Growth, Surface Structure and Morphology of Semiconductor Nano-Structures

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Growth, Surface Structure and Morphology of Semiconductor Nano-Structures

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Growth, Surface Structure and Morphology of Semiconductor Nano-Structures

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Abstract

Self-assembled growth of semiconductor quantum dots has perspective applications in optoelectronic devices and a detailed understanding of their growth mechanisms is of high practical importance. Within this thesis work, the controlled formation and structural characterization of self-organized semiconductor nano-structures are discussed with special focus on their surface properties. Two types of semiconducting nano-structures have been investigated namely as Si–Ge based as well as GaN based quantum dot structures. In addition, GaN growth on Si(111) for integration of nitride semiconductors into Si technology has also been studied.

Self-organized nano-patterning of Ga/Si(111) surfaces after submonolayer Ga deposition has been studied by STM, LEEM and XPEEM. The surface defects of the Si(111)-7×7 surface (steps and the domain boundaries) play an important role in the initial Ga nucleation. Post-deposition annealing of Ga/Si(111) surface or elevated temperature Ga deposition on Si(111) leads to a 2D phase separation and surface nano-patterning. Varying the amount of Ga coverages, structures of the Ga/Si(111) nano-patterns can be controlled. Subsequent Ge deposition on partially $\sqrt{3} \times \sqrt{3}$-Ga covered nano-patterned substrate leads to a selective nucleation of 3D Ge islands and thus to the formation of an array of highly aligned Ge dots. The formation of the nano-patterns can be explained in terms of surface stress and surface free energy.

The structure, morphology and stoichiometry of silicon nitride films prepared by plasma assisted reactive growth on the Si(111) surface at elevated temperatures have been examined using LEED, STM and ESCA microscopy. Low temperature nitridation results in smooth silicon nitride films of poor crystallinity, whereas nitridation at high temperatures leads to the formation of crystalline Si$_3$N$_4$ layers but with a rough surface morphology. To facilitate the wurtzite GaN growth on Si(111), various silicon nitride inter-layers have been used as a buffer and a significant improvement of the subsequently grown GaN films morphology is obtained for Si(111) nitridation at higher temperatures.

In-situ cleaning and surface defects characterization of MOVPE grown GaN(0001)/sapphire templates and subsequent homo-epitaxial growth of thin GaN layer using MBE have been studied using XPS and STM and RHEED. A combination of initial plasma assisted active nitrogen cleaning at low temperature followed by a short duration high temperature cleaning leads to an efficient removal of surface oxide while maintaining a smooth surface morphology. For a smooth template surface, a layer-by-layer growth morphology of GaN has been achieved for Ga-rich growth condition.
MOVPE grown self-organized $\text{In}_x\text{Ga}_{1-x}\text{N}$ nano-islands on GaN(0001) templates have been investigated using STM. The morphology and density of these $\text{In}_x\text{Ga}_{1-x}\text{N}$ nano-islands can be controlled by the choice of proper MOVPE growth conditions such as temperature, $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit, growth rate and III-V flux ratio. With decreasing growth temperatures, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ island size is reduced and the homogeneity of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface is improved. Homogeneous nucleation of small $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands of high densities ($10^{12}/\text{cm}^2$), suitable for three-dimensional quantum confinement is found for growth at $600^\circ\text{C}$ at a low In partial pressure. However, these nano-islands do not show quantum-dot like emission after overgrowth. Instead, two-dimensional (2D) $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands grown at $700^\circ\text{C}$ show a sharp photoluminescence (PL) emission lines, indicative of single dot emission, after the GaN capping process.
Contents

Abstract IX

1 General Background 1
   1.1 Abstract ................................................. 1
   1.2 Semiconductor nano-structures ................................ 2
      1.2.1 Nano-structures for quantum confinement ............... 2
      1.2.2 GaN based quantum dot nano-structures .................. 3
      1.2.3 Si–Ge based quantum dot nano-structures .................. 4
   1.3 Growth mechanism and nano-structures formation .............. 4
      1.3.1 Thermodynamics: growth modes .......................... 5
      1.3.2 Kinetics: surface morphology ........................... 7
      1.3.3 Role of surface reconstructions and defects ............ 9
   1.4 Carrier confinements within nano-structures .................. 9
      1.4.1 Density of states (DOS) ............................... 10
      1.4.2 Density of states for 3D, 2D, 1D, and 0D nano-structure .... 11
Bibliography ................................................. 14

2 Instrumental methods 17
   2.1 Abstract ............................................... 17
   2.2 Scanning tunneling microscopy (STM) ........................ 18
      2.2.1 Mode of operation ....................................... 19
      2.2.2 Theoretical expression of tunneling current .......... 21
   2.3 Low energy electron diffraction (LEED) ...................... 23
   2.4 X-ray photoelectron spectroscopy(XPS) ....................... 24
   2.5 High energy electron microscopy ............................ 25
      2.5.1 Transmission electron microscopy (TEM) ................. 27
      2.5.2 Scanning electron microscopy (SEM) ..................... 28
## Contents

2.6 SPELEEM .................................................. 30
  2.6.1 Low energy electron microscopy (LEEM) ............... 30
  2.6.2 X-ray photoemission electron microscopy (XPEEM) ........ 32
2.7 ESCA microscopy ............................................. 33
2.8 Molecular beam epitaxy (MBE) .................................. 34
2.9 Metal organic vapour phase epitaxy (MOVPE) .................... 35
2.10 Nitrogen plasma sources ....................................... 36
  2.10.1 Radio frequency (RF) plasma source ...................... 37
  2.10.2 Electron cyclotron resonance (ECR) plasma source ........ 38
2.11 Evaporator .................................................... 39
  2.11.1 Knudsen/effusion cell ..................................... 39
  2.11.2 E-beam evaporator .................................... 39
Bibliography ..................................................... 40

3 Surface nano-patterning of Ga/Si(111) for Ge-epitaxy .......... 43
  3.1 Abstract ................................................. 43
  3.2 Introduction .............................................. 44
    3.2.1 Si(111)-7\times7 surface .................................. 44
    3.2.2 Ga/Si(111) ........................................... 47
    3.2.3 Ge on Si(111) ......................................... 51
  3.3 Experimental details ........................................ 51
  3.4 Results and discussion ...................................... 53
    3.4.1 Increasing amount of Ga deposit ......................... 53
    3.4.2 Room temperature Ga deposition (0.33 ML) .............. 54
    3.4.3 Room temperature Ga deposition (< 0.33 ML) .......... 55
    3.4.4 Ga/Si(111) nano-patterning (< 0.33 ML) .............. 59
    3.4.5 Room temperature Ga deposition (> 0.33 ML) .......... 65
    3.4.6 Elevated temperature Ga deposition and nano-structuring (>0.33 ML) .... 70
    3.4.7 Hetero-epitaxial growth of Ge on Ga:Si(111) ........... 71
    3.4.8 Ge quantum dot on nano-patterned Ga-Si(111)surface .... 74
  3.5 Conclusions ................................................. 79
Bibliography ..................................................... 80

4 Growth, structure and morphology of thin silicon nitride films .... 83
  4.1 Abstract ................................................. 83
  4.2 Introduction .............................................. 84
## Contents

4.2.1 Motivation ........................................ 84
4.2.2 Structure and properties .......................... 84
4.2.3 Previous work ..................................... 85
4.2.4 Surface reconstruction of Si$_3$N$_4$(0001) .......... 86
4.3 Experimental details ................................. 88
4.4 Results ............................................... 89
  4.4.1 LEED results .................................... 89
  4.4.2 STM results .................................... 90
  4.4.3 ESCA results .................................. 109
4.5 Discussion ........................................... 111
4.6 Conclusions .......................................... 114
Bibliography ............................................. 114

5 Growth and morphology of MBE grown GaN on Si(111) surface 117
  5.1 Abstract ........................................... 117
  5.2 Introduction ....................................... 118
    5.2.1 Motivation .................................... 118
    5.2.2 Conventional substrates ...................... 118
    5.2.3 Silicon as a substrate ....................... 119
  5.3 Experimental details ................................ 121
    5.3.1 Preparation ................................... 121
    5.3.2 Characterization procedure .................... 122
  5.4 Results ............................................ 123
    5.4.1 ESCA results ................................ 123
    5.4.2 LEED results ................................ 127
    5.4.3 STM results ................................ 128
    5.4.4 SEM results ................................ 132
    5.4.5 TEM results ................................ 133
  5.5 Discussion .......................................... 135
  5.6 Conclusions ....................................... 137
Bibliography ............................................. 137

6 GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy 141
  6.1 Abstract .......................................... 141
  6.2 Introduction ...................................... 142
    6.2.1 Motivation .................................... 142
Chapter 1

General Background

1.1 Abstract

This chapter is focused on some of the basic phenomena of semiconductor nano-structures which can be used for multi-dimensional charge carrier confinement. Various growth mechanisms and epitaxial nano-structure formations are discussed in terms of thermodynamics and surface kinetics. The influence of surface reconstructions and defects on the growth process is mentioned. The quantum confinement of the charge carriers and the dependence of the available electronic energy density of states (DOS) on the size and shape of the nano-structures are also elucidated.
1.2 Semiconductor nano-structures

Semiconductor nano-structures and nano-technology have attracted worldwide attention and constitute a frontier area of research. This research promises to extend device physics to one- (quantum wells), two- (quantum wires) or three-dimensional (quantum dots) confinements for electronic devices. It has long been predicted that the multi-dimensional confinement in these low-dimensional structures can alter the transport and optical properties significantly, compared to the bulk or planar hetero-structures [1]. In addition, the effect of quantum charge transport in small semiconductor quantum dots has stimulated much research in single-electron devices [2]. For this kind of device, the transfer of a single electron is sufficient to control the device performance. However, the rapidly expanding semiconductor band-gap-engineering [3] is the most important factor driving the active research in quantum effect. Modern epitaxial growth techniques such as molecular beam epitaxy (MBE) and metal-organic vapour phase epitaxy (MOVPE) make this research work more realistic.

1.2.1 Nano-structures for quantum confinement

The growth sequences of many ultra-thin epitaxial layers with atomically sharp interfaces and thickness control down to the monolayer (ML) level are routinely required for nowadays solid state devices. Alternating layers of wide bandgap and narrow bandgap semiconductors are used to tailor the electronic properties within it. For this super lattice structure, charge carriers can be quantum confined within the low bandgap regions. Using this concept and depending on the shape and size of the nano-structures, carriers can be confined in two-dimension (2D), one-dimension (1D) or zero-dimension (0D) and the corresponding structures are called quantum wells (QWs), quantum wires or quantum dots (QDs), respectively.

A quantum well is a small potential well in which carrier particles can move freely sideways, i.e., in the plane of the thin 2D layer, but are confined in the forward-backward direction. The quantum wells have many useful properties because it is possible to engineer the forward-backward confinement exactly and they are relatively easy to prepare. As a result they are now widely used to make semiconductor lasers and other useful devices. To take the confinement level one step further, by making a thin narrow ‘wire’ instead of a thin 2D layer (QW) of the preferred semiconductor, particles can be quantum-confined in 2D and the carrier is only free to travel along the wire. To prepare a good quantum-wire is technologically challenging and is an active area of research. The next step of quantum-confinement (3D) is to make quantum dots, where the carrier is quantum-confined within a tiny dot of material. Within a QD, carriers are in confined states and not freely moving anymore, which means they behave in a very new way as discussed below.
1.2. Semiconductor nano-structures

Quantum dots

With dimensions of 1–100 nanometers and containing somewhere between $10^3$ and $10^6$ atomic nuclei in a crystalline lattice, semiconductor ‘quantum dots’ are often described as artificial, solid-state atoms [4]. An electron in a quantum dot can be described by a quantum wave function that is similar to that used for an electron in a single atom, although its energy is spread coherently over the lattice of the atomic nuclei. Quantum dots are made of many thousands of atoms but they have a countable number of allowed states. Each state is separated from the others. This means that it is more like a single atom than many atoms. Because of this, a quantum dot system may make the ideal laser material. Also, it may be an ideal building block for a quantum-computer.

1.2.2 GaN based quantum dot nano-structures

GaN based wide-bandgap materials (III-nitrides) have a direct energy band gap which makes them attractive candidates for exciting applications in optoelectronic devices such as visible and ultraviolet light emitting diodes and laser diodes [6, 7]. The high defect density of GaN initially made this material not a likely candidate for light emitting diodes (LEDs) and lasers of good luminescence efficiency. But unlike the majority of semiconductors, in GaN, dislocations did not seem to degrade the optical and electrical properties. An excellent luminescence efficiency from GaN LEDs was obtained despite the high dislocation densities ($10^{10}/\text{cm}^2$). Thereafter, GaN based semiconductors are at the forefront of semiconductor science for optoelectronic devices. The band gap energy of $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ ternary alloys at room temperature can be varied from 0.7 to 6.2 eV depending on its composition. Therefore, III-nitride semiconductors are particularly useful for light-emitting diodes (LEDs) and laser diodes (LDs) in this wavelength region [8, 9]. A schematic diagram of the bandgap energy against the lattice parameter of group-III nitrides is shown in figure 1.1. Among the ternary alloys, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have attracted great attention due to their wide use as multiple quantum well (MQW) active layers in light emitting devices and much work has been devoted to commercialize them. Now, the LED output intensity can highly be increased by further confinement of the carriers by using QDs, instead of MQW. This improves the device performance as it prevents carriers
from a non-radiative recombination at crystal defects. In addition, the use of QDs instead of QWs is expected to reduce the threshold current density of laser diodes [1]. Furthermore, AlGaN/GaN based hetero-structure field effect transistors are very well suited for high-temperature, high-power and high-frequency electronic devices [10, 11].

1.2.3 Si–Ge based quantum dot nano-structures

More than 90% of all semiconductor devices are based on silicon and hence Ge/Si hetero-epitaxial layers can be applied for new device concepts [12]. First industrial applications of Ge/Si hetero-epitaxial layers were hetero-bipolar transistors with an epitaxially grown Ge/Si basis [12, 13]. The compatibility of the Ge/Si system with the standard CMOS technology is one of the most important aspects as it is widely used for the production of many semiconductor devices. However, a major hurdle in the silicon based optoelectronic device has been a consequence of the indirect band gap of this material. Recent reports suggest that indirect-to-direct conversion can be realized for zero dimensional (0D) quantum confined structures such as quantum dots [14, 15]. Theoretical calculations also predict that an indirect-to-direct conversion of the optical transition of Ge QDs would occur if the number of atoms in QDs is below 3100 [16, 17]. Hence, new devices employing Ge/Si epitaxial nano-structures are expected to overcome this restriction [18, 19] and application of Ge/Si may be found in silicon-based optoelectronics. For example, Ge islands embedded in Si layers can be used for light emission where electron–hole pairs are captured in Ge islands and recombined by light emission.

1.3 Growth mechanism and nano-structures formation

In most of the technologically relevant cases, the growth of perfectly flat, 2D layers is a stringent requirement for functionality. The rare examples where a 3D growth morphology is desired are semiconductor quantum dots, which are becoming more relevant for optoelectronic devices or single electron transistors. For nano-structural fabrication, usually a thin epilayer is grown on a substrate which is used to fabricate lower dimensional structures like quantum wires or dots by lithographic techniques. To achieve a 3D confinement effect at room temperature within QDs, a dense array of small islands of only a few nanometers with a narrow size distribution is desirable, which is below the limits of conventional lithography. An alternative way to achieve this is the self-assembly of 3D islands during epitaxial growth. For appropriate growth conditions, self-assembled epitaxial islands can be grown with a reasonably well-controlled narrow size distribution which is also an essential condition for most optoelectronic applications. The ability to grow such size-controlled islands makes the self-assembly an attractive route for the fabrication of devices based on nano-structures.

Molecular beam epitaxy (MBE) or vapor phase epitaxy (VPE) can be used for the growth of thin epitaxial films and artificial multilayers on single crystal substrate surfaces. These
growth techniques are able to control the film thickness down to an atomic monolayer scale. In MBE, the substrate surface is held in ultra high vacuum (UHV, typically at ≈ $10^{-10}$ mbar) while being exposed to a vapor of molecules or atoms of the growing material. Whereas for VPE, precursor molecules are thermally decomposed in a continuous flow oven in a background atmosphere of clean inert gas. However, the control over growth process and film morphology is a major challenge in both growth techniques, which requires knowledge of thermodynamics as well as of surface kinetics.

1.3.1 Thermodynamics: growth modes

The understanding of epitaxial growth has been developed by three major thoughts. Using the elasticity theory, Frank and van der Merwe derived the concept of a critical misfit below which monolayer-by-monolayer growth appears [20]. Applying the nucleation theory, Volmer and Weber assumed that crystalline films grew from 3D nuclei and their relative number and growth rate were determined by interfacial and surface free energies [21]. From atomistic calculations Stranski and Krastanov showed that initially a few pseudomorphic 2D layers are formed, on top of which 3D crystals with their natural lattice constant will grow [22]. Each of these three scenarios is actually observed. After unification to the epitaxy theory, Bauer predicted the growth mode, considering the thermodynamic quantities involved in epitaxy, i.e., three free surface energy per unit area $\sigma_o$, $\sigma_i$, and $\sigma_s$ at the overlayer–vacuum interface, the overlayer–substrate interface, and the substrate–vacuum interface, respectively [23]. Results give rise to the following three growth modes of epitaxy:

(i) Frank–van der Merwe (FM) growth mode (2D morphology, layer-by-layer or step-flow growth)

(ii) Volmer–Weber (VW) growth mode (3D morphology, island growth)

(iii) Stranski–Kranstanov (SK) growth mode (initially 2D, after critical thickness, 3D morphology, layer-plus-island growth).

![Figure 1.2: Schematic representation of the three thermodynamic growth modes](image)

If $\sigma_o$ and $\sigma_i$ are small compared to $\sigma_s$ the system gains energy when totally covered by the overlayer. Otherwise, the substrate surface will only partly be covered by the deposited
material. For a film composed of \( n \) layers the criterion of the FM growth mode is

\[
\sigma_{o(n)} + \sigma_{i(n)} \leq \sigma_s \tag{1.1}
\]

The equality in Eqn. (1.1) holds for the trivial case of homo-epitaxy. This reveals the FM growth mode for growth conditions close to the thermodynamic equilibrium. In the hetero-epitaxial case the obvious condition for FM growth is that \( \sigma_{o(n)} \ll \sigma_s \). The inequality in Eqn. (1) has to be large since in general \( \sigma_{i(n)} \) is positive and non-negligible. The VW mode, case (ii), results if this growth condition is not fulfilled, i.e., \( \sigma_{o(n)} \sigma_s \) and three-dimensional crystals form immediately on the substrate. Close to thermodynamic equilibrium, such 3D island shape is comparable to that of liquid droplets and the contact angle (\( \theta \)) between the cluster surface and the substrate is determined by [24]

\[
\cos(\theta) = \frac{\sigma_s - \sigma_i}{\sigma_o} \tag{1.2}
\]

For a system with different crystallographic structures and/or lattice constants of the overlayer and the substrate, satisfying equation 1.1 results in a different way. The structural mismatch between the substrate and the overlayer leads to the formation of lattice strain and the \( n \)-dependence of \( \sigma_o \) reflects possible changes in the lattice constant and/or structure at the overlayer surface. The thickness dependence of \( \sigma_i \) mainly originates from: (1) the true interface energy caused by the lattice mismatch and (2) the volume strain accumulated in a pseudomorphic overlayer which is conveniently incorporated in \( \sigma_{i(n)} \) [25]. As the film grows in thickness, it stores an increasingly large strain energy. Equation 1.1 implies that this leads to an unstable situation at a critical thickness \( n_c \) where \( \sigma_{o(n)} + \sigma_{i(n)} > \sigma_s \) and the system switches from 2D to 3D growth morphology. This type of growth mode is known as Stranski–Krastanov growth (case (iii)), where a 2D wetting layer initially grows followed by 3D islands formation.

![Figure 1.3: Partial reduction of lattice strain by forming (a) 3D mound (elastic relaxation) [26] and (b) misfit dislocation at interface (plastic relaxation).](image)

The transition from 2D to 3D morphology for the SK growth mode can be explained by two possible reasons. On the one hand, the first few monolayers of the film material can
1.3. Growth mechanism and nano-structures formation

grow in a very different crystallographic structure as compared to its bulk structure [27]. In this case, the crystallographic change of the initial film back to its bulk lattice structure takes place after a certain thickness $n_c$. This induces an abrupt increase in free energy at the interface between the two crystal structures and changes the energy balance to favor 3D growth. On the other hand strain relief by the formation of 'mounds' can be the deciding factor for SK growth. The strained epilayer system can lower its total energy by forming isolated thick islands as can be seen in figure 1.3(a). For the case of compressive strain, how mounds can efficiently regain their bulk lattice constant by increasing the surface area and reduce the volume strain is shown here. This 3D island growth presents a significant issue in the fabrication of coherently strained device structures and is beneficial for the self-assembly of quantum dots into arrays with sharp size and distance distributions. Compared to mounds, it is much harder to relieve strain in a perfect 2D layer. In the best cases strained epitaxial layers exhibit a smooth transition in the lattice constant from the substrate value over several weakly incommensurate phases (moire structures or networks of partial surface dislocations) towards its bulk value [28]. Strain relief in a 2D layer often implies the introduction of structural defects [29] such as bulk dislocations as shown in figure 1.3(b), which generally hamper the device functionality.

1.3.2 Kinetics: surface morphology

All the above mentioned considerations and the classification of various growth modes such as FM, VW, and SK growth modes are only valid for growth conditions close to the thermodynamic equilibrium, i.e., for a high substrate temperature with a slow growth rate. At equilibrium condition condensation and desorption have equal probabilities. Hence, the term growth mode is only justified for growth conditions close to the equilibrium condition (just below). In case of growth conditions far from the equilibrium, the morphology is mainly influenced by kinetics instead of thermodynamics and the term growth mode should be replaced by growth morphology, which depends on the various reaction paths available during growth. For a metastable film morphology, surface kinetics play a very crucial role and mainly control the growth. As an example, if material $A$ perfectly wets material $B$, because $\gamma_A \ll \gamma_B$, then the layer of material $B$ will not be wetting the underlying $A$. In this case it has to be stabilized in a 2D film by controlling the surface kinetics. In case of miscible materials, inter-diffusion results in a rough and not so well defined interface. This problem can be inhibited by lowering the growth temperature.

Various individual atomic processes involved during epitaxial growth are discussed as follows. In case of MBE growth, evaporated material’s vapour in contact with the substrate results in epitaxial growth, which is mainly determined by the surface kinetics such as deposition/adsorption of source atoms, diffusion/migration of adsorbed atoms and nucleation/incorporation into crystal lattice. However, in the case of MOVPE growth there are in addition thermal dissociation, diffusion, and desorption of the precursor molecules.

Evaporated atoms are immediately thermalized onto the substrate and their subsequent 2D diffusion rate $D$ over the atomic terraces can be calculated as [30]
Chapter 1. General Background

\[ D = \frac{\langle r^2 \rangle}{4t} = \frac{d_{nn}^2 \nu_0}{4} e^{-E_m/KT} \]  

where \( E_m \) is the activation energy for migration, \( T \) is the substrate temperature and \( d_{nn} \) the surface nearest neighbour distance. The pre-exponential factor \( \nu_0 \) is the vibrational frequency of the atom in the initial state (\( \sim 10^{13} \)Hz). A similar relation also holds for interlayer diffusion across monoatomic steps.

(a) Step flow  
(b) Layer-by-layer  
(c) Multilayer

Figure 1.4: Schematic representation of the three kinetic growth morphologies: (a) step flow, (b) layer by layer and (c) multilayer growth morphology, respectively.

The final film morphology in the kinetic growth regime is determined by the competition between the activation barriers which define the surface diffusion rate \( D \) and the deposition rate/flux \( F \). The mean distance \( \lambda \) of a monomer travel before encountering one of its own or an existing nucleus is described as \( \lambda \approx (D/F)^{1/6} \) ([30]). Firstly, if \( \lambda \) is larger than the terrace width, no islands are formed since all atoms reach the ascending substrate steps to which they attach. This growth kinetic is called step-flow growth and the surface roughness remains constant during growth (fig. 1.4(a)). In case of \( \lambda \) smaller than the terrace width, deposited atoms form nuclei on the terrace surface and two other possibilities of growth morphology can be found. Periodic monolayer oscillations of the surface roughness appear when the film grows from nuclei and stays 2D during their growth until they coalesce (fig. 1.4(b)). This implies that all atoms deposited on top of the islands can descend. This type of growth morphology is known as layer-by-layer growth where the roughness has its maximum just before island coalescence and a minimum when an integer layer is completed (fig. 1.4(b)). Finally, the other type of growth morphology, i.e., so-called kinetic roughening or multilayered growth is characterized by a monotonically increasing surface roughness as shown in fig. 1.4(c). After the first layer nuclei have reached a certain size, atoms deposited on top can no longer descend quickly enough, leading to the critical monomer density on top of the island for the second layer nucleation.
1.3.3 Role of surface reconstructions and defects

Apart from the general thermodynamics and surface kinetics, surface defects and reconstructions can also influence the growth process. However, mostly these affects the surface kinetics.

The termination of bulk crystals of covalent materials such as semiconductors, by a free surface, leads to the formation of surface reconstructions in order to achieve the energetically most favourable configuration for the surface. Usually this is achieved if the number of dangling bonds is minimized. The surface reconstructions of semiconductors can be changed by adsorption of foreign atoms. This can also be modified by varying the deposition temperature and the coverage of the adsorbates. For different surface reconstructions, the surface chemical reactivity or free energy changes which finally influences the surface diffusion process during growth. As an example, the adsorption of Ga on Si(111) has been shown to lead to a narrowed 3D island size distribution during subsequent Ge epitaxy [31].

In case of a dislocation–free surface, the steps are the only defects and terrace structures should be uniform with a terrace width inversely proportional to the miscut angle of the substrate. However, other surface defects are also formed, mainly due to the relaxation of the surface strain, minimization of surface chemical energy (domain boundary formation during the 7×7→1×1 transition for Si(111)) [32] or due to improper growth conditions (threading dislocations or 'V-defects' formation for GaN growth at lower temperature). In general, the dangling bond density is larger at the defect sites which makes it chemically more active. Additionally, defects also restrict the diffusion process. Finally, these effects result in a defect induced nucleation or growth. Different types of dislocation mediated GaN surface structures such as pinned steps, spiral hillocks and surface depressions have been observed [33].

1.4 Carrier confinements within nano-structures

Spatial confinement of electrons in semiconductor nano-structures leads to remarkable changes in their quantum states. This results in considerable modifications in their electronic properties and consequently their linear and nonlinear optical response.

In quantum-mechanics every phenomenon is described by wave-functions. Confinement in a small volume means that only particular types of wave-functions are allowed, where each of them follows exactly the right length and shape to satisfy the Schrödinger’s equation. In addition, every wave function has a particular energy which finally forms an energy 'ladder' with discrete states of energy. Depending on the details of the situation, the spacing between the energy states can vary.

In case of quantum wells (QWs), charge carriers are confined within a thin two-dimensional (2D) semiconductor layer, where they can move freely sideways in the plane of the layer. Whereas for quantum wires, carriers are further confined and can only move in one-dimension (1D) along the wire. A quantum dot is the final step of confinement, where carriers are totally confined within a quasi zero-dimensional tiny dot of material. Carriers
cannot move freely anymore and as a result the system behaves in a very different way. This small quantum-dot, made of a few thousand atoms, exhibits a countable number of allowed energy states and each state is separated from the others. This means that it appears more like a single atom than many atoms. Quantum confinement effects become pronounced in the region of strong confinement, where the size of the quantum dot is less than the exciton Bohr diameter of the semiconductor. The band picture is no longer strictly valid in the case of quantum confinement and transitions between excitonic levels gain in oscillator strength even at room temperature. These effects can easily be seen in optical absorption and photoluminescence spectra.

1.4.1 Density of states (DOS)

Before calculating the density of carriers in a semiconductor, the number of available states at each energy can be estimated. The number of electrons at each energy then can be obtained by multiplying the number of states with the probability that an electron occupies a state. Since the number of energy levels is very large and dependent on the size of the semiconductor, the number of states per unit energy and per unit volume, i.e., density of states (DOS) can be used for the calculation.

The density of states in a semiconductor equals the density per unit volume and energy of the number of solutions to Schrödinger’s equation. It can be assumed that the semiconductor is modelled as an infinite quantum well in which electrons with the effective mass \( m^* \) are free to move. The energy in the well is set to zero. The semiconductor is assumed as a cube with side \( L \). This assumption does not affect the result since the density of states per unit volume should not depend on the actual size or shape of the semiconductor.

The solutions of the Schrödinger wave equation, where \( V(x) = 0 \), can be described as

\[
\Psi = A \sin(k_x x) + B \cos(k_x x) \quad (1.4)
\]

The wave function must be zero at the infinite barriers of the well, i.e., at \( x=0 \) and \( x=L \). These boundary conditions yield the following possible values for the wave number, \( k_x = \frac{n \pi}{L} \), where \( n = 1,2,3,... \).

In case of a three-dimensional calculation, this analysis can now be repeated in the \( y \) and \( z \) direction and each possible solution corresponds to a cube in \( k \)-space with size \( n \pi / L \) as indicated on figure 1.5.

The total number of solutions with a different value for \( k_x \), \( k_y \) and \( k_z \), and with a magnitude of the wave vector less than \( k \) is obtained by calculating the volume of one eighth of a sphere with radius \( k \) and dividing it by the volume corresponding to a single solution \((\frac{\pi}{L})^3\), yielding [34]:

\[
N = 2 \times \frac{1}{8} \times \left( \frac{L}{\pi} \right)^3 \times \frac{4}{3} \pi k^3 \quad (1.5)
\]
1.4. Carrier confinements within nano-structures

Figure 1.5: Schematic diagram for the calculation of the number of states with wave number less than $k$ [34].

A factor of two is added to account for the two possible spins of each solution. The density per unit energy is then obtained using the chain rule:

$$\frac{dN}{dE} = \frac{dN}{dk} \frac{dk}{dE} = \left(\frac{L}{\pi}\right)^3 \pi k^2 \frac{dk}{dE}$$  \hspace{1cm} (1.6)

The kinetic energy $E$ of a particle with mass $m^*$ is related to the wave number $k$ and can be described as $E(k) = \hbar^2 k^2 / 2m^*$. Therefore, the density of states per unit volume and per unit energy, $g(E)$, becomes:

$$g(E) = \frac{1}{L^3} \frac{dN}{dE} = \frac{8\pi\sqrt{2}}{\hbar^3} m^{*3/2} \sqrt{E}, \text{ for } E \geq 0$$  \hspace{1cm} (1.7)

The same analysis also applies to electrons in a semiconductor. The effective mass takes into account the effect of the periodic potential on the electron. The minimum energy of the electron is the energy at the bottom of the conduction band, $E_c$, so that the density of states for electrons in the conduction band is given by:

$$g_c(E) = \frac{1}{L^3} \frac{dN}{dE} = \frac{8\pi\sqrt{2}}{\hbar^3} m^{*3/2} \sqrt{E - E_c}, \text{ for } E \geq E_c$$  \hspace{1cm} (1.8)

1.4.2 Density of states for 3D, 2D, 1D, and 0D nano-structure

Using the earlier concepts that the density of electrons in k-space is constant and equal to the physical length of the sample divided by $2\pi$ for each dimension, the density of states in 3D, 2D and 1D nano-structures can be obtained [34,35]. Schematic diagrams of various nano-structures in k-space are shown in figure 1.6.

Bulk structures (3D)

For a 3D bulk structure, hence, the k-space can be filled with a cubic unit cell of volume $(\frac{2\pi}{L})^3$. Now, to calculate the number of allowed states between $k$ and $k+dk$, it is worthwhile to obtain the volume $dV_{3D}$ between the two spherical shells of radius $k$ and $k+dk$, which is given by
Therefore, the total number of states between $k$ and $k+dk$ can be derived by dividing this volume by the unit cell volume [34]. A additional factor of two has to be added to account for the two possible spin states.

$$
\frac{dN_{3D}}{dE} = 2 \times \frac{dV_{3D}}{(2\pi)^3} = 2 \times \left(\frac{L}{2\pi}\right)^3 \times 4\pi k^2 dk = \frac{L^3 k^2 dk}{\pi^2}
$$

Now, eliminating $k$ using the $E(k) = \hbar^2 k^2/2m^*$ relation, the density of states per unit volume per unit energy, can be derived as:

$$
g_{c,3D} = \frac{dN_{3D}}{dE} = \frac{8\pi \sqrt{2}}{\hbar^3} m^{*3/2} E^{1/2}
$$

Quantum well structures (2D)

For a 2D quantum well structure, a similar kind of approach can be used to obtain the density of states, keeping in mind that one of the k-space components is fixed here (fig. 1.6(b)). Hence, the k-space can be filled with a square unit cell of area $(2\pi)^2$ instead of a cube for the 3D structure. Here, the number of allowed states between $k$ and $k+dk$ can be obtained by measuring the area $dV_{2D}$ of the annular disc of radius $k$ and $k+dk$, which is given by

$$
dV_{2D} = 2\pi k dk
$$

The total number of states between $k$ and $k+dk$ can be derived by dividing this area by the unit cell area and adding the spin component [34].

$$
dN_{2D} = 2 \times \frac{dV_{2D}}{(2\pi)^2} = 2 \times \left(\frac{L}{2\pi}\right)^2 \times 2\pi k dk = \frac{L^2 k dk}{\pi}
$$
1.4. Carrier confinements within nano-structures

Now, the density of states per unit volume per unit energy, can be derived as:

\[ g_{c,2D} = \frac{dN_{2D}}{dE} = \frac{4\pi m^*}{\hbar^2} \]  

(1.14)

From this expression it is realized that the density of states does not depend on the energy. As the top of the energy gap reaches the next eigenenergy values, there is immediately a significant number of available states. Taking this effect into account for all other available energy levels in the quantum well, the density of states becomes a staircase like function as can be derived by [34]

\[ g_{c,2D} = \frac{4\pi m^*}{\hbar^2} \sum_i H(E - E_i) \]  

(1.15)

where \( H(E - E_i) \) is the Heaviside function which has a value of zero for \( E < E_i \) and one for \( E \geq E_i \). \( E_i \) represents the \( i \)-th energy level within the quantum well.

Quantum wire structures (1D)

In the case of quantum wires, the k-components are fixed for two directions as can be seen in figure 1.6(c). Therefore, the k-space volume for bulk 3D structures or the k-space area for 2D quantum wells becomes a length for 1D quantum wires. Hence, the k-space can be filled with a line unit cell of length \( \frac{2\pi}{L} \). Therefore, the number of allowed states between \( k \) and \( k + dk \) can be obtained by measuring the length \( dV_{1D} \) of the line covered between radius \( k \) and \( k + dk \), which is given by

\[ dV_{1D} = 2dk \]  

(1.16)

The total number of states between \( k \) and \( k + dk \) can be derived by dividing this length by the unit cell length and adding the spin component [34].

\[ dN_{1D} = 2 \times \frac{dV_{1D}}{2\pi} = 2 \times \left( \frac{L}{2\pi} \right) \times 2dk = \frac{2Ldk}{\pi} \]  

(1.17)

and the density of states per unit volume per unit energy, can be derived as:

\[ g_{c,1D} = \frac{dN_{1D}}{dE} = \sqrt{\frac{2\pi m^*}{\hbar^2}} E^{-1/2} \]  

(1.18)

Similar to the quantum wire structure, taking into account the higher energy levels, the density of states function becomes

\[ g_{c,1D} = \sqrt{\frac{2\pi m^*}{\hbar^2}} \sum_i n_i H(E - E_i) \]  

(1.19)
where $H(E - E_i)$ is again the Heaviside function, $E_i$ is the $i$-th energy level within the quantum wire and $n_i$ is the degeneracy factor [34].

Quantum dot structures (0D)

In case of 0D semiconductor nano-structures, i.e., quantum dot structures, the $k$-components are quantized in all directions (fig. 1.6(d)). All the available states exist only at discrete energies and can be represented by a delta function.

$$g_{c,0D} = \delta(E)$$ (1.20)

Taking the higher energy eigen values into account, the density of states function can be represented in a series of delta functions as

$$g_{c,0D} = \sum_i \delta(E - E_i)$$ (1.21)

In reality, however, the size distribution of the quantum dots leads to the broadening of this function. Schematic drawing of the density of states for various nano-structures have been shown in figure 1.7.

Figure 1.7: Density of states (DOS) versus energy ($E$) for semiconductor nano-structures of different dimensionality which offers different levels of quantum confinements

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Chapter 2

Instrumental methods

2.1 Abstract

The working principle and instrumental details of various instruments, which have been used for the experimental works of this thesis are discussed here. A major part of the experimental characterization has been carried out with a scanning tunneling microscope (STM) which gives information about atomic reconstructions, structure and morphology of the surface down to atomic scale. Overall information about the surface reconstructions and crystalline quality of the samples have also been examined using low energy electron diffraction (LEED). In addition, X-ray photoelectron spectroscopy (XPS) has been applied to get the chemical information of the samples. Low energy electron microscopy (LEEM) and X-ray photoemission electron microscopy (XPEEM) at the 'Nanospectroscopy' beamline at ELETTRA allow to observe directly the structural evolution and surface kinetics during the growth and the chemical information of the surface with nanometer scale accuracy. Whereas ESCA microscopy has been utilized to get the chemical as well as the morphological information on a larger scale. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been used to gather structural information of the surface and its underneath. For sample preparation and growth, molecular beam epitaxy (MBE) techniques have been used with various effusion cells as material sources. Radio frequency (rf) and electron cyclotron resonance (ECR) nitrogen plasmas have been utilized as active nitrogen sources for nitride growths and cleaning. Samples grown by metal-organic vapour phase epitaxy (MOVPE) have also been studied.

STM results have been presented throughout the thesis for all kind of material systems, whereas LEED has been performed mainly for Ga/Si(111) nano-patterning and subsequent Ge-growth (chapter 3) as well as for silicon nitride formation on Si(111) and subsequent GaN growth (chapter 4 and 5). LEEM and XPEEM measurements have been carried out only for Ga/Si(111) nano-patterning for selective growth of Ge nano-islands (chapter 3). XPS has been used for in-situ cleaning studies of GaN/sapphire templates (chapter 6) and for GaN growth on nitrified Si(111) substrate (chapter 5). Some parts of the nitridation process of Si(111) followed by GaN growth have also been characterized using ESCA microscopy (chapter 4 and 5). TEM and SEM have been used for structural characterization of InGaN nano-islands (chapter 7) as well as for the GaN growth on Si(111) (chapter 5).
2.2 Scanning tunneling microscopy (STM)

In March 1981, two IBM scientists, Gerd Binnig and Heinrich Rohrer, developed a new technique for studying the surface structure - "Scanning Tunneling Microscopy" (STM) [1, 2]. Only a few years later in 1986, they were awarded the Nobel Prize for this development. The development of this technique has undoubtedly been the most important event in the surface science field in recent times and opened up many new areas of science and engineering at the atomic and molecular level. This invention was quickly followed by the development of a whole family of related techniques which together with STM, may be classified in the general category of Scanning Probe Microscopy (SPM) techniques.

The revolutionary invention of the scanning tunneling microscope (STM) makes it possible to obtain atomically resolved images of metal and semiconductor surfaces in real space. In addition to structural properties, it can also provide information about the local electronic states of the surface down to the atomic scale. Finally, the abilities of monitoring surfaces with atomic resolution combined with the tip positioning with atomic accuracy makes the STM capable of doing direct and controlled manipulation down to atomic scale to create atomic scale devices. A detailed overview of the STM and its various applications is presented by Wiesendanger. [3, 4]

STM is one of the few instruments that can give atomic-scale structural and electronic information of a surface in ultra high vacuum (UHV) to atmospheric pressures and beyond [5, 6]. In addition, it can also be used in liquids. Furthermore, STM enables the study of surface atomic structures ranging from cryogenic temperatures [7] to temperatures in excess of 1000 K [8, 9].

The basic working principle of STM is the quantum mechanical tunneling effect of electrons between two conductors in very close physical proximity. STM probes the surface with the tip of an extremely sharp needle (STM tip) which is brought within a few atomic spacings of the investigated material during scanning. The distance from the tip to the sample is so small that the electronic wave functions of the sample surface and the tip overlap. If a voltage (from ∼10 mV to a few volts, depending on the sample material) is applied between the tip and sample surface (bias voltage), electrons tunnel through the vacuum barrier from the tip to the sample or vice versa. The current generated from this electron tunneling is called the tunneling current, which is typically of the order of ∼10 pA to 1 nA. The electronic wave function overlapping decreases more or less exponentially with the distance which makes the tunneling current extremely sensitive to the distance between the tip and the surface. By precisely controlling the relative position of the tip and scanning over the surface, a height map of the probed area can be measured with atomic scale accuracy. A schematic illustration of the STM is shown in figure 2.1.

Although apparently very simple, in reality there are a lot of difficulties to achieve the atomic resolution. Firstly, the mechanical vibration from the housing or acoustic noise is one of the most serious problems. For high resolution STM applications, picometer scale vertical stability of the tip-sample spacing is required which is six order of magnitude lower than the typical floor vibration (∼µm). This problem has been overcome by an effective...
vibration-isolation system using four-spring suspension and eddy-current damping method with a rigid design of the instrument. Secondly, the precise control (about 0.1 Å) over the three-dimensional (3D) positioning of the tip and the movement of the scanning unit, is a major challenge. Usually this is achieved by using piezoelectric devices. Thirdly, as the tunneling current is only of the order of pA, it is very difficult to sense without any electrical noise pickup. To avoid the noise signal the tunneling current is measured by a preamplifier (gain $10^6 - 10^9$ V/A) placed very closely to the tip (sensor) directly on the STM scan unit. At the same time, a feedback loop is used to maintain a constant tunneling current during the scanning (constant current mode imaging) by moving the tip up and down depending on the nature of the surface. Fourthly, the STM tip must be very sharp, ideally terminating in just one single atom at its apex (closest point of approach to the surface) to sense the atomic scale height difference. Additionally, the radius of curvature of the tip apex and the cone angle have to be sufficiently low for proper imaging of larger structures [11]. Generally, an electro-chemically etched metallic wire [12] is used as STM tip. As there is always some probability to have contact between tip and sample surface, the choice of the materials for the STM tip is, in general, hard materials such as tungsten. There are also several processes for tip preparation such as electro-chemical etching or mechanical cut. Finally, a fully computer automated STM system induced data acquisition, analysis, processing and visualization is required to run a modern STM successfully. A detailed discussion on various problems of STM experimental methods and the solutions can be found in the literature [3, 13].

### 2.2.1 Mode of operation

STM is a versatile instrument which offers various modes of operation depending on the matter of interest. From the observation point of view the modes can be divided mainly into two types: (i) **microscopic mode or topography** and (ii) **spectroscopic mode**. In case of microscopic imaging mode, it mainly deals with the surface structural properties, whereas the spectroscopic mode gives information about the surface electronic states. Also there are many more options to use STM, such as spin polarized scanning tunneling microscope (SPSTM), Ballistic electron emission microscope (BEEM), scanning field emission microscope (SFEM) and more [3].
Chapter 2. Instrumental methods

For the topographic imaging there are two possibilities of data acquisition depending on the activity of the feedback loop. If the feedback loop is kept active, the tunneling current remains constant and the imaging mode is called **constant current mode**. On the other hand, if the feedback loop is switched off, the tip scans over the surface at a constant height and then the imaging is called **constant height mode**. The movement of the tip with respect to the surface during scanning in both cases is shown in figure 2.2. The tunneling current not only depends on the tunneling-gap and the local barrier height of the tip-surface junction, but there also exists a bias voltage dependence. For a metal-metal tunneling junction in a low bias voltage regime, the current-voltage (I-V) curve is linear, i.e., of ohmic nature, whereas for higher bias voltage and particularly for semiconductor samples, the I-V curve generally does not follow the ohmic behaviour. Hence, the STM image can depend critically on the applied bias voltage. Studying this bias voltage dependence in detail allows extraction of the spectroscopy with high spatial resolution. Similar to microscopy, there are also different modes of spectroscopy and mainly two types are quite well known. Variation of tunneling current with respect to the bias voltage is measured at a fixed point, keeping the tip height constant (feedback loop off) which is known as **I-V spectroscopy** and gives information about the surface electronic properties such as the position of the valance and the conduction band. Alternatively, if the variation of tunneling current with respect to the tunneling gap is measured keeping the bias voltage constant, the mode is called **I-Z spectroscopy** which provides the information about the local barrier height. In the following, two microscopic modes are discussed in detail.

![Figure 2.2: Schematic drawing of the tip movement for (left) constant current mode and (right) constant height mode STM operation [14].](image)

**Constant current mode**

The first and most widely used imaging mode is the constant current mode. From the typical name of this mode it is quite clear that the tunneling current remains constant during the entire scanning. Hence to keep the tunneling current constant, a feedback loop is used. This helps to move the tip up and down depending on the surface roughness and to maintain the tunneling gap constant. The height adjustment is performed by applying an
2.2. Scanning tunneling microscopy (STM)

appropriate voltage $V_z$ to the $z$-piezo while the lateral tip position $(x,y)$ is determined by the corresponding piezo-voltages, $V_x$ and $V_y$. Afterwards, the recorded signal $V_z(V_x,V_y)$ can be translated into the topographic image format $z(x,y)$ by appropriate calibration of the different piezo-sensitivity. The scan speed for this mode is limited by the response time of the feedback loop.

**Constant height mode**

The limitation in the scan speed due to the slow response of the feedback loop is a significant drawback of the constant current mode for imaging of rapidly changing surfaces. Hence to overcome this problem the ‘constant height mode’, is used. In this case, the feedback loop is switched off and the tip moves at a constant height during the scan. The tunneling current is recorded simultaneously which exponentially depends on the tip-sample tunneling gap. Afterwards, the variation of the tunneling current with respect to the lateral tip position reflects the surface topography. This imaging mode is generally used for very flat surfaces and very much useful for video STM.

All the STM work in this thesis has been done using a commercial variable temperature scanning tunneling microscope (VT-STM) from Omicron NanoTechnology. The picture views of the STM base platform hanging with four springs and the STM analysis chamber are shown in figure 2.3. This VT-STM has the ability to scan at high temperatures. Although it can be operated in various modes, mainly the constant current mode imaging is used for data collection.

2.2.2 Theoretical expression of tunneling current

The theoretical expression for the tunneling current of STM in general, is very complicated. Anyway, mathematically it is approached using the three dimensional quantum mechanical tunneling effect through a potential energy barrier. With the help of Bardeen’s formalism [15], the tunneling current $I$ can be evaluated using first order time dependent perturbation theory to

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} \{f(E_\mu)[1 - f(E_\nu + eV)] - f(E_\nu + eV)[1 - f(E_\mu)]\}|M_{\mu\nu}|^2 \delta(E_\nu - E_\mu) \quad (2.1)$$
where \( f(E) \) is the Fermi function, \( V \) is the applied bias voltage, \( M_{\mu\nu} \) is the tunneling matrix element between the unperturbed electronic wave functions \( \psi_{\mu} \) of the tip and \( \psi_{\nu} \) of the sample surface. \( E_{\mu} \) and \( E_{\nu} \) are the energies of the states \( \psi_{\mu} \) and \( \psi_{\nu} \), respectively, in absence of any tunneling. The delta function represents the energy conservation for the case of elastic tunneling. According to Bardeen, the tunneling matrix can be written as

\[
M_{\mu\nu} = -\frac{\hbar^2}{2m} \int dS \cdot (\psi^*_\mu \nabla \psi_{\nu} - \psi_{\nu} \nabla^* \psi_{\mu})
\] (2.2)

where the integral has to be evaluated over any surface lying entirely within the vacuum barrier region separating tip and sample surface. The quantity in parentheses can be represented as the current density \( j_{\mu\nu} \). To derive the matrix element \( M_{\mu\nu} \), the explicit wave function of tip \( \psi_{\mu} \) and sample surface \( \psi_{\nu} \) are required. In general, the atomic structure of the tip is not known which makes it very difficult to derive the expression.

Tersoff and Hamann [16, 17] first applied the simplest possible model for the tip with a local spherical head of local radius of curvature \( R \) located at the center \( r_0 \) to evaluate the tunneling matrix. For a spherical head tip, an s-type wave function is used and the angular dependence is neglected. Now, considering the case of low temperature and low bias voltage (metal-metal tunneling), the tunneling current can be derived as

\[
I = \frac{2\pi e^2 V}{h} \sum_{\mu,\nu} |M_{\mu\nu}|^2 \delta(E_{\nu} - E_{\mu}) \delta(E_{\mu} - E_F)
\] (2.3)

Within this s-type wave function approximation for the tip, the tunneling current can finally be obtained as

\[
I \propto V \cdot n_t(E_F) \cdot exp(2\chi R) \cdot \sum_{\nu} |\psi_{\nu}(r_0)|^2 \delta(E_{\nu} - E_F)
\] (2.4)

where \( \chi = (2m \phi)/\hbar \) and \( \phi \) represent the decay rate of the wave function and the local effective potential barrier height and \( n_t(E_F) \) is the density of states of the tip at the Fermi level. Also the surface local density of states (LDOS) at Fermi level \( E_F \), evaluated at the center of curvature can be written as

\[
n_s(E_F, r_0) = \sum_{\nu} |\psi_{\nu}(r_0)|^2 \delta(E_{\nu} - E_F)
\] (2.5)

Therefore, in case of STM images obtained in constant current mode at low bias voltage, the contour map of the surface is represented by the LDOS at \( E_F \) evaluated at the center of the curvature of the tip. As the wave function decays exponentially in the z direction normal to the surface it can be written as

\[
\psi_{\nu}(r) \propto exp(-\chi z)
\] (2.6)

and at the center of the local tip-sphere it can be found that

\[
|\psi_{\nu}(r_0)|^2 \propto exp[-2\chi(s + R)]
\] (2.7)
2.3. Low energy electron diffraction (LEED)

where $s$ is the constant distance between the tip and sample surface (constant current mode) and hence the tunneling current becomes exponentially dependent on the gap distance $s$ as can be expressed as

$$I \propto \exp(-2\chi s)$$ (2.8)

Anyway, this simple interpretation of the tunneling current given by Tersoff and Hamann for constant current imaging is no longer valid for high bias voltages and tip wave functions with angular dependence, e.g. for semiconductors or d-metals.

2.3 Low energy electron diffraction (LEED)

Low energy electron diffraction (LEED) is a well established technique for the investigation of the periodicity of solid surfaces. By the principle of the wave-particle duality, an electron beam may be equally regarded as a succession of electron waves incidents normally on the sample surface. These waves will be scattered by regions of highly localized electron density, i.e. the surface atoms, which can therefore be considered to act as point scatterers. More precisely, the scattering mechanism is scattering at an electrostatic potential $V(\vec{r})$ which is continuous in space. Electrons of kinetic energies in the range of 10 eV to 300 eV have de Broglie wavelengths $\lambda = h/p$ comparable to interatomic distances,

$$\lambda = h/p = h/(2 \cdot m \cdot e \cdot V)^{1/2}$$ (2.9)

where $V$ is the acceleration voltage. This is a necessary condition for diffraction effects associated with atomic structures to be observed. The sample itself has to be a single crystal with a well-ordered surface structure in order to generate a back-scattered electron diffraction pattern. If the crystalline surface is illuminated with a mono-energetic electron beam of low energy, a well defined diffraction pattern of elastically scattered electrons can be observed. As a result of the short mean free path of electrons in this energy region, this scattering process only probes the surface layers of crystals. If only the uppermost atomic layer is involved in the scattering process, it can be shown that the diffraction spots appear when the parallel components of the wave vectors of incoming ($\vec{k}_0$) and outgoing ($\vec{k}_{out}$) electron waves fulfil Laue’s diffraction condition

$$\vec{k}_{out}|| - \vec{k}_0|| = G_{2D||}$$ (2.10)

where $G_{2D||}$ is a reciprocal mesh vector. Hence a constructive interference of the backscattered electrons scattering from the periodic lattice of the sample surface occurs and the diffraction pattern represents the reciprocal lattice vectors of the surface [18].

The basic principle of a typical LEED experiment and an Omicron spectra LEED system is shown in figure 5.6. A filament emits electrons which are accelerated by a variable bias voltage and focussed on the sample surface with deflection electrodes. The lower energy secondary electrons are removed by energy-filtering grids placed in front of the fluorescent screen. Finally, the electrons passing the grids are accelerated onto the fluorescent screen, where they are converted into visible intensity variations [18]. The sample is placed at
2.4 X-ray photoelectron spectroscopy (XPS)

Electrons and photons are the most easily available probes to investigate matter. Hence, many spectroscopic techniques involve the use of these two types of particles. Photoelectron spectroscopy (PES) is one of the spectroscopic techniques that utilizes photoionization and energy-dispersive analysis of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample. In the PES experiment, photons (ultraviolet (UV), X-rays) are the incoming particles and electrons are the outgoing particles to be analyzed. The working principle of PES is based on the photoelectric effect, which was detected by Hertz in 1887. In 1905, Einstein proposed the concept of the "photon" and explained the photoelectric effect through the quantum nature of light using the following simple formula:

\[ E_k = h \nu - E_B - W_O, \]  

where \( E_k \) is the kinetic energy of the photoelectron, \( h \nu \) is the photon energy, \( E_B \) is the
2.5. High energy electron microscopy

binding energy of the electron (with respect to the Fermi level) and $W_O$ is the work function of the material. The emitted photoelectrons are detected and analyzed in terms of their kinetic energy. Small shifts in the element specific core or valence band energies signalize changes and can give detailed information about the chemical environment of the atoms. Different designs of electron energy analyzer exist but the preferred option for photoemission experiments is a concentric hemispherical energy analyzer, which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy. This design offers a high energy resolution together with a relatively high intensity.

![Figure 2.5: Schematic drawing (left) and view (right) of an XPS chamber at Foundation Institute of Material Science in Bremen](image)

Depending on the incoming photon energy range, when X-rays are used as a photon source, this method is traditionally called X-ray photoelectron spectroscopy or X-ray photoemission spectroscopy (XPS). Sometimes it is also referred to as electron spectroscopy for chemical analysis (ESCA). This method was developed in the mid 1960s by K. Siegbahn and he was awarded the Nobel Prize in 1981 for this work. The photon energy in XPS is usually more than 1000 eV. X-rays in this energy range can be obtained using the characteristic X-ray lines of the targets in X-ray tubes. The most commonly used target materials are Al and Mg, with $K_\alpha$ line energies of 1486.6 eV and 1253.6 eV, respectively. To a large extent, however, these photon sources are now being replaced by synchrotron radiation sources, which allow a continuous variation of the photon energy that cover the whole spectral range from the near-UV to the far X-ray regime. XPS is a method providing information of depths of typically a few monolayers and therefore offers a special instrument for surface sensitive chemical analysis of heterogeneous materials.

The essential parts of the experimental set-up are a monochromatic x-ray source, the sample contained in an ultra high vacuum (UHV) vessel to maintain clean surface conditions and an electron energy analyzer, as illustrated in Fig. 2.5. The XPS studies in this thesis were recorded partially at the Foundation Institute of Material Science (IWT) in Bremen and partially using the ESCA microscopy beamline at the ELETTRA synchrotron light source in Triest, Italy.

2.5 High energy electron microscopy

The magnification of light microscopes is restricted by the diffraction of the light waves and limited to a resolution of about 0.2 micrometers. In the early 1930’s this theoretical
Chapter 2. Instrumental methods

limit had already been reached. Due to the limitation of the resolving power by light microscopy, other sources of illumination with shorter wavelengths than visible light have been investigated. Early experiments using X-rays of extremely short wavelengths were not pursued further because of the inability to focus these rays. The first breakthrough in this development of the electron microscope came when Louis de Broglie advanced his theory that the electron has a dual nature with characteristics of a particle or a wave. The demonstration by Busch that a beam of electrons could be focussed by magnetic or electric fields, opened the way for the development of the first electron microscope.

The electron microscope is a scientific instrument having a working principle very similar to the optical/light microscope except that it uses a beam of highly energetic electrons instead of light waves to examine objects on a very fine scale. By taking the advantage of very short wave lengths of rapidly moving electrons and the ability to focus them by magnetic or electric fields, it improves the image magnification by $10^4$ times higher compared to the optical microscope. The resolution is primarily limited by the spherical and chromatic aberrations. There are several steps involved in all types of electron microscopy which are as follows. Firstly a monochromatic beam of electrons is formed using an electron gun. These electrons are accelerated towards the specimen using a high voltage. The beam of electrons is confined into a thin, focussed beam using metal apertures and magnetic lenses. Secondly, this focussed/parallel beam interacts with the sample, which ultimately affects the electron beam by loss, scattering, absorption of electrons, etc. Finally, the interactions with the specimen are detected and transformed into an image.

In electron microscopy, where the electron beam interacts with the specimen, there are several interaction paths which can occur as shown in figure 2.6. In case of thicker samples, the upper part of the interactions (secondary electrons, Auger electrons, backscattered electrons and X-rays) is used to investigate using a specialized way called scanning electron microscopy (SEM), whereas for thinner specimens, the transmitted part of the interaction (non-scattered, elastically-scattered and inelastically-scattered electrons) can be utilized in a different type of microscopy called transmission electron microscopy (TEM). Details of the two different types of EMs are described below.
2.5. Transmission electron microscopy (TEM)

The Transmission Electron Microscope (TEM) is the first type of electron microscope that had been developed in 1931 by Max Knoll and Ernst Ruska [19]. For this achievement, Ernst Ruska was also awarded the Nobel Prize in 1986. Its working principle is similar to the light transmission microscope (LTM) except that a beam of electrons is used instead of light for imaging. As the transmitted part of the interacting electron beam is used here (2.6), the materials for TEM must be specially prepared to thicknesses typically of the order of a few hundred atomic layers, which allow electrons to transmit through the sample. During transmission, electrons interact with matter and the scattering process occurs. The elastically scattered electrons keep their energy and only change the direction which is similar to the Rutherford scattering experiment, where $\alpha$-particles were used. This scattering process is highly dependent on the atomic mass of the scatterer. Hence a mass dependent contrast can be obtained after proper imaging which gives the information about the different materials. In case of a crystalline specimen the scattering process can lead to the formation of diffraction patterns following the Bragg reflection of the electrons wave functions during transmission. Details of the diffraction pattern and switch-over to the imaging mode is discussed below.

![Figure 2.7: Schematic drawing of the two basic operations of the transmission electron microscopy system involving (A) diffraction patterns and (B) image formation [20].](image)

The electron gun produces a stream of monochromatic electrons. This stream is transformed into a small, thin, focussed/parallel coherent beam by the use of condenser lenses. The beam is restricted by the condenser aperture (usually user selectable), suppressing high angle electrons (those far from the optic axis). The beam strikes the specimen and parts of it are transmitted. A schematic drawing of the TEM electron optics is shown in figure 2.7, which shows the two basic operations of the transmission electron microscopy system: (A) the diffraction and (B) the image formation, after the specimen is illuminated.
Chapter 2. Instrumental methods

by a parallel beam of electrons. The transmitted part of it is focused by the objective lens. Optional objective and selected area diffraction (SAD) apertures can restrict the beam. The diffraction pattern is formed in the back focal plane of the objective lens which represent the image of the reciprocal lattice space. The selected area aperture is introduced into the image plane of the objective lens which virtually reduces the illuminated area of the specimen contributing to the diffraction and enables to examine the periodic diffraction of electrons from the lattice plane. In general, the diffraction pattern contains the bright specular reflected (00) beam at the center and the other diffracted beams of higher orders. For direct space imaging in TEM, either the central (00) beam is selected for imaging and the mode is called ”bright field” image or other higher order diffracted beam/beams is/are used for imaging in the ”dark field” mode. The selection of the diffracted beams to form the image is done by introducing an objective aperture within the back focal plane of the objective lens. The objective aperture enhances the contrast by blocking out all the diffraction patterns except the selected one. The selection of the diffraction spot can be obtained either by moving the objective aperture or tilting the incident electron beam. The diffraction pattern/image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The beam finally strikes the phosphorus image screen and light is generated, allowing the user to see the image. In this way TEM can reveal the finest details of internal structures. Recently, high voltage/high resolution TEMs, utilizing electron energies from 200 keV to 1 MeV, have permitted the routine imaging of atomic structures with a lateral resolution of 1.9 Å and the resolution is mainly restricted by spherical aberration.

In the field of experimental semiconductor physics, TEM is a very powerful tool gaining an increasing significance for the understanding of a variety of phenomena such as crystal structure, interfaces, defects, inclusions, etc. Whereas most of the other microscopic techniques are restricted to the surface, TEM measurement offers the possibility of an insight into the volume material. Phase determination as well as defect and precipitate orientation are typical outcomes of conventional TEM experiments. Microstructural characterization including unit cell periodicity can be readily determined using various combinations of imaging and electron diffraction techniques. TEM results presented here were performed using a commercial CM20 Phillips microscope with a beam energy up to 200 kV.

2.5.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most versatile and widely used techniques of modern science which probes the surface using a scanning electron beam. Although TEM had been successfully developed in 1931, the first and true SEM was developed and described by Zworykin et al. in 1942 [21]. Its late development was due to the electronics involved in ”scanning” the beam of electrons across the sample. SEM is working the same way as the reflecting light microscopes and yields information about the topography/morphology, material composition, crystal structures etc. In this case of electron beam interactions with matter, only the upper part of the interacted beams are utilized for the investigation (fig. 2.6). Therefore, the sample thickness needs not to be
2.5. High energy electron microscopy

specific and the preparation is non-destructive in contrast to the TEM sample preparation. The typical energy of the scanning electron beam ranges from 0.5 keV to 30 keV and a lateral resolution of nominally 1 nm can be achieved with SEM.

![Figure 2.8: Schematic drawing of a scanning electron microscope [22].](image)

Basically SEM is working by scanning a focused electron probe across a specimen and detecting the emitted secondary electrons. An electron gun [at the top] emits a beam of high energy electrons in vacuum which travels downward through a series of magnetic lenses. The beam is collimated by an electromagnetic condenser lens and focused to a very fine spot by an objective lens. Near the bottom, a set of electromagnetic deflection coils (scanning coils) move the focused beam back and forth across the specimen to scan over the surface. As the electron beam hits each spot on the sample, secondary electrons are generated. The surface imaging is obtained by collecting these secondary electrons. They are detected by a scintillation material that produces flashes of visible light when hit by the electrons. The light flashes are then detected and amplified by a photomultiplier tube. The final image is built up from the number of electrons emitted from each spot on the sample. For SEM imaging, the sample surface has to be conducting to avoid charging. In case of non-conducting samples usually a very thin layer of gold is sputtered on the surface prior to the imaging. Figure 2.8 shows a schematic drawing of the scanning electron microscope.

There are various possibilities to use the SEM, designed for specific purposes ranging from routine morphological studies to high-speed compositional analysis. Monitoring the secondary electrons across a specimen, high resolution images of the morphology or topography of a specimen can be obtained. Compositional analysis of a material may also be obtained by monitoring the energy dispersive analysis of secondary X-rays (EDAX). SEM results presented within this thesis were recorded using a commercial instrument from FEI Nova NanoLab combined with focused ion beam.
2.6 Spectroscopic photoemission and low energy electron microscopy (SPELEEM)

The spectroscopic photoemission and low energy electron microscopy (SPELEEM) is a unique multi-method instrument which combines microscopy and spectroscopy with high spatial and energy resolution, respectively, with low energy electron diffraction (LEED) and energy-selected photoelectron angular distribution from selected small areas. With this single instrument it is possible to investigate the structure and the morphology by LEEM (low energy electron microscopy) / LEED and the local chemical composition and chemical state by XPEEM (X-ray photoemission electron microscopy) on the same area of the surface down to a few nanometer scale. This experimental technique is of particular importance when the chemical identification of the structural features is necessary for the understanding of a surface or thin film process. LEEM can be easily combined with LEED, photoemission electron microscopy (PEEM) and other emission microscopies which allow a large variety of in-situ studies over a wide temperature range. This combination of imaging, diffraction and spectroscopy modes is presently possible with the instrument at the "Nanospectroscopy" beamline at the synchrotron radiation light source ELETTRA in Trieste, Italy, operating successfully since 1997. An improved version of this microscope has been installed in 2000 which can now be used alternately for XPEEM, LEEM, LEED, MEM (mirror electron microscopy) and other imaging modes, depending upon the particular problem studied.

The X-ray light is provided by a third generation electron storage ring operating at about 2.0 GeV and at 200 mA beam current and the covered energy range is 50-1000 eV for this beamline. The typical spatial resolution for the ELMITEC LEEM instrument at the "Nanospectroscopy" beamline is about 15 nm, whereas for XPEEM it is about 40 nm and with energy peak shifts of less than 0.2 eV. Details of the SPELEEM instrumentation at ELETTRA can be found in the reference [23]. Figure 2.9 shows a schematic view of the SPELEEM optics (top) and the microscope (bottom).

2.6.1 Low energy electron microscopy (LEEM)

Using the wave properties of the electron, in 1962 [24], Ernst Bauer had invented a new technique for surface imaging known as low energy electron microscopy (LEEM). Although it makes use of electron lenses as in conventional high energy electron microscopes it differs from them in using electrons that have a very low energy of some eV up to \(~100\) eV only when they interact with the surface. This difference makes this method very much surface-sensitive and the probing depth can be tuned by varying the electron energy. The imaging contrast is mainly produced by the low energy electron diffraction process. The resolution is determined mainly by the chromatic and spherical aberration of the decelerating/accelerating field in front of the specimen. The theoretical limit of the resolution is about 4 nm at a beam energy of 10 eV. One of the greatest advantages of this method is the rapid image acquisition that allows the study of surface processes such as adsorption, phase transitions, chemical reactions, thin film growth etc. in real time.
In LEEM, collimated beams of high energy electrons are generated in the similar way as in high energy electron microscopy. This beam is then deflected by the magnetic beam separator and decelerated in front of the specimen from 10-20 keV to a kinetic energy of typically ranging from 0 to 15 eV using a cathode lens. Then the slowly moving electrons are reflected from the surface providing information about the low energy electron interaction with the surface atoms. Afterwards, the reflected electrons are accelerated to 10-20 keV (operated at 18 keV) again, deflected by the beam separator and separated from the incident beam and then moved into the image column. Finally it is transferred via the energy analyzer into the image on the screen (micro channel plate), as shown in figure 2.9. The (real space) imaging or (reciprocal space) diffraction pattern is obtained in the similar way as in TEM except using the reflected electron beam instead of the transmitted beam. The reflection of the low energy electrons at the surface gives a LEED pattern which is imaged by the objective lens into its back focal plane and after passing a micro channel plate (MCP) can be imaged on the phosphorous screen by changing the excitation of the intermediate lens. The beam separator and the transfer lens transfer...
the LEED pattern into the field lens, in which a so-called contrast aperture is inserted in order to optimize resolution and contrast. By selecting the proper mode for imaging, the "bright" and "dark" field image can be obtained which is similar to the TEM imaging. The contrast in the LEEM represents the topography and crystal structure of the surface. In addition to the diffraction contrast, interference contrast is available which allows one to image surface steps and thickness differences in thin films with atomic depth sensitivity. In reference [25] the details of the LEEM imaging and information extraction is discussed.

The combination of LEEM with LEED is one of the advantages of LEEM over other cathode lens imaging methods such as PEEM. The possibilities of LEED are greatly enhanced in a LEEM instrument. In many cases a characteristic LEED pattern can be obtained from a small surface feature (one micron in diameter or less) and its crystal structure, orientation, shape and the composition can be identified by this selected area LEED. When compared to a standard LEED system, LEED in a LEEM instrument has the advantage that the positions of the LEED spots on a flat surface do not change with energy. This makes it easy to take, for example, $I$(intensity) versus $V$(voltage) curves and to identify facets. Other advantages are that the (00) beam intensity can be measured at normal incidence and the LEED pattern can be studied from 0 eV upwards. Detailed information on the basics of LEEM optics, instrumentation and its various modes of operation with applications have been reported by E. Bauer [25, 26].

2.6.2 X-ray photoemission electron microscopy (XPEEM)

One basic instrumental feature of LEEM, the cathode lens, provides the possibility of combining LEEM with all forms of emission microscopy, foremost photoelectron emission microscopy (PEEM) [27]. For PEEM measurements, samples need not to be crystalline. The increasing availability and brightness of synchrotron radiation has extended PEEM into the photon energy range up to 1000 eV which is called X-ray (generated) photoemission electron microscopy (XPEEM) [23, 27]. The high brightness of third generation synchrotron radiation sources has opened the door to chemical and magnetic surface imaging using XPEEM with resolutions in 40 nm range and a chemical shift sensitivity of a few tenths of an eV, provided the instrument is equipped with an imaging energy filter. The element-selective magnetic imaging can also be done by circularly and linearly polarized synchrotron light, which makes use of circular and linear magnetic dichroism and has successfully been applied in a LEEM instrument. In this imaging method the photon-excited secondary electrons are used for imaging so that no energy filter is required.

XPEEM is an attractive method currently being installed in many synchrotron sources such as Elettra Light Source (Italy), Swiss Light Source (Switzerland), Diamond Light Source (UK) and the Brookhaven National Laboratory (USA). In XPEEM, the surface is illuminated by a monochromatic beam of soft X-rays and as a result electrons emit from the surface. The kinetic energy of the emitted electrons ranges from zero up to the photon energy (neglecting the work function). Electrons within a narrow energy window of as low as 0.5 eV at a pass energy of 1800 eV are selected for imaging using an electron energy analyzer which on the one hand reduces chromatic aberration effects and on the other hand gives the possibility of imaging with selected core level electrons.
The energy window can be set between less than 0.5 eV and a few eV by varying the adjustable slit in the dispersive plane. Even smaller energy windows can be used by selecting a lower pass energy which, however, results in a decrease of the intensity and diminishes the spatial resolution. Minute details of the microscope settings and imaging of SPELEEM at ELETTRA have been discussed in reference [23]. By selecting kinetic energies corresponding to core levels, images reveal pure element contrast. Chemical peak shifts can be used to map the chemical state of elements. In order to obtain the full spectroscopic information about an area of interest, a series of images is collected with different energy spectra.

2.7 ESCA microscopy

The 'ESCA microscopy' beamline at the ELETTRA synchrotron light source allows chemically surface sensitive measurements with high spatial resolution. The working principle of ESCA microscopy is someway similar to XPEEM, but the scanning ability of the sample offers imaging over a larger scan area. In general, it works with a relatively higher energy range and at 400 mA maximum beam current. In addition, high resolution XPS spectra of a selected area can be obtained. A lateral resolution of about 100 nm and an energy sensitivity within 400 meV have been achieved. The insertion device is a 81 period undulator with a 5.6 cm period divided in three sections. The X-ray source covers an energy range of 200-1400 eV and is optimized for 400-700 eV. A variable angle spherical grating monochromator with fixed entrance and exit slits operates in the photon energy range from 350 to 650 eV using one grating with 600 grooves/mm. The beam is focused by a Fresnel zone plate which is used to demagnify the source into a microprobe. A schematic of the microscope optics and the beamline is shown in figure 2.10.

The experimental apparatus allows to carry out a manifold of experiments, aiming at quantitative and qualitative chemical characterizations of morphologically complex natural and fabricated materials. It also probes the chemical reactions and mass transport processes leading to lateral changes in composition, morphology and electronic properties of materials.

The experimental station at the ESCA microscopy beamline at Elettra consists of different UHV coupled chambers such as scanning photo-electron microscopy (SPEM), sample preparation and characterization and load lock for sample insertion. The SPEM is exclusively used for the X-ray photoelectron (XPS) microscopy. The sample positioning and scanning is controlled by a combination of mechanical stepper motors (1µm) and piezo-driven motors (nm). A hemispherical energy analyzer of 100 mm with 48 channels of a micro channel plate with a striped anode is used to have an energy resolution of 50 meV. The sample preparation chamber is equipped with Auger electron spectroscopy (AES), LEED and PEEM facilities. Both the microscope and the preparation chamber exhibit a ultra high vacuum (UHV) with a base pressure of about $10^{-10}$ mbar and are interconnected with an in-situ transfer system. The details of the experimental instrumentation of the ESCA microscopy beamline have been discussed in references [28, 29].
Chapter 2. Instrumental methods

2.8 Molecular beam epitaxy (MBE)

Growth of thin films under ultra high vacuum (UHV) conditions is of high interest as it allows to prepare clean surfaces by evaporation and condensation processes. Depending on the substrate surface and on the evaporation conditions, epitaxial films can be amorphous, poly-crystalline or mono-crystalline. When the epitaxial films grows on a substrate of the same material, the film is called "homo-epitaxial"; alternatively, if it grows on a substrate of a different material, it is called "hetero-epitaxial". Moreover, MBE is not only applicable to the growth of epitaxial films but also to the preparation of adsorbate systems with high precise control.

The method of MBE is a specialized technique for controlled vacuum deposition with high material purity. The concept of MBE was first invented by Günther et al. in 1958 [31] and the first mono-crystalline films were achieved by Davey and Pankey in 1968 [32]. The MBE growth process takes place by the reaction of molecular beams of the constituent elements with a crystalline substrate surface held at a suitable substrate temperature under UHV conditions. The molecular beams are generated from sources contained in effusion cells, which are aimed towards the heated substrate. The flux intensity of each
evaporated beam is controlled by adjusting the temperature of its effusion cell. The substrate temperature provides sufficient thermal energy to the deposit for migration and dissociation over the surface to incorporate in preferred lattice sites and start growing. The elements, which are not incorporated to the growth can also be thermally desorbed. MBE growth is carried out under conditions far from the thermodynamic equilibrium, and is governed mainly by the kinetics of the surface processes occurring when the impinging beams react with the outermost atomic layer of the substrate crystal. This is in contrast to other epitaxial growth techniques, such as liquid phase epitaxy (LPE) processes which occur in the crystallizing phase surrounding the substrate [33]. The UHV environment during growth helps to maintain the high material purity and the various available in-situ characterization techniques make the MBE an excellent research tool. The photograph of the MBE growth and analysis chamber of the STM laboratory is shown in fig. 2.11.

2.9 Metal organic vapour phase epitaxy (MOVPE)

A different technique for crystal growth, based on the thermally activated chemical reaction of metal-organic molecules containing the metal of interest with other chemical gases, is called metal organic vapour phase epitaxy (MOVPE). The origin of MOVPE was first established in late 60’s by Manasevit et al. [34, 35], when MBE was the most preferable tool of choice for highest quality semiconductor structure production. Nowadays MOVPE is the main production tool for the growth-III nitrides. It is more stable and once the growth parameters are optimized, the reproducibility is ensured over longer periods of time than for MBE.

Generally, the metal-organic molecules of relatively high vapour pressure are transported to the substrate using some carrier gases such as H\textsubscript{2} and N\textsubscript{2}. The metal-organic molecules consist of methane or ethane as organic groups which are bonded to the metal atoms. The bonding between the metals and organic groups are weakest and break thermally apart well below the growth temperature, ensuring that the organic groups are not involved in the growth reaction. The substrate is kept at high temperature to induce the growth reaction. For lower growth temperatures the growth rate is limited by the kinetics of the
reaction, whereas for intermediate temperatures the reaction is sufficiently fast and the growth rate is limited by the diffusive transport across the boundary layer. In case of higher growth temperatures thermal desorption starts to dominate.

All the MOVPE grown GaN and InGaN samples studied within this thesis were grown in a commercial ‘Thomas Swan’ MOVPE system of the Semiconductor Epitaxy group of Prof. Hommel, within a 3×2” close-spaced showerhead reactor. Trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia (NH₃) were used as source materials for Ga, In and N, respectively. A simple example of the chemical reactions for GaN growth is shown in equation 2.12, although in practical, there are several multi-step decomposition processes. A photograph of the MOVPE growth system is shown in fig. 2.12.

\[
Ga(CH_3)_3 + NH_3 \rightleftharpoons GaN + 3CH_4
\]  

(2.12)

2.10 Nitrogen plasma sources

The nitrogen plasma source is of high importance in the semiconductor technology for the growth of III-nitrides (GaN, AlN, InN) and their alloys, silicon nitride, and other nitride materials as well as for doping (ZnSe), cleaning or etching processes. For the nitride growth, the most simple and cheapest chemical nitrogen precursor is ammonia (NH₃) which is widely used for the MOVPE growth of III-nitrides. But its high thermal stability significantly restricts the growth temperature as well as it introduces surface impurities for the molecular beam epitaxy (MBE). Additionally, the chemical reactivity of NH₃ may be another drawback to handle it. Hence, an alternative nitrogen source is required and the easiest one would be the pure nitrogen gas (N₂). As the molecular nitrogen is itself chemically inactive, some technique, such as glow discharge plasma formation, is required for the activation. A gas plasma at low pressure is an effective tool for the conversion of highly stable source gases such as N₂ to more active atomic and molecular species suitable for MBE growth.

In the plasma source, electrons acquire energy from an electric field and collide with gas molecules which causes excitation and ionization of the gas molecules. The reciprocal of the time constant with which the charged particles within a plasma (electrons and ions) can respond to the alternating electric field is called the ’plasma frequency’. There are
two very crucial parameters for plasma such as the plasma frequency for electrons ($\omega_e$) and that for ions ($\omega_i$). For a typical ac discharge, the driving frequency ($\omega$) is applied in between these two frequencies ($\omega_i < \omega < \omega_e$) [36]. Depending on the plasma frequency, basically two types of nitrogen plasma sources are available: (a) the radio frequency (rf) plasma source activated by a rf generator of the discharge frequency 13.56 MHz and (b) the electron cyclotron resonance (ECR) plasma source using a microwave frequency of 2.45 GHz.

2.10.1 Radio frequency (RF) plasma source

In case of a radio frequency (rf) plasma source, the driving frequency (13.56 MHz) $\omega$ has a typical value close to the plasma frequency of ions $\omega_i$ ($\omega_i \approx \omega < \omega_e$), where electrons oscillate in the high frequency field and ions feel mainly the time average field [36].

Figure 2.13: Schematic illustration of radio frequency plasma formed within the PBN plasma bulb (left) and the Epi, Uni-Bulb rf-plasma source with matching / control unit (right) used in this study [37].

Figure 2.13(top) illustrates the principle of a radio frequency (rf) plasma discharge. The rf power, usually at a frequency of 13.56 MHz, is applied through a matching network, which is inductively coupled by a coaxial rf coil to the plasma chamber.

A commercial Uni-Bulb plasma cell from Applied Epi (presently Veeco), was employed for this study as a rf-plasma source to generate an active nitrogen flux (fig.2.13, bottom) [37,38]. The dual coaxial rf coil with integral water cooling design allows an effective heat dissipation and the possibility for more coils to be confined in a smaller area to enhance the power coupling up to 600W. A leak valve is used to control the flow rate of pure N$_2$ gas to the plasma bulb via a single metal tube. The PBN (pyrolytic boron nitride) plasma bulb and gas inlet prevent leakage of inactive nitrogen, providing a consistent gas flow and a minimized chamber background pressure. The plasma is confined within the PBN bulb due to the higher local gas pressure. Then the nitrogen atoms created by the plasma source come out through the pin holes of the aperture and are directed towards the substrate because of the pressure difference between the plasma cell and the growth chamber.

The design of the source promotes efficient electron-nitrogen collisions and results in the plasma stability and reproducibility which provides about 70% of atomic nitrogen,
25-30% of N$_2^+$-ions and 0.1% of N$^+$-ions at the beam outlet of the PBN bulb (front of the aperture) [38]. The operating pressure of our plasma chamber in fig. 2.11 (MBE growth chamber pressure is one order lower) with a turbo-molecular pumping system was maintained within the range of 5×10$^5$ to 5×10$^6$ mbar.

### 2.10.2 Electron cyclotron resonance (ECR) plasma source

For the electron cyclotron resonance (ECR) plasma source with the microwave discharge, the driving frequency (2.45 GHz) $\omega$ approaches the plasma frequency of the electron $\omega_e$ ($\omega_i \ll \omega \approx \omega_e$) [36]. In this case, the electrons also cannot fully follow the time varying field and get partially trapped within the plasma, resulting in an increase in plasma density (charged particles within plasma) with frequency.

![Figure 2.14: Schematic of the enhancement of plasma density using a magnetic quadrupole (left) and drawing of an ECR plasma source from Tectra (right), employed in this study [14] (direction of the plasma beam is normal to the page).](image)

As an alternative source of active nitrogen, an ECR plasma source from Tectra is also used for this study [39, 40]. Here, the driving frequency is generated by a microwave magnetron and coupled through a resonant coupler into a coaxial feed-through (antenna). This antenna guides the microwaves into the vacuum within the boron nitride discharge chamber, where the plasma is ignited and the microwaves absorbed. Similar to the rf-source, the plasma is also confined within the BN discharge chamber and directed towards the substrate through the pin holes of the aperture. In addition, the plasma density is also enhanced by the magnetic quadrupole (QP) arranged around the discharge chamber. This QP magnets generate a 87 mT magnetic field inside the discharge tube, where electrons in a 2.45 GHz microwave field undergo an electron cyclotron resonance [40]. This forces the electron to move in a spiral way and hence greatly enhances their path length. Therefore, the probability of further collisions of electrons with other molecules is increased and results in an enhanced plasma density. A schematic drawing of the plasma discharge and the Tectra ECR plasma source is shown in figure 2.14. The operating pressure for the ECR plasma chamber was maintained about one order higher than the rf-source and ranging from 3×10$^4$ to 7×10$^5$ mbar. The instrumentation of both rf and ECR plasma source is also discussed elsewhere [14].
2.11 Evaporator

For the MBE system, any kind of deposition regarding epitaxial growth of semiconductor films or adsorbates on a crystalline surface under UHV conditions, requires the use of several techniques to evaporate material from the condensed phase. The evaporation can be achieved by direct or indirect heating of the material at high temperatures. However, evaporation from a free surface is isotropic, termed as Langmuir evaporation, where a very small fraction of the evaporant vapour molecules reach the object surface. In 1909, Knudsen invented a technique to enhance it and the corresponding evaporation source is called a Knudsen cell.

2.11.1 Knudsen/effusion cell

In a Knudsen cell, a somewhat directional evaporation is achieved using the technique of evaporation through an orifice by which the area of the orifice appears as an evaporation source. The large mean free path of the vapour molecules under UHV conditions helps to maintain the direction and appears to the object surface without any collision. An evaporator system needs a water cooling system for the dissipation of heat generated at the crucible and a mechanical shutter which allows the evaporant flux to be rapidly modulated. In addition, a thickness monitor can be used to get a systematic idea on the flux of evaporant vapour molecules. The evaporation from the effusion cell can be achieved by either resistive or radiative heating evaporation or electron beam (e-beam) evaporation. The resistive heating evaporation is basically limited to evaporate material of high vapour pressure and lower melting point. The heating is obtained by passing a relatively high current through the filament made of tungsten, tantalum or molybdenum wire.

![Schematic drawing of an electron beam evaporator](image)

2.11.2 E-beam evaporator

For the evaporation of materials with a low vapour pressure or a high melting point, an electron beam evaporator is required, where high temperatures can be achieved by local bombardment of the evaporant material with high energy electrons. The electron beam evaporator can also be used to achieve higher growth rates. It is used especially, if ultra-high purity evaporants are required. A relatively high voltage is applied to the target
material up to a few kilovolts (kV). Electrons are generated from a resistive heating filament. These electrons are accelerated by the high voltage and collide with the evaporant material, which results in a local generation of heat and maintains the high purity of the evaporant. A schematic drawing of an electron beam evaporator is shown in figure 2.15.

Within this thesis, most of the depositions were carried out using an Omicron single (EFM 3,4) and triple (Triple EFM) e-beam evaporator for different materials. The flux was measured using an integrated flux monitor. A very low current (∼nA) originated from the evaporant ions existing within the evaporation beam is measured by the flux monitor. In some cases, a home build radiative heating evaporator was also used and the flux was measured by a quartz microbalance thickness monitor.

Bibliography

Bibliography


[30] Homepage of ELETTRA synchrotron light source, Trieste, Italy: www.elettra.trieste.it


Chapter 3

Surface reconstructions and nano-patterning of Ga/Si(111) for Ge-epitaxy

3.1 Abstract

The structure and formation of temperature induced self-organized 2D nano-patterns and the phase separation of the Ga/Si(111) system at submonolayer Ga coverage have been investigated by scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM). Depending on the Ga deposit, two types of phase separation between the domain areas to the initial domain boundary and the step edge regions of the Si(111)-7×7 are observed. The amount of 1/3 ML Ga deposit seems to play a key role for surface reconstructions during phase transition. For Ga coverages below 1/3 ML, Si(111)-7×7 reconstructed domain areas with specific shape and orientation are surrounded by $\sqrt{3} \times \sqrt{3}$-Ga structures at the domain boundary and step edge regions of the initial Si(111)-7×7. If the Ga coverage exceeds 1/3 ML, the reconstructions change and a $\sqrt{3} \times \sqrt{3}$-Ga structure is found within domains surrounded by a 6.3×6.3-Ga structure at the initial domain boundary and the step edge regions of the Si(111)-7×7. For Ga coverages below 1/3 ML, the shape and size of the Ga/Si(111) surface nano-pattern can be controlled by the choice of surface miscut orientation and miscut angle. These patterned substrates have been used as a template for the subsequent growth of Ge and as a result selective nucleation and alignment of 3D Ge islands is achieved. The findings are explained in terms of surface stress, surface free energy, miscut direction, surface diffusion and energetics. Some parts of the result presented here have already been published [1–4]
3.2 Introduction

The termination of the bulk crystals of covalent materials such as semiconductors, by a free surface, leads to the formation of surface reconstructions in order to achieve the energetically most favourable configuration for the surface. Usually this is achieved if the number of dangling bonds is minimized. The surface reconstructions of semiconductors can be changed by adsorption of foreign atoms. In order to understand growth phenomena it is necessary to identify the relevant reconstructions of the surface and their impacts on the growth. Scanning tunneling microscopy (STM) is a very useful tool for the direct observation of the surface structure with atomic resolution for metallic and semiconducting surfaces. The ability of probing the surface structure at variable temperatures helps to determine temperature induced phase transitions and surface reconstructions directly.

The nanometer scale patterning of semiconductor surfaces is one of the most challenging tasks in modern semiconductor research. Adsorption or rearrangement of adsorbates on a semiconductor surface lead to variations in the surface chemical and physical properties. In general, adsorbate terminated semiconductor surfaces are chemically less active than the clean surface because of the termination of dangling bonds. These changes in the surface chemical states can highly influence the subsequent growth process, which may result in a selective adsorption or growth of nanometer scale structures such as nano-dots or nano-wires. Different routes have been taken towards surface patterning: single atom manipulation [5, 6], electron or ion beam lithography [7, 8] and self-assembly [9, 10] of surface patterns. Self-assembly or self-organizing processes are especially promising with respect to technological applications as they offer the possibility to open the gate towards massive parallel fabrication of device structures. One of the main mechanisms behind self-organized surface nano-patterning is the reduction of surface stress in combination with the minimization of the total surface free energy by the adsorbate.

3.2.1 Si(111)-7×7 surface

Since the first LEED observation that the annealed Si(111) surface reconstructs with a 7×7 surface cell [11], a large amount of effort has been expended trying to understand this important surface. The nature of the Si(111)-7×7 surface reconstruction itself has been the subject of intense study for more than 30 years and the role of STM was very important to resolve this problem. In the past several years, a variety of experimental techniques have been employed and there were various proposed structural models to study this 7×7 surface reconstruction. But the most widely acceptable dimer-atom-stacking-fault (DAS) model was first introduced by Takayanagi et al. [12, 13] in 1985 derived from the transmission electron diffraction (TED) measurements which can explain the atomic structure correctly. The DAS model for the 7×7 unit cell is shown in figure 3.1(a). In the Takayanagi model, there are two triangular subunits each surrounded by 9 dimers. In addition there is a stacking fault in one of these triangles (right triangle) called as faulted half, whereas the other triangle is referred to as unfaulted half of the unit cell, respectively. The top layer is composed of 12 Si adatoms and 6 triply coordinated Si rest atoms. At the corner of the unit cell there are vacancies usually referred to as corner holes. It is assumed
that the surface reconstructions are usually formed to reduce the total surface stress. But in case of the Si(111) surface, the surface chemical energy plays the most crucial role behind the formation of $7 \times 7$ reconstructions. The most important chemical effect of this reconstruction is a severe reduction in the number of surface dangling bonds. While an unreconstructed Si(111)-$1 \times 1$ surface exhibits 49 dangling bonds, only 19 are found in the $7 \times 7$ unit cell. Of these, 12 are located on the adatoms, six on the rest atoms and one on the atom at the bottom of the corner hole. It has been reported that the Si(111)-$7 \times 7$ surface exhibits a tensile stress. Atomically resolved empty and filled state STM images of Si(111)-$7 \times 7$ surface are shown in figure 3.1(b). In both imaging conditions, each half of the unit cell contains six adatoms but in case of the filled state imaging the adatoms of the faulted halves appear brighter than those of the unfauluted halves as depicted in 3.1(b).

![Figure 3.1: (a) Dimer adatom stacking fault (DAS) structural model (top view) for the Si(111)-$7 \times 7$ surface reconstruction according to ref. [12], (b) Atomically resolved STM images of Si(111)-$7 \times 7$ surface reconstructions with empty and filled state imaging conditions, respectively.](image)

**Phase transition**

After flashing the sample at a high temperature (~1200°C) and subsequent cooling down at about 830°C, the phase transition of Si(111) between $1 \times 1$ to $7 \times 7$ occurs. In figure 3.2, LEEM images of various stages of the Si(111) surface during the phase transition from $1 \times 1$ to $7 \times 7$ reconstruction are shown. The Si(111) surface miscut angle is about 0.02° along the [112] crystal direction. The nucleation of the $7 \times 7$ phase starts at the step edges (runs upper left to lower right). In fig. 3.2(a), the initial nucleation of the $7 \times 7$ reconstruction appears as white parallel lines. Slowly these structures flow over the terrace area and $7 \times 7$-domains of triangular shape are formed, facing away from the steps towards the higher terrace, as can be seen in fig. 3.2(b). Towards the end of the phase transition, $7 \times 7$ domains meet each other and form the Si(111)-$7 \times 7$ domain boundaries.
Figure 3.2: LEEM images of the Si(111) surface during the progress of phase transition from $1\times1$ to $7\times7$ surface reconstruction from (a) starting, (b) intermediate to (c) completion. Field of view $5 \mu$m and electron energy of 11.5 eV. Bright area shows the $7\times7$ reconstruction and grey the $1\times1$, respectively.

which can be seen as dark lines (running more or less perpendicular to surface steps) in fig. 3.2(c).

Figure 3.3: STM images of the Si(111) surface of $7\times7$ domains separated by domain boundaries (a) surface overview ($750\times750$ nm$^2$) and (b) closer look ($100\times100$ nm$^2$), respectively.

Domain boundary

As it has already been mentioned that during cooling down of the Si(111) surface the $7\times7$ domains start to nucleate at about 830°C and below this temperature the Si(111) surface exhibits domains of $7\times7$ with different sizes and shapes. Each of these are separated from the others through narrow lines of surface defects which are called domain boundaries. In figure 3.3(a) STM images of $7\times7$ domains separated by domain boundaries (faint white lines) are shown. A closer look of the $7\times7$ domains and the domain boundaries is presented in fig. 3.3(b). It can be noticed from the high resolution STM image that the rotational symmetry follows from one domain to the other domain across the domain boundary but, a translation shift of the atomic rows may occur across it.
3.2. Introduction

Surface steps

Apart from the domain boundaries, the other dominating surface defects which also termi-
minate the evolution of $7 \times 7$ domains are the surface steps. STM images of Si(111)-$7 \times 7$
surface steps are shown in figure 3.4. In general, steps are running parallel to each other
and the average separation \textit{i.e.}, the terrace width is reduced with the increase of the
miscut angle. In fig. 3.4(a) a large area STM image shows the Si(111) surface steps with
an average terrace width of about 200-300 nm. A closer look of a single surface step with
a corresponding line scan height profile is shown in fig. 3.4(b) and 3.4(c), respectively.
In the line scan profile, the Si(111) surface appears with a single bilayer step of about
3.2 Å height, which is in good agreement with the measured value of fig.3.4(c). Steps of
monolayer height are not feasible for the Si(111)-$7 \times 7$ surface.

![Figure 3.4](image1.png)

Figure 3.4: (a) Large scan area (1000×1000 nm$^2$) STM image of Si(111)-$7 \times 7$ shows the
surface steps separated by a terrace width of about 200-300 nm. (b) Closer look of the
surface step (45×45 nm$^2$) with line scan and (c) corresponding line scan height profile,
respectively.

3.2.2 Ga/Si(111)

In some of the recent works it is seen that most of the group-III metals form self-organized
ordered arrays of nano-clusters (\textit{i.e.}, magic clusters) on Si(111)-$7 \times 7$ surfaces during low
temperature deposition with sub-monolayer coverage [14–17]. These clusters with a spe-
cific number (magic number) of atoms exhibit an electronic as well as an atomic close-cell
structure and hence a remarkable stability. Annealing above certain temperatures, the
clusters break and form different surface reconstructions. Among the various surface
structures, the Ga induced reconstructions of the Si(111) surface are of particular interest
due to the existence of five different commensurate and incommensurate phases within
a narrow range of Ga coverage, as well as it’s use in the surfactant mediated epitaxial
(SME) growth of Ge [18,19]. Detailed studies of Ga induced magic clusters on Si(111)
surface have been done by Lai et al. [17,20–23]. Various reconstructions of Si(111)-Ga
surface have been studied by Golovchenko, Zegenhagen and coworkers [24–30].
In case of the Si(111)-Ga surface, at lower Ga coverages a structure consisting of so-called magic clusters is formed. For the magic clusters the nominal saturation coverage is approximately 0.24 ML, whereas for a slightly higher Ga coverage of about 0.33 ML, the $\sqrt{3} \times \sqrt{3}$ R30°-Ga reconstruction is observed. In case of further increase in Ga coverages different incommensurate structures of 6.3x6.3-Ga surface reconstruction start to appear. From 0.5 ML to 0.65 ML of Ga coverages, the surface exhibits a mixture of the $\sqrt{3} \times \sqrt{3}$-Ga and the γ-phase of the 6.3x6.3-Ga structures. For Ga coverages of about 0.7 to 0.8 ML, the surface shows the coexistence of the γ-phase and the β-phase of the incommensurate 6.3x6.3-Ga structure. For a Ga coverage between 0.8 ML and 1.0 ML the most Ga saturated ∆-phase of the 6.3x6.3-Ga structure is observed. In case of Ga coverage exceeding 1 ML, Ga droplets are formed on the surface.

**Self organized 2D nano-cluster:**’Magic cluster’

The initial stage of nucleation of Ga on Si(111) surface at room temperature (RT) leads to the formation of self organized nano-clusters. These nano-clusters always appear with a fixed number of Ga adatoms (6 atoms) which accounts for the nomenclature as ‘magic clusters’. They have an extraordinary thermal stability up to about 400°C as well. The magic cluster structure consists of 12 Ga adatoms per 7x7 unit cell, 6 Ga-atoms in the center of each half of the unit cell. The 7x7 unit cell basically is not affected by the magic clusters. A structure model of this magic cluster has been proposed by Lai *et al.*, [17] as shown in fig. 3.5(a). In case of RT Ga deposition on Si(111)-7x7, for up to 0.2 ML of Ga coverage the surface exhibits only magic clusters. For higher coverages Ga-islands start to appear.

![Figure 3.5: (a) Structural model (top view) for Ga induced magic clusters according to ref. [17], Ga(2a1s) indicates the Ga-atom bonded with two atop and one substrate Si atom, whereas Ga(1a2s) is the reverse. (b) Empty state STM images of Ga magic clusters at 300°C 50x50 nm² (inset shows a closer look of magic clusters).](image)
3.2. Introduction

An empty state STM image of magic clusters is presented in figure 3.5(b). The clusters are triangular in shape and form at the center of each half of the Si(111)-7×7 unit cell. Each of the faulted and the unfaulted half contains a triangular cluster with three Si atoms surrounded by six Ga atoms, among which the central three Ga atoms appear brighter than the outer three in the STM images as can be seen in the inset of fig. 3.5(b). These findings also support the structural model for the magic clusters.

√3 × √3-Ga R30° reconstruction

1/3 ML of Ga deposition at a higher temperature (>400°C) or post deposition annealing at 600°C after room temperature Ga deposition, leads to the formation of the most thermally stable (up to 670°C) Ga-induced surface reconstruction of Ga/Si(111) which is called √3 × √3 R30°-Ga. For the √3 × √3 R30°-Ga structure, the Ga adatoms occupy T_4 sites forming a tetrahedron with three neighbouring Si atoms, as can be seen in the schematic structural model in fig. 3.6(a). The surface lattice vector of the √3 × √3 structure is √3 times of the Si-1×1 unit lattice and also rotated by 30° with respect to the 1×1 lattice. Details of the structure and the position of the adatoms have been discussed elsewhere [28, 31]. Theoretical calculation predicts a large tensile stress for this reconstructed Ga/Si(111) surface. Atomically resolved empty state STM image of the √3 × √3-Ga R30° reconstruction is shown in figure 3.6(b), whereas a close-up view can be seen in 3.6(c).

6.3×6.3-Ga reconstruction

For Ga coverages above 1/3 ML and a low deposition/annealing temperature (T< 570°C), various incommensurate structures of 6.3×6.3-Ga reconstruction have been observed. In the case of the 6.3×6.3-Ga phases the top layer Si atoms are replaced by Ga atoms forming a Ga-Si double-layer structure [29, 30]. A schematic structural model of this structure has been shown in figure 3.7(a). In this structure, the surface Ga-Si bilayer is vertically compressed (compared to Si-Si bilayer) which results in a compressive surface stress of
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

this structure. The compressive stress in the double layer causes a lateral expansion and the transverse relaxation of the surface results in the formation of domains separated by light walls, i.e., regions with local lower Ga concentration. The resulting stress of the 6.3×6.3-Ga structure is partially reduced by the formation of domain boundaries of the incommensurate structure. In figure 3.7(b), an empty state STM image of the 6.3×6.3-Ga reconstruction has been presented. Depending on the local Ga concentration, different types of incommensurate structures such as (i) γ-phase, (ii) β-phase and (iii) Δ-phase of 6.3×6.3-Ga can be formed as discussed below [20].

![Structural model](image)

**Figure 3.7:** (a) Structural model (side views) of the 6.3×6.3-Ga reconstruction where Ga atoms take the substitutional sites. Empty state STM images of 6.3×6.3-Ga (b) 100×100 nm², closer look of (c) γ-phase 27×24 nm² and (d) β-phase 20×20 nm² of 6.3×6.3-Ga reconstructions, respectively.

### γ-phase of 6.3×6.3-Ga

The so called γ-phase of 6.3×6.3-Ga appears at a Ga coverage up to ∼0.7 ML and the STM image consists of hexagonally close-packed domains as shown in figure 3.7(c). In the case of the γ-phase the registration of the Ga-Si bilayer is unfaulted with respect to the underlying Si because such stacking is energetically favourable.

### β-phase of 6.3×6.3-Ga

In case of the β-phase the Ga coverage is about 0.7–0.8 ML and the β-phase STM image consists of a tiling of triangular domains as can be seen in figure 3.7(d). For the β-phase, only one half of the unit cell shows unfaulted stacking and for the other half a faulted stacking is found which is energetically unfavourable. In some sense, this observation suggests that the Ga coverage of the β-phase has reached ”saturation”. 

50
### 3.3. Experimental details

**3.3. Experimental details**

#### ∆-phase of 6.3×6.3-Ga

In addition to these two phases, another incommensurate structure for an "oversaturated" Ga coverage between 0.8 and 1 ML, appears on the surface, which is called ∆ phase for the shape of its domains. For the ∆-phase, the surface is saturated with Ga and the domains are a collection of isolated triangles in an alternating faulted and unfauluted stacking which are quasi-periodically distributed on the surface. As the Ga coverage for the ∆-phase is "oversaturated", a coexistence of Ga-droplets is also possible which might impede the STM studies.

#### 3.2.3 Ge on Si(111)

Nano-scale three-dimensional Ge islands on Si substrates are of great interest, mainly due to their potential for opto-electronic applications \[37, 38\]. A variety of approaches have been used in order to improve the uniformity and correlation of such islands. Most of them rely on pre-patterning of the Si substrates. Artificial structures can be formed, e.g. by direct manipulation via an AFM probe \[39\] or by conventional electron beam lithography and reactive ion etching processes \[40, 41\]. Although these techniques offer precise control and alignment of Ge islands, they are hardly scalable. In this respect, self-organizing processes are more promising. In most cases, self-organized alignment is achieved by a strain modulation of the substrate. This can be obtained by deposition of coherent Si\(_{1-x}\)Ge\(_x\) layers, which due to growth instabilities exhibit a surface undulation \[42\]. Alternatively, incoherent, i.e. dislocated Si\(_{1-x}\)Ge\(_x\) layers grown on Si(001) can be used \[43\]. A third approach exploits the interaction of vertically stacked layers of GeSi clusters, which leads to a vertical alignment of these clusters and through a self-organized ordering process \[44\] improve the lateral alignment and size distribution in the upper layers \[45\]. In all these cases, a periodic strain modulation of the substrate offers energetically preferential sites for Ge island nucleation and thus promotes island alignment. Surface energetics can also lead to an ordered growth of Ge islands, as has been observed on spontaneously facetted surfaces which can be obtained after Si buffer layer growth on vicinal Si(001) surfaces \[46\].

As far as ordering effects are concerned, less attention has been paid to the influence of surface kinetics. However, it is well known that smaller islands with higher density can be achieved when using Sb as a surfactant \[47, 48\], which is known to reduce the effective surface diffusion of Ge \[49\]. The adsorption of Ga on Si(111) is of specific interest because it has been shown that depending on Ga coverage, it can sharpen the island size distribution during subsequent Ge epitaxy \[19\].

#### 3.3 Experimental details

The experiments have been carried out in two parts. One part was performed in an ultra-high vacuum (UHV) chamber with a base pressure of 5×10\(^{-11}\) mbar equipped with a variable temperature scanning tunneling microscope (Omicron VT-STM) and low energy
electron diffraction (LEED) at Bremen University. Other part of the experiment was
performed using the spectroscopic photoemission and low energy electron microscope
(SPELEEM) at ELETTRA’s undulator beamline 1.2 [50, 51]. SPELEEM imaging was
done with assistance of beamline scientists Dr. A. Locatelli and Dr. S. Heun, as well as
the interpretation of these results were done in close collaboration with Dr. Th. Schmidt.

Highly oriented p-type silicon (111) wafers with an absolute miscut angle of about 0.02°
were used as substrates. After cleaning with methanol, the samples were loaded into the
UHV chamber. Then the samples were degassed for at least 12 hours at 600°C. A clean
7×7 surface reconstruction was prepared by 2–3 short flashes to 1200°C for up to 30 sec
to remove the native oxide. This preparation was checked by LEED and/or STM/LEEM,
and a clean 7×7 structure was observed reproducibly. Deposition of high purity Ga and
Ge was performed using an effusion cell heated by electron beam bombardment. Substrate
temperature was measured by an infrared pyrometer with an absolute uncertainty of ±
25°C.

For the STM experiments, Ga was deposited at room temperature and then the sample
was transferred to the STM. Here, the temperature of the sample was increased slowly
and stepwise by direct current heating in the STM head. At the same time, the STM
measurements were performed. During scanning, the heating current was maintained
constant. The heating current was increased in steps of 10 mA, with a maximum current
of 0.1 A corresponding to 400°C. At the onset of the phase transformation at about 400°C,
the temperature was kept constant and the surface was repeatedly scanned for a long time
to monitor the transition.

For the LEEM studies, Ga was deposited at elevated sample temperature, using e-beam
heating, during the LEEM imaging. The sample temperature was set close to the Ga
redesorption threshold (≈ 650°C for $\sqrt{3} \times \sqrt{3}$-Ga and 550°C for 6.3×6.3-Ga), i.e. very
close to thermodynamic equilibrium conditions.

The values of the absolute Ga coverages given here have been determined from the
area fractions of the $\sqrt{3} \times \sqrt{3}$-Ga structure appearing in the LEEM and STM images,
which is known to have a local coverage of 1/3 ML (1 ML=7.83×10^{14} atoms/cm^{2}). Ge
was deposited at a substrate temperature of about 450°C for both STM and LEEM
experiments.

Figure 3.8: LEED patterns of (a) Si(111)-7×7, (b) $\sqrt{3} \times \sqrt{3}$-Ga and (c) 6.3×6.3-Ga surface,
respectively.
3.4 Results and discussion

As mentioned earlier, the initial stage of nucleation of Ga on the Si(111) surface at room temperature leads to the formation of magic clusters. For Ga coverage above 0.3 ML, Ga-islands also appear on the surface. As these clusters are thermally stable only up to 400°C, Ga deposition above 400°C results in direct nucleation of \( \sqrt{3} \times \sqrt{3} \)-Ga instead of magic clusters. If the Ga coverage exceeds 0.33 ML, the other reconstruction of \( 6.3 \times 6.3 \)-Ga starts to nucleate. It has been observed that the \( 6.3 \times 6.3 \)-Ga structures are thermally stable up to 570°C and for higher temperatures only \( \sqrt{3} \times \sqrt{3} \)-Ga are found. Above 670°C, thermal desorption dominates over the nucleation process and Ga is not sticking anymore on Si(111). LEED patterns of Ga-induced various surface reconstructions of Si(111) are shown in figure 3.8.

![Figure 3.9: Empty state (−2 V) STM images of Ga on the Si(111) surface at 200°C after room temperature deposition of Ga with an increasing amount of deposit of (a) 0.2 ML , (b) 0.27 ML, (c) 0.34 ML and (d) 0.41 ML, respectively. Scan areas are about 100×100 nm².](image)

3.4.1 Increasing amount of Ga deposit

The dependence of the surface structure on the Ga deposit after room temperature Ga deposition is shown in figure 3.9. The STM images shown in figure 3.9 are recorded at a substrate temperature of 200°C. In case of Ga deposition of about 0.2 ML, the surface is partially covered by magic clusters. The density of the clusters is enhanced at the domain boundaries (fig. 3.9(a)) of the initial Si(111)-7×7 reconstruction, (To realize the position of the initial domain boundary of Si(111)-7×7 see fig. 3.10 and henceforth it will be referred to as domain boundary), whereas a larger density of vacancies in the magic cluster network is found in the center of the domains of the initial 7×7 reconstruction. (Henceforth it will be referred to as domain). If the Ga deposit is increased to about 0.27 ML, magic clusters are uniformly formed and mostly cover the Si(111) domains, while
excess Ga leads to Ga-induced island formation preferentially at the domain boundaries (fig. 3.9(b)). With increasing deposits above 0.3 ML, excess Ga forms islands not only near the 7×7 domain boundaries but also within the domains. For Ga deposit of 0.34 ML, the domain boundaries are totally covered with Ga induced islands and some of the islands are also found within the domain area (fig. 3.9(c)). For deposits significantly above 0.4 ML excess Ga forms more and more islands within the domains (fig.3.9(d)) [52, 53]. Hence we can conclude that the domain boundaries are the most preferential nucleation sites.

3.4.2 Room temperature Ga deposition (0.33 ML)

After deposition of 1/3 ML at room temperature most of the surface is covered with magic clusters and excess Ga forms islands. The appearance of the magic clusters in STM images is strongly bias-dependent as can be seen in figure 3.10. The filled state STM image is shown in fig. 3.10(A), whereas in fig. 3.10(B) an empty state STM image of the same surface area (50×50 nm²) is presented. This is an indication for the semiconducting nature of this surface although it needs to be confirmed by spectroscopic measurements. In figure 3.10 one can also see that the structure at the domain boundary is different from the center of the domains where magic clusters are found. Excess Ga is found in islands (white spots in fig. 3.10) located at the domain boundaries (indicated by black arrows) as well as within the domains, however with a clear preference for the domain boundaries.

![Figure 3.10: (A) Filled state (+2V) and (B) empty state (−2V) images of Ga magic clusters on Si(111)-7×7 (50×50 nm²). Atomic rows (white lines) are shifted across the domain boundary (indicated by black arrow) and mostly Ga-islands (very bright spots) are formed predominantly along the domain boundary.](image)

With increasing substrate temperature, magic clusters start to decay at about 400°C (transition temperature) and a rearrangement of the surface Ga atoms takes place. This process results in the formation of various surface reconstructions and finally the total surface is covered with $\sqrt{3} \times \sqrt{3}$-Ga reconstructions.

The amount of Ga deposition at room temperature plays a crucial role on the subsequent evolution of surface morphology during annealing at transition temperature (400°C). It has been observed that the Ga coverage of 0.33 ML is the key coverage and Ga coverages below and above this value lead to two different types of two dimensional phase separation and surface nano-patterning. In the following, the evolution of the Ga/Si(111) surface structure with substrate temperature for Ga deposit slightly below and above 1/3 ML will be discussed in details.
### 3.4.3 Room temperature Ga deposition (< 0.33 ML)

Within this section, changes in the Ga/Si(111) surface morphology with Si(111) substrate temperature and orientation (miscut) have been discussed for a Ga coverage of about 0.3 ML. Starting from a room temperature Ga deposition and thermal phase transition at 400°C, finally the resulting two dimensional surface phase separation and nano-patterning have been investigated by elevated temperature STM. Whereas the dependence of the nano-pattern shape on Si(111) miscut (step) orientation has been studied using LEEM.

![Empty state STM images of the Si(111)-Ga surface at (a) as-deposited, (b) 200°C and (c) 400°C, respectively, after room temperature deposition of 0.3 ML Ga.](image)

**Figure 3.11:** 100×100 nm² empty state STM images of the Si(111)-Ga surface at (a) as-deposited, (b) 200°C and (c) 400°C, respectively, after room temperature deposition of 0.3 ML Ga.

**Effect of annealing**

The dependence of the surface structure on the substrate annealing temperature after room temperature deposition of 0.3 ML Ga is shown in figure 3.11. The surface morphology of the as-deposited Ga/Si(111) surface is shown in fig. 3.11(a). Within domain areas uniformly distributed magic clusters and very small Ga islands are found, whereas at the domain boundary region an enhanced density of the Ga islands is observed. If the temperature is slowly increased up to about 200°C, the surface structure is more or less stable and no changes were recorded during STM imaging except for a decrease of the Ga-island density within the domain, as well as enhanced island nucleation at the domain boundaries. The average size of the island is also increased at the domain boundary region due to the coalescence effect as can be seen in fig. 3.11(b). After a further temperature increase to about 400°C, the island density within the domains is drastically reduced. Near the domain boundary, however, the situation is different and the Ga islands coalesce and form larger islands with bilayer steps (fig.3.11(c)). Near 400°C the transition starts, and the magic clusters begin to break apart. In figure 3.11(c) one can see a snapshot of the surface at the beginning of the transition process where some magic clusters have disappeared, leaving behind vacancies in the magic cluster network within the domains. At the domain boundary region the islands transform to a $\sqrt{3} \times \sqrt{3}$-Ga structure with a bilayer step height (see below).
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

To identify the surface structure of the Ga-island of bilayer height a STM image of Ga/Si(111) at the beginning of the surface phase transition at 400°C and a closer look of the selected area with larger magnification (fig. 3.12(b)) are shown in figure 3.12. From fig. 3.12(a), a 2D phase separation of magic clusters within the domain areas with the Ga-islands at the domain boundaries is clearly observed. A $\sqrt{3} \times \sqrt{3}$-Ga surface reconstruction is atomically resolved on top of the Ga-islands, which can clearly be seen in fig. 3.12(b). As the nominal Ga coverage of the $\sqrt{3} \times \sqrt{3}$-Ga phase (0.33 ML) is comparatively higher than that of magic clusters (0.24 ML), it can be concluded that the domain areas of lower Ga concentration are surrounded by relatively Ga rich domain boundary regions at the beginning of the phase transition.

Two-dimensional (2D) phase separation

Empty state STM images of the phase transition of the Ga/Si(111) surface at 400°C, after room temperature deposition of 0.3 ML of Ga on Si(111)-7×7, are shown in figure 3.13. As mentioned earlier, at the beginning of the transition the domains are mostly covered with magic clusters and the domain boundary regions with Ga-islands. At the transition temperature of about 400°C, magic clusters break apart and rearrange over the surface. It has already been discussed that domain boundaries act as preferred nucleation site for the $\sqrt{3} \times \sqrt{3}$-Ga reconstruction in this context. In the following we will show that also at a certain temperature range the step edges are playing an important role in the nucleation of the resulting $\sqrt{3} \times \sqrt{3}$-Ga reconstruction. Fig. 3.13(a), 3.13(b) and 3.13(c) show the surface overview at the various stages of the phase transition from magic clusters to a $\sqrt{3} \times \sqrt{3}$-Ga surface, whereas fig. 3.13(d), 3.13(e) and 3.13(f) show zooms into some areas selected from the earlier images. In figure 3.13(a), 3.13(b) and 3.13(c), one can clearly see that the domain boundary region and the step edges are covered with $\sqrt{3} \times \sqrt{3}$-Ga reconstruction (grey areas) and a few $\sqrt{3} \times \sqrt{3}$-Ga bilayer islands (bright island-like spots), whereas the domain areas are partially covered with magic clusters (small white dots in fig. 3.13(d) and 3.13(e)) and the bare Si(111)-7×7 surface is reappearing (darker grey areas). With time, the $\sqrt{3} \times \sqrt{3}$-Ga reconstructed areas grow in size as can be seen by comparison of fig. 3.13(a) to 3.13(c). This can be interpreted in a picture where more and more magic clusters break and Ga atoms move away from the central part of the domains.
3.4. Results and discussion

These Ga atoms prefer to re-nucleate at the domain boundary region as well as at the step edges area. Looking at the STM images of fig. 3.13, it can be seen that the $\sqrt{3} \times \sqrt{3}$-Ga reconstructions appear in triangular shape (grey overlapping/triangular patches), which is clearly seen in figure 3.13(d) and 3.13(e). At the end of this transition the central portion of the domains is free of magic clusters, instead clean Si(111)-7×7 reconstructed areas with a preferential shape of an equilateral triangle (vertexes point towards the equivalent [1\(\bar{1}\) 2] directions) are found surrounded by $\sqrt{3} \times \sqrt{3}$-Ga reconstructions as seen in fig. 3.13(e) and 3.13(f). The boundary line between the $\sqrt{3} \times \sqrt{3}$-Ga and Si(111)-7×7 reconstructions is always aligned along the [1\(\bar{1}\) 0] and its equivalent directions. It can also be observed that the number and size of the $\sqrt{3} \times \sqrt{3}$-Ga bilayer islands decrease with transition time and no more bilayer-islands are found at the end of transition. The final result of this process is a 2D nano-patterning of the surface into the Si(111)-7×7 area bounded by domains of the $\sqrt{3} \times \sqrt{3}$-Ga reconstruction located at the initial domain boundaries and step edge regions.

A closer look STM image of the surface during the phase transition is shown in figure 3.14(a) and a selected area of this surface is further zoomed in 3.14(b), where the $\sqrt{3} \times \sqrt{3}$-
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

Figure 3.14: ((a) and (b)) Empty state STM images of the Si(111)-Ga surface during phase transition at 400°C after room temperature deposition of 0.3 ML Ga. (c) Schematic drawing of the structure model for the boundary lines of the $\sqrt{3}\times\sqrt{3}$-Ga and Si(111)-7×7 reconstruction.

Ga and the Si(111)-7×7 structures are nicely resolved. At the domain boundary regions, $\sqrt{3}\times\sqrt{3}$-Ga reconstructions with bilayer islands are observed, whereas inside the domain a clean Si(111)-7×7 reconstruction is found. (fig. 3.14(b)). It should be noted that the boundary line between the $\sqrt{3}\times\sqrt{3}$-Ga and the Si(111)-7×7 reconstruction is always straight and of minimum length of twice the lattice constant of the 7×7 unit cell, along the equivalent [110] directions. Another observation is that the boundary line of 7×7 and the $\sqrt{3}\times\sqrt{3}$-Ga areas is constructed of faulted halves of the Si(111)-7×7 unit cell in contact with the $\sqrt{3}\times\sqrt{3}$-Ga areas only. The bilayer $\sqrt{3}\times\sqrt{3}$-Ga islands, which are not connected to the Si(111)-7×7 reconstruction are of arbitrary shape and mostly found to be completely surrounded by the $\sqrt{3}\times\sqrt{3}$-Ga reconstructions. A model structure for the boundary lines of the $\sqrt{3}\times\sqrt{3}$-Ga and Si(111)-7×7 reconstruction is given in figure 3.14(c). The equilateral triangle represents the Si(111)-7×7 area, the outer boundary lines are made of the border line of the faulted halves of the Si(111)-7×7 unit cells.

Preferential nucleation and temperature induced segregation of Ga atoms on the Si(111) surface at the defect site i.e., initial domain boundaries and step edges can be explained in terms of dangling bonds and surface stress. In general, defect sites have more dangling bonds than Si(111)-7×7 domains which cause more nucleation of adsorbate around it to reduce the surface chemical free energy. Additionally, surface stress and energetic can play an important role for the stabilization of Ga reconstructions against thermal decay. As the surface stress of the $\sqrt{3}\times\sqrt{3}$-Ga surface (1.35 eV/(1×1) cell) [32, 33] is significantly lower than that of the Si(111)-7×7 surface (2.56 eV/(1×1) cell) [56], in case of Ga coverage below 0.33 ML, the nucleation of $\sqrt{3}\times\sqrt{3}$-Ga structures at the domain boundary and step edge region can partially lower the tensile stress of initial Si(111)-7×7 domains and thereby lower the total surface free energy. Decay of magic clusters within domain areas supplies not only the six Ga atoms but also three Si atoms. These 3 Si atoms occupy the adatom position and rebuild the Si(111)-7×7 structure within the domain. But the Ga atoms move towards the defect site (initial domain boundaries and step edges) and form $\sqrt{3}\times\sqrt{3}$-Ga reconstructions. A transformation of the Si(111)-7×7 structure to the
3.4. Results and discussion

$\sqrt{3} \times \sqrt{3}$-Ga structure leaves 12 Si adatoms free for each $(7 \times 7)$ unit cell, which initially results in the formation of the bilayer steps and hence of $\sqrt{3} \times \sqrt{3}$-Ga bilayer islands. The atomic arrangement of Si beneath the $\sqrt{3} \times \sqrt{3}$-Ga is believed to be similar to the bulk terminated Si(111)-$1 \times 1$ structure, without any stacking fault. This can act as a un-faulted half and prefers to make bonding with the faulted half of the bare Si(111)-$7 \times 7$ area to reduce the dangling bonds by forming the dimer rows. As a result, the boundary line between the $\sqrt{3} \times \sqrt{3}$-Ga and the Si(111)-$7 \times 7$ reconstruction is always found with the faulted half of the Si(111)-$7 \times 7$ unit cell [35] along [112] direction which also makes the minimum length of any kink on this boundary line twice the length of the Si(111)-$7 \times 7$ unit cell. It is assumed that the step formation is energetically unfavourable for the surface under tensile stress. Hence, the bilayer $\sqrt{3} \times \sqrt{3}$-Ga islands, which initially formed at the beginning of the phase transition, are not stable for a longer time and decay with transition time. This produces some additional Si and Ga atoms. The Si atoms move towards the step edges and absorb in step flow growth, whereas Ga atoms are involved for further $\sqrt{3} \times \sqrt{3}$-Ga reconstructions. The preferential shape of an equilateral triangular Si(111)-$7 \times 7$ domain surrounded by $\sqrt{3} \times \sqrt{3}$-Ga with a long straight boundary line can be explained by the kink formation energy. As the kink formation is energetically unfavourable, the surface would prefer to minimize the number of kinks and for the best to have an equilateral triangular shape. Details of this will be discussed later.

3.4.4 Ga/Si(111) nano-patterning ($< 0.33$ ML)

In the earlier section it has already been demonstrated that a 2D nano-pattern can be achieved for the Ga/Si(111) system after RT Ga deposition and subsequent annealing at the transition temperature of 400°C, using the self organized surface phase separation. For this specific adsorbate system of Ga/Si(111), it has been reported that the miscut direction can affect the shape of the Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$-Ga domains [36] after room temperature saturation and (partial) thermal redesorption of gallium. Within this section, it will be discussed how the nano-pattern shape can be controlled during Ga deposition at elevated temperature. In addition, the mechanism responsible for this type of nano-pattern formation will also be elucidated.

The structural evolution during Ga deposition on the Si(111) surface at elevated temperature with increasing time, studied by low energy electron microscopy (LEEM), will be discussed here. Ga was deposited during imaging in the LEEM, at a sample temperature of 650°C which is very close to the thermodynamic equilibrium conditions for the $\sqrt{3} \times \sqrt{3}$-Ga structure. As the temperature is higher than the transition temperature, magic clusters are not forming anymore and the initial Ga nucleation on Si(111) starts with the $\sqrt{3} \times \sqrt{3}$-Ga structure.

Surface miscut orientation along [112]

The topography of a Si(111) surface with a miscut orientation towards [112] and its evolution during Ga deposition at about 650°C is shown in Fig. 3.15. For the electron energy
Figure 3.15: Bright-field LEEM images of Si(111) during Ga deposition at about 650°C. (Field of view: 2.5 µm, $E=3.5$ eV). Step edges run from bottom left to top right, the miscut (step down) direction is towards [112]. (a) Ga-terminated $\sqrt{3}\times\sqrt{3}$ domains (dark) nucleate at the initial domain boundaries (IDBs) of the $7\times7$ reconstruction (bright). From (a) to (d) the Ga coverage increases. $\sqrt{3}\times\sqrt{3}$ and remaining $7\times7$ domains are composed of equilateral triangles in a christmas-tree arrangement.

chosen here, the $\sqrt{3}\times\sqrt{3}$-Ga reconstruction appears dark, whereas the $7\times7$ superstructure appears bright. The nucleation of the $\sqrt{3}\times\sqrt{3}$ structure takes place both at initial domain boundaries (IDBs) of the $7\times7$ reconstruction and on the lower terrace side of the step edges. At the beginning, the $\sqrt{3}\times\sqrt{3}$ domains are composed of equilateral triangles with the outward normal of the edges pointing along (112). As can be seen from the images, the $\sqrt{3}\times\sqrt{3}$ areas grow with comparable speed at the step edges and at the domain boundaries. It is also obvious that at the step edges the growth proceeds only towards the lower terrace, whereas at the domain boundaries, the $\sqrt{3}\times\sqrt{3}$ structure develops on both the [110] and the [110] direction. As soon as the $\sqrt{3}\times\sqrt{3}$ reconstruction dominates the surface topology, the remaining patches of the $7\times7$ form equilateral triangles with the outward normal of the edges pointing along (112), which is identical with the earlier STM finding (fig. 3.13(f)).

These LEEM findings (fig. 3.15) are very similar and in agreement with the earlier STM studies of a Si(111) surface with miscut along [112], monitored during thermal annealing at about 400°C, after room temperature deposition of less than 1/3 ML Ga (fig. 3.13), where both the $\sqrt{3}\times\sqrt{3}$ domains and the remaining the $7\times7$ domains form equilateral triangles for this miscut orientation.

Surface miscut orientation along [112]

A different surface topology is observed, however, if the miscut points to the opposite direction: Figure 3.16 shows the evolution for the same preparation conditions as in fig. 3.15, but for a surface with a miscut along [112]. Again, the formation of a nano-
pattern of $\sqrt{3} \times \sqrt{3}$ domains is observed. The $\sqrt{3} \times \sqrt{3}$ structure again grows from step edges (on lower terraces) and domain boundaries (both towards [110] and [1̅10] direction) but the growth rate at step edges is much smaller than at the domain boundary and the triangular shape of the domains is less pronounced. This leads to the formation of a rather rectangular or stripe pattern.

Surface miscut orientation along [1̅10]

Yet another finding is observed for a miscut along a perpendicular direction, as depicted in fig. 3.17. Again, the $\sqrt{3} \times \sqrt{3}$ areas grow on the lower terrace side of step edges, i.e., towards [1̅12], and with comparable rate at the domain boundaries. However, the growth at the domain boundaries proceeds mainly along the [112] direction, whereas the growth towards the opposite direction, [1̅12], is almost completely suppressed. As a result, $\sqrt{3} \times \sqrt{3}$ patches form equilateral triangles at the domain boundaries and right-angled triangles at the step edges. Consequently, the remaining patches of the $7 \times 7$ structure tend to resemble right-angled triangles, as can be seen from fig. 3.17(b).

From all the LEEM images shown above, it can be concluded that the shape of the self-organized nano-pattern can be chosen by the miscut orientation. For conditions close to thermal equilibrium, the structural size of the pattern is determined on the one hand by the terrace length, which can be controlled via the miscut angle, and on the other hand by the width of the initial $7 \times 7$ domains on the terraces, which to some extent can be tuned e.g. by the cooling rate at the $1 \times 1$ to $7 \times 7$ phase transition. Especially, for larger miscut angles in the range of a few tenths of a degree, our findings imply that pattern length...
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

Figure 3.17: Bright-field LEEM images taken under similar conditions as in fig. 3.15 and fig. 3.16, but with a miscut towards [110]. (Field of view: 2.5 \( \mu \)m, \( E=3.5\) eV.) From (a) to (b), the Ga coverage increases.

scales below 100 nm can be achieved. Moreover, the choice of the deposition temperature would be less crucial in this case: Such a temperature has to be chosen that homogeneous nucleation within the initial 7×7 domains is suppressed. Hence, for larger miscut angles, a wider temperature range could be used.

**Growth scheme of \( \sqrt{3}\times\sqrt{3} \) with miscut orientation**

In order to understand the dependence of the domain shape on the miscut orientation, a growth model has been proposed by Schmidt et al. [2]. Within this model, the similarities in the findings for all different miscut orientations are considered. Firstly, the domain boundaries between \( \sqrt{3}\times\sqrt{3} \) and 7×7 always run along \( \langle 1\bar{1}0 \rangle \), with the outward normal of the \( \sqrt{3}\times\sqrt{3} \) pointing towards \( \langle 1\bar{1}2 \rangle \). Secondly, the domain boundaries are very straight, i.e. they do not exhibit many kinks. To a large extent, the kinks observed can be attributed to the coalescence of different \( \sqrt{3}\times\sqrt{3} \) domains. Thirdly, the \( \sqrt{3}\times\sqrt{3} \) structure always nucleates both at the lower terrace side of the step edges as well as at the initial domain boundaries, and the step edges act as efficient barriers for \( \sqrt{3}\times\sqrt{3} \) growth.

From the observation that long straight domain boundaries between \( \sqrt{3}\times\sqrt{3} \) and 7×7 are preferred over kinky short ones, it can be concluded that kink formation is energetically unfavourable. Starting with an ideal \( \sqrt{3}\times\sqrt{3} \) domain with only straight domain

Figure 3.18: Sketch of a growth model proposed by Schmidt et al. [2] showing subsequent stages (I to V) of the evolution of a \( \sqrt{3}\times\sqrt{3} \) domain (dark), for different orientations (a) to (d) with respect to 1D defects (fuzzy yellowish lines), i.e., either step edges or initial domain boundaries. (I) Ideal \( \sqrt{3}\times\sqrt{3} \) domain without kinks. (II) A single kink nucleates at the 1D defect, which then (III) propagates towards the apex while the next kink is injected. (IV) and (V): further evolution. In cases (a)–(c), the domain shape and aspect ratio is preserved, whereas for (d) a narrow stripe along the 1D defect evolves. The less probable case of double kink formation is shown in (d').
3.4. Results and discussion

boundaries, growth can only take place by kink formation, i.e., by single kink formation at defects like existing kinks (which are not available for an ideal $\sqrt{3}\times\sqrt{3}$ domain), step edges, or domain boundaries. The alternative mechanism, namely double kink formation at the straight edges is strongly suppressed due to the large kink energy mentioned above. The $\sqrt{3}\times\sqrt{3}$ domain then grows while the single kink propagates, until it reaches an apex of the $\sqrt{3}\times\sqrt{3}$ domain; growth around such apexes is again suppressed because it includes an intermediate double-kink-like stage. The injection of kinks from step edges and domain boundaries is also promoted by an increased local adsorbate concentration at these defects [1], which can as well be regarded to drive the initial nucleation of $\sqrt{3}\times\sqrt{3}$ domains.

Within this model, which is also sketched in Fig. 3.18, all the different growth speeds and domain shapes can be well explained. An azimuthal orientation of the miscut along [112] (cf fig. 3.15) leads to a $\sqrt{3}\times\sqrt{3}$ domain growth at the step edges as depicted in fig. 3.18(a). This results in the formation of equilateral triangles at the step edges. It has to be kept in mind that the $\sqrt{3}\times\sqrt{3}$ domains grow towards the lower terrace only. In contrast, the $\sqrt{3}\times\sqrt{3}$ structure can grow towards both directions at the domain boundaries. Therefore, at the domain boundaries the domains grow as shown in fig. 3.18(b) and fig. 3.18(c). This allows for a symmetrical growth around the domain boundaries leading to the christmas-tree arrangement observed in fig. 3.15.

For a miscut along [112] (cf. fig. 3.16), a domain boundary segment parallel to the step edges will hardly move away from the step edge, since the only way to do so is via double kink formation [see fig. 3.18(d')]. Instead, a long stripe parallel to the step edge slowly evolves by repeated kink injection from the step edge, as shown in fig. 3.18(d). At the domain boundaries, again fig. 3.18(b) and 3.18(c) apply, which leads to equal growth in [110] and [110] directions.

If the miscut is perpendicular to [112] (cf. 3.17), the growth at the step edges proceeds as either sketched in fig. 3.18(b) or 3.18(c). At the domain boundaries, figure 3.18(a) and 3.18(d) apply for growth towards [112] and [112], respectively. Therefore, the growth at the domain boundaries cannot be symmetrical for such a miscut orientation. The domains hardly grow towards the [112] direction and equilateral triangles are formed much faster on the [112] side.

Generalizing the growth scheme

The growth mechanism proposed here is based on generic properties of the surface system, i.e., the line and kink energies of the $\sqrt{3}\times\sqrt{3} - 7\times7$ domain boundary and their anisotropy. This explains why similar results are found for this system under quite different experimental conditions. Though the structures after room temperature deposition and annealing 400°C are smaller than those obtained after deposition at 650°C, this clearly reveals that the surface topology is governed by energetics, not by surface kinetics.

An even more general scheme of the pattern formation is obtained when comparing the results shown so far to LEEM images obtained during the phase transition of the bare substrate from 1×1 to 7×7 at 830°C, such as the one shown in fig. 3.19. Here, 7×7...
domains nucleate at the upper terrace side of the step edges [54] (i.e. the 1×1 reconstruction remains at the lower terrace side), forming either stripes or triangles, depending on the orientation of the meandering step edges. The domain boundaries are very straight and run along ⟨110⟩ directions. The outward normal orientation of the 7×7 domains is identical to the one observed during the 7×7 to $\sqrt{3} \times \sqrt{3}$ transition. All these similarities indicate that the interactions between 7×7 and 1×1 domains on one hand, and 7×7 and $\sqrt{3} \times \sqrt{3}$ domains on the other hand, are comparable. As an important interaction between the different phases, surface stress has to be considered [55]. With respect to the 7×7-Si(111) reconstruction, both the $\sqrt{3} \times \sqrt{3}$-Ga/Si(111)- as well as the 1×1-Si(111) reconstruction impose less tensile surface stress. For $\sqrt{3} \times \sqrt{3}$-Ga/Si(111), this stress relief has been reported to amount to 80 meV/Å² [56] and corresponding values for 1×1-Si(111) range from 30 to 60 meV/Å² [57, 58].

Regarding the kink energies and the anisotropy of the line energies, the local atomic arrangement at the domain boundaries is essential. From this point of view, it is noteworthy that the arrangement of the silicon atoms within the $\sqrt{3} \times \sqrt{3}$ and the 1×1 reconstruction is more or less identical. In this respect, the $\sqrt{3} \times \sqrt{3}$ structure with Ga on T₄ sites can be regarded as a ”distorted bulk-terminated structure”. Since this allows for similar atomic arrangements at the domain boundaries, our findings are explained in terms of generic properties of the Si(111) surface, namely the high kink energies and anisotropy of the 1×1-7×7 domain boundaries, which are preserved after Ga adsorption. Following this scheme, the formation of nano-patterns, like the ones observed here, could as well be expected for similar adsorbate structures, as long as the adsorbate-induced distortion of the bulk-terminated structure does not lead to too strong tensile surface stress.

Figure 3.19: Bright-field LEEM image obtained during the 1×1 to 7×7 phase transition of the bare Si(111) substrate at $\approx$830°C. (Field of view: 5 µm, $E$=12.1 eV.) 1×1 domains appear dark, 7×7 domains appear bright and are attached to the upper terrace side of the step edges [54]. Depending on the step edge orientation, either a stripe-like (region A) or a triangular (region B) domain shape is found.

Figure 3.20: Bright-field LEEM images of Si(111) during indium deposition at about 450°C. (Field of view: 5 µm, $E$=11.1 eV). (a) In/Si(111)-$\sqrt{3} \times \sqrt{3}$ domains (dark) nucleate at step edges and domain boundaries of the 7×7 reconstruction. (b) After further In deposition, different pattern shapes evolve for different step edge orientations (compare the regions labelled A and B).
In order to verify the scheme described above, similar adsorption experiments using indium instead of gallium were also performed. Typical results are shown in fig. 3.20. Like with Ga, high temperature low coverage adsorption of In leads to the formation of a $\sqrt{3} \times \sqrt{3}$-R$30^\circ$ reconstruction [59]. Obviously, the nucleation and growth behaviour of this In/Si(111)-$\sqrt{3} \times \sqrt{3}$ structure is equivalent to Ga/Si(111)-$\sqrt{3} \times \sqrt{3}$. In the sample area depicted in fig. 3.20, different orientations of the step edges are found simultaneously. In striking agreement with Ga, the shape of the nano-pattern formed by In adsorption depends on this orientation. It is remarkable that the average local In coverage at the stripe-pattern [see area ”A” in fig. 3.20 (b)] is much lower than at the triangular pattern regions (e.g. area ”B” in the same image). On the one hand this reflects the different growth velocities mentioned above, on the other hand this concentration gradient clearly shows that the adsorbate mobility is high enough to allow diffusion in the micrometer range. This can be regarded as a further important prerequisite for the presently observed pattern formation.

### 3.4.5 Room temperature Ga deposition (> 0.33 ML)

As described earlier, after deposition of about 0.35 ML of Ga at room temperature, the surface is mostly covered with magic clusters and excess Ga forms islands mainly found near the domain boundaries. However, some of the islands are also located within the domain areas.

![Figure 3.21](image)

Figure 3.21: Empty state (-2V) STM images of the Si(111)-Ga surface at (a) 300°C (60×60 nm$^2$), (b) 350°C (55×55 nm$^2$) and (c) 400°C (50×50 nm$^2$) after room temperature deposition of 0.35 ML Ga. The presence of domain boundaries is indicated by white lines as in fig. 3.10.

**Effect of annealing**

If the temperature is slowly increased up to about 400°C, the structure within the domains is more or less stable and no changes are recorded during STM imaging except for a decrease of the Ga-island density as can be seen in fig. 3.21. Near the domain
boundary, however, the situation is different. As the temperature is increased from room temperature to 300°C, slowly the Ga islands start to coalesce and larger islands (fig. 3.21(a)) are formed. After a further temperature increase to about 350°C, the islands partially transform to domains of 6.3×6.3-Ga structure (fig. 3.21(b)). At about 400°C the magic clusters start to decay. In figure 3.21(c) one can see a snapshot of the surface at the beginning of this transition process: some magic clusters have disappeared, leaving behind vacancies in the magic cluster network within the domains. At this temperature a 6.3×6.3-Ga structure is found near the domain boundaries with a few islands (bright spots). This finding is very different from the earlier results obtained for a Ga coverage of 0.3 ML, where only the $\sqrt{3} \times \sqrt{3}$-Ga structure was observed at the domain boundary regions.

Phase transition at 400°C

In figure 3.22 one can see the surface at an intermediate stage of the phase transition. For clarity the domain boundary region has been highlighted. In some parts at the inner side of the domain, the magic clusters have vanished (as started in fig. 2(c)) and the Si(111)-7×7 structure has reappeared. In the area (marked as 4) corner holes are clearly resolved. At other parts of the surface the $\sqrt{3} \times \sqrt{3}$ structure (marked as 3) is observed now instead of magic clusters which can also still be found on the surface, e.g. in the area marked as 5, where magic clusters are visible as faint wide spots at this tunneling condition.

![Figure 3.22: Empty state (-2V) STM image of the Si(111)-Ga surface (35×30 nm²) showing co-existence of various types of reconstruction during the phase transition (400°C). $\sqrt{3} \times \sqrt{3}$-Ga (marked by 1) and 6.3×6.3-Ga (2) structures are observed at the domain boundary. Within the domains $\sqrt{3} \times \sqrt{3}$-Ga (3), Si(111)-7×7 (4) and magic clusters (5) are found.](image)

At the domain boundary region, however, the findings are different again. Here a mixture of mostly 6.3×6.3-Ga areas (marked as 2) with some very small patches of $\sqrt{3} \times \sqrt{3}$-Ga structure (marked as 1) is found in between, depending on the local Ga coverage. At the chosen tip bias, the contrast within the 6.3×6.3 structure is weak. The Ga coverage at the inner of the domains is smaller than 1/3 ML, there a mixture of Si(111)-7×7, $\sqrt{3} \times \sqrt{3}$-Ga structure and magic clusters is found. Distinctively the Ga coverage in the domain boundary region is significantly larger. Here a mixture of $\sqrt{3} \times \sqrt{3}$-Ga and 6.3×6.3-Ga (γ-phase) structures is found, with an estimated average Ga coverage near 0.5 ML.
3.4. Results and discussion

The rearrangement of Ga atoms on the surface during the transition has been monitored directly in figure 3.23. Two 40×46 nm² images of the same surface area were recorded subsequently at a time interval of 10 minutes, while the sample temperature was kept constant at approximately 400°C. Again, the borderline between the domain boundary region and its neighbouring domains has been indicated by curly white lines. The two images are similar, but slight changes are observed reflecting the mobility of Ga atoms on the surface. Magic clusters in the vicinity of the domain boundary region are found at different positions in fig. 3.23(B) as compared to fig. 3.23(A), which can be seen clearly in the area labelled 5. Within this white box the rearrangement of magic clusters has been marked by white arrows. As the magic clusters are too big for a collective motion, we conclude that at this temperature the magic clusters break apart and renucleate. Consistently, the total number of magic clusters decreases with time. The rate of thermal decay of magic clusters at the transition temperature has been determined to be 1.57×10⁻³/sec, from which the activation energy for the decay has been estimated to about 2.05±0.15 eV assuming a trial frequency of 10¹²±1 /sec.

Another process can also be identified from a careful comparison of the area labelled 1 (white ellipse) in fig. 3.23(A) to fig. 3.23(B). Few small bright spots at the domain boundary region within the ellipse of fig. 3.23(A), which is believed to be a √3×√3 reconstruction, seems to be thermally unstable and slowly converts to a 6.3×6.3 reconstruction in fig. 3.23(B). This finding is further confirmed by the images shown in fig. 3.24.

After RT deposition of about 0.35 ML Ga on Si(111), temperature induced movements of Ga atoms and phase transition at a time interval of about one hour are shown in figure 3.24. Fig. 3.24(a), 3.24(b) and 3.24(c) show the starting, whereas 3.24(d), 3.24(e) and 3.24(f) represent towards completion of the Ga/Si(111) phase transition at 400°C. Some selective area of fig. 3.24(a) (white circle) is magnified in fig. 3.24(b) and further zoomed in fig. 3.24(c). The same procedure has been followed for fig. 3.24(d) to fig. 3.24(f). At the beginning of the phase transition the initial Si(111)-7×7 domain areas were totally covered by magic clusters with few Ga-islands while the step edges and initial domain boundaries (IDBs) were mostly decorated by 6.3×6.3-Ga reconstructions (fig. 3.24(a) and 3.24(b)). Depending on the local Ga coverage, few patches of √3×√3-Ga
structures were also found within the 6.3×6.3-Ga reconstructed domain boundary region (fig. 3.24c). Comparing fig. 3.24(c) (before transition) to fig. 3.24(f) (after transition), it is clearly observed that the $\sqrt{3} \times \sqrt{3}$-Ga reconstructed area at the domain boundary region totally converted to the 6.3×6.3-Ga reconstruction after keeping the surface at transition temperature for 60 min.

Finally at the end of the transition, again a self-organized 2D-phase separation is observed, with spatial variation of Ga coverage. The $\sqrt{3} \times \sqrt{3}$-Ga reconstructions within domain areas are surrounded by 6.3×6.3-Ga reconstructions along the domain boundaries and the step edges. A closer view of the Ga/Si(111) surface after the phase transition is shown in figure 3.25. Clearly resolved 6.3×6.3-Ga structures are found at the domain boundaries and the step edges, whereas $\sqrt{3} \times \sqrt{3}$-Ga reconstructions are observed within the domain areas. It can also be noted that the 6.3×6.3-Ga structures at the domain boundary region always appear with a bilayer step height and at the step edges they appear in the upper terrace of the steps. Even if the temperature is further increased (up to 500°C), this domain boundary structure remains stable for long times. All these findings are very different from the earlier 2D phase separation (fig. 3.13) where the Ga coverage was below 0.33 ML.

After keeping the surface at the transition temperature, the magic clusters break apart
3.4. Results and discussion

![Figure 3.25: Empty state STM image of the Si(111)-Ga surface at the end of the phase transition at 400°C after room temperature deposition of 0.35 ML Ga. Scan area 90×60 nm².](image)

and the density of the Ga-islands becomes lower within the domains. Simultaneously, the reconstruction of domain boundaries changes from $\sqrt{3} \times \sqrt{3}$-Ga (nominal coverage 1/3 ML) to 6.3×6.3-Ga (nominal coverage 1 ML) reconstructed area. This can be concluded as a net flow of Ga atoms from the initial Si(111)-7×7 domain regions towards the step edges and initial domain boundary regions. We attribute this to a significant mass transport of Ga either from the magic clusters or from the residual Ga-islands within the domain to the domain boundaries.

The 2D phase separation of Ga/Si(111) can be explained in terms of surface stress, which leads to a stabilization of a patchwork of 6.3×6.3-Ga and $\sqrt{3} \times \sqrt{3}$ areas against thermal decay. From theoretical investigations it is known, that both the $\sqrt{3} \times \sqrt{3}$ and the Si(111)-7×7 surface are under tensile stress of about 1.35 eV/(1×1 cell) [32,33], and 2.56 eV/(1×1 cell), respectively. For the Si(111)-7×7 an experimental value of 2.37 ± 0.15 eV was reported [56] in quite good agreement with theory. For Ga in a substitutional site, i.e. a surface Ga-Si bilayer, a large compressive stress of about 4.45 eV/(1×1 cell) was predicted [32]. Due to the formation of an incommensurate surface structure with a large number of domain boundaries, the actual stress of the 6.3×6.3-Ga structure will be significantly lower. However, it will still be substantially compressive in nature. Hence, by the nucleation of 6.3×6.3-Ga domains at the initial Si(111)-7×7 domain boundaries, the Si(111) surface can partially lower its tensile stress which arises from domains of 7×7 and $\sqrt{3} \times \sqrt{3}$-Ga structure and thereby lower the total surface free energy. As for both of 6.3×6.3-Ga and $\sqrt{3} \times \sqrt{3}$-Ga structures (γ-phase) stacking fault does not exist anymore, there is no such specification for the shape or growth direction like in the earlier case. During the formation of 6.3×6.3-Ga structures the top layer Si atoms are replaced by Ga atoms, which leads to a surplus of Si atoms on the surface. These Si atoms preferentially form bilayer steps as seen in the domain boundary regions. Additionally, the 6.3×6.3-Ga surface which is under strong compressive stress, might prefer to be on top of bilayer steps where it can partially reduce the surface stress through incommensurate structure formation. Similar explanations can also be applicable for the 6.3×6.3-Ga structure growth at the upper terrace of the step edges.
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

Figure 3.26: LEEM images show the evolution of the $6.3 \times 6.3$-Ga surface reconstruction on the $\sqrt{3} \times \sqrt{3}$-Ga surface at 550°C. The bright areas represent the $6.3 \times 6.3$-Ga reconstructed area and dark areas are the $\sqrt{3} \times \sqrt{3}$-Ga phase. The upper left part is higher than the lower right part and steps are along the bright line in fig. (a). Field of view 2.5 $\mu$m and electron energy 3.5 eV.

3.4.6 Elevated temperature Ga deposition and nano-structuring (>0.33 ML)

In case of Ga deposition (up to 1/3 ML) on Si(111) at elevated temperature (400°C < T < 650°C), the changes in the surface structure are similar to them discussed in the section "Ga/Si(111) nano-patterning (<0.33 ML)" (fig. 3.30–fig.3.32). For further Ga deposition at 650°C no significant changes have been observed as the excess Ga does not stick anymore on the surface at this temperature. However, if the substrate temperature is slightly reduced (550°C) and Ga deposition continued, a further structural evolution starts as shown in figure 3.26. LEEM images of the various growth stages of the $6.3 \times 6.3$-Ga structure at 550°C on the $\sqrt{3} \times \sqrt{3}$-Ga surface are shown here. After the $\sqrt{3} \times \sqrt{3}$-Ga structure is completed, nucleation of the $6.3 \times 6.3$ structure begins, strongly preferred at the surface steps as shown in figure 3.26(a). The bright narrow lines (from left to right) along the steps represent the $6.3 \times 6.3$-Ga structures over the $\sqrt{3} \times \sqrt{3}$-Ga dark background. Here we found that the effect of domain boundary of the initial Si(111)-7×7 surface is no longer present and only surface steps influence the nucleation of the $6.3 \times 6.3$-Ga structure, which is significantly different from the STM observation in figure 3.24. Figure 3.26(b) shows a somewhat later stage where the steps are completely decorated by bright islands of $6.3 \times 6.3$-Ga structure). Additionally, the nucleation of the $6.3 \times 6.3$-Ga structures has also appeared within the terrace area (few bright spots away from the steps). For a further continuation of the Ga deposition, the $6.3 \times 6.3$-Ga structure from the steps slowly flows over the lower terraces and appears wider. The region with higher step density is nearly covered with the $6.3 \times 6.3$-Ga phase, whereas a $\sqrt{3} \times \sqrt{3}$-Ga structure is still visible for the wider terraces as can be seen in fig. 3.26(c). The $6.3 \times 6.3$-Ga phase is completed at this temperature after deposition of about 0.8–1.0 ML of Ga. The fine grainy structure within the large terraces in fig. 3.26(d) nearly obliterates the step contrast. This may be due to the bilayer step formation and surface roughening occurring during the formation of the $6.3 \times 6.3$-Ga structure or due to the very small size of the $6.3 \times 6.3$-Ga domains.
3.4. Results and discussion

For elevated temperature Ga deposition (> 0.33 ML), 2D phase separation and surface nano-patterning is found again. But only the surface steps can influence the initial nucleation of 6.3×6.3-Ga here. For Ga deposition at elevated temperatures, if the Ga coverage exceeds 0.33 ML the $\sqrt{3} \times \sqrt{3}$-Ga terminated Si(111) surface acts as a substrate for further nucleation of Ga atoms. Since there are no initial domain boundaries of Si(111)-7×7 left when the surface is totally covered by $\sqrt{3} \times \sqrt{3}$-Ga, only the steps can further influence the Ga nucleation as seen in LEEM observation.

3.4.7 Hetero-epitaxial growth of Ge on Ga:Si(111)

Ga induced various surface reconstructions and nano-patterning of Si(111) are of high practical importance as the amount of Ga coverage can largely impact the subsequently grown Ge film quality. Moreover, Ga/Si(111) nano-patterned substrates can also influence the Ge growth process due to local variations of the surface chemical properties, which may lead to selective Ge growth. For a better understanding of the selective growth phenomena, the knowledge of Ge films growth on various Ga-reconstructed Si(111) surfaces is highly desirable.

Ge growth on clean Si(111)

The evolution of the surface morphology, after thin layer of Ge deposition on clean Si(111)-7×7 surface at 450°C, is shown in figure 3.27. In case of Ge coverage of about 0.8 ML, the surface exhibits large overlapping triangular 2D islands of bilayer step height within the center portion of the terraces as can be seen in fig. 3.27(a). At the step edge region, a denuded zone has been observed for both upper and lower terraces. Additionally, step edge roughening results in the formation of meandering surface steps. Some selected surface area of fig. 3.27(a) is shown in fig. 3.27(b), with larger magnification. Similarly, some selected area of fig. 3.27(b) is further zoomed in fig. 3.27(c), where only an atomically resolved 7×7 surface reconstruction has been observed both within the terrace as well as on top of the islands of bilayer step height. For Ge coverage of about 1.6 ML, the overall surface morphology looks similar but a higher density of Ge island is found as shown in fig. 3.27(d). Here, large islands have also appeared at the steps and no more denuded zones can be found. Furthermore, nucleation of the next Ge bilayer has already started before completion of the first layer. This results in the formation of small Ge islands on top of the larger triangular islands (fig. 3.27(e)). Atomically resolved 5×5 surface reconstructions are observed on top of the small Ge islands (fig. 3.27(f)). A coexistence of 7×7 patterns can also be seen at the upper right corner of this figure.

Ge growth on 6.3×6.3-Ga terminated Si(111)

To investigate the effect of Ga adsorbates on subsequent Ge hetero-epitaxy, a similar kind of Ge growth experiments on 6.3×6.3-Ga terminated Si(111) surfaces have been performed and the corresponding surface morphological evolution is shown in figure 3.28. After 0.8 ML of Ge deposition at 450°C, a smooth surface morphology with some vacancy islands of depth of bilayer step have been observed (fig. 3.28(a)). Meandering of the surface steps
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

Figure 3.27: Empty state STM images of the Si(111) surface after deposition of 0.8 ML ((a)–(c)) and 1.6 ML ((d)–(f)) of Ge, respectively, on a clean Si(111)-×7 surface at 450°C. Some selected area of Fig. (a) is zoomed in fig. (b), which is further magnified in fig. (c). Similar procedure is also followed for fig. (d) to (f).

After 0.8 ML of Ge deposition on clean Si(111)-×7 surface at 450°C

After 1.6 ML of Ge deposition on clean Si(111)-×7 surface at 450°C

can also be seen. In closer look, a 6.3×6.3 structure has been observed throughout the surface. In case of Ge coverage of about 1.6 ML, the surface morphology looks similar, but vacancy islands are not found anymore, instead 2D islands of bilayer step height have been observed on the surface (fig. 3.28(a)). In closer look again a 6.3×6.3 surface reconstruction is observed. All the structures shown here are identified as a β-phase of the 6.3×6.3-Ga/Ge(111) reconstructions.

Ge growth on $\sqrt{3} \times \sqrt{3}$-Ga/Si(111)

To understand the effect of Ga coverages for Ge epitaxy on Ga covered Si(111), similar growth experiments have also been tested on the $\sqrt{3} \times \sqrt{3}$-Ga/Si(111) surface and the corresponding surface structures are shown in figure 3.29. Fig. 3.29(a) shows the surface overview after 0.8 ML of Ge deposition. At the step edges a different contrast has been
3.4. Results and discussion

After 0.8 ML of Ge deposition on 6.3×6.3-Ga/Si(111) at 450°C

After 1.6 ML of Ge deposition on 6.3×6.3-Ga/Si(111) at 450°C

Figure 3.28: Empty state STM images of the Si(111) surface after deposition of 0.8 ML ((a)–(c)) and 1.6 ML ((d)–(f)) of Ge, respectively, on the 6.3×6.3-Ga/Si(111) surface at 450°C.

observed which is identified as a 6.3×6.3 reconstruction. Within the central part of the terrace area, similar kinds of patches can also be seen. Some of these patches contain a small bright spot. A larger magnification STM image of this type of patch is shown in fig. 3.29(b), where the bright spots appear as 2D islands of bilayer height surrounded by 6.3×6.3-Ga reconstructions. A closer look of the 2D islands is shown in fig. 3.29(c) where a $\sqrt{3} \times \sqrt{3}$ surface reconstruction is mainly resolved on top of the 2D islands. However, a 5×5 structure is also found along the outer border of the 2D islands (fig. 3.29(c)). In case of a Ge coverage of 1.6 ML, the surface overview is shown in fig. 3.29(d). The surface morphology appears rougher with 2D islands around the step edges and vacancy islands within the terrace area. A $\sqrt{3} \times \sqrt{3}$ structure is not found anymore, whereas small patches 5×5 reconstruction surrounded by 6.3×6.3 structures are found throughout the surface (fig. 3.29(f)). The 6.3×6.3 structures are not properly resolved for this tunneling condition.

From all three sets of Ge growth experiments, it can be concluded that bare Si(111)-7×7 leads to the formation of large Ge island followed by thin wetting layer growth.
Chapter 3. Surface nano-patterning of Ga/Si(111) for Ge-epitaxy

![Images of STM images](image1)

Figure 3.29: Empty state STM images of the Si(111) surface after deposition of 0.8 ML ((a)–(c)) and 1.6 ML ((d)–(f)) of Ge, respectively, on the $\sqrt{3} \times \sqrt{3}$-Ga/Si(111) surface at 450°C.

For 6.3×6.3-Ga terminated Si(111) substrate, a surfactant mediated epitaxial growth of smooth Ge films occurs with Ge islands/pits of only bilayer step height. However, a rough growth front with a variation in local Ge coverages is observed for Ge growth on $\sqrt{3} \times \sqrt{3}$-Ga/Si(111). An enrichment of the Ge nucleation along the outer border of the $\sqrt{3} \times \sqrt{3}$ islands is found, which finally leads to the formation of Ge islands. The lateral size of these islands is much smaller than those formed on the bare Si surface, whereas the density is higher.

### 3.4.8 Ge quantum dot on nano-patterned Ga-Si(111)surface

It has already been discussed how the Ga coverage can influence the surface morphology of Ge growth on Si(111). Depending on the Ga coverage, the island size distribution during subsequent Ge epitaxy can be sharpened [19]. In the following, it will be discussed how a modulation of the surface properties by submonolayer adsorption of Ga on Si(111) can be used for selective growth of Ge islands. In comparison to strain-based 3D island growth
techniques, the approach presented here is expected to leave more freedom to tune the electronic properties of the system, as will be explained below.

Prior to the Ge growth, nano-patterning of the Ga/Si(111) surface has been obtained by submonolayer coverage Ga deposition on Si(111) at 650°C as shown in figure 3.30. With increasing Ga coverage the $\sqrt{3}\times\sqrt{3}$-R 30° patches (dark areas) grow in size. In Fig. 3.30 (c) a typical shape of the $\sqrt{3}$ domains becomes visible. The Ga deposition is stopped before the $\sqrt{3}\times\sqrt{3}$-Ga reconstruction extends over the whole surface. The domain shape of the nano-pattern has already been discussed earlier [2].

![Figure 3.30: Bright-field LEEM images of Si(111) during Ga deposition at about 650°C. (Field of view: 5 µm, $E=3.1$ eV). Step edges run bottom up, domain boundaries of the initial 7×7 run from left to right. (a) Prior to Ga deposition, (b) nucleation of Ga $\sqrt{3}$ domains (dark) at step edges and 7×7 domain boundaries, and (c) later stage of the nano-pattern development after further Ga deposition. (For display reasons, the grey scale contrast in (a) has been enhanced by a factor of 3 with respect to (b) and (c)).](image)

A low-energy electron diffraction (LEED) pattern of the surface shown in fig. 3.30 (c) is presented in fig. 3.31 (a). It clearly reveals the coexistence of 7×7 and $\sqrt{3}\times\sqrt{3}$ R 30° reconstructed areas on the surface. Dark-field LEEM data obtained using one of the $\sqrt{3}$ superstructure spots are shown in fig. 3.31 (b). This result unambiguously confirms that $\sqrt{3}\times\sqrt{3}$ domains have formed at step edges and domain boundaries of the initial 7×7 reconstruction.

The evolution of the surface structure and morphology during Ge deposition onto a Ga/Si(111) nano-pattern is depicted in fig. 3.32. In fig. 3.32 (a), the surface has already undergone a transformation. This can directly be seen from the drastic change in contrast (as compared to fig. 3.30 (c) which was obtained at the same electron energy). Moreover, in an experiment which was performed under the same preparation conditions, the growth of Ge was interrupted in a stage comparable to that of fig. 3.32 (a), and the LEED pattern (cf. fig. 3.32 (b)) did no longer show $\sqrt{3}\times\sqrt{3}$ contributions, but only a diffuse 7×7-like pattern. This indicates that Ge is incorporated preferentially at the former $\sqrt{3}\times\sqrt{3}$ patches. This leads to a site exchange of Ge and Ga, and thus to the formation of a
Figure 3.31: Ga/Si(111) nano-pattern after preparation. (a) LEED pattern ($E=26$ eV) showing both $7 \times 7$ and $\sqrt{3}$ periodicity of the surface. An integer order spot and a $\sqrt{3}$ superstructure spot are labelled. (b) Dark-field LEEM image ($E=28$ eV, $5 \mu$m field of view) taken using one of the $\frac{1}{3}$ order spots. Areas with $\sqrt{3}$-periodicity therefore appear bright.

Ga/Ge/Si(111)-6.3$\times$6.3 structure [18]. Due to the presence of relatively strong $7 \times 7$ LEED pattern contributions, the 6.3$\times$6.3 structure can hardly be detected by LEED, therefore no clear indication for a 6.3$\times$6.3 structure is found in fig. 3.32(b). The 6.3$\times$6.3 structure has a larger local Ga coverage as compared to Ga/Si(111)-$\sqrt{3}$, which leaves behind a patchwork of Ga-terminated 6.3$\times$6.3 domains as well as Si(111)-$7 \times 7$ or Ge/Si(111)-5$\times$5 areas. In the LEEM image in fig. 3.32(a), the spotty appearance of the former $\sqrt{3} \times \sqrt{3}$ regions might be a further indication for such a patchwork with a length scale near the resolution limit of the microscope.

Upon further Ge deposition, the contrast in the LEEM images becomes weaker (see figs. 3.32(c) and (d)), which we attribute to a high density of mobile Ge adsorbate atoms on the surface. In fig. 3.32(e), small bright spots appear which are identified as Ge islands as will be shown below. The nucleation of these Ge islands is almost complete in fig. 3.32(f), and the contrast in the image increases again. This might point to a lattice relaxation of the islands which makes them stable against decay and energetically attractive to Ge adatoms. From figs. 3.32(f) to 3.32(h), the number of islands remains almost constant and the lateral size of the islands increases only slightly, which indicates a three dimensional island growth.

In order to unambiguously determine the nature of the bright spots referred to as Ge islands so far, a LEEM micrograph is compared to an x-ray photoemission electron micrograph (XPEEM) in fig. 3.33(a) and 3.33(b). The images shown in fig. 3.33(b) and fig. 3.33(c) were obtained using Ge 3$d$ and Ga 3$d$ photoelectrons, respectively, and therefore directly provides chemical contrast. Taking a slight drift between the two images (fig. 3.33(a) and 3.33(b)) into account (see black circles), virtually every bright spot in the LEEM image can be identified as a Ge-rich region. This proves that the spots observed in LEEM are indeed Ge islands. The rather weak overall contrast of the XPEEM image in fig. 3.33(b) is attributed to the existence of a Ge wetting layer between the islands. A dark contrast appears at the right hand side of these islands. Since the sample is illuminated from the left hand side under an incident angle of 16° with respect to the surface, this dark contrast reveals the three-dimensional nature of the islands. At a photon energy of 120 eV, the attenuation length in Ge is about 30 nm, which is in the order of the lateral dimension of the Ge islands (about 50 nm FWHM). Hence the dark contrast is identified as a shadowing effect. The preferential nucleation of Ge islands observed here is also related to the presence of Ga on the surface. This finding is in good agreement with
3.4. Results and discussion

Figure 3.32: (a) and (c)–(h) Bright-field LEEM image taken during Ge deposition at about 450°C onto the surface shown in Fig. 3.31(c). (Field of view: 5 μm, E=3.1 eV). The Ge deposition time is indicated in each image. (b) LEED pattern after growth interruption at stage (a), obtained from an experiment performed under nearly identical conditions.

the earlier STM observation (fig. 3.29(c)). Comparing the XPEEM images in fig. 3.33(b) and 3.33(c), a clear correlation between the Ge 3D islands and Ga-rich regions is revealed. This further confirms that the nucleation of such islands in Ga-rich regions is energetically less expensive than on Ga-depleted areas.

In order to explain the preferential nucleation of Ge islands at the former $\sqrt{3} \times \sqrt{3}$ reconstructed areas, either the minimization of the surface free energy, including surface strain energy, or growth kinetics have to be considered as a driving force. A close look e.g. at fig. 3.32(h) reveals that 3D islands start to evolve at the centers of the initial 7×7 domains as well; however, there are denuded zones at the borders of these domains. The width of the denuded zones, which can be interpreted as an effective diffusion length, is found to be about 90 nm for the growth conditions used here. Within the smallest of the initial 7×7 domains, virtually no 3D islands are found. Moreover, many 3D islands on top
of the formerly √3-reconstructed areas (Ga-rich regions) are located near the boundary towards the initial 7×7 domains. These observations imply that there is a net Ge mass transport from the interior of the initial 7×7 domains towards the Ga-rich regions. This leads to an enhanced density of Ge ad-species at the 6.3×6.3 domains and hence it is most likely that the 3D growth is initiated at the 6.3×6.3 domains.

Possible reasons for this kind of net mass transport are either (a) a slower diffusion of Ge on the 6.3×6.3 domains, or (b) a more attractive chemical potential for Ge on these Ga-rich regions as compared to the Ga-depleted areas. Site exchange processes between Ga and Ge are energetically favourable, as has been concluded from the observation of an efficient Ga segregation [19]. This can be interpreted as a hint for the validity of scenario (b). Nevertheless, as has been shown for Si homoepitaxy on As-terminated Si(111) [60], Ge–Ga re-exchange processes can be activated thermally, resulting in temporarily trapped Ge atoms and hence in a reduced effective diffusion length. Therefore, a final decision between kinetics and energetics as the reason for the observed selectivity of the 3D nucleation process might be difficult from a fundamental point of view.

Finally, a larger scale view of the surface as shown in fig. 3.34 clearly demonstrates the quality of alignment which can be achieved. For substrates with larger vicinality, the average terrace width becomes smaller. Hence, the initial 7×7 domain size can be made smaller than the denuded zone width, resulting in a completely heterogenous nucleation. Using this approach, it will be possible to overcome kinetic limitations of the ordering process. Moreover, due to step-step interaction, larger miscut angles lead to more regular terrace width distributions, which should result in even better ordered structures than those presented here. The approach of an adsorbate pre-patterned surface may in principle
Figure 3.34: Bright-field LEEM image taken after Ge deposition (Field of view: 20 µm, $E=6.9\text{ eV}$), showing the alignment of Ge islands (bright spots).

also be applied to Si$_{1-x}$Ge$_x$ alloys. Superior to strain-based approaches, the pattern size could then be tuned independently of the chemical composition, leaving this parameter free for tailoring of the electronic properties.

3.5 Conclusions

The structure and formation of nanometer scale surface patterning by temperature induced 2D phase separation of Ga/Si(111) surfaces has been investigated. Thermal phase transitions of the Ga/Si(111) surface after RT Ga deposition on Si(111)-7×7 have been studied by STM. Depending on the amount of Ga coverage, two types of 2D phase separation and nano-patterning are observed. In case of Ga coverage less than 1/3 ML, mostly triangular Si(111)-7×7 reconstructed areas (within the domain region) are surrounded by $\sqrt{3} \times \sqrt{3}$-Ga structures (at the domain boundary and step edge regions of the initial Si(111)-7×7 surface). For higher Ga coverages ($> 1/3$ ML) the $\sqrt{3} \times \sqrt{3}$-Ga reconstructed areas (within the domain region) are surrounded by 6.3×6.3-Ga structures (at the domain boundary and step edge regions of the initial Si(111)-7×7 surface).

For elevated temperature (400°C $< T < 650$°C) Ga deposition up to 1/3 ML, a similar kind of surface nano-patterning has also been observed using LEEM. The shape of a Ga/Si(111) surface nano-pattern can be tuned by an adequate surface miscut orientation. The pattern formation is based on a heterogeneous nucleation at domain boundaries of the initial 7×7 reconstruction and at step edges. Therefore, the size and shape of the nano-pattern can be tuned by the modulus of the miscut angle. A model for the underlying mechanism of pattern formation has been proposed which predicts that other adsorbates on Si(111) could exhibit a similar behaviour. This prediction has been confirmed replacing Ga with In, supporting the validity of the model. However, for a Ga deposit exceeding 1/3 ML during an elevated temperature deposition (400°C $< T < 550$°C), only the surface steps can play a dominating role on phase separation. Controlling the amount of Ga deposit, nano-pattern with special variation of Ga coverage such as 6.3×6.3-Ga recon-
structured nano-wire (at the step edge) separated by $\sqrt{3} \times \sqrt{3}$-Ga reconstructed structures (separation gap is about the terrace width) can be obtained.

Ga-induced surface nano-patterning of Si(111) allows for a further degree of freedom for subsequent processing, e. g. for the growth of Ge 3D nano-structures. It is shown that partially $\sqrt{3} \times \sqrt{3}$-Ga covered nano-patterned Si(111) substrates successively act as templates for selective nucleation and alignment of 3D Ge islands. In contrast to many other approaches, the underlying mechanism is not based on (volume) strain modulation, but on the modulation of surface properties.

Bibliography


Chapter 4

Growth, structure and morphology of thin silicon nitride films

4.1 Abstract

The growth, structure and morphology of ultra-thin silicon nitride (Si$_3$N$_4$) films grown on Si(111) substrates have been investigated using low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and ESCA microscopy. The nitridation of Si(111) surfaces has been carried out using a radio frequency nitrogen plasma source as well as an electron cyclotron resonance plasma source. The nitridation temperatures were ranged from 600°C to 1050°C, whereas the growth time also varied from 5 sec for starting the initial nucleation up to the saturation thickness.

The initial nucleation stage, thickness and temperature dependent changes in the films structure and morphology, the surface atomic structures and the films chemical composition of silicon nitride films are discussed within this chapter. Initial Si$_3$N$_4$ nucleation always starts at the steps with a nucleation patch, i.e., either at the step edges of the Si(111) surface or on the terrace area by forming an etch pit. With increasing nitridation temperature, the size of the nucleation patches are enlarged but the number is decreased. The shape of the nucleation patches becomes more regular, of an equilateral triangle. The nitride film crystalline quality improves with increasing substrate temperature but the surface morphology degrades and appears rougher with holes and grooves forming on the surface. Honey-comb like ”8×8” surface reconstructions are observed for thin nitride films, whereas for thicker films ”8/3×8/3” super structures are obtained for higher nitridation temperature. The chemical homogeneity of the silicon nitride films is tested and a homogeneous film with a stoichiometry of Si$_3$N$_4$ is found. All findings are explained in terms of thermally activated inter-diffusion of Si and N atoms and surface adatom diffusion/mobility. Some parts of the result presented here have already been published [1–4]

83
4.2 Introduction

4.2.1 Motivation

In semiconductor technology, insulating films are of high practical importance for the implementation of virtually all kinds of integrated circuit devices. Due to the miniaturization of ultra large scale integrated (ULSI) circuits all the device components are getting smaller. To achieve a high level of integration and speed the thickness of the insulating films need to be controlled down to nanometer scale. The ultra-thin insulating films not only help to minimize the devices size, but also provide the opportunity for novel device development such as barrier material in resonant tunneling diodes [5] or magnetic tunnel junction memory devices [6].

The high quality and superior homogeneity of SiO$_2$ on silicon (Si) made it the most useful insulating material in the integrated microelectronic devices for the last few decades. The continued approach of device size miniaturization requires a thickness of the corresponding oxides of a few atomic layers. Therefore, the homogeneity in terms of film morphology and chemical composition becomes more and more pronounced. Small fluctuations in oxide layer thickness play a crucial role since they may lead to the break-down of a device, for instance due to enhanced electron tunneling through the extremely thin insulating barriers or capacitors.

To overcome this problem, a search for new materials with a higher dielectric constant is required in order to replace the SiO$_2$ layer. Among the various possible candidates, silicon nitride (Si$_3$N$_4$) received considerable attention due to its compatibility with Si processing technologies. The larger dielectric constant of Si$_3$N$_4$ compared to SiO$_2$ could be useful for replacing the thin SiO$_2$ layers by thicker Si$_3$N$_4$ layers. This can reduce the charge losses due to tunneling currents through the ultra-thin insulator films without any change in the capacitance of the device. Recently, ultrathin Si$_3$N$_4$ and silicon oxynitride films gathered increasing attention for replacing SiO$_2$ as a gate dielectric material [7, 8] because of its higher dielectric coefficient and diffusion resistive passive materials properties. In addition, the high thermal stability of silicon nitride makes it of high technological demand for its various application as high temperature structural ceramics. Furthermore, the high refractive index makes it capable for anti-reflective coating materials. Finally, thin Si$_3$N$_4$ layers on Si can serve as a substrate for GaN growth [9] to integrate the optoelectronic devices to the well–established silicon technology. Hence, for a better understanding of growth, structural and chemical properties in a very local scale, detailed studies of the Si$_3$N$_4$ films are highly motivated.

4.2.2 Structure and properties

Silicon nitride is one of the new high temperature structural ceramics developed for its high mechanical strength at room and elevated temperature as well as for its high fracture toughness. It is thermally stable up to 1600$^\circ$C in air and has a larger dielectric constant ($\epsilon=7.5$) with respect to SiO$_2$ ($\epsilon=3.8$). The energy band gap of this semiconducting mate-
The crystal structure of $\beta$-Si$_3$N$_4$ has been described by various groups and for bulk crystals, the lattice constant $'a'$=7.595 Å in the lateral (X-Y) plane and $'c'$=2.902 Å in the vertical (Z) direction are obtained [10]. A top view schematic model of the $\beta$-Si$_3$N$_4$ structure containing 14 atoms in the lateral plane (normal to c-axis) is shown in figure 4.1. Half of the atoms are placed in the $Z=-c/4$ plane where the other half is in the $Z=c/4$ plane. Local geometric configuration indicates $sp^3$ and $sp^2$ hybridized orbitals for Si and N atoms, respectively. The structure can also be imagined as a complex network of SiN$_4$ tetrahedrons connected at the corners. Structural information about the $\beta$-phase of silicon nitride and its relation to the $\alpha$-phase can also be found elsewhere [10, 11].

### 4.2.3 Previous work

Various methods have been used for the growth of silicon nitride films. In case of chemical vapour deposition from a mixture of silicon-hydrogen (SiH$_4$, Si$_2$H$_6$, Si$_3$H$_8$) and nitrogen-hydrogen (NH$_3$, N$_2$H$_4$, HN$_3$) compounds, it has been observed that the resulting films are usually amorphous, non stoichiometric and contaminated [12]. Nitride layers can also be obtained without supplying any Si source compound, only by direct nitridation of a Si substrate. The three fold rotational symmetry of Si(111) and its 2×2 unit cell of only about 1.1% lattice mismatch with 'a' axis of hexagonal Si$_3$N$_4$ make it a very compatible substrate for the growth of Si$_3$N$_4$ films in (0001) direction. This has been done by exposing the Si substrate to various reactive gases such as NH$_3$ [14–20], NO [21–24] and other gaseous N-compounds at high temperatures or by post-annealing. Other methods such as ion bombardment [25–28] or sputter deposition have also been employed. However, the simplest and easiest way could be to use the pure nitrogen gas for the nitridation. But due to the inertness of molecular nitrogen, a very high growth pressure is required, which might cause severe contamination in nitride film purity. This problem has recently been solved by providing an atomic nitrogen exposure from active nitrogen flux using nitrogen plasma sources. The atomic nitrogen exposure at low temperatures has been
performed on Si(111) and Si(001) surfaces, which leads to the formation of amorphous nitride with a disorder interface of nitride/Si. However, a crystalline interface and well ordered, hexagonal, smooth $\beta$-Si$_3$N$_4$ films have only been observed for a nitridation at a temperature higher than 700°C [16–20, 25–30].

Several methods have been employed to study the growth process and structural characterization of thermally grown nitride layers with laterally averaging surface probing instruments such as low energy electron diffraction (LEED), reflected high energy electron diffraction (RHEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), photoelectron spectroscopy with X-ray (XPS) and ultraviolet light, thermal desorption spectroscopy (TDS) etc. Regarding the growth kinetics and direct microscopic information in atomic scale low energy electron microscopy (LEEM), atomic force microscopy and scanning tunneling microscopy have been utilized. Some studies on X-ray reflectivity (XRR) have also been carried out for information about the film thickness and the subsurface interface. A detailed investigation on structural and chemical information of silicon nitride has also been reported in an earlier master thesis from our working group [31, 32].

### 4.2.4 Surface reconstruction of Si$_3$N$_4$(0001)

From all the above mentioned experimental observation it has been found out that the Si$_3$N$_4$ films are usually amorphous at lower growth temperatures and crystalline Si$_3$N$_4$ films are only formed at relatively high growth temperatures. Depending on the growth temperatures, crystalline Si$_3$N$_4$(0001) films grown on Si(111) have shown two different types of surface reconstruction. Using various methods these two well known surface reconstructions, (i) "8×8" and (ii) quadruplet structures (3/4×3/4), have been observed. In some cases also doublet or sextet structures have been found. It has been reported that the "8×8" reconstruction appeared at relatively low growth temperatures and the quadruplet structures are favourable for higher growth temperatures with a slight surface contamination. The details of the two main surface reconstructions are discussed below.

#### "8×8" reconstruction

By nitrifying the Si(111) surface or post annealing the nitrogenated Si(111) surface above 700°C the ordered "8×8" structure appears in LEED. The quotation marks are used for the coincidence of the unit cell lattice vector with the 8×8 unit cell of the unreconstructed Si(111)-1×1 surface of unit cell 3.84 Å. From various observed experimental results, several structural models have been proposed to explain the "8×8" structures of Si$_3$N$_4$/Si(111) and some of them are contradicting the others.

Considering the LEED and EELS results, Nishijima et al. [22] first proposed a structural model accounting for the "8×8" structure where 11 unit meshes of the nitrified surface match with 8 unit cells of the unreconstructed Si(111)-1×1 surface. Hence the basic unit cell of "8×8" structure is determined as 8/11×3.84 Å, i.e., 2.79 Å with a periodicity of 8×Si(111)-1×1 unit cell (30.2 Å). Additionally, the triangular pyramids of Si$_3$N separated
by 2.79 Å in a quasi-planar silicon nitride surface exhibiting a $sp^3$ hybridization have also been proposed. But afterwards Bauer et al. [16] observed superstructures of "8/3×8/3" lattice periodicity in STM imaging and 8×8 structures in LEED. As the structural model proposed by Nishijima et al. could not explain the 8/3×8/3 structure, they proposed a new model for the 8/3×8/3 structure. Within this model, Si atoms are found at the center of the Si-N honeycomb which is effectively acting as tunneling site for the STM and appear as bright spots with 8/3×8/3 periodicity of Si(111)-1×1 unit cell (3.84 Å). To explain the 8×8 LEED spots with the 8/11 unit cell, Morita et al. [29] proposed a different model modifying the Nishijima model, taking into account the interaction of the Si(111) substrate with the top most nitride layer. They explain the appearance of 8/3×8/3 structures by isolated dangling bonds between the subsurface interface and the nitride layer. Wang et al. [18] have proposed a model with a 4×4 surface reconstruction of Si$_3$N$_4$ to explain the "8×8" structures. Recently Ahn et al. [20] have proposed a structure model with nine adatoms for the "8×8" structures of Si$_3$N$_4$ using Kikuchi electron holography (KEH), STM and ab initio calculation. They also proposed from scanning tunneling spectroscopy that the tunneling site in the STM image is the N-atom, which appears bright in the 8/3×8/3 superstructure. A new model based on x-ray standing wave measurements has also been proposed [31].

Quadruplet structure or 3/4 ×3/4 reconstruction

The other surface reconstruction of Si$_3$N$_4$/Si(111), reported to appear at higher growth temperatures (above 950°C), is the quadruplet structure with a lattice unit cell of 3/4 times of the Si(111)-1×1 unit cell, i.e., 2.88 Å(3/4×3.84 Å). The quadruplet surface has been found to be a 3/4×3/4 triangular lattice with rotations of ±5° and ±10°. It has also been reported that the quadruplet structure preferentially appeared for a contaminated Si(111) surface. Similar to the "8×8" structural model, Nishijima et al. [22] have also proposed a structural model based on LEED and EELS studies. The proposed structure consists of a $sp^2$ hybridization of the Si-N network of flat structure as compared to the $sp^3$ pyramidal structure of the "8×8" phase. Recently Morita et al. [30] have successfully resolved the atomic structures of the quadruplet structures using STM. Depending on the bias dependency of the STM image appearance, they have also proposed a new structural model modifying the earlier proposed model of Nishijima et al. (fig. 4.2).

Figure 4.2: Structural model of the quadruplet structure of Si$_3$N$_4$ proposed by Morita et al. [30] with a hexagonal pyramidal structure. The large open and shaded circles corresponds to the top and bottom Si atoms, whereas small open circles correspond to the nitrogen atoms. The unit vector of the $3\sqrt{3}/4 \times 3\sqrt{3}/4$ structure is super imposes and a hexagonal pyramid is indicated by a dotted line.
4.3 Experimental details

The major parts of the experiments were carried out in the STM chamber of our institute at Bremen University. The STM chamber is \textit{in-situ} connected to the preparation chamber with a base pressure of $5 \times 10^{-11}$ mbar, equipped with small evaporators for MBE growth. For characterization, variable temperature scanning tunneling microscope (Omicron VT-STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) are available. Some of the experiments were also done at the ESCA microscopy beamline at the ELETTRA synchrotron light source, Trieste, Italy with assistance of beamline scientists Dr. L. Gregoratti, Dr. A. Barinov and Dr. L. Aballe.

Highly oriented ($0.02^\circ$ miscut) boron doped p-type silicon (111) wafers were used as substrates. The typical sample size for our experiments was about $10 \times 2$ mm$^2$. After \textit{ex-situ} cleaning with methanol, the samples were loaded into the UHV chamber for degassing at 600$^\circ$C for more than 12 hours. By three to four times short flashing at about 1200$^\circ$C the native oxide was removed from the silicon surface and the clean Si(111) surface with $7 \times 7$ reconstruction was prepared prior to the nitridation process. The sample heating was performed using resistive heating by passing a direct current through the sample and the temperature was measured by a infrared pyrometer with an uncertainty of $\pm 30^\circ$C. This preparation was checked by LEED and STM, and a clean $7 \times 7$ reconstruction was observed reproducibly.

The nitridation process of the Si substrate was done by exposing the clean Si(111) surface to active nitrogen flux at different elevated growth temperatures. Two types of commercial plasma sources: (i) a radio frequency (RF) plasma source from Epi Uni-bulb and (ii) an electron cyclotron resonance (ECR) plasma source from Tectra electronics were used as active nitrogen sources. In both cases the pressure within the plasma chamber was controlled by a leak valve with an inlet line of N$_2$ gas. Dry nitrogen gas of high purity was introduced to the nitrogen plasma chamber through the leak valve. The rf-plasma was operated at about $10^{-5}$mbar under 450W rf-power during the formation of Si$_3$N$_4$, whereas the working pressure for the ECR plasma was one order higher and was maintained to about $10^4$ mbar with a plasma current of about 40 mA. The flux of active nitrogen was calibrated and found one order higher for the rf-plasma source with respect to the ECR plasma source. Details about the plasma sources can be seen in chapter 2.

The exposure time of the Si substrate under the active nitrogen flux was varied. By this procedure coverages starting from sub-monolayer silicon nitride coverage up to saturation thickness were realized. Depending upon the nitridation temperature, post annealing and the duration of plasma exposure time, the surface morphology of silicon nitride changed. The average crystallinity and the surface reconstructions were characterized by LEED. The surface morphology, growth kinetics, nucleation process and the real space atomic structure were investigated by \textit{in-situ} STM measurements. Auger electron spectroscopy (AES) was measured for surface chemical information. ESCA microscopy and X-ray photoelectron spectroscopy were employed to get information about the chemical composition, stoichiometry, film thickness and homogeneity of the surface.
4.4 Results

4.4.1 LEED results

The overall information about the surface reconstruction and the crystalline quality of Si$_3$N$_4$ films on Si(111) with nitridation temperatures ranging from 600°C to 1100°C, have been studied by low energy electron diffraction (LEED). Prior to the surface nitridation the degassed Si(111) samples have been flashed at 1200°C for 3-4 times to achieve a clean silicon surface with a sharp 7×7 LEED pattern. For both the rf and ECR plasma sources, nitridation below 600°C shows a very faint ”8×8” reconstructed LEED pattern, indicating a poor crystallinity of the nitride films and mostly amorphous silicon nitrides are formed. With increasing nitridation temperature, the crystallinity of the nitride films improved and the ”8×8” LEED patterns become sharper. Using the rf-plasma source for nitridation about 15 min, the evolution of the ”8×8” structures depending on the nitridation temperature have been shown in figure 4.3. For clean Si(111)-7×7, the LEED patterns have been shown in fig. 4.3(a) where the yellow and cyan circles correspond to the (0,0) and (1,0) diffraction spots of the Si(111) surface. After nitridation at 700°C, faint (1,0) diffraction spots of Si$_3$N$_4$"8×8" structure have been observed as shown by the purple circles in fig. 4.3(b). By increasing the nitridation temperature to 800°C the LEED spots appeared brighter and a faint additional superstructure of "8/3×8/3" has been found, as indicated by the red circles (fig. 4.3(c)). In case of a further increase of the nitridation temperature to 920°C (fig. 4.3(d)), the LEED patterns sharpen significantly. The "8/3×8/3" superstructures (red circles) appeared much brighter and dominant for the lower electron beam energy. From the position of the various diffraction spots of the Si$_3$N$_4$"8×8" structure and comparing it to the Si(111) diffraction spots, a periodicity of about 2.79 Å is found for the "8×8" structures. However for "8/3×8/3" super structures a periodicity of 10.2 Å has been observed.

Figure 4.3: LEED patterns show the evolution of the Si$_3$N$_4$"8×8" structure with increasing nitridation temperature. The yellow and cyan circles correspond to the (0,0) and the (1,0) diffraction spots of Si(111). The purple circles corresponds to the (1,0) diffraction spots of Si$_3$N$_4$"8×8" structures, whereas the "8/3×8/3" superstructures are indicated by red circles. The nitridation temperatures for the corresponding LEED images are (a) clean silicon, (b) 700°C, (c) 800°C and (d) 920°C, respectively. The electron beam energies for all the images are about 43 eV.

In case of surface nitridation at even higher temperatures (≥950°C) the other type of
Si$_3$N$_4$/Si(111) surface phase appears which is known as the 'quadruplet structure' or 3/4×3/4 reconstruction in coexistence with the "8×8" structure. With increasing nitridation temperature, the "8×8" patterns become faint and a clear quadruplet structure starts to dominate in the LEED patterns only above 1000°C. In figure 4.4, the LEED patterns of the Si$_3$N$_4$ surface are shown for 12 min nitridation at 1050°C. Quadruplet structures have appeared in bright spots (marked by the blue ellipse) with rotations of the crystalline domains ±5° and ±10° to the underlaying silicon lattice vector as mentioned earlier. The coexisting (1,0) spots of the Si$_3$N$_4$ "8×8" structure can also be found within the purple circles. By comparing the LEED spots of the quadruplet structure with the (1,0) diffraction spot of Si(111), a lattice spacing of about 2.88 Å has been observed for quadruplet structures. It has been reported that the quadruplet structures preferentially occur with a contaminated surface sometimes even at lower temperatures [16, 33].

![LEED patterns of the silicon nitride film obtained by nitridation of Si(111) at 1050°C showing the intense quadruplet structure with a faint coexistence of the "8×8" pattern. The yellow and the cyan circles correspond to the (0,0) and the (1,0) diffraction spots of Si(111). The quadruplet structures are indicated by blue ellipses, whereas the (1,0) diffraction spots of the Si$_3$N$_4$ "8×8" structure are represented by the purple circles. The electron beam energy for the LEED image is 52 eV.](image)

4.4.2 STM results

STM studies of various silicon nitride films grown using both rf and ECR plasma are presented here. Nitride films grown at a wide range of nitridation temperatures and thicknesses from submonolayer coverage up to the saturation thickness are studied. The initial stage of nucleation, growth, surface morphology and atomic structures of silicon nitride are discussed.

**Initial nucleation**

After exposure of the Si(111) surface to atomic nitrogen at elevated substrate temperatures silicon nitride structures are formed. A clear understanding of the growth mechanism and the structural properties of silicon nitride on Si(111) is of high fundamental interest in order to know how the initial nucleation process takes place and the N atoms adsorb on the Si surface. Hence for submonolayer coverage, the initial stage of nucleation and the formation mechanism of Si$_3$N$_4$"8×8" structures on the Si(111) surface have been studied and will be discussed in this section.

In figure 4.5, the evolution of the Si(111) surface morphology with increasing nitridation temperatures of (i) 720°C, (ii) 760°C, (iii) 800°C and (iv) 850°C, after rf-plasma exposure for 5 sec are shown. The surface exhibits many small nucleation pits within the Si(111)
4.4. Results

(i) Nitridation at 720°C, using rf-plasma for 5 sec

(ii) Nitridation at 760°C, using rf-plasma for 5 sec

(iii) Nitridation at 800°C, using rf-plasma for 5 sec

(iv) Nitridation at 850°C, using rf-plasma for 5 sec

Figure 4.5: STM images of submonolayer coverage silicon nitride nucleation with increasing nitridation temperature (i) 720°C, (ii) 760°C, (iii) 800°C and (iv) 850°C, respectively, using rf-plasma exposure for 5 sec.
terrace (appearing as dark spots) as well as discrete patches of nucleation at the step edges (appearing in lower contrast) within the upper terrace. Henceforth for simplicity dark dot-like structures within the terrace area will be mentioned as ‘nucleation pits’ and those for the step edge will be referred to as the ‘nucleation patches’. In case of nitridation at higher temperatures of 800°C and 850°C, the numbers of nucleation pits within terraces and nucleation patches at the step edges are drastically reduced, whereas the average sizes are highly enlarged as compared to the lower nitridation temperature of 720°C and 760°C. Comparing all the images from 720°C to 850°C, it is clearly observed that the density of the nucleation pits within terraces and the nucleation patches at step edges are decreased, whereas the average size is increased with increasing nitridation temperature. Usually, nucleation patches appear larger in size than the nucleation pits. In addition, from a careful observation it can also be noticed that the larger etch pits are preferentially located along the initial domain boundaries of the Si(111)-7×7 surface. Moreover, the shape of the nucleation pits becomes more regular for higher nitridation temperatures (800°C to 850°C) and in general these appear as equilateral triangular patterns. Also at the step edges, the triangular nucleation patches are observed at the upper terrace and the apex of the triangles pointing away from the steps towards the [112] crystal direction. The crystal directions can be determined by comparison of the faulted and unfaulted half of the Si(111)-7×7 unit cell. This finding is similar to the nucleation of 7×7 domains during phase transition from (1×1) to (7×7) of the Si(111) surface at about 830°C. The orientation is also valid for most of the triangular pits within the terrace.

![Figure 4.6: Closer view STM images (-2.5 V) of the nucleation pits within the Si(111)-7×7 terrace after nitridation at 760°C for 5 sec using a rf plasma source. The black arrows indicate the initial silicon nitride nucleation in the vicinity of the etch pits.](image)

The closer view STM images of the nucleation pits within the Si(111) terrace formed after nitridation at 760°C are shown in figure 4.6. The Si(111) surface appears with etch pits of arbitrary shape. Surprisingly, a clean Si(111)-7×7 reconstruction is found within the pits. The Si(111)-7×7 structures within the etch pits follow the same rotational symmetry as the surrounding Si(111)-7×7 terrace. From this finding, we can conclude that the initial N exposure leads to the surface etching, which results in the evolution of vacancy islands (nucleation pits) by local removal of the top Si layer. This is accompanied by the formation of silicon nitride, preferentially in the vicinity of the nucleation pits as indicated by black arrows within fig. 4.6(b). A similar kind of observation is also found for plasma treatment at 720°C (image is not shown). But the nucleation pits appear only in a smaller size with a higher density. For the step edge nucleation patches no regular structures are observed.
4.4. Results

Nitridation at 760°C for 5 sec

![Large area STM images and line scan height profiles of the nucleation pits within the Si(111)-7×7 terrace after nitridation at 760°C for 5 sec using rf plasma source.](image)

The depth profiles of the nucleation pits are shown in figure 4.7. To give an idea of the height scale, a comparison of the height difference between the S(111) bilayer step (3.14 Å) and the nucleation pit has been chosen. Most of the pits in STM observation are appeared about 1.5 Å deeper than the Si(111)-7×7 terrace. Some of the nucleation pits appear deeper than 1.5 Å in the line profile due to the formation of further holes within them.

![Closer view STM images of the nucleation pits within the Si(111)-7×7 terrace and at the step edge after nitridation at 800°C for 5 sec using rf plasma source.](image)

The closer view STM images of the surface for a nitridation temperature of 800°C are shown in figure 4.8. For both images nucleation etch pits of an equilateral triangular pattern are observed. In general, most of the nucleation pits show a clean Si(111)-7×7 structure with a height difference of 1.5 Å, similar to the earlier observation (fig. 4.6). Si and/or N adatoms are found preferentially located around the periphery of the 7×7 nucleation pits and appear as bright dots within the STM image (fig. 4.8(a)). Sometimes, generally for the larger nucleation pits, adatoms can also be found within the 7×7 nucleation pits. For nucleation patches at the step edges generally a disordered structure of the nitrided Si(111) surface appears in the STM images. However, in some cases a very
interesting finding can be observed as shown in fig. 4.8(b). Here a transition period of 7×7 nucleation patches to "8×8" structures at the step edge is presented. An atomically resolved Si(111)-7×7 structure is observed at the inner side, whereas a Si₃N₄-"8×8" is observed at the outer side of the step edge. Comparing the height difference of the 7×7 reconstructed area within this nucleation patch to the upper and lower terrace it is confirmed that the structure appears in the same height scale as the nucleation pits, i.e., about 1.5 Å lower or higher than the upper or lower terrace, respectively. Furthermore, the Si(111)-7×7 structure within nucleation pits or nucleation patches exhibit the same rotational symmetry of the Si(111) terrace structure, only with a translational shift.

In case of nucleation at 850°C, atomically resolved honey-comb like "8×8" structures of Si₃N₄ are observed for both cases of nucleation within terraces and at the step edges. Si(111)-7×7 structures are not found within the nucleation site anymore.

(i) Nitridation at 800°C for 30 sec
(ii) Annealing at 850°C for 60 sec
(iii) Further annealing at 900°C for 60 sec

Figure 4.9: STM images of the structure and evolution of the Si(111) surface morphology after nitridation at 800°C for 30 sec using rf-plasma (i) and subsequent post annealing at 850°C (ii) and 900°C (iii) for 1 min, respectively.

Effect of annealing

From earlier observations it is realized that the substrate temperature can significantly influence the growth and initial nucleation of silicon nitride. This finding highly motivates the attempt to gather the knowledge on how the annealing temperature affects the
4.4. Results

The evolution of surface structures. Within this section the effect of the post-annealing at different temperatures on the submonolayer coverage silicon nitride surface grown at 800°C is discussed.

In figure 4.9, STM images show the Si(111) surface after nitridation at 800°C for 30 seconds exposure under rf-plasma and subsequent post-annealing at 850°C and 900°C for one minute. After nitridation at 800°C for 30 sec, nucleation pits within the terraces and nucleation patches at the upper terrace of step edges are formed (fig. 4.9(i)). However, the size and density of the triangular nucleation pits and patches are distinctly enhanced as compared to the earlier observation for 5 sec nitridation (fig. 4.5(i)). In case of annealing at 850°C for 1 min, the surface adatoms get mobile and due to high thermal diffusion, change the surface morphology (fig. 4.9(ii)). The triangular nucleation pits, which are located away from the lower steps, are not changed so much, but mainly the nucleation patches at steps and the nucleation pits in close proximity to the lower steps are highly affected. Some of the nucleation patches get detached from the upper terrace and stay as free standing nitride islands in the lower terrace. In addition, the size of the free standing islands has increased due to the coalescence of the nucleation patches and nucleation pits. By comparing with initial images (fig. 4.9(i)) a local retraction of the surface steps towards the upper terrace has been observed which results in the formation of free standing islands on the lower terrace now. The triangular shape of the nitride pits has also changed in the free standing islands which is discussed later. For further annealing to 900°C for another minute the changes in the surface morphology continued as shown in fig. 4.9(iii). The size enlargement of the free standing islands as well as the movement of the surface steps further progressed, which sometimes leads to a breaking of the terrace structures. It can be noticed that the nucleation of N adatoms is also started at the domain boundary regions connected between nitride nucleation pits (bright dots within the terrace in 0.2×0.2 μm² STM image of fig. 4.9(iii)). Depending on the tunneling bias voltage the appearance of the free standing islands in STM imaging can be altered as can be seen in the middle and right column of figure 4.9(ii).

(a) 65×65 nm² (b) 150×150 nm²

Figure 4.10: Closer view STM images of a silicon nitride film surface after nitridation at 800°C using rf-plasma exposure for 30 sec.

The closer look STM images of the surface after nitridation at 800°C for 30 sec are shown in figure 4.10. In contrast to the earlier observation of fig. 4.8, a honeycomb-like ”8×8” structure of Si₃N₄ is usually found within the nucleation pits (fig. 4.10(a)). The diminished quality of the ”8×8” structure indicates a pour crystallinity of the silicon
nitride at this nitridation temperature. In few cases, the Si(111)-7×7 etch pits are only partially filled by the Si$_3$N$_4$ structure. The Si$_3$N$_4$ structure appears at a darker contrast within the pits as shown in fig. 4.10 (b). Comparing these results to fig. 4.8 it can be concluded that the "8×8" silicon nitride prefers to nucleate within the nucleation pits rather than on the normal 7×7-Si(111) terraces.

(a) 150×150 nm$^2$ (b) 60×60 nm$^2$

(i) Annealing at 850°C for 60sec

(c) 150×150 nm$^2$ (d) 50×50 nm$^2$

(ii) Further annealing at 900°C for 60 sec

Figure 4.11: Closer view STM images of a nitrified silicon surface, subsequently annealed at 850°C and 900°C for 1 min, respectively.

The closer look STM images of the nitrified Si(111) surface after subsequent annealing steps are shown in figure 4.11. After post-annealing at 850°C for 1 min, significant changes in the structure and the surface morphology of the nucleation pits are observed. Etch pits, which were partially filled with disordered Si$_3$N$_4$ structures, are now completely covered with Si$_3$N$_4$ showing an ordered honeycomb-like "8×8 atomic arrangement (fig. 4.11(i)). Si(111)-7×7 structures are not found anymore within the etch pits. A sharper appearance of the "8×8" structure indicates an improvement in the crystalline quality. Apart from the structural properties, the size and shape of the nitride nucleation centers have also been altered. The shape of the "8×8" nucleation pits remains triangular. However, the morphology of the free standing islands turned towards a rather hexagonal shape by forming a truncated equilateral triangle as shown in fig. 4.11(ii). For second step annealing at 900°C, silicon nitride nucleation also starts at the initial domain boundary regions of the 7×7 terrace. This area connects the different nucleation pits. The structural symmetry of the "8×8"-Si$_3$N$_4$ is also improved. The improvement in the crystalline quality with nitridation/annealing temperature observed here is also in agreement with the conclusion drawn from LEED observation.
4.4. Results

(i) Nitridation at 850°C, using rf-plasma for 5 sec

(ii) Nitridation at 850°C, using rf-plasma for 20 sec

(iii) Nitridation at 850°C, using rf-plasma for 30 sec

(iv) Nitridation at 850°C, using rf-plasma for 120 sec

Surface morphology with increasing thickness

In the previous section it has been realized that the increase of the plasma exposure time from 5 sec to 30 sec highly influenced the structure and surface morphology of the nitrified Si(111) surface. Hence, the morphology of the Si₃N₄ surface can be modulated by varying the thickness of the nitride films and is of high practical interest. It has also been noticed
that for a higher nitridation temperature of 850°C, the crystallinity of the "8×8"-Si₃N₄ structure is improved. Within this section morphological evolutions of the nitrified Si(111) surface at 850°C with increasing rf-plasma exposure time have been compared. Starting from 5 sec for initial nucleation, the Si(111) surface was exposed under rf-plasma up to 45 min for a saturation coverage of the nitride film.

In figure 4.12, STM images show the structure and morphological evolution of the Si(111) surface, nitrified for (i) 5 sec, (ii) 20 sec, (iii) 30 sec and (iv) 120 sec, respectively, using rf-plasma exposure at 850°C. For 5 sec exposure, the surface exhibits triangular nucleation pits within the terrace area as well as nucleation patches at the step edges (fig. 4.12(i)). Both structures show an atomic structure of honeycomb-like "8×8"-Si₃N₄. Sometimes a small area of the Si(111)-7×7 surface reconstruction is also observed within the Si₃N₄ nucleation patch at the step edges. For a longer exposure of 20 sec, the structures appear larger and for some cases the nucleation patches at the step edge reach the next step and that results in the breaking of the Si(111) terrace (fig. 4.12(ii)). For 30 sec of nitridation, the coverage of the "8×8"-Si₃N₄ reconstructed area increased and the nucleation patches at the step edge cross the next step (fig. 4.12(iii)). This causes a damage in the Si((111) terrace structure which results in formation of 2D islands and eventually step bunching. After 2 min of exposure, the surface is totally covered by "8×8" structures (fig. 4.12(iv)). The terrace structure totally breaks and large islands with atomically flat top surfaces are observed. Due to step bunching some of the islands appear with a height of a few bilayer step-height of Si(111). In closer view, atomically resolved honeycomb-like "8×8" structures of Si₃N₄ are obtained throughout the surface.

In case of even longer plasma exposure, the nitride layers become thicker and the morphology of the silicon nitride surface for (i) 4 min, (ii) 8 min, (iii) 12 min and (iv) 45 min of nitridation is shown in figure 4.13. After 4 min of nitridation, the surface morphology appears rough with grooves and holes on the surface and the terrace structures are partially broken as can be seen in fig. 4.13(i). Occasionally, some small bright spots also appear on the surface. For continuing nitridation up to about 8 min the terrace structures have severely been damaged and the location and topology of the steps on the nitride film have no correlation with the steps of the original Si(111) surface (fig. 4.13(ii)). An even longer nitridation of 12 min results in completely broken terrace structures and the formation of 2D islands with flat surfaces (fig. 4.13(iii)). The step heights for the nitride islands are observed to be in integer multiple of 2.9 Å, indicating multiple layer films of β-Si₃N₄. The step height also suggest the correlation of the nitride film with the Si(111) substrate as Si₃N₄(0001)||Si(111). In addition, the holes and grooves on the surface appear larger and deeper and the border of the islands appears mostly in a straight line. The structure within the holes and grooves is very similar to that on the islands, which confirms the nucleation of nitride within the holes/grooves and the formation of a continuous layer of Si₃N₄. Furthermore, the size of the bright spots also enlarges and is preferentially found on top of the islands. Details about the appearance of the bright spots will be discussed later. For 45 min of nitridation, the nitride film thickness becomes saturated and the morphology changes drastically (fig. 4.13(iv)). The overall surface roughness is decreased as the holes/grooves are partially filled and become smaller and shallower. However, the top surface becomes very rough and appears with many small
4.4. Results

Nitridation at 850°C, using rf-plasma for increasing duration

(i) 4 min (ii) 8 min (iii) 12 min (iv) 45 min

Figure 4.13: STM images of the silicon nitride film surface with increasing duration of rf-plasma exposure.

granular structures. Surprisingly, all nitride films of fig. 4.13 do not show any atomically resolved "8×8" honeycomb-like Si₃N₄ structures in STM imaging in contrast to the earlier findings of the nitrified Si(111) surface of up to monolayer coverage (fig. 4.12).

Surface morphology with increasing growth temperature

It has already been observed that the Si(111) substrate temperature can highly influence the crystalline quality and surface morphology of the silicon nitride film. Within this section the temperature dependent morphological evolution of two types of nitride films grown using a rf-plasma source is discussed. Firstly, the thin nitride films of a few atomic layer thickness (~1 nm) grown after 12 min of nitridation at substrate temperatures from 700°C to 850°C are studied. Later, silicon nitride films of saturation thickness (~2.1 nm) grown at temperatures ranging from 830°C to 1040°C for 45 min of plasma exposure are discussed.

Thin Si₃N₄ films (~1 nm)

In figure 4.14, thin nitride films for 12 min of rf-plasma exposure at (i) 700°C, (ii) 750°C, (iii) 780°C, (iv) 800°C, (v) 820°C and (vi) 850°C, respectively, are shown. In case of nitridation at 700°C (fig. 4.14(i)), the film surface appears atomically flat with bilayer steps of Si(111). At the same time, two dimensional (2D) islands with flat surfaces and
Chapter 4. Growth, structure and morphology of thin silicon nitride films

(i) Nitridation at 700°C, using rf-plasma for 12 min

(ii) Nitridation at 750°C, using rf-plasma for 12 min

(iii) Nitridation at 780°C, using rf-plasma for 12 min

(iv) Nitridation at 800°C, using rf-plasma for 12 min

(v) Nitridation at 820°C, using rf-plasma for 12 min

(vi) Nitridation at 850°C, using rf-plasma for 12 min

Figure 4.14: STM images of silicon nitride film surface morphology with increasing nitridation temperature using rf plasma for 12 min.
very tiny holes within the terrace area are observed. In addition, some very bright spots in
the STM image also appeared, mostly located on top of the 2D islands. If the nitridation
temperature is increased to 750°C (fig. 4.14(ii)), the surface morphology does not change
significantly but the 2D islands and small holes are not found anymore. However, the
bright spots appear in smaller size with higher density, randomly distributed throughout
the terrace area. It has been noticed that the bright spots are preferentially located
within the terrace area and denuded zones usually form along the surface steps. The
bilayer steps of the Si(111) substrate are visible in the STM image but appear not so
smooth as compared to the steps of clean Si(111). Local retreat of the step edge at
the upper terrace or kink formation can also be observed. For nitridation at 780°C (fig.
4.14(iii)), the local retreat and removing of the upper terrace at the steps are enhanced
and the holes reappear on the surface with a larger size. The nucleation of the holes is
strongly preferred at the step edges. The bright spots are also found, preferentially within
the terrace area with a larger size. In case of nitridation at 800°C, the surface morphology
changes significantly as can be seen in fig. 4.14(iv). Local retreat or removal of the upper
terrace at the steps are getting larger and for a few cases reach to the next step, which
results in the formation of free standing islands. The holes appear with a larger size and
a deeper depth not only at the steps but also on the terrace areas. The average size of
the holes located at the surface steps is usually larger than that of the holes found on
the terrace areas. The 2D islands with flat top surface are again found with larger size
and height. Bright spots are also observed preferentially, but not exclusively, on top of
the islands. The morphology after nitridation at 820°C (fig. 4.14(v)) appears in general
with holes/grooves at the step edges with even larger size and deeper depth. In a few
cases they may cross the next step which causes the breaking of terrace structures. Small
2D islands with flat top surfaces are not found within the terrace areas. The holes are
mostly found along the surface steps. For 850°C nitridation temperature (fig. 4.14(vi)),
the breaking of the terraces is largely enhanced and this causes the formation of large
2D islands with flat surfaces. Height scale of the large islands indicates the formation of
multilayered nitride films as discussed in the earlier section. In some cases bright spots
of even larger size appear on top of the 2D islands.

**Thick Si₃N₄ films (~2.1 nm)**

STM images of a silicon nitride film of saturation thickness grown at (i) 830°C, (ii) 900°C,
(iii) 960°C and (iv) 1040°C, respectively, using rf-plasma for 45 min are shown in figure
4.15. In case of nitridation at 830°C (fig. 4.15(i)), the steps of the initial Si(111) determine
those of the nitride surface. Holes and grooves are also found within the terrace area as
well as at the steps. In contrast to the earlier result of thin films, the holes appear
shallower. The surface morphology of the terrace area appears rough with small granular
structures as shown in the 200×200 nm² scan area STM image of fig. 4.15(i). The
surface morphology of the nitride films changes drastically if the substrate temperature
during exposure is increased to 900°C (fig. 4.15(ii)). Due to breaking of the terraces any
correlation of the steps of the nitride films with the initial steps of the Si(111) substrate
is not found. The number of holes is drastically reduced as compared to the earlier result
Chapter 4. Growth, structure and morphology of thin silicon nitride films

(i) Nitridation at 830°C, using rf-plasma for 45 min

(ii) Nitridation at 900°C, using rf-plasma for 45 min

(iii) Nitridation at 960°C, using rf-plasma for 45 min

(iv) Nitridation at 1040°C, using rf-plasma for 45 min

Figure 4.15: STM images of saturation coverage silicon nitride film (45 min rf plasma exposure) with increasing nitridation temperature.
of 830°C of fig. 4.15(i). The top surface looks also rough and many small pits are found within the large flat 2D islands. For 960°C nitridation temperature, the terrace structures of the Si(111) surface break completely and large flat islands are formed (fig. 4.15(iii)). Deep holes and grooves are almost filled and not found anymore. The small pits on the top surface decreased in number but increased in size as compared to the results of 900°C of fig. 4.15(ii). Closer view STM image indicates an incomplete growth of the top layers. For nitridation at 1040°C, the surface morphology appears very different compared to earlier results. Due to the high growth temperature the LEED pattern were also changed and a coexistence of quadruplet structures coexisting with ”8×8” patterns are found. In STM, the surface morphology appears with very deep cracks. Additionally, very large islands (up to few µm) with flat top surfaces have been observed, as shown in fig. 4.15(iv). Only some part of the island is shown here in the STM image. The cracks are sometimes deeper up to even a few 10 nm.

Surface reconstructions of β-Si₃N₄

The most important and interesting part of any kind of STM investigation is the atomically resolved surface reconstruction, as it is a direct evidence of the high crystalline quality and a key element for the understanding of atomic structures and local electronic properties of the material surface. Within this section we will discuss the surface reconstructions of the β-Si₃N₄ film.

Depending on the growth conditions such as nitridation temperature and plasma exposure time, two types of surface reconstructions of ”8×8” structures such as honeycomb-like structures with a surface periodicity of 30.7 Å and ”8/3×8/3” superstructures of 10.2 Å surface periodicity have been observed for Si₃N₄ films, as discussed in the following. In case of high temperature nitridation (≥ 1000°C) of Si(111), the so called ”quadruplet structures”, i.e., 3/4×3/4 surface reconstructions are found in LEED but atomically resolved structures are not observed in STM.

Honeycomb-like ”8×8” reconstruction

Honeycomb-like ”8×8” surface structures are only found for very thin Si₃N₄ films of coverages below 2 ML. For nitridation temperatures below 800°C, the honeycomb-like structures appear with high defect density and a poor order of crystal symmetry. Whereas a higher nitridation temperature or post-nitridation annealing at higher temperatures helps to improve the order of structural symmetry. For thicker nitride films, this type of surface structures are not well resolved in STM imaging and the Si₃N₄ surface appears with a disordered surface structure.

Empty state STM images of honeycomb-like ”8×8” surface structures of the Si₃N₄ surface of submonolayer coverage, grown at 850°C for 30 sec of rf-plasma nitridation are shown in figure 4.16. A large scale surface overview in fig. 4.16(a) shows the broken terrace structure crossing over the surface steps of Si(111). The nitride nucleation takes place at the upper terrace of the step edges. A closer view of the Si₃N₄ nucleation area is
Chapter 4. Growth, structure and morphology of thin silicon nitride films

Figure 4.16: Empty state STM images of the Si$_3$N$_4$ surface showing honeycomb like "$8\times8$" reconstructions. (a) Surface overview of submonolayer coverage Si$_3$N$_4$ film, (b) honeycomb-like "$8\times8$" surface reconstruction (3V) and (c) closer view.

presented in fig. 4.16(b) where a defective quasi-periodic network with local disordering can be observed. For a further zoom into the honeycomb-like surface area, nicely resolved atomic structures are found as depicted in fig. 4.16(c). It can also be observed that the loop like structures are having short range disorders in lattice symmetry and we assume this as an interfacial state of Si$_3$N$_4$/Si(111). An autocorrelation of fig. 4.16(c) and the corresponding line scan profile is presented in figure 4.17, where a surface periodicity of about 30.6 Å is clearly observed, indicating a "$8\times8$-Si$_3$N$_4$ structure.

(a) autocorrelation   (b) line profile

Figure 4.17: (a) Autocorrelation display of the honey-comb like "$8\times8$"-Si$_3$N$_4$ structure (STM image of fig 4.16(c)) and (b) line scan profile of the marked area in fig.(a), showing a surface periodicity of about 30.6 Å.

"$8/3\times8/3$" surface reconstruction

Apart from the 'honeycomb'-like structures, in some cases another type of "$8\times8$" surface structures with 10.2 Å surface periodicity is also observed, which is known as "$8/3\times8/3$" superstructure. This type of surface structure is observed for relatively thick Si$_3$N$_4$ films formed at a higher nitridation temperature (900-980°C). Long range symmetry of this type of surface structure indicates highly crystalline Si$_3$N$_4$ films can be formed by a proper choice of growth parameters.

Empty state STM images of "$8/3\times8/3$" reconstructed a Si$_3$N$_4$ surface grown at 950°C by 20 min of rf plasma exposure are shown in figure 4.18. In fig. 4.18(a), atomically flat surfaces with multi-layered steps are observed. The minimum step height is found to
4.4. Results

Figure 4.18: Empty state STM images of \(8/3 \times 8/3\) reconstructed Si\(_3\)N\(_4\) surfaces. (a) Surface overview (b) \(8/3 \times 8/3\) reconstructions (4V) and (c) closer view.

be about 2.9 Å, which is the lattice unit cell of \(\beta\)-Si\(_3\)N\(_4\) along (0001) direction, indicating crystalline film growth. A long range atomic symmetry of nicely resolved \(8/3 \times 8/3\) reconstructions with a lattice periodicity of 10.2 Å is shown in fig. 4.18(b). Few defects such as vacancies (dark areas) or adatoms (bright areas) are also visible. A closer look of the \(8/3 \times 8/3\) surface reconstruction is presented in fig. 4.18(c) where a weak 3-fold modulation can also be seen. This might be a reason for the appearance of \(\times 8\) LEED spots together with \(8/3 \times 8/3\) superstructure spots observed for this type of nitride films. An autocorrelation of this superstructure is also done, as shown in fig. 4.19(a) and a structural periodicity of about 10.2 Å is found, as can be seen in the line scan profile in fig. 4.19(b), which confirms the \(8/3 \times 8/3\) superstructure formation. A structural model of the \(8/3 \times 8/3\)-Si\(_3\)N\(_4\) reconstruction has been proposed by Bauer et al. [16] as shown in fig. 4.19(c). According to this model the Si atoms (open circles) located at the center of the Si-N honeycomb act as a tunneling center in STM imaging. Within this structure, each N-atom (filled circles) is surrounded by three Si-atoms and the surface composition of this structure is Si\(_5\)N\(_3\). The \(8/3 \times 8/3\) unit cell is also outlined within the image.

Figure 4.19: (a) Autocorrelation display of the \(8/3 \times 8/3\)-Si\(_3\)N\(_4\) superstructure (STM image of fig 4.18(c)) and (b) corresponding line scan profile of the marked area in fig.(a), showing a surface periodicity of about 10.2 Å. (c) A structure model of the \(8/3 \times 8/3\) reconstructed structure proposed by Bauer et al. [16]. The filled circles represent the N-atoms, whereas the open circles stand for the Si-atoms.
Nitridation of Si(111) using ECR plasma

Nitridation experiments of Si(111) surfaces have also been performed using an electron cyclotron resonance (ECR) plasma source from Tectra electronics. Similar kind of STM and LEED investigations have been performed to compare the effect of the ECR plasma instead of the rf source. The operating pressure within the ECR plasma chamber for plasma ignition was about $\sim 10^4$ mbar which is one order higher than the operating pressure of the rf-plasma chamber.

![Figure 4.20: Empty state STM image of the Si(111) surface after exposure under ECR plasma for 1 min at 750°C. (3V, 200×200 nm²).](image)

Similar to the earlier observations, the initial nucleation of silicon nitride on Si(111) using an ECR plasma source also occurs by forming triangular nucleation pits on Si(111) as can be seen in figure 4.20. As discussed earlier, the apex of the triangular nitride nucleation centers are facing along the $(\bar{1} \bar{1} 2)$ crystalline direction within the Si(111) surface. However, the average flux of active nitrogen with an ECR plasma source is found to be significantly lower (about one order) than that of the rf-source.

As the nitridation temperature is the most determining factor for the crystalline quality and surface morphology, detailed STM investigations of Si$_3$N$_4$ films surface morphology with nitridation temperatures are discussed in this section. The Si(111) surface has been exposed under ECR plasma for 15 min and the nitride film thickness is expected to be very thin, only a few atomic layers ($<1$ nm). The nitridation temperatures were varied from 600°C up to 775°C with a temperature interval of 25°C and the dependence of the Si$_3$N$_4$ surface morphology on nitridation temperature is discussed based on STM topography.

In figure 4.21, STM images of Si$_3$N$_4$ surfaces grown at (i) 600°C, (ii) 625°C, (iii) 650°C, (iv) 675°C, (v) 700°C and (vi) 725°C, respectively, are shown. In general, for lower nitridation temperature the Si$_3$N$_4$ surface morphology appears atomically flat and the steps and terrace structures are followed. For a higher nitridation temperature, the surface morphology appears rougher with the insertion of holes and grooves as discussed here. For 600°C nitridation temperature, the surface morphology strictly follows the Si(111) surface (fig. 4.21(i)). For 625°C, additionally two dimensional (2D) islands with flat surfaces and very tiny holes within the terrace have been observed (fig. 4.21(ii)). In some cases, bright spots on top of the 2D islands are also found. In case of a nitridation temperature of 650°C, the nitrified Si(111) surface looks very similar to that of 600°C, only the number and size of the 2D islands as well as the holes within the terrace area have increased (fig. 4.21(iii)). For 675°C, the surface morphology differs drastically. The holes and 2D islands have almost disappeared. Only few islands of a larger size are found...
4.4. Results

(i) Nitridation at 600°C, using ECR-plasma for 15 min

(ii) Nitridation at 625°C, using ECR-plasma for 15 min

(iii) Nitridation at 650°C, using ECR-plasma for 15 min

(iv) Nitridation at 675°C, using ECR-plasma for 15 min

(v) Nitridation at 700°C, using ECR-plasma for 15 min

(vi) Nitridation at 725°C, using ECR-plasma for 15 min

Figure 4.21: STM images of the silicon nitride film surface morphology with increasing nitridation temperature, using ECR-plasma for 15 min.
(vii) Nitridation at 750°C, using ECR-plasma for 15 min

(viii) Nitridation at 775°C, using ECR-plasma for 15 min

Figure 4.22: STM images of the silicon nitride film surface morphology for nitridation temperature of (vii) 750°C and (viii) 775°C, using ECR-plasma for 15 min.

but bright spots on island-tops are not present anymore (fig. 4.21(iv)). In some cases local retreat of upper steps or kink formation at the step edges are also observed (fig. 4.21(iv)). For a nitridation temperature of 700°C (fig. 4.21(v)), the surface morphology appears very similar and the 2D islands have totally disappeared. The steps appear in a more meandering way by further retreat of the upper terrace. Few tiny bright spots on the terrace area have also been found. After nitridation at 725°C (fig. 4.21(vi)), the surface morphology appears very similar to that of 650°C (fig. 4.21(iii)), except the holes are larger and deeper.

By a further increase of the nitridation temperature to (vii) 750°C and (viii) 775°C, the changes in the silicon nitride surface morphology are shown in figure 4.22. After nitridation at 750°C (fig. 4.22(vii)), again the 2D islands disappear, which is similar to that of 675°C (fig. 4.21(iv)). But the surface exhibits many holes, preferentially at the steps. Due to an enhanced retreat of the upper terrace and hole formation at the steps, the nitride surface steps run in curly/meandering way forming rough steps. Finally at 775°C, the retreat of the steps reach to the next step which causes a totally broken terrace structure and hence the formation of large flat islands (fig. 4.22(viii)). The initial steps of Si(111) cannot be observed anymore and additionally some bright spots at the center of the flat 2D islands are observed. In closer view STM images, the formation of a multilayered Si$_3$N$_4$ film with holes can also be observed.
4.4.3 ESCA results

Apart from the direct imaging of surface crystalline properties, ESCA microscopy technique has also been employed in order to investigate the surface chemical properties of the thin silicon nitride films on Si(111). In general, microscopic techniques can only provide the morphological and structural properties, whereas using ESCA microscopy technique, it is possible to investigate the chemical composition of the nitride films with a spatial resolution of 100 nm. Information regarding the film thickness and surface morphology can also be obtained using this technique. The large area scanning facility also gives an opportunity to have an average chemical mapping of the nitride films up to a millimeter level.

The experiments have been carried out at the ESCA microscopy beamline at ELETTRA synchrotron light source in Italy. A photon energy of 495 eV was selected for the measurements. Actually two types of measurements have been performed such as (a) microscopy mode: scanning the sample keeping the analyzer at a particular energy and (b) spectroscopy mode: scanning the analyzer energy with a fixed sample position. Anyway, spectroscopic information can also be obtained from the images as a multi channel analyzer was used for image detection. The contrast within the ESCA microscopy image is mainly arising from two factors: (a) chemical inhomogeneity, i.e., fluctuation in chemical composition and (b) fluctuation in the film thickness or surface roughening. For ESCA microscopy measurements, samples have been prepared using an ECR plasma source and the measurements were performed under UHV conditions. Two types of silicon nitride samples have been tested: (a) flat and smooth nitride film surfaces grown at a relatively low nitridation temperature (700°C) and nitride surfaces with a rough morphology grown at a higher nitridation temperature of 950°C.

![Image](image.png)

Figure 4.23: 12.8×12.8 μm² spectro-micrographs from a Si₃N₄ surface grown on Si(111) at 700°C showing a very weak contrast. The imaging was done at the same scan area using different photoelectrons of (a) N-1s line, (b) nitride component of Si-2p line and (c) Si-2p bulk component, respectively.

In figure 4.23, spectro-micrographs of silicon nitride films grown at 700°C using ECR plasma are shown, obtained with different photoelectrons. Using both Si-2p bulk and nitride components as well as N-1s, a very weak contrast can be seen, which is an indication of surface homogeneity. Smooth surface morphology is also expected for a relatively low nitridation temperature of the Si(111) substrate. To confirm the chemical homogeneity
Chapter 4. Growth, structure and morphology of thin silicon nitride films

Figure 4.24: XPS spectra of the Si-2p line of the silicon nitride film grown at 700°C using ECR plasma for one hour exposure have been checked at three different locations. The spectra are shifted by 0, 5000 and 10000 units for display.

of the nitride film, high resolution XPS spectra of Si-2p photoemission have also been checked for three different locations as shown in figure 4.24. On the higher kinetic energy region, bulk components of Si-2p spectra appear with doublet splitting, which is arising from the non-reacted Si atoms underneath the nitride film. However, for a lower kinetic energy region a broad chemically shifted dominant peak of this spectra is found. This peak-shift can be attributed to the photoelectrons emitting from the Si-atoms, which have already reacted with N-atoms and formed the nitride layer. From the chemical shift of about 2.9 ±0.1 eV within the Si-2p spectra, the information about the nitride film stoichiometry can also be obtained which is in good agreement with Si$_3$N$_4$ as mentioned in the literature [34, 35]. With this known stoichiometry, it is also possible to get an information about the nitride film thickness from the integral intensity ratio of two Si-2p components as shown in equation 4.1. The details of the thickness calculation process can be found elsewhere [4]. For SiN film thickness

$$d = \lambda_{SiN}\cos(\theta)\log\left(\frac{\lambda_{bulk}}{\lambda_{bulk}}\frac{I_{SiN}}{I_{SiN}} + 1\right)$$ (4.1)

where $\lambda_x$ and $\varrho_x$ denote the attenuation length of the Si-2p photoelectron and the Si-atom density within material $x$, respectively and $\theta$ is the detection angle with respect to the surface normal.

Figure 4.25: 12.8×12.8 µm$^2$ spectro-micrographs from a same Si$_3$N$_4$ surface are using different photoelectrons of (a) N-1s line and (b) Si-2p bulk component, respectively. The nitride film was grown by exposing the Si(111) surface under ECR plasma for 10 min at 950°C.

In case of silicon nitride films grown at a higher nitridation temperature, a very different type of ESCA microscopy images is observed as compared to the earlier findings of low temperature nitridation. In figure 4.25, spectro-micrographs of silicon nitride films grown at 950°C are shown using two photoelectron signals: (a) N-1s line and (b) Si-2p bulk line. A strong contrast for ESCA microscopy images can be observed. Both the image
patterns in fig. 4.25 are similar but the contrast is reversed, which can be explained in terms of thickness fluctuation of the nitride film. The existence of a bare Si(111) surface after this nitridation process can be excluded from the STM results of a similar kind of nitride film, where a continuous silicon nitride film with a thickness fluctuation has been observed. In case of a nitride film of uniform thickness, the image contrast within the N-1s image is attributed to the chemical inhomogeneity, i.e., film stoichiometry. But in that case, imaging with the Si-2p bulk component is expected to be homogeneous without any contrast as the attenuation of Si-2p bulk photoelectrons is more or less homogeneous. The small changes in the attenuation lengths of the Si-2p signal due to chemical inhomogeneity is negligible. But, a strong contrast is also observed for the Si-2p bulk image, which suggests the thickness fluctuation within the nitride film instead of chemical inhomogeneity. However, a further investigation concerning the film thickness variation is shown in figure 4.26. A closer view ESCA micrograph of N-1s line and two individual the Si-2p XPS spectra measured at the corresponding bright and the dark areas of ESCA micrographs are presented. The correlation between the ESCA image and the Si-2p spectra recorded in different spots clearly indicates that the contrast within the ESCA images is dominated by the lateral fluctuation in the film thickness. The rough surface morphology of the nitride film is also expected at this high nitridation temperature.

![ESCA microscopy image and Si-2p XPS spectra](image)

Figure 4.26: (a) ESCA microscopy image (1.6×1.6 μm²) using the N-1s line and (b) Si-2p XPS spectra at the corresponding location mentioned within the image, for a silicon nitride film grown at 950°C using ECR plasma exposure for 10 min.

### 4.5 Discussion

From all the STM images of silicon nitride initial nucleation (fig. 4.5 – fig. 4.8) it is realized that the initial nucleation always occurred at the steps of the Si(111) surface in two ways: (a) either directly at the initial step edges of the Si(111) surface or (b) within the Si(111) terrace areas by forming the 7×7-Si(111) etch pits which finally results also in surface step formation. The nucleation at the steps can be attributed to defect induced nucleation. In general, more dangling bonds are present at the steps with respect to the 7×7-Si(111) domains, which make the steps chemically more active and hence might facilitate the initial nitride nucleation. Additionally, step induced nucleation is also favourable as it gives more degrees of freedom for the relaxation of strain governing from the lattice mismatch between the deposit material and the substrate.

The appearance of the etch pit at about 1.5 Å deeper than the terrace height within STM images 4.7 and a Si(111)-7×7 structure inside the pit is not very clear. As the monolayer
step height is not likely for the Si(111)-7×7 surface, it is assumed to be more electronic effect than the morphology. This may cause by trapping of some very small atoms (H) within the pit, which enhance the tunneling probability during STM imaging and hence reduce the bilayer step height (3.2Å) of the Si(111) surface to about 1.5Å.

The decrease in number and increase in size of nucleation centers with increasing nitridation temperature can be explained in terms of thermal diffusion length. For higher substrate temperature, the thermal diffusion is enhanced which causes the reduced number with enlarge size. Only at low nitridation temperature below 720°C, homogeneous nucleation of the silicon nitride pits is possible. At intermediate temperatures, between 760°C and 800°C, thermal diffusion starts to dominate and as a result heterogeneous nucleation at substrate defects, i.e. at domain boundaries of the Si(111)-7×7 surface and its surface steps governs nucleation. At even higher nitridation temperature, the nucleation of Si₃N₄ occurs at surface steps exclusively. This can easily be understood since the 7×7 structure is not present on the surface due to the 7×7→1×1 phase transition occurring at 830°C [36]. The larger surface diffusion at higher nitridation temperature also influence the shape of the etch pits in favour of equilateral triangles according to the three-fold crystal symmetry of Si(111)-7×7.

The changes in surface morphology and structural quality on the post-annealing effect (fig. 4.9 – fig. 4.11) can also be explained in terms of temperature induced surface adatom diffusion. The high temperature annealing offers a better surface diffusion of Si atoms and hence a proper supply of addatom species as required for the formation of the crystalline Si₃N₄ surface, which results in an improvement in crystalline quality of the nitride film surface. A similar explanation can also be applicable for the LEED observation (fig.4.3). The retreat or removal of the upper terrace is related to the supply of Si atoms to form the further nitride formation. Initially some of the nucleation pits were partially covered with Si₃N₄ (fig.4.10) which were later transferred totally into the nitride nucleation pit. The nitride nucleation patches or free standing islands have also increased in size either by coalescence effect or local regrowth of silicon nitride. The change in the shape of free standing islands from triangular to truncated-triangular/distorted-hexagonal shape can be related to the hexagonal structural symmetry of the Si₃N₄ crystal. However, the nitride pits within the terrace areas still remain triangular, which is in agreement with the three fold crystal symmetry of Si(111). The nucleation of nitride pits around the initial domain boundary of Si(111)-7×7 can also be explained in terms of defect induced nucleation as discussed earlier for surface steps.

The dependence of the silicon nitride surface morphology on the nitridation temperature using both rf (fig. 4.14 – fig. 4.15) and ECR (fig. 4.21 – fig. 4.22) plasma sources can be explained in terms of the thermally activated outer diffusion of Si atoms and the inner diffusion of N-atoms through the nitride overlayer. The inter-diffusion process can also be influenced by the N-plasma energy. As the average energy of the N-atom from ECR-plasma is significantly higher than that from the rf source, the changes in the nitride surface morphology appear at a relatively lower nitridation temperature (about 75°C) for the ECR source. For a nitridation process at a lower substrate temperature (up to 700°C for ECR and 780°C for rf plasma), the outer diffusion of Si atoms beneath the nitride layer is thermally restricted, as they do not have sufficient energy to overcome the
In that case only the inner diffusion of the N-atoms occur during the nitride growth, which results in a smooth surface morphology. With increasing nitridation temperature the outer diffusion starts to dominate by forming holes and grooves within the nitride films (700-750°C for ECR and 780–850°C for rf plasma). Accordingly, with increasing temperature, the holes get larger and deeper and the nitride layer exhibits a rougher surface morphology. For further increase in substrate temperature, the Si(111) terrace structure becomes 'softer' and can easily be damaged/broken by the N-plasma. This results in 2D islands with multiple step formation on the Si(111) surface where the step-edges are acting as a source for the outer diffusion of Si-atoms (above 750°C for ECR and 820°C for rf plasma). With an increase in nitridation temperature, these steps are getting larger and deeper and finally this leads to the deep crack formation which is generally found for 'quadruplet structures' grown above 1000°C (fig.4.15).

In case of nitridation at lower temperatures, as long as the Si(111) terrace structure is present, occasionally flat 2D islands and bright spots are found. The 2D islands indicate the layer by layer growth mode of nitride films. Line scan height profile of the bright spots obtained in STM imaging shows a very high peak. This finding can be explained as not a pure morphology rather than an electronic effect involved during the imaging process. This bright spot might be a cluster of non-reacted Si atoms which is replaced from the Si(111) surface during nitridation and acts as a source for a higher tunneling current during STM imaging. In most of the cases, bright spots are also located at the center of the 2D island. This finding can be attributed to the segregation of replaced Si-atoms during the nitridation of the 2D island surface. The Si-atoms near the outer region of 2D islands are mostly absorbed at the steps. In most of the cases 2D islands are also attached to the holes, which makes the concept even more clear that the holes acted as a source for raw Si-atoms. However, for nitride films of saturation thickness a little roughening within the flat terrace area is found, which may be caused by ion induced damaging from the plasma source.

The honey-comb like "8×8" atomic structures of the β-Si₃N₄(0001) (fig. 4.16) surface only appeared for very thin films (coverage below 2ML) in a loop like way. Additionally, no real long range symmetry can be observed. The appearance of honeycomb-like atomic structures with local disordering can be explained in the following way. On the one hand, the structures observed in STM may be related to states of the Si₃N₄–Si(111) interface, which has a highly distorted bonding configuration due to the substrate-epilayer lattice mismatch. On the other hand the STM image can also be influenced by the local electronic states of the underlying Si(111) substrate (only valid for thin overlayer). However, for "8/3×8/3" superstructures (fig. 4.18) a clear long range symmetry of the atomic reconstructions with a weak threefold modulation is observed for thicker nitride films. The background electronic influence from the Si(111) substrate can be neglected as the nitride film is sufficiently thick. The structure can be explained by the proposed structural model of Bauer et al. [16].

The ESCA microscopy results suggest a surface roughening of silicon nitride films for higher nitridation temperatures, which is in agreement with the STM findings. The contrast in the ESCA images of the nitride layer (fig. 4.25) can be explained in terms of thickness fluctuation of the nitride film. The stoichiometry of the nitride films has
been tested and found to be Si$_3$N$_4$ for both, smooth films grown at lower nitridation temperatures as well as for nitride films of inhomogeneous thickness formed at higher nitridation temperatures.

4.6 Conclusions

In summary, thin silicon nitride films of high crystalline quality have been successfully formed on Si(111) by exposing the surface to nitrogen plasma at elevated substrate temperatures. The initial stage of nucleation, thickness and temperature dependent films structure and morphology, surface atomic structures and chemical properties of the Si$_3$N$_4$ films on Si(111) have been studied by STM, LEED and ESCA microscopy measurements. It has been found that the initial Si$_3$N$_4$ nucleation always occurs at the upper terrace at the step edges of Si(111) or within the terrace area by forming nucleation pits. A lower nitridation temperature results in nitride films of poor crystalline quality with a smooth surface morphology. Whereas the Si$_3$N$_4$ film crystallinity greatly improves at a higher nitridation temperature, at the same time the surface morphology gets rough by forming holes and grooves. For very thin Si$_3$N$_4$ films, a honeycomb-like atomic structure of ”8×8” surface periodicity is observed. However, for thicker films of higher nitridation temperature an atomically resolved ”8/3×8/3” superstructure is obtained in STM. Both the findings are in good agreement with LEED results. The stoichiometry of Si$_3$N$_4$ has been found in ESCA microscopy measurements of nitride films and a thickness fluctuation for a higher nitridation temperature is found. This type of crystalline Si$_3$N$_4$ films on Si(111) may have the potential to serve as a substrate for the growth of crystalline GaN films to integrate the optoelectronic devices to the well established Si technology.

Bibliography


Chapter 5

Growth and morphology of MBE grown GaN on Si(111) surface

5.1 Abstract

GaN based hetero-structures are of great potential for light emitting devices and lasers for the blue to UV spectral region. So far commercial applications of GaN are based on structure grown on sapphire or SiC substrates. A step of great technological and commercial potential is a further integration of laser structures and data processing devices. Hence, the implementation of GaN into the well established Si technology is highly desirable. However, due to strong structural differences of the two materials, the growth of GaN on Si is a major challenge. Different inter layers have been tested to achieve epitaxial growth of GaN on Si. Among them, Si$_3$N$_4$ films appear promising and have already been tested for the single crystal wurtzite GaN growth on Si(111) substrates.

Within this work wurtzite GaN films were grown by rf plasma-assisted MBE on nitrified as well as Ga-terminated Si(111) surfaces. ESCA techniques have been used to study the initial GaN nucleation on a thin Si$_3$N$_4$ buffer layer, which indicates an inter diffusion at the Ga/Si interface as well as the initial GaN nucleation achieved only at lower temperature (<650°C). STM results point towards a high structural quality as well as LEED indicates an improvement in crystalline quality after introduction of a Si$_3$N$_4$ interface layer. An atomically resolved 3×3 reconstruction for thin GaN film and flat homogeneous growth for the thicker film is obtained. In agreement with STM results, SEM measurements confirm the structural improvement of GaN film growth using a Si$_3$N$_4$ buffer layer. A spontaneous formation of a silicon nitride interface is found in TEM study even for a preparation where the Si(111) surface was covered with a 6.3×6.3-Ga reconstruction. The possibility of polycrystalline GaN growth can also be suppressed by the intentional introduction of a high quality Si$_3$N$_4$ buffer layer. Some parts of the result presented here have already been published [1].


## 5.2 Introduction

### 5.2.1 Motivation

The wide range of direct band gap (0.7-6.2 eV) makes group-III nitride based semiconductors class, a promising candidate for the total color display (red to ultraviolet) in light emitting diodes (LED) and laser diodes (LD) [2,3]. Nitrides are being developed for electronic applications due to their high electron saturation velocity, large breakdown field, high thermal stability and good conductivity, which make these materials ideal for high temperature and high power devices (HEMTs and HBTs) [4,5] needed for automobile engines and electric vehicles. Furthermore, they have significantly different properties to the conventional III-V semiconductors such as hexagonal wurtzite structure, wide band gap, high piezo-electric constants and strong $k$-dependence of carrier effective masses. All these scientific and industrial concerns make it of high practical as well as fundamental interest.

The interesting properties and growing application in device technology have motivated the epitaxial growth of gallium nitride (GaN) films using molecular beam epitaxy technique (MBE). The MBE growth process of the high quality semiconductor growth is preferable for several reasons. Firstly, precise control over the amount of deposit in the sub-monolayer level. Secondly, less contamination within the semiconductor as it is grown in ultra high vacuum (UHV) environment. Finally, \textit{in-situ} characterization during the various stage of the growth process.

### 5.2.2 Conventional substrates

Although growth of large bulk GaN single crystals is presently a research area of great effort and the single crystal GaN of sufficient size is not well available, most of the GaN growth is performed by hetero-epitaxy. Various substrates have been tried to grow good quality wurtzite GaN films. Among them the most widely used are c-plane sapphire (0001) and 4H- and 6H-silicon carbide (0001) (SiC), which show promising results and are used as the conventional substrate for GaN epitaxy. It has been reported that the epitaxial GaN growth is also attempted on alternative substrates such as Silicon [6–21], GaAs [22–26], ZnO [27–29], MgO [30], LiGaO$_2$ [31,32] and other materials.

Sapphire (Al$_2$O$_3$), single crystal aluminium oxide, was the original substrate used in the pioneering study of GaN epitaxy by Marsuska \textit{et al}. in 1969 [33]. Still it remains the most common substrate for GaN epitaxy. On the basis of usual assumptions made in choosing a substrate for epitaxy, the properties of the sapphire substrate are not very suitable for GaN growth. The choice of sapphire is mainly due to its hexagonal symmetry and high thermal stability. But the large lattice mismatch (16%) and the large difference in thermal expansion coefficient leads to a high dislocation density and crack formation in the GaN epitaxial films. Low thermal conductivity of sapphire makes it relatively poor at dissipating heat compared to other substrates. Due to its insulating nature, all the electrical contacts must be made to the front side which complicates the device fabrication.
5.2. Introduction

Apart from sapphire substrate, silicon carbide (both 4H- and 6H-polytype) is the most common choice as a substrate material for wurtzite GaN epitaxial growth. It holds several advantages over sapphire such as a lower lattice mismatch and higher thermal conductivity. In addition, as a semiconductor, it can be conducting which makes device designing easier. But the main drawback is the presence of various polytypes and the difficulty to stabilize a single polytype, which makes it much more expensive. Furthermore, the lower surface energy of the SiC(0001) results in a poor wetting of Ga on the SiC surface [34]. This effect may cause to the 3D randomly oriented independent GaN islands formation upon the onset of nucleation, eventually leads to textured or poly-crystalline growth.

5.2.3 Silicon as a substrate

The favourable physical properties, high quality, and low cost of silicon make it a very attractive substrate for GaN based devices. A step of great technological and commercial potential is a further integration of laser structures and data processing devices. For this purpose, the implementation of GaN into the well established Si technology is highly desirable. Silicon wafers are available in very large sizes and at a low price due to the mature development and large scale production. The crystal perfection of Si is the best within all materials. Also it has very good thermal stability under the GaN growth conditions. However, due to strong structural differences and the different thermal expansion coefficient of the two materials the growth of GaN on Si is a major challenge. Different Si surfaces have been tried for the single crystalline GaN growth.

GaN growth on Silicon: Previous work

Despite of the high practical importance of GaN growth on silicon, much more studies have been devoted to GaN growth on sapphire, SiC or GaAs substrates as compared to silicon. It has been found that the zinc blend structure of GaN is usually formed on the diamond lattice of Si(001) substrate, keeping the (001) plane of GaN parallel to the substrate. But for the Si(111) substrate, a wurtzite structure of GaN can be achieved as the Si(111) plane has nearly the same symmetry (3-fold symmetry with hexagonal structure) as the c-plane of the wurtzite GaN. As described earlier for other substrates, the nucleation and growth of GaN on highly mismatched silicon substrate is highly problematic. This problem has also been approached by the use of various intermediate layers, (buffer layers), as tried for other substrate materials.

Lei et al. [17] have reported the growth of thin films of zinc blend GaN on Si(001) substrate using an ECR-plasma nitrogen source. It is also possible to grow zinc blend GaN epitaxial films on β-SiC coated Si(001) substrates using a molecular beam epitaxy approach [18,19]. A comparative study of GaN growth on Si(001) and Si(111) has been done by Yodo et al. [20,21] and found Si(111) to be better suited for wurtzite GaN growth than Si(001).

Single crystal Wurtzite GaN growth on Si(111) substrate has been approached by different groups using both molecular beam epitaxy (MBE) and metal-organic chemical vapour
Chapter 5. Growth and morphology of MBE grown GaN on Si(111) surface

deposition (MOCVD). Various buffer layers have been tested to achieve epitaxial growth of GaN on Si(111). The AlN layer is by so far the most widely employed buffer layer for GaN growth [7–11]. However, other materials such as SiC [12, 13], GaAs [14], or other materials [15, 16] have also been tried as buffer layers. But the silicon nitride formation by substrate nitridation could be a new and a simple solution to overcome the problem of the large lattice mismatch between GaN films and Si(111), as it only requires exposure of the substrate to the nitrogen source prior to the GaN growth.

Nakada et al. [6] suggested a thin Si₃N₄ buffer layer to improve the crystalline quality of GaN films on Si(111) grown by RF-plasma assisted MBE growth process. Zhang et al. [35, 36] observed a good quality GaN film grown on nitrified Si(111) substrate using a growth process similar to hot wall epitaxy (HWE). Yodo et al. investigated the influence of substrate nitridation before growth of GaN on Si(111) and found that it facilitates the wurtzite GaN growth accompanying the improvement of crystalline quality [20, 21]. Rawdanowicz et al. [37] reported that controlled silicon nitride growth on Si(111) helps to improve the crystallinity of a subsequently grown GaN layer by domain matching epitaxy (DME). Atomically resolved structures of the GaN surface grown on nitrified Si(111) substrate have recently been reported by Wang et al. [38]. However, there are also few reports that the formation of amorphous silicon nitride should be avoided to achieve good quality GaN growth.

In case of most GaN samples, an undesirable broad sub band-gap luminescence centered around ~550 nm (photon energy of about 2.2 eV) is observed, which is known as yellow luminescence (YL). The origin of this YL is not yet very clear. Qiu et al. [39] reported that YL correlates with dislocation densities while Li et al. [40] argued that YL is due to impurities rather than dislocations. Anyway, the ratio of band-edge and YL peak intensities can be used as an informal figure of merit, indicating the film quality [41, 42]. A clear improvement of the crystalline quality as well as a suppression of yellow luminescence has been observed by introducing a thin Si₃N₄ buffer layer by Zhao’s working group [43, 44].

Recently, the epitaxial lateral overgrowth (ELO) technique has also proved to be extremely effective in reducing the dislocation density of GaN films on Si(111) substrate [45–51]. Kawaguchi et al. [45] demonstrated the growth process for selective area growth of GaN on dot-patterned silicon substrate whereas Honda et al. [46] used this technique for the growth of ELO-GaN crystal on striped-patterned Si substrate. In both the cases the improvement of the properties of ELO-GaN crystal is confirmed. Kung et al. [47] also obtained an ELO-GaN crystal on GaN template previously grown on Si(111) substrate where they found the lateral growth rate is much higher as compared to the growth rate along the vertical direction.
5.3 Experimental details

5.3.1 Preparation

The growth experiments were carried out in a molecular beam epitaxy (MBE) chamber with a base pressure of $5 \times 10^{-11}$ mbar equipped with a variable temperature scanning tunneling microscope (Omicron VT-STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The active nitrogen was supplied through a commercial radio frequency (RF) plasma source (Epi Uni-bulb) with a pressure controlled inlet line of N$_2$ gas. In some cases also an electron cyclotron resonance (ECR Tectra) plasma was used. Deposition of high purity Ga was performed using an effusion cell heated by electron beam bombardment.

Substrate cleaning

The first step for a good epitaxy is the cleanliness of the substrate surface. Highly oriented (0.02° miscut) boron doped p-type silicon (111) wafers were used as substrates. The typical sample size for our experiments was about $10 \times 2$ mm$^2$. After ex-situ cleaning with methanol, the sample was loaded into the UHV chamber to degas at 600°C for more than 12 hours. The sample heating was performed by passing a direct current through it and the temperature was measured by an infrared pyrometer with an uncertainty of ±30°C. Clean Si(111) surface with 7×7 reconstruction was prepared by 2-3 short flashes to 1200°C for up to 30 sec to remove the native oxide prior to the growth process. This preparation was checked by LEED and STM, and a clean 7×7 reconstruction was observed reproducibly.

Substrate processing

In order to achieve a two-dimensional nucleation of single crystal GaN on Si(111), the wetting between the substrate and the nucleation layer has to be improved, which can be done by substrate processing. In this study we used two different types of substrate processing before GaN growth on Si(111). In one case, a thin silicon nitride (Si$_3$N$_4$) buffer layer is grown by exposing the Si(111) surface to an atomic nitrogen source at elevated substrate temperature. The other approach was to grow GaN directly on the Si(111) surface without the silicon nitride formation. To avoid the spontaneous formation of silicon nitride the technique of GaN growth on Ga covered Si(111) surface was used.

Various types of Si$_3$N$_4$ buffer layers were grown by nitridation of the Si(111) surface at different temperatures ranging from 700-1050°C using a nitrogen plasma source. Basically two types of silicon nitride films: (I) thin layer for 5 min of nitridation and (II) films of saturation thickness for 45 min of nitridation were used. For both the preparations, the Si$_3$N$_4$ surface morphology was tuned by varying the substrate temperature (for details see chapter 4) and was tested for GaN growth. The rf-plasma was operated at about $10^{-5}$ mbar and the rf-power was maintained at 450W during the formation of the Si$_3$N$_4$ layer.
In case of GaN growth directly on Si(111), the initial Si(111)-7×7 surface was totally covered with Ga in order to avoid the spontaneous silicon nitride formation. More than 1 ML of Ga was deposited at room temperature and then annealed at about 550°C. A 6.3×6.3-Ga pattern appeared in LEED and atomically resolve 6.3×6.3-Ga reconstructions were observed by STM throughout the surface. For Ga coverage exceeding 1 ML, Ga droplets are usually formed on Si(111) surface.

**GaN nucleation and growth**

In order to study the influence of the substrate nitridation on the film quality, GaN growth was tested on nitrified as well as on Ga-terminated Si(111) surfaces. The growth process was performed in two steps: (a) initial GaN nucleation at relatively low temperature for 30 min and (b) subsequent growth of GaN epi-layer at a higher temperature. The low temperature process is used to make the GaN nucleation layer thermally stable over the silicon nitride surface as well as to promote the wetting process between substrate and deposit. For the initial nucleation of GaN on a nitrified Si(111) surface, substrate temperatures were varied between 500-650°C. As the 6.3×6.3-Ga surface is thermally stable only up to 620°C, the initial nucleation of GaN is done at 500°C, much lower than the desorption temperature. It will be shown later that this low temperature nucleation leads to the formation of a thin, uniformly grown homogeneous GaN film which can serve as a seed layer for the homo-epitaxially grown GaN epi-layers to reduce the surface stress. The higher growth temperatures (750-800°C) during epi-layer growth are expected to improve the structural perfection and increase the growth rate of the GaN film. If the growth temperature exceeds 850°C, however, no real growth of GaN was observed, probably due to the strongly increased desorption rate of GaN, as will be shown later. During GaN growth, the rf-power of the plasma source was reduced to 300W to avoid the ion induced damage and surface roughening, whereas the operating pressure was kept about 5×10^{-6} mbar. After growth, the samples were kept at 800°C (growth temperature) for 5 min to dissolve the excess metallic Ga from the surface.

**5.3.2 Characterization procedure**

The various stages of growth have been characterized *in-situ* by LEED (low energy electron diffraction) and VT-STM (variable temperature scanning tunneling microscopy). The overview of the surface crystallinity was studied by LEED, whereas STM was used for the characterization of the morphology and surface reconstruction down to the atomic scale. *Ex-situ* ESCA (electron spectroscopy for chemical analysis) measurements were performed at the 'Institute of Materials Science, University of Bremen', to get the chemical information of the film. The initial growth stage of GaN on Si₃N₄, using ECR plasma, was also studied *in-situ* at the 'ESCA microscopy beamline in Synchrotron Light Source, Trieste, Italy' with help of beamline scientists Dr. L. Gregoratti, Dr. A. Barinov and Dr. L. Aballe. Scanning electron microscopy (SEM) was used to have large area surface topographs of the GaN films. Focussed ion beam (FIB) was employed to prepare the samples for selected area cross-sectional transmission electron microscopy (TEM), which was done in collaboration with Dr. R. Kröger at the 'University of Bremen' to get the information about the interface and film crystalline quality.
5.4 Results

5.4.1 ESCA results

Initial growth stage of GaN on Si$_3$N$_4$ buffer layer

To investigate the initial stage of GaN nucleation on nitrified Si(111) surface and the interdiffusion of deposit species at the interface, in-situ ESCA studies have been performed at the ESCA microscopy beamline in synchrotron light source, Trieste, Italy. A photon beam energy of 495 eV was selected for this measurement. An ECR plasma source was used as an active nitrogen source. The Si$_3$N$_4$ buffer layers have been grown by nitridation of Si(111) at 900$^\circ$C for 10 min. The pressure (within the plasma chamber) was maintained at about $8 \times 10^{-5}$ mbar during the GaN growth. After the Si$_3$N$_4$ buffer layer formation, 2 ML of Ga have been pre-deposited on the surface at room temperature prior to the GaN growth. The initial GaN nucleation layer has been grown at a lower substrate temperature of 450$^\circ$C for 15 min and then the growth temperature has been increased for the epilayer growth.

![ESCA spectra](image)

Figure 5.1: (a) ESCA results of GaN growth on nitrified Si(111) (a) Si2p spectra before and after GaN growth where initial GaN nucleation starts at 450$^\circ$C for 15 min and then the epilayer is grown at 700$^\circ$C for 1 hour. (b) Ga3d spectra after GaN growth at 450$^\circ$C for 1 hour on Si$_3$N$_4$ buffer layer and subsequent annealing steps.

The ESCA study of Si2p spectra before and after the GaN growth is shown in figure 5.1(a). The initial GaN nucleation was started at 450$^\circ$C for 15 min followed by the epilayer growth at 700$^\circ$C for 1 hour. An increase of the Si$_3$N$_4$ peak intensity is surprisingly observed after the GaN growth. This is a clear indication for Si nitridation occurring instead of GaN growth, even though the initial surface was covered with 2 ML of Ga. A small shift in the peak position towards the lower binding energy is also observed which can be related to the film stoichiometry and oxidation state of the surface Si atom.

The ESCA study of Ga3d spectra of a GaN film grown at 450$^\circ$C for 1 hour on a Si$_3$N$_4$ buffer layer and the effects of subsequent annealing steps are presented in figure 5.1(b).
Metallic Ga is found on the surface after GaN growth at 450°C, which can be thermally dissolved by post annealing as described in fig.5.1(b). Various annealing steps are shown and it is found that an annealing at 750°C for few min allows to dissolve the metallic Ga from the surface. The intensity of the GaN-Ga3d line is very weak even after one hour of growth which indicates a very thin GaN layers (only few atomic layers). From both the ESCA results it can be concluded that the real GaN growth starts only after the saturation of Si₃N₄ layers.

Figure 5.2: ESCA microscopy images of (a) Si₃N₄ surface and (b) subsequently grown GaN films. GaN film was grown at 450°C for 1 hour on a Si₃N₄ buffer layer and was post annealed at 750°C to remove the metallic Ga.

The lateral chemical homogeneity of the film before and after the GaN growth on a nitrified Si(111) surface have been investigated by ESCA microscopy as shown in figure 5.2. The spectro-micrographs of the film surfaces are imaged using the kinetic energy of a specific photoemission line and the contrast indicates the surface inhomogeneity. There are mainly two effects which can lead to contrast in the micrographs: (a) fluctuations of the chemical composition and (b) fluctuations of the film thickness.

In figure 5.2(a) the silicon nitride surface grown at 900°C is imaged using the nitride component of the Si-2P line. A strong contrast is observed within the 12.8×12.8 µm² scan area ESCA image which suggests an inhomogeneous growth of the silicon film. The fluctuation within the layer thickness is the key element behind the image contrast as has been described by Schmidt et al. [52]. The thickness fluctuation is also expected for silicon nitride growth at higher nitridation temperature.

A very different image is observed for the subsequently grown GaN film after the removal of metallic Ga by post-annealing. Figure 5.2(b) shows a region of 12.8×12.8 µm² on the GaN film where a Ga-3D photoemission line is used for imaging. A very weak contrast is found within the ESCA image, which is an indication of a smooth and homogeneous growth of the GaN film on the nitrified Si(111) surface.

Substrate temperature for the initial nucleation layer

Ex-situ ESCA studies of GaN films grown on Si(111) using rf-plasma assisted MBE have been done at the Institute of Materials Science, University of Bremen. Nitridation of the Si(111) surface was done with rf-power of 450 W for 45 min to have a Si₃N₄ buffer layer of saturation thickness (~2.1 nm) prior to the GaN growth. The surface morphology of the Si₃N₄ inter-layer can be tuned by varying the substrate temperature as discussed earlier (chapter 4). The initial nucleation layer of GaN films has been grown for 30 min on saturated Si₃N₄ layers with a reduced rf-power of 350 W at different growth temperatures.
from (500-670)°C. Later the temperature was increased to (780-800)°C for the growth of epitaxial layers. After growth, the samples were annealed at 800°C for 5 min to dissolve the excess metallic Ga.

The samples have been exposed to air in order to transfer them from the growth chamber into the ESCA analysis system. There, the samples were degassed at 600°C in order to reduce the surface contamination prior to the ESCA measurements. An overview of the surface chemical composition of GaN films with different initial nucleation temperatures is obtained from the survey scan as shown in figure 5.3. We found that the surface contains almost no Ga (absence of Ga-3d, Ga-3s, Ga-LM2 peaks) for an initial nucleation layer growth higher than 650°C, as shown in fig. (c). The ESCA results show that the surface consists mostly of silicon nitride (presence of Si-2p, N-1s, N-KL1 peaks) with surface oxide (O-1s and O-KL1 peaks) and carbon contaminations (C-1s). Whereas for the nucleation temperature of 500°C (fig. (a)) and 550°C (fig. (b)), the ESCA results clearly indicate the growth of GaN as the surface material contains Ga (Ga-3d, Ga-3s, Ga-3p and Ga-LMM) and N (N-1s, N-KL1) species. From all these observations it is clear that GaN growth only starts below 650°C initial nucleation temperature and the surface gets oxidized during the transport.
In figure 5.4 detail scans of Ga-3d and Si-2p spectra are shown. Fig. 5.4(a) clearly shows the GaN growth on a nitrified Si(111) surface for initial nucleation temperatures of 500°C and 550°C. Whereas for the initial nucleation at 650°C, non-existence of Ga-3d spectra indicates that the GaN nucleation does not occur at this temperature. A similar finding can be observed in fig. 5.4(b), where only Si-2p peaks of bulk and nitrified silicon are found for the initial nucleation at 650°C. But in case of initial nucleation at 500°C and 550°C, Si-2p photoelectrons are mostly attenuated by the GaN overlayer and a strong Ga-3p photoemission peak appears.

**Thickness of the GaN film**

The ESCA results of GaN samples with different deposition times show the variation in the peak intensity, resulting in a variation of the film thickness. A rough estimation of the film thickness is done using the attenuation of Si-2p photoelectron by the GaN overlayer. The photocurrent exponentially decays with the overlayer GaN thickness ‘d’ as described by equation 5.1.

\[ I(d) = I_0 \ast \exp(-d/\lambda) \]  

where \( I_0 \) is the photocurrent without any attenuation and \( \lambda \) is the inelastic mean free path (IMFP) of the Si-2p photoelectron within the GaN layer. The IMFP of the Si-2p photoelectron within the GaN for a Mg K\( \alpha \) radiation source has been calculated to about 25Å using the following relation

\[ \lambda = E/[E_p^2\{\beta ln(\gamma E) - (C/E) + (D/E^2)\}] \]  

where \( E \) is the kinetic energy of the Si-2p photoelectron, \( E_p \) is the free electron plasmon energy of GaN and \( \beta, \gamma, C \) and \( D \) are some constant parameters, depending on the material properties of GaN. Details of the various parameters are given in ref. [53].

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**Figure 5.5:** Gaussian fit (a) Si-2p and (b) Ga-3d spectra of GaN films grown on nitrified Si(111) for three different deposition times of 45 min, 90 min and 120 min, respectively.
In figure 5.5(a), the attenuation of the Si-2p photoelectron for three different growth durations of the GaN layer is presented. For a growth duration of 45 min to 90 min, the peak intensity does not decrease significantly, whereas for 120 min of growth time it is almost absorbed. An increase in thickness from 90 min to 120 min of GaN growth is estimated to be about 53 Å, whereas from 45 min to 90 min it increases only by about 9 Å. This effect can be explained differently: (a) slower growth rate for initial growth stage of GaN (b) an incomplete / inhomogeneous growth (3D island growth) of the GaN layer and (c) interface inter-diffusion during GaN layer growth.

For a comparative study of GaN growth with respect to the earlier results and to get an idea about the total GaN coverage Ga-3d spectra have also been taken into account as shown in fig. 5.5(b). Here also we found a comparable coverage of GaN for 45 min and 90 min of GaN deposition. Whereas for 120 min of deposition, it increases only by a factor of two which might be due to the saturation depth of the Ga-3d photoelectron for ESCA measurements. The escape depth of the Ga-3d photoelectron is estimated to be about 26Å in the GaN layer. For a more detailed understanding of the growth process and an estimation of the growth rate in a more precise way a more systematic investigation would be needed.

Figure 5.6: LEED images of (a) Si(111)-7×7, (b) ”8×8” -Si$_3$N$_4$, (c) 1×1 GaN. The Si(111) was nitrified at 960°C for 30 min. Initial GaN nucleation was started at 500°C for 30 min and then the temperature was increased to 780°C for 180 min of epi-layer growth. The electron beam energies are for figure (a) 35 eV, (b) 49 eV and (c) 47 eV, respectively.

5.4.2 LEED results

To get an overall information of the surface crystalline quality of various stages of GaN growth on Si(111) using Si$_3$N$_4$ as a buffer layer, low energy electron diffraction (LEED) has been used as illustrated in figure 5.6. After flashing the degassed Si(111) surface at 1200°C for 3-4 times, a sharp LEED pattern of 7×7 structure is observed as shown in fig. 5.6(a). The LEED pattern changes to a ”8×8” Si$_3$N$_4$ structure after surface nitridation at elevated temperature (700-1000)°C. Fig. 5.6(b) shows the LEED patterns of a silicon nitride buffer layer prepared at 950°C using a rf-plasma source. The LEED pattern of GaN films grown on a Si$_3$N$_4$ buffer is not very clear for thin layers. Whereas for thicker GaN layers the LEED patterns change to a 1×1(fig. 5.6(c))structure indicating crystalline
growth of the GaN layer. It is found that the GaN film quality is very much dependent on the Si$_3$N$_4$ buffer layer and the best results concerning the crystalline quality of GaN films are obtained for growth on 8×8 Si$_3$N$_4$ layers prepared at a temperature above 850°C. LEED patterns of a GaN film grown at 780°C on "8×8" Si$_3$N$_4$ structure are shown in fig. 5.6(c). In case of GaN growth on 6.3×6.3-Ga/Si(111), LEED patterns are rather diffuse indicating a poor crystallinity.

### 5.4.3 STM results

Here we discuss the STM results on two types of GaN/Si$_3$N$_4$ films, (a) ‘thin film’ and (b) ‘thicker film’. For thin films we have used a thinner silicon nitride buffer layer and the GaN film is also very thin, only a few nanometers. For the thicker films, the silicon nitride buffer layer is of saturation thickness and the GaN film thicknesses are in the order of 10 nm.

![STM images](image)

Figure 5.7: STM images of Si$_3$N$_4$ buffer layer before any GaN deposition (fig. (a) and (b)), GaN nucleation layer (fig. (c) and (d)) and subsequently grown GaN epilayer (fig. (e) and (f)). The Si$_3$N$_4$ buffer layer was grown by nitrifying the Si(111) surface at 850°C for 12 min (fig. (a) and (b)). The GaN nucleation was performed at 500°C for 10 min and then subsequently increased to 650°C for 30 min (fig. (c) and (d)) and further increased to 750°C for another 30 min (fig. (e) and (f)).
5.4. Results

(a) Thin films

The surface morphology of the different growth stages of thin GaN films on Si$_3$N$_4$ buffer layers has been monitored by scanning tunneling microscopy (STM). In figure 5.7, empty state STM images of the surface structure comparing the surface morphology of the silicon nitride (fig. 5.7(a) and 5.7(b)), after low temperature (650°C) nucleation of the GaN film (fig. 5.7(c) and 5.7(d)) and after high temperature (775°C) GaN growth (fig. 5.7(e) and 5.7(f)) are presented. The surface structure of the GaN film is found to be determined by the Si$_3$N$_4$ morphology and growth temperature. After the low temperature layer nucleation, a smooth flat surface with atomic steps and small shallow holes is found. For a large scan area the surface step edges appear curly (fig. 5.7(c)). In closer look STM image small islands are resolved (fig. 5.7(d)). After subsequent growth of the epitaxial layer at 775°C the surface pattern changes. It appears as flat areas with large holes and grooves (fig. 5.7(e) and 5.7(f)). In average, the holes are becoming larger and deeper as compared to the low temperature growth, whereas the hole density is decreased with growth temperature.

![Figure 5.8: STM image of 3×3 atomic reconstruction of thin GaN film grown on silicon nitride buffer layer (scan area 20×20 nm$^2$).](image)

A closer look of the surface, i.e. empty state STM images of the GaN atomic reconstructions are shown in figure 5.8. An atomically resolved 3×3 reconstruction is identified in fig.(a) with a strong modulation of background contrast. The strong background contrast in the STM images is most likely due to the unintentional Si doping through the thin Si$_3$N$_4$ layer. The underlying Si$_3$N$_4$ layer may also influence the STM tunneling condition locally. A structural model for the 3×3 surface reconstruction of GaN has already been reported by the Feenstra group [54]. This type of surface reconstruction for a GaN film is only observed in the N-polar GaN(000$\bar{1}$) face where Ga adatoms are placed on the Ga adlayer as shown in figure 5.9. Ga atoms of the adlayer are placed just above the surface N atom, i.e. at the T$_1$ site position. The Ga adatoms of the top most layer occupy the T$_4$ site position. Hence the total Ga coverage on the 3×3 GaN surface is about 1.33 ML.

For thin GaN film growth directly on the 6.3×6.3-Ga/Si(111) surface, the formation of homogeneous films with three dimensional small granular islands is found. In figure 5.10, one can see the surface structure of the various stages of GaN growth on a Ga-terminated Si(111) surface. Before GaN growth, the initial 6.3×6.3-Ga reconstructed Si(111) surface looks atomically flat with silicon bilayer steps (fig. 5.10(a)). The surface is totally covered with an incommensurate 6.3×6.3-Ga reconstruction, as seen in fig. 5.10(b). After initial nitridation of the 6.3×6.3-Ga surface at low temperature (500°C), the surface is covered...
Chapter 5. Growth and morphology of MBE grown GaN on Si(111) surface

Figure 5.9: Schematic structure model of (a) 1×1 and (b) 3×3 reconstructions. Upper images represent the top view and lower images the side view [54].

with small uniform granular islands (fig. 5.10(c) and (d)). After GaN growth at 750°C, the surface morphology changes and appears flat and with homogeneous small islands (fig. 5.10(e)). On a closer look, only small granular islands are found of sizes up to 25 nm (fig. 5.10(f)). At an even higher resolution, no atomic reconstructions could be observed (images not shown).

6.3×6.3-Ga After nitridation After GaN growth

Figure 5.10: STM images of 6.3×6.3-Ga reconstructed Si(111) (fig. (a) and (b)), after nitridation of the Ga-terminated surface (fig. (c) and (d)) and overgrown thin GaN films (fig. (e) and (f)).

Thicker films

Within this section, the surface morphology of the thicker GaN films grown on saturated Si₃N₄ buffer layers is discussed. For GaN growth on Si₃N₄ buffer layers, the Si(111) surface was exposed to atomic nitrogen for 45 min at different substrate temperatures to reach the saturation thickness (~2 nm). However, the thickness of this GaN (thicker) films presented here is relatively thick and estimated to be about 10 nm.
5.4. Results

Si₃N₄ buffer layers grown at different temperatures

"8×8"  "8×8"  'quadruplet'

Subsequently grown GaN films on Si₃N₄ buffer layers

Figure 5.11: STM images of Si₃N₄ buffer layers formed by 45 min nitridation of the Si(111) surface at three different temperatures and the subsequently grown corresponding GaN surfaces. Initial GaN nucleation was started at 540°C for 30 min followed by GaN growth at 750°C for three hours.

STM images showing an overview of the surface morphology of saturated Si₃N₄ buffer layers and the subsequently grown GaN films are shown in figure 5.11. In the following, three types of Si₃N₄ layers were used as a substrate for GaN nucleation: (i) low temperature (800°C) grown Si₃N₄ layer ("8×8"), (ii) high temperature (950°C) grown "8×8" reconstructed Si₃N₄ layer and (iii) even higher temperature (1040°C) grown 'quadruplet' structure. The Si₃N₄ surface grown at 800°C contains Si(111) terrace structures and small holes (fig. 5.11(a)). Holes are preferentially located around the surface steps. For Si₃N₄ growth at 950°C, the surface morphology shows flat, two-dimensional (2D) islands with smaller holes. However, holes appear here within the terrace areas and with higher density (fig. 5.11(c)). The quadruplet structured silicon nitride surface grown at 1040°C appears with large flat terraces and deep crack-like features as shown in fig. 5.11(e). Details of the various types of saturation thickness Si₃N₄ films can be seen in chapter 4.

The surface morphology of the subsequently grown GaN films on different silicon nitride buffer layers shows a strong dependency on the initial substrate properties. For GaN growth on low temperature (800°C) Si₃N₄ layers, homogeneous surfaces with large 3D-islands are observed (fig. 5.11(b)). The island diameter (φ) ranges from 15–30 nm with a height (h) variation between 4–6 nm. For 950°C grown "8×8" reconstructed Si₃N₄ substrate, a smooth and homogeneous GaN film surface is found appearing with a triangular tile-like pattern (φ ~ 30–40 nm and h ~ 1–2 nm) as can be seen in fig. 5.11(d). The tiles are have a three fold symmetry and consist of smaller islands of diameter φ ~ 7–10
nm and height < 1 nm. In case of quadruplet silicon nitride substrate, the GaN growth mode leads to the formation of inhomogeneous GaN layer growth and a rough surface containing big islands. Islands of $\phi \sim 40–80$ nm and $h \sim 6–10$ nm are found.

GaN growth experiments without any silicon nitride buffer were also performed and the surface morphology has been compared. The STM image shows a rather rough and inhomogeneous GaN layer growth for 6.3×6.3-Ga reconstructed Si(111) substrate as presented in figure 5.12. Before GaN growth, the 6.3×6.3-Ga/Si(111) surface looks extremely flat, only with bilayer steps as shown in figure 5.12(a). But the surface morphology of the subsequently grown GaN film appears to be quite rough containing large mounds ($\phi \sim 100$ nm, $h \sim 10$ nm) and deep valleys ($\sim 6$ nm) (fig.5.12(b)).

Figure 5.12: STM images of 6.3×6.3-Ga/Si(111) surface (a) and overgrown GaN films surface (b). The initial GaN nucleation was started at 500°C for 30 min and then the growth was performed at 750°C for two hours. Scan areas 1000×1000 nm².

The surface morphology of the GaN films grown both on nitrified as well as Ga-terminated Si(111) substrates has been investigated by STM at room temperature. The GaN films were grown on different types of Si₃N₄ buffer layers. The surface morphology of Si₃N₄ can be tuned with growth temperature as discussed in chapter 4. The STM measurements indicate that the GaN film morphology is more homogeneous (smoother) for the growth on ”8×8”-Si₃N₄ buffer layers prepared at a higher nitridation temperature ($\geq 850$ºC). In case of GaN growth directly on Ga-terminated Si(111), an inhomogeneous layer growth and rough surface morphology with big islands and holes are observed even for larger GaN deposition.

5.4.4 SEM results

To investigate the characteristic microstructure resulting from the two different growth processes: (i) GaN films grown on nitrified Si(111) or (ii) Ga terminated Si(111), scanning electron microscopy (SEM) has been used. The initial nucleation layer was grown at 500°C for 30 min and then the growth temperature was increased up to 750°C for 2 hours. The samples were exposed to air for the transfer from the growth chamber to the SEM analysis chamber.

A distinct change in the surface morphology is observed in figure 5.13, when the GaN films were grown directly on Ga terminated Si(111) instead of growth on a silicon nitride buffer layer. For GaN growth without any silicon nitride buffer (fig. 5.13(a) and 5.13(b)), the growth leads to the formation of large GaN 3D islands. The surface appears to be very rough and a cratered morphology is observed with deep holes on the surface. Figure 5.13(a) shows the surface overview SEM image of a GaN film directly grown on Si(111)
and a closer look of a $300 \times 300 \text{nm}^2$ scan area is shown in fig. 5.13(b). The surface shows a rough morphology and contains mostly 3D islands of a diameter of about 50 nm. Large holes of similar diameter are also found on the surface. A ring-like guard wall is always found surrounding the holes (fig. 5.13(b)), which may be related to local charging effects of the surface during measurements. After introduction of a $\text{Si}_3\text{N}_4$ buffer layer prior to GaN growth, the surface morphology of the subsequently grown GaN films surface homogeneity drastically improves as shown in fig. 5.13(c) and 5.13(d). Smooth and homogeneous growth of GaN is observed and the large area of flat surface with smaller pits is formed. Figure 5.13(c) shows the SEM overview image of a GaN film growth on Si(111) using silicon nitride buffer layers, whereas in fig. 5.13(d) a closer look image of the surface is shown. The surface shows large flat terraces with few circular pits (diameter $\sim 30 \text{nm}$) appearing as dark dots. As we have seen, for both cases GaN films contain holes on the surface but the average size and depth is much larger and deeper for GaN growth without a $\text{Si}_3\text{N}_4$ buffer layer.

5.4.5 TEM results

To investigate the interface between the GaN films and the Si(111) substrate, high resolution cross sectional transmission electron microscopy (XTEM) measurements have been performed. In figure 5.14, TEM images show the GaN-Si(111) interface for GaN growth without any silicon nitride buffer. A $6.3 \times 6.3$-$\text{Ga/Si}(111)$ reconstructed surface has been used as a substrate for initial GaN nucleation. The initial GaN nucleation was started at $500^\circ\text{C}$ for 30 min followed by a high temperature GaN growth at $750^\circ\text{C}$.
The TEM images clearly show a thin layer of silicon nitride interface formation underneath the GaN layer even if the initial Si(111) surface was covered by 1 ML of Ga. It can also be seen that the Si(111)–silicon nitride interface is atomically flat but the interface between silicon nitride–GaN is a little more rough than the earlier interface (fig. 5.14(b)). Also, near the interface, partly cubic or poly-crystalline wurtzite GaN can be found. In fig. 5.14(b), the orientation of the GaN atomic rows at the upper left corner does not match with the orientation at the upper right corner. This is an indication of poly-crystallinity of the GaN films.

In figure 5.15, a closer look HRTEM image of the film–substrate interface is shown where a mostly amorphous silicon nitride interface layer is found (fig. 5.15). These unintentionally formed Si₃N₄ layers are of amorphous nature as they are grown during the low temperature GaN nucleation at 500°C. However, a wurtzite GaN is also observed on top of the amorphous silicon nitride layer. In case of GaN growth on a Si₃N₄ buffer layer, things happened someway differently. As the interface silicon nitride layer is grown at a relatively high temperature (950°C), it is expected to be a crystalline Si₃N₄ layer (image is not shown). This may be an important reason why the crystalline quality of subsequently grown GaN films is better for the Si₃N₄ substrate. This finding is also in agreement with the LEED results.
5.5 Discussion

From ESCA (fig. 5.1) and TEM (fig. 5.14 and 5.15) results it is clearly observed that always a silicon nitride interface layer is formed during the initial nucleation of GaN on Si(111). In case of initial GaN nucleation on a very thin (< 1 nm) silicon nitride layer a further continuation of Si$_3$N$_4$ growth occurs instead of GaN growth. On the other hand, TEM results confirm the formation of silicon nitride during the GaN nucleation on a 6.3×6.3-Ga reconstructed Si(111) surface. This effect may be due to the high inter-diffusion at the interface and a strong chemical reactivity between Si and atomic nitrogen. By inter-diffusion of N through the Ga layer at elevated temperature, it is possible to supply free N atoms to the unbound Si atoms and the strong chemical reactivity of Si with active N prefers Si-N bonding over the GaN growth and forms silicon nitride.

ESCA results show that the initial nucleation of GaN on a silicon nitride buffer layer only starts if the substrate temperature is kept below 650°C (fig. 5.3 and 5.4). This can be attributed to a thermal desorption of Ga atoms on the silicon nitride layer in the UHV condition. Also the lower substrate temperature can help to improve the wetting of Ga on the surface, which is necessary to stick the initial GaN nucleation layer for the growth process. The thickness and growth rate calculation of the GaN film on Si$_3$N$_4$ shows a slow growth at the initial nucleation stage and then increased for thicker layers (fig. 5.5). This might be due to the strong inter-diffusion at the interface and lower sticking of deposit material on Si$_3$N$_4$. In a later stage (for longer duration of deposition) the diffusion process completes and the sticking effect is enhanced as the deposition continued on the GaN covered surface instead of Si$_3$N$_4$.

In the LEED results (5.6), an indication of the improvement in the crystal perfection of the GaN film is obtained in case of GaN growth using Si$_3$N$_4$ buffer layers. TEM study shows that an interface silicon nitride layer is spontaneously formed even if the GaN nucleation is initiated on a Ga-terminated Si(111) surface. As the initial nucleation layer is grown at sufficiently low temperature (about 500°C), the interface silicon nitride layer is also formed at a relatively low temperature. This leads to the formation of mostly amorphous Si$_3$N$_4$ growth. But in case of higher temperature substrate nitridation (850–1000°C) prior to GaN growth, the crystallinity of the Si$_3$N$_4$ interface layer is improved. This effect may help to improve the crystallinity of the GaN growth and suppress the polycrystal formation within the GaN films. A 1×1 pattern in the LEED is indicating the N-polar GaN surface, which is also in agreement with the finding of a 3×3 surface reconstruction in STM [54].

The surface morphology of the GaN films highly depends on the initial substrate processing as discussed in the sections about the corresponding STM and SEM studies. We observed that a initial substrate nitridation at high temperature (950°C) improves the surface homogeneity drastically. This can be explained in terms of the crystalline quality of the interface Si$_3$N$_4$ layer as discussed earlier. In case of thin GaN layer growth on a crystalline silicon nitride buffer, it is quite usual to follow the surface morphology of the underlying layer as it offers a high crystallinity in the growth layer. As a result, an atomically resolved STM image of a 3×3 reconstructed pattern is observed, which is also an indication of the N-polar surface reconstruction usually found in the MBE growth. The
strong background contrast in the STM images is most likely due to the unintentional doping through the thin Si$_3$N$_4$ layer or interface state as the GaN film is also very thin. But for the case of GaN growth on a Ga-terminated Si(111) surface, an unintentional silicon nitride interface is formed which is mostly amorphous. We have already discussed earlier that the low temperature silicon nitride growth leads to a flat homogeneous surface. This amorphous layer may also be very flat which leads to the homogeneous GaN films with 3D island growth. At the same time high temperature grown silicon nitride offers a patterned substrate with flat island and grooves/holes for the GaN growth, which is someway similar to the epitaxial lateral overgrowth (ELO) technique. This may help to reduce the dislocation density during the thicker GaN growth and as a result a smoother surface morphology is observed.

The closer view TEM image (fig. 5.15) shows a crystalline GaN film growth even on a amorphous or partially crystalline silicon nitride layer. It is an open and very important question why and how crystalline GaN is formed on amorphous silicon nitride and also follow the hetero-epitaxial crystal relationship (GaN(0001) $\parallel$ Si(111) and GaN(11$ar{2}$0) $\parallel$ Si(1$ar{1}$0)) with the underlaying Si(111). There are two possible ways to explain this phenomenon. Firstly, some small parts of the Si$_3$N$_4$ layer show a crystalline structure, which can transfer the crystal orientation of the Si(111) substrate to the overgrown GaN layer. Secondly, the local tetrahedral coordination of each atom within the interface layer may be maintained in short range order. An improvement in GaN crystalline quality and surface homogeneity after introduction of a high temperature Si$_3$N$_4$-layer is also in agreement with the crystalline interface formation to transfer the hetero-epitaxial relation. The STM investigation of silicon nitride growth at 950$^\circ$C shows an atomically reconstructed "8×8" surface as discussed in chapter 4, which is a clear evidence of a crystalline interface layer. Whereas for GaN growth on Ga-terminated Si(111) surfaces, spontaneous formation of a Si$_3$N$_4$ layer at low temperature results in an amorphous interface causing worse quality GaN growth. However, still the growth process of single crystal GaN on Si(111) substrate is not yet very clear.

As we already discussed the effect of the silicon nitride buffer layer on the quality of the GaN epilayer, two possible reasons may be responsible for it. Firstly, the "8×8" reconstructed Si$_3$N$_4$ lattice constant in the a-axis (0001 lattice plane) is about $a_{\text{Si}_3\text{N}_4}$=2.79 Å which is closer to the GaN lattice constant of GaN $a_{\text{GaN}}$=3.18 Å as compared to the Si(111) lattice constant $a_{\text{Si}(111)}$=3.84 Å. This close lattice matching helps to reduce the stress governing from the misfit. On the other hand, the six fold symmetry of "8×8"-Si$_3$N$_4$ crystal can be more convenient for wurtzite GaN growth compared to the bare Si(111) surface of three fold rotational symmetry. In this way the interface silicon nitride layer greatly reduces the possibility of dislocation formation and provides a better platform for initial nucleation during the GaN growth. Furthermore, a large number of dangling bonds of N on the silicon nitride surface at high temperature can also provide a good substrate for initial GaN nucleation, which later serves as a good template for the GaN hetero-epitaxy.
5.6 Conclusions

In summary, crystalline GaN films have been successfully grown on Si(111) substrate by plasma assisted MBE. Various growth stages of GaN films have been studied by ESCA, STM, LEED, SEM and TEM measurements. Strong diffusion at the subsurface interface and high chemical reactivity of Si with atomic N is observed, which causes the spontaneous formation of a silicon nitride interface layer even if the surface is covered by Ga. How the introduction of a thin silicon nitride buffer layer can influence the GaN growth is discussed in details. High temperature Si$_3$N$_4$ buffer layer formation during substrate nitridation greatly improves the GaN film quality. $3\times3$ reconstructed STM images are observed for thin GaN films as an indication of N-polar surface. For thicker GaN layers, the surface morphology also improves by the introduction of a Si$_3$N$_4$ buffer layer and an ordered pattern of triangular islands with three fold symmetry is observed upon initial GaN growth. GaN growth without substrate nitridation leads to inhomogeneous film growth and causes a phase mixing and poly-crystalline GaN formation near the interface. Various possible reasons behind the improvement of the film quality as well as the hetero-epitaxial relationship between substrate and epilayer have also been discussed. Among these, an improvement in crystallinity of the silicon nitride buffer layer by high temperature substrate nitridation being the most plausible.

Bibliography


Chapter 6

GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy

6.1 Abstract

Radio frequency (rf) N plasma-assisted in-situ cleaning of GaN templates and its impact on the surface morphology have been investigated using XPS, RHEED and STM. Additionally, various types of surface defects of the GaN templates and their influence on the MBE grown thin GaN films morphology have been studied by STM. Furthermore, the dependence of the MBE growth parameters such as growth temperatures and V/III flux ratios on the surface structures and morphologies of the GaN films have also been examined using STM.

In-vacuo thermal degassing of the GaN templates at 600°C partially removes the surface oxides/adsorbates whereas atomic nitrogen exposure at elevated temperature appears very promising for the removal of surface native oxides. By using plasma cleaning process at low temperature (≤300°C) surface oxide is not removed completely. Whereas the high temperature cleaning (≥700°C) is able to remove it but causes a severe surface roughening. A combination of initial low temperature plasma cleaning followed by a high temperature cleaning of short duration shows an optimization for the cleaning process. Among the surface defects mainly large defects of screw/threading pits and holes of different sizes as well as small defects of screw/mixed and edge dislocation are observed. The larger surface defects promote a defect induced growth process after deposition of thin GaN layer using MBE. Within the terrace area, a flat GaN surface consisting of atomic steps and screw dislocations is observed, whereas an inversion domain of GaN surface is found in the vicinity of the substrate pits/holes. In case of GaN substrates consisting of smaller defects, a layer-by-layer growth mode is observed for Ga rich growth conditions. For growth at 750°C, an atomically resolved 4×4 surface reconstruction with a high defect density is found. However, subsequent growth at 790°C forms one-dimensional nano-clusters. For GaN growth at a lower Ga-flux, a rougher surface morphology and three dimensional growth is observed. Independent of the Ga flux, one-dimensional nano-structures appear after prolonged growth at higher temperature. Some parts of the result presented here have already been published [1, 2].
6.2 Introduction

6.2.1 Motivation

Before 1990, GaN was not considered as a likely candidate for blue light emitting diodes (LEDs) and lasers as it contained too many defects and was too difficult to process. Good luminescence efficiency regardless of the semiconductor was thought to require very low dislocation densities, less than $10^6$/cm$^2$. However, unlike the majority of semiconductors, in GaN, dislocations did not seem to degrade its optical and electrical properties and an excellent luminescence efficiency from GaN LEDs was obtained [3, 4], despite the dislocation densities of four orders of magnitude higher ($10^{10}$/cm$^2$). The first GaN LEDs were developed at a small company, Nishia, by Shuji Nakamura, in 1994 and his demonstration of the world’s first ultraviolet semiconductor laser in 1996 resulted in a revolution in the field of display technology. Suddenly, GaN was at the forefront of semiconductor science. Since that time onwards sapphire was, and still remains, the most common substrate for GaN nitride based semiconductor material growth despite its large lattice constant and thermal expansion coefficient mismatches with GaN which is not suitable, based on the usual assumptions made in choosing a substrate for epitaxy.

Apart from the optoelectronic applications, AlGaN/GaN based heterostructure field effect transistors are very well suited for high-temperature, high-power and high-frequency electronic devices [5, 6]. Furthermore, they have significantly different properties to the conventional III-V semiconductors such as the hexagonal (wurtzite) structure, wide band gap, high piezo-electric constants and strong $k$-dependence of carrier effective masses. All these scientific and industrial concerns make it of high practical as well as fundamental interest.

6.2.2 GaN(0001)/sapphire template layer

As large bulk GaN single crystals are currently a research area of great effort and the single crystal GaN of sufficient size is not well available, GaN growth is mostly performed by hetero-epitaxy. As mentioned earlier, sapphire ($\text{Al}_2\text{O}_3$), single crystal aluminium oxide is the most commonly used substrate for GaN growth. Among the growth process, metal organic vapour phase epitaxy (MOVPE) is one of the most developed techniques for GaN growth and has largely been accepted by the industry. Hence for all kinds of GaN nitride based homo- and/or hetero-epitaxial growth experiments as well as for device fabrication, MOVPE grown template layers of sub-micron thickness GaN(0001) on sapphire can serve as pseudo-substrates and play a very important role in further epitaxy.

The MOVPE growth process of GaN films on c-plane sapphire was performed in a vertical close spaced showerhead reactor (Thomas Swan Sci. Eq., UK) using ammonia and trimethyl gallium as precursors and hydrogen as the carrier gas. Several experimental steps were carried out for the GaN template layer growth. Prior to any GaN growth, firstly the sapphire substrate was thermally annealed at about 1070°C under H$_2$ ambient to remove the surface oxides and other contaminations. This process also stabilizes an Al-
terminated sapphire surface. Secondly, the substrate nitridation following the annealing steps was performed at about 800°C to prepare a thin AlN layer which might play an important role on the polarity determination and the quality of the subsequently grown GaN layer [7]. After proper substrate nitridation, the initial nucleation of the GaN layer, i.e., the nucleation layer (NL) growth was performed at a relatively low growth temperature of about 550-600°C in order to obtain a thin and homogeneous layer and the thickness of the nucleation layer was optimized to about 25-50 nm. Annealing of the as-grown nucleation layer under NH₃ and H₂ gas atmosphere was performed, which is called the recrystallization process, before the high temperature GaN growth starts. This process can highly influence the GaN films crystallinity and leads to the formation of nucleation centers for the subsequently grown high temperature (1050°C) GaN epilayer growth [7]. Finally, the high temperature GaN epilayer of 2-5 μm thickness was grown. The high temperature growth initially leads to the formation of large GaN islands, later followed by island coalescence which results in a smooth and flat GaN surface of homogeneous film thickness [8]. An in-situ reflectometry setup was used to determine the layer thickness at coalescence. A detailed study of the GaN template layer growth process is presented in ref. [7]. This type of GaN(0001) layer on sapphire substrate is known as template layer which can be used as a substrate for further homo- and hetero-epitaxial growth experiments of GaN nitride based materials. In the following an in-situ cleaning process of the template layers and various types of surface defects found on this template layer have been discussed.

6.2.3 Surface cleaning

The cleanliness of the sample is very crucial for any kind of semiconductors as it highly affects the surface structure, electronic properties and the reactivity [9], which are important factors for subsequent processing. In particular, highly cleaned semiconductor surfaces are generally required prior to metallization since the metal-semiconductor interface plays an important role determining the overall performance [10, 11]. Among various contaminants, native oxide formation is one of the major issues for virtually all kind of metal and semiconductor surfaces and demands a proper cleaning process if further ex-situ processing is required. In the following, the removal of surface oxide and the cleaning process of GaN template layers will be discussed.

Surface oxidation

In contrast to the results typically observed for the cleaning of GaAs or Si by thermal oxide desorption, a complete removal of oxygen species from air-exposed GaN surfaces is not possible using in-vacuo heating alone. Only a partial removal can be achieved up to the GaN decomposition threshold temperature at about 850°C. Hence, additional or alternative cleaning methods are necessary to obtain spectroscopically clean GaN surfaces.

Several surface cleaning methods have been tried for GaN, such as ex-situ chemical etching [11–13], Ga deposition and re-evaporation [14], sputtering with nitrogen [15–17], xenon [15] or argon [15] ions, or annealing in ammonia (NH₃) [16–18]. Plasma-assisted
cleaning methods have also been employed, using a mixture of H and He [19] or N [21, 22, 25] exposure at elevated substrate temperature. In most reports, the authors concentrate on the chemical surface properties. An interlink of the cleaning process and its impact on the surface structure and morphology is still missing. In order to bridge this gap, we will present an efficient technique to remove the surface oxide using an exposure to activated nitrogen from a radio frequency (rf) plasma source at elevated substrate temperature. To investigate the impacts of the cleaning process on the structural and morphological quality of the surface, reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED), as well as scanning tunneling microscopy (STM) have been used, combined with x-ray photoelectron spectroscopy (XPS) for chemical analysis.

6.2.4 Surface defects

Any kind of surface defects on GaN template layers can highly influence the subsequent growth process, the surface carrier mobility, the luminescence efficiency as well as many other aspects which make the investigation of the surface defects of high fundamental as well as practical importance. In case of a dislocation-free GaN surface, the step-terrace structures should be uniform with a terrace width inversely proportional to the miscut angle of the substrate. However, in case of MOVPE grown template layers, a highly non-uniform terrace morphology dominated by the dislocation mediated intersection of free surface structures is observed. The surface defect structures can play an important role on the dislocation mediated surface features and as a result can diminish the performance of quantum hetero-structures.

Different types of dislocation mediated GaN surface structures such as pinned steps, spiral hillocks and surface depressions and their impact on the device performance have been discussed [23]. Termination of surface steps by the screw component of a threading dislocation results in the formation of pinned steps. These structures may increase the interface roughness scattering that reduces the carrier mobility in quantum hetero-structures [24]. In case of GaN growth by MBE growth system on templates, defect mediated formation of spiral hillocks have been found which results in substantial thickness variations in quantum wells [25]. This thickness variations within the quantum wells may cause luminescence line-width broadening of optoelectronic devices. The formation of spiral-hillocks also increases the planar step density near the center of each spiral, which may lead to fluctuations in the compositions of group III-nitride ternary alloys and dopant concentrations. Formation of ”V-defects” in InGaN/GaN multi-quantum well structures [26], AlGaN/GaN hetero-structures and GaN grown at low temperature may originate from the surface depression of the GaN templates. All these defects create inhomogeneities in the surface topography as well as in the luminescence wavelengths for quantum hetero-structures. Hence, a further understanding and control of these surface features may lead to the improvement of the performance of nitride-based quantum hetero-structures.

Within this study, various types of surface defects of MOVPE grown GaN template layer have been characterized using UHV scanning tunneling microscopy (STM).
6.2.5 GaN homo-epitaxy using MBE

For a better understanding of the GaN growth process it is important to know the effect of growth parameters e.g. substrate morphology, substrate temperature and flux ratios on the morphology and structure of GaN films. In general, the growth mechanism can largely differ by the different choice of substrate material. Therefore, to eliminate the influence of different substrate materials such as sapphire, SiC or GaAs, it is useful to conduct a homo-epitaxial growth experiment of GaN. Moreover, the lattice mismatch induced film stress is not a factor in homo-epitaxy. Hence a homo-epitaxial growth of GaN is of high practical interest.

The MBE growth technique has several inherent advantages that have driven the continued development of GaN growth by MBE. One of the main advantages is the lower growth temperature of MBE (500°C–750°C) compared to MOVPE (900°C–1100°C). The high temperatures of MOVPE can lead to dopant redistribution within layers, limitations in alloy incorporation and film cracking due to thermal mismatch. Low levels of impurities in the ultra high vacuum environment of MBE are also advantageous. Additionally, for p-type doping with Mg within the GaN layer, formation of a H-Mg complex is commonly found for the MOVPE growth system. To activate the p-type GaN, a post-growth high temperature annealing is required to drive out the H from the material, which is not needed in MBE because of the lack of H in the growth chamber [27]. Other advantages of MBE growth include a high degree of interface control and layer thickness and the in-situ characterization of the surface structure of the film allowed by reflectance high-energy electron diffraction (RHEED).

6.3 Experimental details

Metal organic vapour phase epitaxy (MOVPE) grown 3-4 µm thick GaN(0001) layers on Al₂O₃ were used as substrates. For STM studies, a 400 nm thick overgrown top GaN layer was doped with silicon. GaN templates were grown at the Semiconductor Epitaxy group of Prof. Hommel using MOVPE, in collaboration with Dr. S. Figge. After growth, the samples were transferred to the STM analysis chamber and then thermally degassed at 600°C under ultra high vacuum (UHV) conditions for more than 12 hours. The sample was heated by passing a direct current through a silicon wafer back-plate which was in direct mechanical contact with the sapphire template. A schematic drawing of the sample heating process is shown in figure 6.1. The temperature of the silicon wafer was measured using an infrared pyrometer of an uncertainty of ±20°C and all the temperature quoted here is the temperature of the Si back-plate. The actual temperature of the GaN surface is expected to be (20-30)°C lower than the measured temperature.

6.3.1 Oxide cleaning procedure

The cleaning experiments were carried out with two different ultra-high vacuum (UHV)
systems having base pressures below $10^{-10}$ mbar. As analytical tools, XPS (Mg K radiation) and RHEED are available in the first system (III-V MBE growth chamber, Epi 930) and the characterization was performed in collaboration with Dr. C. Kruse. The second UHV setup (Omicron microprobe system) is equipped with a STM and a LEED system. Nitrogen rf plasma sources (Epi uni-bulb) and Ga deposition sources are attached to both UHV systems.

All the cleaning experiments were done using MOVPE grown 3-5 $\mu$m thick GaN(0001) films on sapphire substrates. Prior to the experiments, the GaN template layers were exposed to air for a long time (at least several weeks). First, the samples were thermally degassed at 600°C. Then, they were exposed to active nitrogen from the rf-plasma sources at elevated temperatures. RHEED patterns were taken at elevated temperatures during plasma-assisted cleaning, whereas LEED investigations and STM measurements (constant current mode) were carried out at room temperature. For all experiments, the rf power was kept at relatively low values (300 W) in order to minimize the surface damage induced by ions emerging from the plasma sources.

### 6.3.2 Investigation of surface defects

In case of surface defects characterization, MOVPE grown GaN template layers were transferred to the STM analysis chamber under nitrogen ambient to avoid the surface oxidation and other contamination. The experiments were performed in the UHV STM chamber with a base pressure of $5 \times 10^{-11}$ mbar. Prior to the STM measurements, samples were properly degassed. Thin GaN layers were also grown on GaN templates at 750°C. Radio frequency (rf) nitrogen plasma was used as an active nitrogen source and high purity Ga metal was evaporated from an effusion cell heated by electron beam bombardment.

### 6.3.3 GaN homo-epitaxy

Similar to the surface defect investigation, the sample transfer was performed under N$_2$ ambient conditions. GaN growth was carried out on the GaN(0001)/sapphire templates homo-epitaxially to exclude the influence of the sapphire substrate on the following growth
process. The template layer, almost free from large surface defects (see later) was used to avoid the defect induced GaN nucleation. The influence of the Ga and N flux on the GaN surface morphology has been investigated by varying the Ga flux while keeping the N flux constant. GaN growth was done using nitrogen plasma-assisted MBE. The impact of the growth temperature on the growth process has also been studied. After every growth step, the samples were annealed at the growth temperature for a few minutes to remove excess Ga which might form droplets and therefore would impede STM studies. The surface structures and morphology were investigated by LEED and STM.

6.4 Results and discussion

6.4.1 Surface cleaning

Two different cleaning procedures were examined by XPS. In the first case, GaN was thermally degassed at 600°C for 45 min, prior to a low-temperature active-nitrogen exposure at 200°C for 30 min. In the second case, the degassing at 600°C was extended to more than 12 hours, followed by 20 min of high-temperature plasma-assisted cleaning at 700°C (Process-II). In both cases, the O 1s, N 1s and Ga 3d core levels were probed by XPS.

Oxide removal: XPS results

(A) Thermal degassing:

The effect of thermal degassing at 600°C on the removal of surface oxides of GaN templates is shown in figure 6.2. From the comparison it is clearly observed that the thermal degassing for 45 min can only remove a fraction of the surface oxide, whereas prolonged degassing is much more effective to remove the surface oxygen concentration. However, the existence of the oxygen peak even after a significant period of thermal degassing (12 hours) suggests that GaN surface oxides cannot be removed only by in-vacuo degassing. This finding demands an additional cleaning procedure for the GaN surface, which is discussed in the following.

![Figure 6.2: O 1s core level spectra of GaN, shown after thermal degassing at 600°C for 30 min (red) and 12 hours (black), respectively.](image-url)
Chapter 6. GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy

The results obtained before and after the active-nitrogen cleaning using both cleaning processes are presented in fig. 6.3. In fig. 6.3(I), low temperature (200°C) cleaning process (I) is presented, whereas fig. 6.3(II) represents the high temperature (700°C) cleaning process (II).

(B) Plasma cleaning at low temperature (Process-I):

The results for 45 min degassing at 600°C are shown before and after low-temperature active-nitrogen cleaning [fig. 6.3(I)]. It can clearly be seen that the exposure to active nitrogen at 200°C for 30 min reduces the surface oxygen concentration [cf. image (a) of fig. 6.3(I)]. Nevertheless, a significant oxygen peak persists after cleaning, which demonstrates that this process is not able to remove the oxide completely. From an evaluation of the integral O 1s intensities it follows that about 80% of the oxide species are removed employing this plasma-assisted cleaning process. The comparison of the N 1s spectra is shown in image (b) of fig. 6.3(I), where an increase of the N concentration of about 26% is observed after cleaning. Image (c) of figure 6.3(I) shows the Ga 3d spectra, where a slight increase in intensity and a small shift of about 0.15 eV towards the lower binding energies can be found.

(C) Plasma cleaning at high temperature (Process-II):

The results for prolonged degassing at 600°C are shown before and after high-temperature active-nitrogen cleaning [fig. 6.3(II)]. It is evident that the surface oxygen concentration for the starting surface is much smaller than after degassing for only 45 min. Hence, degassing at 600°C for a longer duration (12 hours) is already quite efficient for the removal of the surface oxide. In this respect, the prolonged degassing is even almost comparable to the low-temperature plasma-assisted cleaning. A further removal of the surface oxide from the well degassed sample is observed by plasma-assisted cleaning at 700°C, which leads to a reduction of the integral O 1s intensity by another 85%. In the image (b) of fig. 6.3(II), N 1s spectra are shown and an increase of about 68% of the integral intensity is determined after high-temperature cleaning, which is much higher than the increase found after low-temperature plasma-assisted cleaning. This strong increase can be explained by the efficient removal of the top oxide layer, which leads to a reduced attenuation of the N 1s signal, as well as in terms of a replacement of surface oxygen atoms with nitrogen atoms. This is confirmed by the evolution of the Ga 3d signal, as shown in image (c) of fig. 6.3(II). Apart from an increase in intensity, a peak shift of about 1 eV towards lower binding energies is observed, indicating the replacement of Ga-O bonds by Ga-N bonds.

Plasma-assisted cleaning of GaN templates at low temperature removes only a minor part of the surface oxygen species, whereas for high-temperature cleaning, the removal is almost complete, as demonstrated by our XPS results. In addition, prolonged thermal degassing has almost the same impact on the surface oxygen content as low-temperature plasma-assisted cleaning. These findings indicate that the cleaning process is a combined impact of active nitrogen species together with the thermal activation of the surface species. In case of low-temperature cleaning, the thermal activation energy is the limiting factor for the replacement of O atoms by N atoms. Similarly, degassing at high temperature without any exposure to active nitrogen is not very efficient since it is restricted to thermal desorption. Therefore, plasma-assisted cleaning at high temperature is necessary. This leads to a
6.4. Results and discussion

Figure 6.3: (a) O 1s, (b) N 1s, and (c) Ga 3d core level spectra of GaN, shown before (□) and after (●) N-plasma assisted cleaning. (I) 30 min plasma cleaning at 200°C after 45 min degassing at 600°C. (II) 20 min plasma cleaning at 700°C after 12 hours degassing at 600°C.

change of the surface chemical composition from a Ga₂O₃-like to a GaN stoichiometry, which is supported by a strong increase of the N 1s signal and a moderate rise of the Ga 3d signal, as well as by the observed chemical shift of the Ga 3d line towards lower binding energies.

Effects of plasma-assisted cleaning on structure and morphology

Figure 6.4 shows the RHEED patterns of a well-degassed GaN surface (600°C for more than 12 hours), obtained at elevated temperature before [6.4 (a) and ((b))] and after [6.4 (c) and (d)] the plasma-assisted cleaning at 700°C for 20 min. Images for different azimuthal orientations are shown within the figure. A transition from a streaky to a spotty RHEED pattern is observed which indicates a roughening of the GaN surface due to active-nitrogen exposure at high substrate temperature.

Very similar cleaning experiments were carried out in the STM UHV system. All the samples were degassed at 600°C for about 12 hours. Subsequently, three different plasma-
Chapter 6. GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy

Thermally degassed at 600°C for 12 hours

After plasma-assisted cleaning at 700°C for 20 min.

Figure 6.4: RHEED patterns of GaN templates at elevated temperature, before [(a) and (b)] as well as after [(c) and (d)] high-temperature plasma-assisted cleaning at 700°C for 20 min. V.

assisted cleaning procedures were tested with exposures at 300°C for 30 min [process (a)], 700°C for 30 min [process (b)] and a combination of 375°C for 30 min and 750°C for 10 min [process (c)], respectively.

Figure 6.5: Empty state (−3 V) STM image of a GaN surface (1000×1000 nm²) which has only been treated by thermal degassing without any plasma cleaning.

The STM surface overview of the GaN template layer before any plasma cleaning treatment is shown in figure 6.5. The STM image shows a rough and spotty surface morphology which is an indication of a high surface contamination. In fig. 6.6 (a) and (b), large-scale STM images obtained after cleaning process (a)[300°C for 30 min] and (b)[700°C for 30 min] are shown, respectively. A drastic improvement in the STM image surface morphology has been achieved. In case of low-temperature plasma-assisted cleaning, the surface exhibits small structures. However, some parts of the surface still appear fuzzy, as can be seen e.g. in the lower left corner of fig. 6.6 (a). This may arise from the large residual surface contamination still present, even after the cleaning process. If the cleaning
temperature is raised to 700°C, a slight change of the surface morphology is observed, as shown in fig. 6.6 (b). Again, small islands appear, but now the surface looks relatively clean and to some extent, a faint contrast due to surface step edges can also be resolved.

STM images at larger magnification are shown in fig. 6.7 (a) and (b) for the cleaning process (b)[700°C for 30 min] and (c)[375°C for 30 min, followed by 750°C for 10 min], respectively. From the topograph and the line scan in fig. 6.7 (a), it is obvious that plasma-assisted cleaning at 700°C for 30 min causes a severe surface roughening in agreement with the RHEED observation. Islands of about 20 nm to 40 nm in diameter are found with a height of up to about 1.5 nm. In case of combined low-temperature and high-temperature plasma-assisted cleaning [cf. fig. 6.7 (b)], the surface looks very smooth and exhibits only very small islands and surface steps of monolayer height (2.5 Å). The height of the islands, as determined from the STM data, does not exceed 3 Å.

Figure 6.6: Empty state (−3V) STM images of a GaN surface (1000×1000 nm²) after different plasma-assisted cleaning procedures: (a) 300°C for 30 min and (b) 700°C for 30 min.

Figure 6.7: STM images and height profiles along the indicated lines, recorded after different plasma-assisted cleaning procedures: (a) 700°C for 30 min (300×300 nm² scan area) and (b) 375°C for 30 min, followed by 750°C for 10 min (100×100 nm² scan area).
The smoothness of the surface obtained after cleaning procedure (c) is also reflected in large-scale STM images, such as shown in fig. 6.8. On this scale, the surface appears atomically flat, and step edges are clearly resolved. Dark spots become visible, which from their position at the end of step edges are identified as surficial intersections of screw or mixed-type dislocations, which are common for GaN template layers grown on sapphire.

The exchange of N-atoms with O-atoms leads to the re-structuring and possibly to a thermally activated re-growth of the top GaN layer which occurs under N-plasma. This growth process can be treated as GaN MBE growth under nitrogen rich conditions for which a 3D growth mode is energetically favourable [28]. This explains the rough surface morphology after high-temperature plasma-assisted cleaning as observed both by RHEED and STM. In addition, GaN becomes softer at higher temperatures, which facilitates ion induced etching and surface damaging from the plasma source. Such high-energy nitrogen ion induced processes have already been discussed as a reason behind surface roughening [29].

Figure 6.8: Empty state (−3 V) STM image of a GaN surface (1000×1000 nm²) after plasma-assisted cleaning at 375°C for 30 min followed by 750°C for 10 min.

Optimum results regarding both surface chemistry and morphology are obtained by prolonged thermal degassing, followed by low-temperature plasma-assisted cleaning and a final short high-temperature active-nitrogen cleaning step. This provides a maximum efficiency of thermal surface oxide desorption, together with a subsequent chemical reduction of the surface by active nitrogen species, while minimizing the surface damage and roughening occurring during high-temperature plasma-assisted cleaning.

Growth of thin GaN layers on plasma-cleaned template

A thin homo-epitaxial GaN film (few nm) was grown at 750°C on a GaN template cleaned by combined low-temperature and high-temperature active-nitrogen exposure. Subsequently recorded large-scale STM images showed a very flat surface morphology which is quite similar to fig. 6.8. At a larger magnification, atomically resolved structures with 1×1 periodicity were observed, as can be seen in fig. 6.9 (a). The 1×1 structures appeared only with a local periodicity. The LEED patterns of this surface are shown in fig. 6.9 (b) which also shows a 1×1 reconstruction, in agreement with the finding of STM.

Hence, GaN layers of high structural quality can be grown on template layers cleaned by this combined low-temperature and high-temperature cleaning technique. The appearance of a smooth and flat surface morphology with GaN step and terrace structures is an indication of a step-flow growth mode. The presence of a 1×1 surface reconstruction is
6.4. Results and discussion

Figure 6.9: (a) STM image (15×15 nm², −3 V) of a thin GaN film homoepitaxially grown on a cleaned surface. Local atomic structures with 1×1 periodicity are found. (b) LEED pattern (45 eV) obtained from the same film, showing a 1×1 surface reconstruction.

in agreement with the as-grown 1×1 GaN surface reported by Xue et al. [30]. From all the findings it is also clear that the in-situ plasma cleaning method is a highly effective surface cleaning process for GaN template layers and the cleaned GaN templates can be used for further UHV investigations.

6.4.2 Surface defects of GaN(0001) templates

Within this section, various types of surface defects of different GaN templates observed during STM investigations will be discussed. For all these STM studies, the GaN sample mounting as well as transfer to the STM analysis chamber have been carried out under nitrogen ambient condition in order to avoid any kind of surface contamination. For the larger defects, ‘screw/threading pits’ and ‘surface holes’ of different shape and depth are observed. For smaller defects, ‘screw/mixed’ and pure ‘edge’ type dislocations are found.

(a) 1000×1000 nm²  (b) 180×180 nm²  (c) 220×160 nm²

Figure 6.10: (a) Empty state (−4 V) STM images of a GaN surface showing large screw pits. Closer look of (b) single and (c) dipole screw pits, respectively.

Large screw pits

Fig. 6.10 shows the STM images of a GaN template having large screw/threading pits. In fig. 6.10(a), the MOVPE grown GaN template surface overview consists of single and dipole screw pits of a diameter of 60–90 nm and depth up to 3 nm. The surfaces appear quite smooth, consisting of an array of terraces separated by monolayer step height (∼0.26 nm). The steps on the MOVPE-GaN surface are predominantly straight and mostly terminated tangentially at the edges of large surface pits/depressions. The screw pits are in general of hexagonal shape and each surface step consists of two interlocking screw pits
of threading of opposite sign. No surface depressions of this type are observed within the terrace area. Closer looks of a single and a double screw pit are shown in fig. 6.10(b) and 6.10(c), respectively. For both cases, hexagonal pits of pinning steps along (000\bar{1}) direction with monolayer step height can clearly be seen.

After deposition of a thin GaN layer (few nm) on this surface, changes in the surface morphology have been shown in figure 6.11. The overall GaN surface appears similar with large pits and flat terraces. But the average terrace size is increased. Similar to earlier observation, again the steps are terminated at the pits. Both effects result in formation of some step bunching. A closer look STM image of a screw pit after GaN deposition is shown in fig. 6.11(b), where a partial filling up of the pits with the deposited material can clearly be observed. In the vicinity of the screw pit, a step bunching process can also be seen.

(a) 1000×1000 nm²  (b) 200×200 nm²

Figure 6.11: Empty state (−4 V) STM images after deposition of a thin GaN layer at 750°C. (a) GaN surface overview and (b) closer look at screw pit.

The formation of large screw pits is very similar to the screw/mixed dislocation commonly formed during GaN growth using MOVPE. The dislocation causes a surface displacement equal to the Burgers vector normal to the surface. The hexagonal shape of the pits may be related to the six fold crystal symmetry of the GaN lattice. Additionally, the pit’s structure looks very similar to the 'V-defects' which may originate from the lower surface diffusion during growth [26]. The top few 100 nm of an overgrown GaN layer were doped with Si for STM measurements. Si doping during GaN growth reduces the surface diffusion which may be the cause for the defects generation. High Si doping can also promote the formation of surface cracks. Furthermore, slightly lower growth temperature can also be a deciding factor. The filling of the screw pits after thin GaN layer deposition can be related to the defect induced GaN nucleation. The widening of the flat terrace area with step bunching may be related to the step flow growth mode which is obstructed by the screw pits. Both the results indicate a high surface diffusion of the deposited materials during MBE growth.

Surface holes with flat bottom surface

Apart from the large screw pit, another type of defect of even larger size, called 'surface holes' has been observed. The main difference of this structure to the earlier pits is the sharp termination of the side walls without any screw threading and an atomically flat bottom surface. The holes appear in different shape, size and depth and the step edges of the GaN surface are terminated at the side wall of the holes. STM images of a GaN
6.4. Results and discussion

(a) $1000 \times 1000 \text{ nm}^2$  
(b) $1000 \times 1000 \text{ nm}^2$  
(c) $1000 \times 1000 \text{ nm}^2$

Figure 6.12: Empty state ($-4 \text{ V}$) STM images of a GaN surface showing shallow holes of different sizes and shapes. (a) Hexagonal holes with flat bottom surface. (b) and (c) Holes of arbitrary shapes having GaN terrace structures even within the bottom surface.

Surface consisting of various types of shallow surface holes are presented in figure 6.12. Surface holes of hexagonal shape with an average diameter of about 150 nm and depth of about 4 nm have been shown in fig. 6.12(a). Shallow holes of arbitrary shape with an extremely large lateral size (up to 500 nm) can be seen in fig. 6.12(b) and 6.12(c). The bottom surface of the holes appears smooth, consisting of atomically flat GaN terrace structures with monolayer step height as can be seen in fig. 6.12(c).

(a) $500 \times 500 \text{ nm}^2$  
(b) $300 \times 300 \text{ nm}^2$  
(c) $50 \times 50 \text{ nm}^2$

Figure 6.13: Empty state ($-4 \text{ V}$) STM images after deposition of a thin GaN layer at $750^\circ \text{C}$. (a) Surface overview, (b) Inversion domain is found at the step edge near the hole and (c) $4 \times 4$ surface structures within the terrace area, respectively. Inset shows a closer look of the surface ($14 \times 14 \text{ nm}^2$).

A very similar kind of GaN growth experiment on this template surface has also been performed using MBE and the changes in the surface morphology have been shown in figure 6.13. Filling up of the surface hole can be found in fig. 6.13(a). A distinct surface morphology has been observed on a GaN terrace in the vicinity of the hole area. The surface appears rougher in contrast to the rest terraces as shown in fig. 6.13(b). Larger magnification STM images of the smooth terrace area show atomic row like patterns with a spacing of a $4 \times 4$ surface reconstruction.

The formation of surface holes is not yet clear. There are some possibilities of the polarity inversion of the GaN(0001) surface which may cause these findings. In case of p-type GaN templates, Mg-induced pyramidal defects are usually found, which may lead to a polarity
Chapter 6. GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy

inversion. As the growth rate of GaN for Ga and N polar face largely differs, the overgrown GaN films may exhibit a thickness difference for the Ga-polar to the N-polar area. This effect may finally result in the surface hole formation. However, more investigations are required for a better understanding of the formation mechanism of the surface holes. The 4×4 reconstruction is an indication of a Ga-polar surface which is in agreement with the earlier results obtained for GaN homo-epitaxy on MOVPE templates. The terrace with a rougher surface morphology may be related to the polarity inversion and formation of the N-polar area originating from the bottom surface of the hole. The N-polar GaN surfaces in general appear with a rougher morphology than the Ga-polar, which is also compatible with the explanation of polarity inversion.

Deep holes with side wall facet

Depending on the thickness of the overgrown GaN films, surface holes of even larger depth (8–16 nm) have also been observed as shown in figure 6.14. The bottom surface of the holes looks also flat. By a careful inspection, side wall facetting of the surface holes can also be observed. The line scan along the side wall and the corresponding height profile are shown in fig. 6.14(c) and fig. 6.14(d), respectively. The line profile suggests a formation of two side facets. The inclination angle of the lower facet to the bottom surface is about 13.4°, whereas the upper facet appears steeper than the lower one and the angle is about 26.8°.

Figure 6.14: Empty state (−4 V) STM images of a GaN surface showing deep holes with side wall facet. [(a)-(c)] STM images and (d) line scan height profile along the side wall.

Screw/mixed and edge type dislocation

By proper choice of the MOVPE growth parameters for GaN growth on sapphire, the formation of all these larger defects can be avoided, which leads to very smooth and atomically flat terrace structures. But due to the lattice mismatch induced strain and the different thermal expansion coefficient of GaN and sapphire, some smaller types of surface defects such as screw, mixed and edge type dislocations always appear after GaN growth using MOVPE.

A typical surface morphology of MOVPE grown GaN template layers without any larger surface defects is shown in figure 6.15(a). The GaN film is quite smooth consisting of
an array of terraces separated by steps of ~2–3 Å height, well in agreement with the monolayer step height (2.6 Å for GaN(0001)). Most of the steps are terminated tangentially at the edges of surface pits/depressions (large black dots). This type of pits can be correlated to screw or mixed-type surface dislocations, which are quite common for GaN template layers grown on sapphire. The density of this dislocation is in the order of $10^9$/cm$^2$. Apart from the screw or mixed-type surface dislocations, some even smaller and shallower pits/depressions (small faint-dark spots marked by arrows) can also be found, which are located within the GaN terrace areas. These smaller pits can be related to pure edge type dislocations of GaN. Since the Burgers vector of pure edge dislocations does not have a component perpendicular to the surface, no steps are generated or terminated. In a high resolution STM image of the GaN surface small granular islands are observed as shown in figure 6.15(b) and the surface structure cannot be resolved atomically.

6.4.3 GaN homo-epitaxy using MBE

To investigate the influence of the Ga/N flux ratio on the surface morphology of homo-epitaxially grown thin GaN films on GaN(0001) templates, basically two different MBE growth regimes were investigated. The active N-flux was kept fixed, whereas the Ga-flux was varied. The GaN growth processes are called as Ga-rich growth for high Ga-flux and N-rich growth for low Ga-flux, respectively. For GaN growth with low Ga flux, the flux monitor current was set to 60% of the value used for the high Ga flux experiments. For each growth regime (a) the initial nucleation of about 4 nm GaN at 750°C and (b) the subsequent growth of about another 4 nm GaN at 790–800°C was studied.

GaN growth with high Ga flux

In figure 6.16, STM images of a homo-epitaxial GaN film grown at 750°C (figure 6.16(a)–6.16(c)) and 790°C (figure 6.16(d)–6.16(f)) with high Ga-flux are presented. The surface of the GaN films appears very smooth and the terrace/step structure typical of GaN templates with dislocation pits is preserved (figure 6.16(a)). On the STM image in figure 6.16(b) a small surface roughness and the formation of small 2D islands with a height of 2.5–5.0 Å can be observed. In figure 6.16(c), an atomically resolved 4×4 surface reconstruction with high defect density is found. After subsequent GaN growth at 790°C, the surface morphology does not change much and still appears with flat terraces and dislocation pits as shown in figure 6.16(d). But at a closer inspection a significant
change in the surface structure is revealed, as shown in figure 6.16 (e). A one-dimensional ordering of nano-clusters of about 3 nm average lateral spacing is observed, which is shown at higher resolution in figure 6.16 (f).

After 4 nm of GaN deposition at 750°C at a high Ga flux
(a) 1000×1000 nm²  (b) 150×150 nm²  (c) 40×40 nm²

Another 4 nm of GaN deposition at 790°C at a high Ga flux
(d) 1000×1000 nm²  (e) 200×200 nm²  (f) 70×70 nm²

Figure 6.16: STM images after MBE deposition of about 4 nm of GaN deposition at 750°C on GaN/sapphire template: [(a)–(c)] as well as after further deposition of about another 4 nm of GaN at 790°C [(d)–(f)], respectively.

The smooth surface morphology with step edges and dislocation pits can be attributed to a layer-by-layer growth mode. For Ga-rich growth condition, the surplus Ga atoms enhance the surface diffusion, which promotes a smooth surface formation [28]. The 4×4 surface reconstruction suggests a Ga-polar GaN(0001) surface, which is in agreement with the earlier reported surface reconstructions. According to the structural model proposed by Xue et al. [31], the 4×4 surface reconstruction is formed by removing Ga-adatoms from the T₄ site of the 2×2 reconstruction. The 1D array of nano-clusters may be attributed to the impact of high-energy ions from the N-plasma source [29], leading to selective growth in a preferential direction, as the substrate was not rotated during GaN growth.

GaN growth with reduced Ga flux

In case of GaN growth with reduced Ga flux, the surface morphology changes and a three-dimensional growth front is obtained that results from the formation of a rough surface with 3D islands of about 1 nm height. The step and terrace structure and the dislocation pits of the GaN template disappeared for this growth condition as shown in figure 6.17 (a).
6.4. Results and discussion

After 4 nm of GaN deposition at 750°C at a reduced Ga flux
(a) 1000×1000 nm²  (b) 290×290 nm²  (c) 75×75 nm²

After 4 nm of GaN deposition at 800°C at a reduced Ga flux
(d) 1000×1000 nm²  (e) 500×500 nm²

Figure 6.17: STM images after MBE growth of about 4 nm GaN at 750°C with a reduced Ga-flux [(a)–(c)] as well as after further deposition of about 4 nm GaN at 800°C [(d) and (e)], respectively.

Figure 6.17 (b) shows the evolution of the surface morphology after deposition of about 4 nm of GaN at 750°C. The 3D islands consist of small terraces separated by monolayer surface steps as can be seen in the high resolution STM image (figure 6.17(c)). The changes of the surface morphologies after further deposition of about another 4 nm GaN at 800°C are presented in figure 6.17 (d). Again, 1D arrays of GaN islands are obtained, which is very similar to growth with high Ga-flux at 790°C. Also, the orientation of the GaN island alignment is identical to the nano-cluster ordering depicted in figure 6.16.

The rough surface morphology and 3D growth for reduced Ga flux is correlated to the reduced surface diffusion of the adatom species. Here, the growth proceeds at rather N-rich conditions, which results in surface roughening. This finding is in good agreement with the theoretical prediction for GaN growth under N-rich growth conditions [28]. The 1D ordering of GaN islands can be related to the N-plasma source induced modifications as discussed earlier. We found such an alignment of nano-clusters or islands only for high-temperature growth. This effect may be related to the GaN surface softening at high temperature, which might facilitate ion induced damage/modification.

In case of GaN growth at 800°C, sometimes nano-wires-like surface structures have also been observed as shown in figure 6.18(a)–6.18(c). The 1D GaN nano-structures are mostly oriented along a direction similar to the earlier ordering of the nano-clusters (upper-right
Chapter 6. GaN(0001)/sapphire templates: cleaning, defects and homo-epitaxy

(a) 190×190 nm² (b) 30×45 nm² (c) 50×30 nm²

Figure 6.18: Empty stage STM images of 1D GaN nano-structures grown at 800°C.

to lower left). The reason behind this type of nano-structuring is not yet clear. However, the orientation of the nano-wires may be related to the plasma induced selective growth. A schematic drawing of the sample surface and the orientation of the plasma beam exposure is presented in figure 6.19.

Figure 6.19: Schematic drawing of the sample surface and plasma beam orientation.

6.5 Conclusions

An efficient removal of the GaN surface oxides while maintaining a flat surface morphology have been achieved by prolonged thermal degassing at 600°C and subsequent plasma assisted cleaning, starting at low substrate temperature (350°C) and followed by a short-period cleaning step at high temperature (700°C). This technique seems very promising for ex-situ cleaning procedures in technological semiconductor processing, as well as for surface science experiments, where a high chemical purity and a high structural quality is required. The structure and formation mechanism of various types of surface defect of the GaN template layer and the subsequent growth of a thin GaN layer have been investigated. In case of GaN homo-epitaxy using MBE, a smooth surface morphology has been observed for Ga-rich growth conditions. In contrast, a tendency towards 3D island growth was encountered for growth with reduced Ga-flux. Growth at relatively high temperatures leads to a one dimensional nano-cluster formation likely induced by high energy N-ions of the plasma source.
Bibliography


Chapter 7

In$_x$Ga$_{1-x}$N nano-islands on MOVPE grown GaN(0001)/Sapphire templates

7.1 Abstract

The morphology and density of In$_x$Ga$_{1-x}$N nano-islands can be controlled by the choice of proper growth conditions for metal organic vapor phase epitaxy. Scanning tunneling microscopy has been used to investigate the In$_x$Ga$_{1-x}$N island morphology in dependence on the growth parameters. The influence of MOVPE growth parameters on the surface morphology of In$_x$Ga$_{1-x}$N films and the shape of various types of In$_x$Ga$_{1-x}$N nano-islands grown on GaN(0001) are discussed in terms of surface diffusivity, thermal decomposition, In incorporation and sticking ability of adsorbate species.

With decreasing growth temperature, the In$_x$Ga$_{1-x}$N island size is reduced and the homogeneity of the In$_x$Ga$_{1-x}$N surface is improved due to lower thermal diffusion. A heterogeneous nucleation of large In$_x$Ga$_{1-x}$N islands with a complex structure is observed after growth at 650°C in conjunction with a high In partial pressure. For 600°C and a low In partial pressure, however, the homogeneous nucleation of small islands of sizes suitable for three-dimensional quantum confinement is found with very high densities around $10^{12}$ cm$^{-2}$. This is discussed in terms of shorter thermally activated diffusion length of adspecies and the lower surface mobility due to a smaller density of In adatoms on the surface. From the structural point of view, these QD-like In$_x$Ga$_{1-x}$N nano-islands are a promising candidate for three-dimensional carrier quantum confinement. This is not confirmed by photo-luminescence (PL) after the capping process for which a relatively high temperature is needed. However, two-dimensional (2D) In$_x$Ga$_{1-x}$N nano-islands grown at 700°C show sharp lines in photo-luminescence (PL) spectra after a proper (‘novel’) capping process. The effect of post-growth annealing on surface morphology and PL peak intensity is also discussed. Parts of the results presented here have already been published [1–5].
7.2 Introduction

It is well known that hetero-epitaxially grown, highly strained material systems can form low-dimensional nano-structures. This nano-structures can provide the possibility for charge carrier quantum confinement, such as quantum wells (QWs), quantum wires, and self-assembled quantum dots (QDs) for one, two, and three dimensional confinement, respectively [6]. Group-III nitride semiconductors of wurzite crystal structure have a direct energy band gap and hetero-epitaxial growth can also be performed systematically. The band gap energy of Al$_x$In$_y$Ga$_{1-x-y}$N at room temperature can be varied from 0.7 to 6.2 eV depending on its composition. Therefore, III-nitride semiconductors are particularly useful for light-emitting diodes (LEDs) and laser diodes (LDs) in this wavelength region [7–10]. Typical high-brightness LEDs have a multiple quantum well (MQW) active region. The MQW LED is a kind of hetero-junction device, in which electrons and holes are confined in the well layers. Thus, one can achieve high quantum efficiency from the MQW LEDs since carrier can recombine easily in the confined well layers [11–14]. Although high-brightness MQW LEDs are already commercially available, the LED output intensity can highly be increased by further confinement of the carriers using QDs, instead of MQW.

In$_x$Ga$_{1-x}$N alloys have attracted great attention due to their use as active layers in light emitting devices. Much work has been devoted to In$_x$Ga$_{1-x}$N/GaN quantum wells (QWs) grown by metal organic vapor phase epitaxy (MOVPE) which allowed for the commercialization of light emitting diodes (LEDs) and laser diodes (LDs) for the blue and ultraviolet spectral range [15, 16]. Also there are some recent reports on In$_x$Ga$_{1-x}$N/GaN multiple QW based LEDs and LDs, grown by molecular beam epitaxy (MBE) [17, 18]. Nanometer-scale fluctuations of the In mole fraction have been found within In$_x$Ga$_{1-x}$N QW structures [19–22], and theoretical calculations predict a high tendency of phase separation within In$_x$Ga$_{1-x}$N alloys [23]. The indium-rich phases in the In$_x$Ga$_{1-x}$N films are discussed to act as centers for carrier localization and exhibit a quantum-dot (QD)-like behavior [21, 22]. This improves the device performance as it prevents carriers from non-radiative recombination at crystal defects. In addition, the use of QDs instead of QWs is expected to reduce the threshold current density of laser diodes [24]. Since the emission characteristics of QDs vitally depend on their structural properties, the controlled growth of In$_x$Ga$_{1-x}$N QDs is of high importance. Recent reports have shown that Stranski-Krastanov-like growth of In$_x$Ga$_{1-x}$N islands is possible [25–29]. Improvements regarding the formation of QDs have been obtained by varying the growth parameters [25, 28] as well as employing special techniques such as growth interruption [26], reduced growth pressure [29] or post-annealing [27]. MBE has also been explored for In$_x$Ga$_{1-x}$N QD formation [30, 31]. Among the remaining problems, predominantly, the low density and a large size of the islands are to be listed. Hence, for a successful growth of In$_x$Ga$_{1-x}$N QDs, a better understanding of the growth mechanisms is highly desirable, which is addressed in the following. For this purpose, the morphology of MOVPE grown In$_x$Ga$_{1-x}$N nano-islands has been characterized by scanning tunneling microscopy for a wide range of systematically varied growth conditions. It will also be shown how high-density arrays of In$_x$Ga$_{1-x}$N quantum dots can be achieved.
7.3 Experimental details

Uncapped In$_x$Ga$_{1-x}$N islands were grown by MOVPE on GaN(0001) template layers of 2.5 μm thickness with a dislocation density of about 10$^9$ cm$^{-2}$. The template layers themselves were grown by MOVPE on c-plane sapphire substrates. Atmospheric pressure MOVPE growth was carried out in a vertical type showerhead reactor (Thomas Swan) using N$_2$ as a carrier gas and trimethyl-gallium (TMGa), trimethyl-indium (TMIn) and ammonia (NH$_3$) as Ga, In and N sources, respectively. Basically three different growth temperatures were used: (i) 700°C, (ii) 650°C, and (iii) 600°C. The MOVPE growth parameters such as amount of In$_x$Ga$_{1-x}$N deposit $t$, growth temperature $T_g$, In partial metal flux $\gamma$ (i.e. the In:(In+Ga) precursor flux ratio), V-III ratio $\eta$, and growth rate $r$ were varied in a wide range. The growth parameters are summarized in detail in table 7.1 for the individual samples that are referred to in the following. All In$_x$Ga$_{1-x}$N samples were grown by Dr. T. Yamaguchi and Dr. S. Einfeldt, in the Semiconductor Epitaxy group of Prof. D. Hommel at the University of Bremen.

<table>
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<tr>
<th>Sample</th>
<th>$t$ (nm)</th>
<th>$T_g$ (°C)</th>
<th>$\gamma$</th>
<th>$\eta$</th>
<th>$r$ (nm/s)</th>
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Table 7.1: Growth parameters of the individual samples. In$_x$Ga$_{1-x}$N deposit $t$, growth temperature $T_g$, In partial metal flux $\gamma$ (i.e. the In:(In+Ga) precursor flux ratio), V-III ratio $\eta$, and growth rate $r$ are listed.

After In$_x$Ga$_{1-x}$N growth, the samples were transferred under dry-nitrogen ambient to the scanning tunneling microscopy (STM) analysis chamber which has a base pressure below 10$^{-10}$ mbar. Prior to the STM experiments, the samples were thermally degassed at 500°C. All STM measurements were performed in constant current mode. The growth rates were calibrated by cross-sectional scanning electron microscopy measurements of thick In$_x$Ga$_{1-x}$N reference layers. For the samples discussed in the following, the nominal
In molar fraction $x$ of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands ranged from 0.2 to 0.5, which was confirmed by transmission electron microscopy and grazing incidence x-ray diffraction.

7.4 Results and discussions

7.4.1 $\text{In}_x\text{Ga}_{1-x}\text{N}$ nano-islands with different growth temperature

The amount of In content within $\text{In}_x\text{Ga}_{1-x}\text{N}$ is the key for optical and electronic properties as well as the determining factor for the strain driven 3D $\text{In}_x\text{Ga}_{1-x}\text{N}$ island growth. In incorporation within $\text{In}_x\text{Ga}_{1-x}\text{N}$ films is highly temperature sensitive and hence the influence of the growth temperature on the film surface morphology is of high practical importance and have been studied. It has already been found that for $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth at higher temperature ($\geq 700^\circ\text{C}$) the amount of In incorporation rapidly decays with the growth temperature. In addition, due to high thermal decomposition of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, In-droplets (metallic indium) are usually formed on the surface. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface grown at a temperature higher than 780$^\circ\text{C}$ does not show any $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands but only pure In droplets are formed along with a two dimensional $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer, which is typically used as quantum well (QW) [5]. Hence for the growth of quantum dot (QD) structures, a lower temperature growth regime will be more effective. In the followings, the growth and surface morphology of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys grown at three different sets of temperatures such as (a) 700$^\circ\text{C}$, (b) 650$^\circ\text{C}$ and (c) 600$^\circ\text{C}$ are discussed.

The surface morphology of a nominally 26 nm thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ film grown at 700$^\circ\text{C}$ on GaN is shown in figure 7.1(a). Different types of $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands are observed and, from the inhomogeneous island size distribution, they can be classified into two types: (i) large islands with approximate diameters of 140–160 nm and (ii) small islands with diameters of about 50–60 nm. In general, large islands exhibit a shape which is in between hexagonal and triangular, in the following referred to as ”truncated hexagonal”. In some cases, truly triangular large islands are also found. These shapes reflect the crystal symmetry. In contrast, the small islands often have a more irregular shape.

By lowering the growth temperature to 650$^\circ\text{C}$ while maintaining all other growth parameters, the changes of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface morphology can be seen in figure 7.1(b). After deposition of nominally 26 nm of $\text{In}_x\text{Ga}_{1-x}\text{N}$ at 650$^\circ\text{C}$, the surface exhibits two typical sizes of $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands, similar to the results obtained for 700$^\circ\text{C}$. However, at 650$^\circ\text{C}$ the lateral sizes of the large and the small islands are decreased to about 80 nm and 30 nm, respectively. The density of the small islands is increased, as compared to the density of the small islands at 700$^\circ\text{C}$.

By further decreasing the growth temperature to 600$^\circ\text{C}$ while keeping the other growth parameters unchanged, the changes of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface morphology can be seen in figure 7.1(c). After nominally 26 nm of $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposition at 600$^\circ\text{C}$, a distinct change in the surface morphology is found and a more homogeneous $\text{In}_x\text{Ga}_{1-x}\text{N}$ nucleation is observed. The larger islands are not found anymore and the $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface exhibits
only the smaller islands of diameter about 30-40 nm. The density and the lateral size of the smaller islands is slightly increased, as compared to that of the small islands at 600°C.

These findings are attributed to the reduced thermal diffusion. In contrast, the density of the large islands is very similar for both the growth temperature of 700°C and 650°C. This indicates a heterogeneous nucleation of these islands (at substrate defects, as will be shown later). Additionally, for these large islands grown at 700°C as well as at 650°C, smoothly curved height profiles are found (similar to those presented in figure 7.6(b)), which we attribute to metallic In droplets on top of these islands. (If no such In droplets are present, a flat top facet of the In\textsubscript{x}Ga\textsubscript{1−x}N islands is observed, as shown in figure 7.6(a).) The formation of In droplets on top of the large islands is explained as follows. The higher growth temperatures promote a significant thermal InN decomposition and provide a high thermally-activated surface mobility. Therefore metallic In can agglomerate into droplets. The preferential nucleation of such droplets on top of large In\textsubscript{x}Ga\textsubscript{1−x}N islands might point to a high In content of these islands.

By lowering the growth temperature, the homogeneity of the In\textsubscript{x}Ga\textsubscript{1−x}N islands is improved and hence it is essential to consider the In\textsubscript{x}Ga\textsubscript{1−x}N growth at lower temperature in order to realize well ordered homogeneous nano-islands. However, for a better understanding of the growth mechanism of In\textsubscript{x}Ga\textsubscript{1−x}N nano-islands knowledge of the initial nucleation stage is also very important as it plays the key role behind the various growth processes. Therefore, samples with a very low In\textsubscript{x}Ga\textsubscript{1−x}N deposit draw considerable attention and have thoroughly been investigated as discussed in the following.

### 7.4.2 In\textsubscript{x}Ga\textsubscript{1−x}N growth at 650°C with high In partial pressure

In case of In\textsubscript{x}Ga\textsubscript{1−x}N growth at a high In partial pressure In:(In+Ga) = 0.85], the V–III ratio was fixed at 2.2×10\textsuperscript{3} and a growth rate of 0.26 nm/sec was measured by cross-sectional scanning electron microscopy measurements of thick In\textsubscript{x}Ga\textsubscript{1−x}N reference layers.
Figure 7.2 shows a STM image for an In$_{x}$Ga$_{1-x}$N deposit of 1.3 nm, grown at 650°C with high In partial pressure (sample B$_1$). Two types of large islands are observed: (i) islands with a spiral arrangement of discs (lateral size $d \approx 80$ nm) and (ii) single islands with a flat top facet ($d \approx 30$ nm). The wetting layer of the In$_{x}$Ga$_{1-x}$N surface appears very smooth and defects assigned to the GaN template layers, especially dislocations (see below), are not found. Additionally, the density of large spiral islands is in the order of $10^9$ cm$^{-2}$ which is quite similar to the dislocation density of the GaN template layers (fig. 6.15(a)).

Spiral islands

Examples of large spiral disc-like islands are shown in figure 7.3. The islands have a diameter of about $d \approx 80 - 100$ nm, and a height of about $h \approx 10$ nm. Moreover, they have a specific structure, which is very different from the reported earlier spiral In$_{x}$Ga$_{1-x}$N islands as found, e.g., by Keller et al. [32]. Here, the spiral disc-like islands are in general of hexagonal shape with a central pit. The discs/terraces are atomically flat, appear to be stacked in a spiral way and are separated from each other by steps of monolayer height (2.5 Å). In fig. 7.3(a), a double spiral In$_{x}$Ga$_{1-x}$N island is shown where the spiral stacking of individual discs is nicely observed. The single spiral island appears with a central pit and individual discs/terrace structure is shown in fig. 7.3(b). This type of In$_{x}$Ga$_{1-x}$N islands presented here is observed for the first time.

The finding of a smooth wetting layer without any visible defects after In$_{x}$Ga$_{1-x}$N growth and an spiral island density similar to the substrate defect density suggests that the large islands preferentially nucleate at defect sites of the GaN template. Moreover, the spiral arrangement of the island-discs with a central pit is likely to be initiated by heterogeneous island nucleation around screw or mixed-type dislocations of the GaN template. This points to a highly activated thermal diffusion at this temperature. Apparently at 650°C, the thermal diffusion length of the surface deposits is larger than the average spacing between the dislocations of the substrate, which is about 100 nm. The hexagonal shape of the spiral islands is attributed to the six-fold crystal symmetry. The presence of a wide and atomically flat (0001) top facet on the large islands is attributed to a minimization
of the total surface free energy. In addition, the relatively In-rich growth conditions can be expected to promote the formation of a smooth and flat surface because In is known to act as a surfactant for GaN growth [33, 34].

**Single flat-top islands (internal structure)**

The single islands with flat top facet have a diameter of about $d \approx 30 \text{ nm}$, and height of about $h \approx 3 \text{ nm}$. In case of the flat-top single islands, the central portion of the top surface appears very smooth with an atomically flat (0001) facet. The detailed surface structure of this type of islands will be discussed later and can be seen in figure 7.11(b). This atomically flat (0001) top facet points to a local In enrichment at the top of such islands as well as minimization of the total surface energy. A high resolution transmission electron microscopy (HRTEM) of a single flat-top island is shown in figure 7.4 which also supports the (0001) top facetting. The TEM results are in good agreement with the island size (lateral and vertical) observed in STM measurements for this island type. Additionally, an increased In incorporation with the island height (along (0001) crystal direction) is also found in digital analysis of high resolution TEM lattice images (DALI), where the lattice parameters were converted into a local indium content. Increase of In concentration along growth direction is an indication of local In enrichment on top of the islands which promotes a smooth surface morphology.
Chapter 7. \textit{In}_x\text{Ga}_{1-x}\text{N} nano-islands on MOVPE grown GaN(0001) templates

Thickness dependence

The changes of the surface morphology with increasing \textit{In}_x\text{Ga}_{1-x}\text{N} deposit under In-rich growth conditions are shown in figure 7.5. After deposition of 1.3 nm of \textit{In}_x\text{Ga}_{1-x}\text{N} (fig. 7.5(a)), large hexagonal \textit{In}_x\text{Ga}_{1-x}\text{N} islands with flat top faceted structure are found and the wetting layer appears very smooth without any visible substrate defects. The inset of fig 7.5(a) shows a large spiral disc-like islands. For thicker \textit{In}_x\text{Ga}_{1-x}\text{N} layers grown under identical conditions, still hexagonal islands are found, but on most of these islands, metallic In droplets have formed. Fig. 7.5(b) shows an overview for a larger \textit{In}_x\text{Ga}_{1-x}\text{N} deposit of 6.5 nm. The density of the larger islands does not change but the top surface of the islands is usually covered with a metallic In droplet. A close-up STM image of a large island with a small In-droplet on top is shown in the inset of fig. 7.5(b). Local roughening of the wetting layer is observed as it contains the initial nucleation stage of further island growth. The surface morphology of the \textit{In}_x\text{Ga}_{1-x}\text{N} film changes drastically after deposition of 26 nm \textit{In}_x\text{Ga}_{1-x}\text{N} as shown in figure 7.5(c). The density of the larger islands remains constant but now these islands are totally covered with In-droplets. The inset of fig. 7.5(b) shows a close-up STM image of a \textit{In}_x\text{Ga}_{1-x}\text{N} island totally covered with a metallic In-droplet on top. (The presence of In droplets is identified by the rather spherical shape of their height profiles, which is discussed later.) The wetting layer exhibits severe roughening which results in the formation of smaller islands throughout the entire \textit{In}_x\text{Ga}_{1-x}\text{N} surface.

(a) 1.3 nm InGaN  (b) 6.5 nm InGaN  (c) 26 nm InGaN

Figure 7.5: Empty state (-2V, 1000×1000 nm2) STM images of the \textit{In}_x\text{Ga}_{1-x}\text{N} surface after growth at 650°C at a high In-flux. The \textit{In}_x\text{Ga}_{1-x}\text{N} deposits are (a) 1.3 nm (sample B\textsubscript{1}), (b) 6.5 nm (sample B\textsubscript{2}) and (c) 26 nm (sample B\textsubscript{4}), respectively. Close-up of a spiral disc-like \textit{In}_x\text{Ga}_{1-x}\text{N} island, an island with a In-droplet on its top facet and an islands totally covered with metallic In are shown in the insets of figs. (a), (b), and (c), respectively.

As it has already been discussed that the large islands (spiral island) are most likely grown around the substrate defects, the density of the large islands does not change with the increasing amount of \textit{In}_x\text{Ga}_{1-x}\text{N} deposit. For smaller \textit{In}_x\text{Ga}_{1-x}\text{N} deposit, the wetting layer exhibits a smoother surface morphology, which can be explained in terms
of suppressed $\text{In}_x\text{Ga}_{1-x}\text{N}$ nucleation within the GaN terrace area. With increasing deposit, $\text{In}_x\text{Ga}_{1-x}\text{N}$ nucleation also takes place within the GaN terrace area which results in wetting layer roughening and finally homogeneous nucleation of smaller islands.

The formation of In-droplets on top of the large islands can be related to an inhomogeneous In-incorporation and a thermal decomposition of the $\text{In}_x\text{Ga}_{1-x}\text{N}$. Moreover, a larger In content is expected on top of the islands as the material there can partially relax the strain arising from the lattice misfit. An increasing In content of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers from the bottom to the top of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands has also been observed in transmission electron microscopy (see above). Details of the In-droplets on top of the islands are discussed in the following paragraph.

**Droplets or islands?**

To distinguish bare $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands from those covered by In-droplets, line scan height profiles of the corresponding islands are shown in figure 7.6. In fig. 7.6(a), the STM image shows large spiral disc-like $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands and the line scan profile (inset) clearly indicates a flat surface with (0001) top-faceted structure of the islands. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands in fig. 7.6(b) are covered with metallic In-droplets and can be identified by a rather spherical shape of their height profile (inset). The lateral size of the In-droplets is similar to that of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands (80-100 nm) but the height scale differs drastically from 8 nm for the islands to 27 nm for the droplet-covered islands.

![Figure 7.6: Empty state (−2 V, 300×300 nm²) STM images of (a) bare $\text{In}_x\text{Ga}_{1-x}\text{N}$ island (sample B₁) and (b) islands covered by metallic In droplet (sample B₄). Height profiles across typical islands are shown below images (c) and (d).](image)

The fact that In droplets are preferentially formed on top of the large islands can be explained in terms of Stranski-Krastanov-like growth. The most effective strain relaxation for a Stranski-Krastanov island is expected to occur at its top, which therefore provides energetically favorable In incorporation sites. This attractive chemical potential leads to a net mass transport of In species from the vicinity towards the top of the island, and hence
Chapter 7. $\text{In}_x\text{Ga}_{1-x}\text{N}$ nano-islands on MOVPE grown GaN(0001) templates

to a locally increased In concentration. As the In-N bonds are much weaker than the Ga-N bonds, the thermal decomposition becomes more effective in the In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$ areas on top of the islands. Furthermore the high surface diffusivity enhances the probability of In-droplet formation. Thus, In droplets form at the top of the islands. Prior to the droplet formation, the local In-enrichment on top of the islands also promotes a smooth and flat surface as In is known to act as surfactant for the growth of GaN [33, 34].

2D to 3D transition

In figure 7.7, the morphological evolution of the wetting layer with increasing $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit is shown. As mentioned earlier, the wetting layer looks very smooth after 1.3 nm $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposition at 650°C as shown in fig. 7.7(a). The line scan height profile also indicates a 2D lateral growth mode. With increasing $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit, 3D growth starts to dominate over lateral growth, which results in a wetting layer roughening and finally in a 3D island growth. Fig. 7.7(b) shows the initial stage of the 3D island formation within the wetting layer after deposition of 6.5 nm of $\text{In}_x\text{Ga}_{1-x}\text{N}$. For an $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit of 13 nm, the surface morphology of the wetting layer is shown in fig. 7.7(c). The island nucleation density has increased drastically and the wetting layer surface mostly exhibits 3D islands with a diameter of 20-30 nm and a height of 2-3 nm. For even larger deposits mostly 3D growth takes place. As a result, the island density does not change, and only the island height is increased. The surface morphology of the wetting layer at this growth stage can be seen in fig. 7.7(d) after deposition of 26 nm $\text{In}_x\text{Ga}_{1-x}\text{N}$. The surface contains a large number of 3D islands with some of them having a height of up to 10 nm. The 3D island growth with increasing amount of $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit can be related to the partial relaxation of the elastic strain arising from the large lattice mismatch between GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ (up to 11% for InN).

Figure 7.7: Empty state ($-2\text{~V}$, $300\times300$ nm$^2$) STM images of the evolution of wetting layer surface morphology with increasing $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit: (a) 1.3 nm (sample B$_1$), (b) 6.5 nm (sample B$_2$), (c) 13 nm (sample B$_3$) and (d) 26 nm sample (sample B$_4$), respectively, grown at 650°C. Height profiles across typical islands are shown below images (c) and (d).
7.4. Results and discussions

Effect of growth rate and V-III flux ratio

In figure 7.8, the STM images show the dependence of the surface morphology on the growth rate and the V-III flux ratio after deposition of nominally 1.3 nm of In$_x$Ga$_{1-x}$N at 650°C. Large spiral islands at substrate defects are found for a growth rate of 0.26 nm/sec and a V-III flux ratio of 2200 as shown in fig. 7.8(left column). Surprisingly, the formation of large In$_x$Ga$_{1-x}$N islands is completely suppressed and only a 2D wetting layer has been formed after In$_x$Ga$_{1-x}$N growth at a lower growth rate of 0.06 nm/sec as can be seen in fig. 7.8(middle column). Some step structures are also visible within the wetting layer. However, the large In$_x$Ga$_{1-x}$N islands reappear for this lower growth rates if the V-III flux ratio is increased to 8900 as depicted in fig. 7.8(right column).

\[ \text{growth rate}(r) = 0.26 \text{nm/sec} \quad r = 0.06 \text{ nm/sec} \quad r = 0.06 \text{ nm/sec} \]

\[ \text{V:III} \ (\eta) = 2200 \quad \eta = 2200 \quad \eta = 8900 \]

Figure 7.8: Empty state (−2 V) STM images of sample B$_1$ [left column], sample H$_1$ [middle column] and sample I$_1$ [right column]. Scan areas for upper row are 1000×1000 nm$^2$ whereas for lower row are 300×300 nm$^2$, respectively.

These observations can be explained by changes of the sticking coefficient of the deposited material and the In incorporation. In case of slow growth, the sticking of In atoms on the surface is restricted by the high thermal desorption. At the same time, the amount of In incorporated into the growing In$_x$Ga$_{1-x}$N layer is also reduced. The reduced In content leads to a diminished driving force for 3D island formation which explains the 2D surface morphology. By increasing the V-III flux ratio, the surface exhibits more active N species, which can readily react with the surface In adatoms and thus reduce the thermal desorption. Hence, more In is incorporated into the In$_x$Ga$_{1-x}$N layer which in turn enhances the formation probability for large islands driven by the partial relaxation of the lattice strain.
7.4.3 $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth at 600°C with high In partial pressure

If the growth temperature for $\text{In}_x\text{Ga}_{1-x}\text{N}$ is reduced to 600°C while maintaining the same In partial pressures [$\text{In}: (\text{In}+\text{Ga}) = 0.85$] and the V–III ratio [$\eta = 2.2 \times 10^3$], a different type of $\text{In}_x\text{Ga}_{1-x}\text{N}$ surface morphology is obtained, as shown in the STM images in fig. 7.9. Again, large islands can be found, but spiral disc-like islands are not observed. The average size of the large islands is reduced by a factor of about 2 ($d \approx 35 \text{ nm}$, $h \approx 3.5 \text{ nm}$). Moreover, the wetting layer appears rougher and exhibits smaller islands ($d \approx 10 \text{ nm}$, $h \approx 2 \text{ nm}$). In contrast to sample B$_1$, defects which can be attributed to the GaN template are visible for this growth condition (dark spots in the STM image). Additionally, the step edges of the underlying GaN template are also visible here. In case of larger $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit, however, In droplets are not found anymore.

The morphological changes of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ films observed by lowering the growth temperature from 650°C to 600°C can be attributed to a reduced thermal diffusion of adatom species and to a reduced $\text{In}_x\text{Ga}_{1-x}\text{N}$ decomposition. The thermal activation at 600°C reduces the diffusion lengths, which prevents the heterogeneous nucleation at defects such that the latter are not covered by islands (as in the case of 650°C) and hence become visible after $\text{In}_x\text{Ga}_{1-x}\text{N}$ growth at 600°C. Due to the smaller diffusion length, the size of the remaining large islands is reduced (for equal deposits). Formation of smaller islands on the wetting layer and the visible GaN terrace structures also indicate more homogeneous $\text{In}_x\text{Ga}_{1-x}\text{N}$ nucleation conditions at lower temperatures. A limited material transport will in addition keep the local In concentration below the critical value for In droplet formation. Finally, the formation of droplets is further suppressed by a reduced thermal decomposition of InN.

Surface morphology with increasing $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit

The changes in surface morphology with increasing amount of $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit is shown in figure 7.10. After deposition of nominally 1.3 nm of $\text{In}_x\text{Ga}_{1-x}\text{N}$, the surface exhibits large and small $\text{In}_x\text{Ga}_{1-x}\text{N}$ islands as well as substrate defect pits. For larger $\text{In}_x\text{Ga}_{1-x}\text{N}$ deposit of 2.6 nm the overall surface morphology looks very similar and a little increase
in the large islands density is observed. However, a significant change can be found by comparing the close-up images (300×300 nm²), where the small islands density increases drastically. In case of further increase in InₓGa₁₋ₓN deposit to 3.9 nm, an increase in the density and the average size of the larger island is observed. Close-up STM image shows that the density of the small islands does not change further and a little increase in average height is found.

![STM images scan areas are 1000×1000 nm²](image1)

![STM images scan areas are 300×300 nm²](image2)

Figure 7.10: Empty state STM images of the InₓGa₁₋ₓN surface with increasing deposit at 600°C at a high In-flux.

The increase in density of the large islands with larger InₓGa₁₋ₓN deposit is very different from the findings of similar growth experiments at 650°C (fig. 7.5) and can be explained by large island nucleation free from substrate defects. In contrast, growth at 650°C leads to the formation of large islands at defects and hence at a constant density (similar to the surface defect density of GaN template) even for larger deposits. However, for InₓGa₁₋ₓN growth at 600°C, the thermal diffusion length of the deposit material is reduced. This promotes a more homogeneous island nucleation. The smaller islands are basically formed by continuous roughening of the wetting layer which helps to partially reduce the strain by elastic relaxation of the InₓGa₁₋ₓN material and hence the island density increases with larger InₓGa₁₋ₓN deposit.
Chapter 7. \textit{In\textsubscript{x}Ga\textsubscript{1-x}N nano-islands on MOVPE grown GaN(0001) templates}

Large \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} islands

For these \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} growth conditions two types of large islands are found: (i) islands with rough surface and (ii) islands with flat top facet. The large \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} islands with rough surface have an average diameter of about $d \approx 30$ nm, and height of about $h \approx 3$ nm, whereas the \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} island with flat top surface have a slightly larger size with an average diameter about $d \approx 40 - 45$ nm, and a height of about $h \approx 4$ nm. Most of the large islands in general have a rough surface and consist of smaller grains as shown in 7.11 (a). Only a minority of the large islands have an atomically flat top facet which is already mentioned earlier as single flat-top islands found for \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} growth at 650°C (sample B\textsubscript{1}, fig. 7.2). One of this type of flat-top islands is presented in fig. 7.11 (b) (sample C\textsubscript{3}). As mentioned above, this points to a local In enrichment at the top of such islands. Despite the moderate image quality, an atomically resolved (1×1) surface reconstruction is observed on the flat top facet, which is shown in the inset of fig. 7.9 (c). This reconstruction is indicative for the formation of an In adlayer on top of an In-terminated \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} surface, confirming locally In-rich growth conditions [35,36].

![Island with rough surface](image1.png)

![Island with flat top](image2.png)

Figure 7.11: Empty state ($-4$ V, 50×50 nm$^2$) STM images of large \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} islands grown at 600°C with high In partial pressure. (a) islands with rough surface (sample C\textsubscript{1}) and (b) islands with flat top surface (sample C\textsubscript{3}). In image (b), the second derivative of the STM data is shown for display reasons. Inset shows an atomically resolved (1×1) surface reconstruction within the flat central region of the island.

Small \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} islands

The small \textit{In\textsubscript{x}Ga\textsubscript{1-x}N} islands have an average diameter of about $d \approx 10 - 12$ nm, and an average height of about $h \approx 2$ nm. As it has been discussed earlier, these islands are formed due to the roughening of the wetting layer. For close-up STM imaging, small islands appear in six additional smaller clusters which may be related to the six-fold
7.4. Results and discussions

crystal symmetry of the GaN based material. Typical surface morphology of the small In$_x$Ga$_{1-x}$N islands is shown in figure 7.12.

![200x200 nm$^2$ and 100x100 nm$^2$ STM images of small In$_x$Ga$_{1-x}$N islands](image)

Figure 7.12: Empty state ($-4$ V) STM images of small In$_x$Ga$_{1-x}$N islands (sample C$_2$).

7.4.4 In$_x$Ga$_{1-x}$N Growth at 600°C with reduced In partial pressure

Reducing the In precursor (TMIn) flux while keeping all the other precursor gas fluxes unchanged, results in a very different surface morphology. For this growth condition, the In partial pressure [In:(In+Ga)] was maintained at about 0.736 resulting in a group V:III material ratio of 3900. As a consequence, the In$_x$Ga$_{1-x}$N growth rate was also reduced and for thick reference sample was measured to about 0.13 nm/sec.

The most uniform island size distribution was achieved under these growth conditions as can be seen in figure 7.13. Corresponding STM images of samples D$_1$–D$_3$ are shown here. The large topograph (1000x1000 nm$^2$) provides an overview of the In$_x$Ga$_{1-x}$N surface. Only homogeneously distributed small islands are found and the nucleation of larger islands is completely suppressed. Defects originating from the GaN template as well as step edges and terrace structures are visible. After deposition of 1.3 nm In$_x$Ga$_{1-x}$N mostly 2D islands are formed and a small roughness of about 2 ML within the wetting layer is found. For larger In$_x$Ga$_{1-x}$N deposits, 3D growth starts to dominate and In$_x$Ga$_{1-x}$N nano-islands are uniformly formed. After deposition of 3.9 nm of In$_x$Ga$_{1-x}$N, homogeneously distributed In$_x$Ga$_{1-x}$N nano-islands with a very high density of about $10^{12}$ cm$^{-2}$ are found. The average diameter of the islands is about 8 nm and the height ranges from 2 to 3 nm. Details of the growth mode and 2D-3D transition of the surface morphology with increasing In$_x$Ga$_{1-x}$N deposit are discussed later. A higher resolution STM image of this type of nano-islands is shown in figure 7.14(a).

The findings for the growth at 600°C with reduced In partial pressure can be explained by a limited surface diffusion due to a low In surface coverage [37] which results in an increased island nucleation density. In addition, a reduced growth rate (cf. table 7.1) will also lead to a reduced In incorporation due to enhanced In redesorption [19]. Moreover, the reduced In partial pressure leads to further nitrogen-enriched growth conditions.
Figure 7.13: Empty state STM images of the In$_x$Ga$_{1-x}$N surface with increasing deposit, after growth at 600°C at a reduced In-flux.

For these conditions, smaller island sizes due to high diffusion barriers for metal atoms have also been predicted by theoretical studies [36]. Thus, the combination of a reduced growth temperature and a reduced In partial pressure leads to very homogeneous nucleation conditions and to the formation of very dense small islands. In an earlier work [29], a decrease of the islands density for reduced In partial pressure was reported. It is noteworthy that this is not contradictory to the results presented here, but even in agreement with the findings discussed above, because the growth rate (30–80 nm/h) was lower and the growth temperature (670°C) was higher as compared to the present study. For such growth conditions, according to our experimental results obtained for 650°C, the thermal decomposition of InN is a limiting factor for the formation of In$_x$Ga$_{1-x}$N islands. Therefore, a higher In vapor pressure is required in order to allow for In$_x$Ga$_{1-x}$N island formation at higher temperature and slower growth rate.

As the frequency of the emitted light is determined by the In concentration within the In$_x$Ga$_{1-x}$N nano-islands, it is very important to know the amount of In incorporation. As it was difficult to directly measure the In content for the small In$_x$Ga$_{1-x}$N islands of thin In$_x$Ga$_{1-x}$N layer, X-ray diffraction (XRD) measurements were performed on thick
7.4. Results and discussions

Figure 7.14: (a) Empty state (−4 V, 100×100 nm²) STM images of sample D₃. (b) X-ray ω-2θ diffraction of 210 nm thick InₓGa₁₋ₓN layer grown at 600°C with low In flux. A phase separation of 36% and 46% In content within the InₓGa₁₋ₓN layer is observed.

InₓGa₁₋ₓN layers, grown at identical growth conditions. It is assumed that the lattice parameters of InₓGa₁₋ₓN are changed in proportion to the In incorporation (Vegard’s law). Hence, using double crystal X-ray diffraction (ω-2θ scan), the actual lattice constants that correspond to the (0002) diffraction lines of ternary InₓGa₁₋ₓN were calculated. In figure 7.14(b), X-ray diffraction results of a 210 nm thick InₓGa₁₋ₓN sample grown with low In flux at 600°C are shown. From figure 7.14(b) it is clear that the InₓGa₁₋ₓN layer exhibits a phase separation of two different In contents such as In₀.₃₆Ga₀.₆₄N and In₀.₄₆Ga₀.₅₄N, respectively. Hence the average In content for the InₓGa₁₋ₓN surface of quantum dot like islands is estimated to approximately 40%. However, the actual In mole fraction within the QD-like InₓGa₁₋ₓN nano-islands may differ from the measured value for a thick reference sample. In this respect transmission electron microscopy (TEM) can provide more insight. In TEM measurements the In content within the InₓGa₁₋ₓN nano-islands was measured to about 30-35% and a relatively thick wetting layer was observed which can be explained by a strong inter-diffusion of metallic adspecies at the substrate–adlayer interface.

2D to 3D transition

In case of InₓGa₁₋ₓN growth at a further reduced In partial pressure, a very similar type of surface morphology has been observed. For this growth condition, the In partial pressure [In/(In+Ga)] was fixed at 0.582, resulting in an increased group V:III material ratio of 6130 and a decreased InₓGa₁₋ₓN growth rate of about 0.08 nm/sec. The evolution of the surface morphology with increasing InₓGa₁₋ₓN deposit is shown in fig. 7.15 for samples E₁ to E₃. Due to the low temperature and the low In partial pressure, again the formation of small and dense InₓGa₁₋ₓN nano-islands is observed.

A 2D–3D transition of the surface morphology with increasing InₓGa₁₋ₓN deposit is also
Chapter 7. \textit{In}_x\textit{Ga}_{1-x}N \text{ nano-islands on MOVPE grown GaN}(0001) \text{ templates}

observed at this growth condition and shown in figure 7.15. After deposition of 1.3 nm, the surface is quite smooth as can be seen from the height profile in fig. 7.15 (a). The vertical roughness is on a single or double monolayer step height range. Nevertheless, a high lateral roughness is observed. Hence, the growth does not proceed by step flow, but rather in a 2D-islands growth mode. According to the results discussed above, this growth mode is in agreement with the small diffusion lengths expected for these growth parameters. When the deposit is increased to 2.6 nm, the islands become higher (about 1 to 1.5 nm), whereas their lateral size remains almost constant, as can be deduced from a comparison of fig. 7.15 (a) with fig. 7.15 (b). This can be interpreted in terms of a 2D to 3D growth mode transition occurring at an \textit{In}_x\textit{Ga}_{1-x}N coverage of \( \sim 2.0 \pm 0.6 \) nm for these growth conditions. The three-dimensional character of the islands is even more emphasized after deposition of 3.9 nm \textit{In}_x\textit{Ga}_{1-x}N, as can be seen in fig. 7.15 (c). The average island height has risen to about 2.5 nm, whereas the lateral size has not increased. Being well known for conventional III-V systems and GeSi growth on Si, this evolution of the island aspect ratio is typical of Stranski-Krastanov island growth, which is driven by the associated elastic strain relaxation.
7.4.5 Prospects and problems

From STM measurements, the aspect ratio (diameter/height) of about 2-2.5 is obtained for the QD-like In$_x$Ga$_{1-x}$N nano-islands which is the lowest in the In$_x$Ga$_{1-x}$N/GaN material system, to best of the knowledge. The wetting layer thickness of about 2-3 nm and the In concentration of 25-35% were derived from TEM investigations. The In$_x$Ga$_{1-x}$N dots themselves were found to be free of misfit dislocations and with pronounced facets from the results of TEM observations [38]. From all these findings it is clear that the QD-like In$_x$Ga$_{1-x}$N nano-islands can successfully be grown using S-K growth. i.e., by forming a strained wetting layer followed by the elastic relaxation through 3D island formation. Therefore, from the structural point of view, these small 3D In$_x$Ga$_{1-x}$N nano-islands of very dense array (10$^{12}$ cm$^{-2}$) would represent a promising candidate for application as active-layer material in highly efficient light emitting devices.

It has already been discussed that the decrease of growth temperature is essential for the formation of homogeneously distributed QD-like In$_x$Ga$_{1-x}$N nano-dots of high density. But in practice, it is problematic for the optical properties. The QDs are embedded by a capping layer for a device application. Significant changes in the size, shape and density of QDs may occur during the capping process due to an intermixing between a QDs layer and a capping layer. In order to minimize the effect of intermixing, the growth temperature of the cap layer is in general kept at a lower temperature than that used for the bulk growth of the cap layer material. However, the low-temperature growth causes a degradation of the structural properties and hence also affect the optical properties. From photo luminescence (PL) measurements it is observed that the luminescence intensity drastically decreases with the growth temperature [39]. The main reasons for this are the difficulties in low-temperature GaN cap layer growth and the inferior crystalline quality of the In$_x$Ga$_{1-x}$N quantum dots as well as of the GaN capping layer. Cubic GaN phases are easily incorporated within the GaN cap layer grown at a low temperature. Hence, a possible solution to overcome this problem is to increase the growth temperature and optimize the In$_x$Ga$_{1-x}$N island growth. In the following sections, In$_x$Ga$_{1-x}$N surface morphology at higher growth temperatures and formation of various types of nano-islands will be discussed.

7.4.6 In$_x$Ga$_{1-x}$N Growth at 650°C at low In partial pressure

For In$_x$Ga$_{1-x}$N growth at 650°C at a reduced In partial pressure [In:(In+Ga)=0.74], the surface morphology of the In$_x$Ga$_{1-x}$N islands changes drastically as compared to the growth at 600°C. For this growth condition, the V-III flux ratio was kept at 3900, and the effective growth rate was calibrated to about 0.13 nm/sec. Again large In$_x$Ga$_{1-x}$N islands are found on the surface but the structure and shape of the islands change completely with respect to the In$_x$Ga$_{1-x}$N islands grown at 650°C with a high In partial pressure. Spiral islands (fig. 7.2) are not found anymore. The In$_x$Ga$_{1-x}$N surface appears with large islands (bright spots) and defects originating from the GaN substrate (dark spots) are visible here. In figure 7.16, STM images show a surface overview after deposition of 3.9 nm of In$_x$Ga$_{1-x}$N where a relatively rough wetting layer can be seen. Mainly two types
Chapter 7. \textit{In}_{x}\text{Ga}_{1−x}\text{N} nano-islands on MOVPE grown GaN(0001) templates

(a) Flat-top hexagon  
(b) Triangular pyramid

Figure 7.16: \textit{In}_{x}\text{Ga}_{1−x}\text{N} surface overviews (1000×1000 nm\(^2\)) after 3.9 nm of deposit at 650\(^\circ\)C with a low \textit{In} partial pressure (sample \(F_1\)). Large \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands (bright areas) and substrate dislocation pits (dark spots) are visible.

of large \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands are observed: (a) hexagonal islands with a flat-top surface (7.16(a)) and (b) triangular pyramidal islands with three side facets (7.16(b)). Details of the shape and structure of these large islands are discussed in the following.

The visibility of dislocations from the substrate and the wetting layer roughening indicate a more homogeneous \textit{In}_{x}\text{Ga}_{1−x}\text{N} nucleation in comparison to the growth with an increased \textit{In} partial pressure (fig. 7.16), which can be attributed to the shorter effective diffusion length of the adspecies. Since the reduced growth rate is expected to result in an even enhanced heterogeneous nucleation, the kinetic limitations observed in the experiment are attributed to the more nitrogen-rich conditions and the reduced \textit{In} partial pressure. Nevertheless, the surface diffusion is still high enough to allow for the formation of large islands.

Large islands

A closer look of different types of large \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands is presented in figure 7.17. The lateral size for all kind of large islands is observed to be about 75 nm (diameter/side). The height (h) of 'hexagonal islands' with a flat-top is about 2-4 nm, whereas the height of 'pyramidal islands' of triangular base is about 12 nm. The top surface of the 'hexagonal islands' is atomically flat having a tilt of a few degrees (up to 2\(^\circ\)) to the wetting layer as shown in figure 7.17(a). In case of the 'pyramidal islands', three smooth side facets can be observed in figure 7.17(c). From the STM image, the angle between the facets and the wetting layer [(0001)-plane] is measured to about 20\(^\circ\). In a few cases \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands of an intermediate shape, i.e. with a hexagonal base and three dominating side facets, have also been observed as shown in figure 7.17(b). The height of the intermediate islands varied from 4-6 nm, which is also in between the height scale of hexagonal and pyramidal islands as given above. All these findings indicate an evolution of large \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands from a hexagonal to a triangular pyramidal shape.

The atomically flat faceted structures of the large \textit{In}_{x}\text{Ga}_{1−x}\text{N} islands indicate a local \textit{In} enrichment at the facet surface and a shape close to the thermodynamic equilibrium. The transition from hexagonal islands with flat top surface to the triangular pyramidal islands with inclined side facets can be explained in the following way. It is assumed that for islands of lower height, the (0001) top facet is energetically favourable whereas for higher
7.4. Results and discussions

(a) Flat-top hexagon    (b) Hexagon, side-facet    (c) Triangular pyramid

Figure 7.17: Close-up STM image (−2 V, 100×100 nm²) of different large islands found after deposition of 3.9 nm of InₓGa₁₋ₓN at 650°C with a low In partial pressure, (sample F₁). (a) hexagonal island with a large flat top facet, (b) island of intermediate shape with hexagonal base and three dominating facets and (c) pyramidal island of triangular base.

islands, the inclined side facet formation dominates over the top facets. Hence, for the shallow hexagonal islands (h=2–4 nm) only (0001) top facet formation take place. For islands of larger height, the side facet formation also starts and as a result an intermediate stage of large islands, i.e., islands of hexagonal base and three dominating side facets are formed. In case of further increase in island height, the side facet formation dominates over the top facets and the islands appear with a triangular pyramidal shape. The slight tilt of the large InₓGa₁₋ₓN islands may be related to the (0001) facet formation and an average miscut of the GaN template.

Similar to the earlier finding, again the capping process at 650°C growth temperature is still very problematic and as a result PL spectra do not show any quantum dot like sharp lines after capping of these InₓGa₁₋ₓN islands. Hence, a further increase of the InₓGa₁₋ₓN growth temperature is required which will be discussed in the following.

7.4.7 InₓGa₁₋ₓN growth at 700°C at low In partial pressure

As the capping process at 650°C was not so successful and no single QD-like light emission was found after capping, the growth temperature was further increased to 700°C. At this growth condition, In partial pressure was kept fixed to [In/(In+Ga)] 0.736 and the resulting group V:III material ratio was maintained to 3900. The effective growth rate was further reduced to about 0.10 nm/sec due to a relatively low sticking coefficient of the adspecies at this temperature.

The morphological changes of the InₓGa₁₋ₓN films after about 1 nm of nominal InₓGa₁₋ₓN deposition at a low In partial pressure and the corresponding PL spectra after subsequent capping is shown in figure 7.18. In fig. 7.18(a), a STM image shows the InₓGa₁₋ₓN surface overview. Large islands are not found anymore, whereas only 2D (two dimensional) islands of diameter \( d \approx 50 – 100 \text{ nm} \), and height up to 2 nm are observed. The terrace
structures and dislocation pits of GaN template layer can be found. A STM image with larger magnification is shown in fig. 7.18(b). From this STM image, it is clearly observed that the many smaller grains / clusters are present on large 2D islands.

The presence of only 2D islands can be explained by high thermal desorption and less sticking of In atoms at 700°C. Additionally, the slower growth rate also leads to a lower In incorporation, which results in less lattice strain and suppresses the 3D island growth. The visible substrate defects and terrace structures indicate homogeneously grown In$_x$Ga$_{1-x}$N 2D islands and the absence of defect induced island nucleation. However, the surface mobility of the adspecies in not sufficient to promote a smooth surface for 2D island which results in smaller clusters / grains formation.

From a structural point of view these 2D islands do not seem to be appropriate for sharp light emission. However, the most exciting result of this structure is the 'single-quantum-dot' like light-emission after the 'novel' capping process. Details of this
7.4. Results and discussions

capping process are discussed in the following. Very sharp photo-luminescence (PL) emission lines with a width down to the order of the spectral resolution of the experimental setup of 0.17 meV at 4 K have been observed as can be seen in fig. 7.18(c).

The appearance of sharp PL peaks for capped layer are attributed to strong localization centers from the quantum dots which can be explained as follows: during the capping process strong inter-diffusion occurs which may cause the formation of some In-rich dots/clusters embedded within the capped layer. However, the actual reason for QD-like emission and its formation mechanism are not yet very clear which needs some more structural characterizations. A more details of the In$_x$Ga$_{1-x}$N QDs formation mechanism are discussed later.

Novel capping process

Taking in consideration the problem of interdiffusion between the In$_x$Ga$_{1-x}$N QDs layer and the GaN capping layer, a novel capping process has been used. After the In$_x$Ga$_{1-x}$N QDs layer growth, a post-growth annealing/growth interruption for 60 sec was carried out. (The effects of the post-growth annealing are discussed in the next section). Afterwards, an 8 nm thick In$_y$Ga$_{1-y}$N capping layer of very low In content (y ≈ 0.02) was initially grown at 700°C above the In$_x$Ga$_{1-x}$N QDs layer, instead of a GaN capping layer. During the In$_y$Ga$_{1-y}$N capping layer growth, the TMIn flow was reduced to 10%, compared to the growth conditions of the In$_x$Ga$_{1-x}$N QDs layer. The In content of the In$_y$Ga$_{1-y}$N capping layer was set much lower than that of the In$_x$Ga$_{1-x}$N QDs layer to avoid any kind of strain driven island growth during the capping process. Finally, the growth temperature was increased to 820°C and a 30 nm thick GaN capping layer was grown on top of the In$_y$Ga$_{1-y}$N capping layer.

To investigate the formation mechanism of QDs like localization center during the capping of 2D In$_x$Ga$_{1-x}$N islands, TEM investigation can play an important role. The direct imaging of the QDs-like localization centers was not successful in TEM because of their low density. A flat interface between the In$_y$Ga$_{1-y}$N capping layer and GaN capping layers has been observed in TEM which suggests a smooth In$_y$Ga$_{1-y}$N capping layer growth. Hence, the localization centers are not related to any kind of island formation during the In$_y$Ga$_{1-y}$N capping layer growth. However, a rough interface between the In$_x$Ga$_{1-x}$N 2D island layer and the In$_y$Ga$_{1-y}$N capping layer is found. This is a clear indication of strong intermixing as well as alloy decomposition which finally results in formation of In rich localization centers. To confirm the effect of the In$_x$Ga$_{1-x}$N 2D island layer on QDs-like localization center formation, the capping process was also performed without the In$_y$Ga$_{1-y}$N 2D island layer growth. But in PL measurements, sharp lines were not detected anymore. Similarly, the effect of In$_y$Ga$_{1-y}$N capping layer was also tested by varying the thickness of the In$_y$Ga$_{1-y}$N capping layer. For a thickness below 2 nm, no sharp PL lines are found. Therefore, we can conclude that the 2D In$_x$Ga$_{1-x}$N islands act as seeds of the QDs. At the same time, the In$_y$Ga$_{1-y}$N capping layer has an effect on the formation of the QDs and also works as a protection layer of the QDs from the GaN capping layer.
Chapter 7. \textit{In}_x\text{Ga}_{1-x}N nano-islands on MOVPE grown GaN(0001) templates

(a) 1000×1000 nm$^2$  (b) 500×500 nm$^2$  (c) PL spectra

(i) Surface morphology (uncapped sample G$_1$) and PL spectra of as grown \textit{In}_x\text{Ga}_{1-x}N sample

(ii) Surface morphology (uncapped) and PL spectra after 1 min post-annealing

(iii) Surface morphology (uncapped) and PL spectra after 5 min post-annealing

Figure 7.19: STM images of surface morphology of the uncapped \textit{In}_x\text{Ga}_{1-x}N sample ((a) and (b)), and the corresponding PL spectra after capping process (c). PL measurements done by K. Sebald, University of Bremen.

Effect of post-annealing

Thermal annealing within the growth reactor immediately after the growth experiment at the same growth temperature can highly influence on the PL intensity as shown in figure

186
7.19. The surface morphology of uncapped In$_x$Ga$_{1-x}$N samples is shown in fig.7.19(a) and (b). The corresponding PL spectra of the sample after capping process is presented in fig.7.19(c). It has already been mentioned above that the as grown In$_x$Ga$_{1-x}$N surface exhibits 2D islands (fig.7.19(i)). We find that post-growth annealing for one minute at the growth temperature does not affect the surface morphology strongly but a significant change and a large enhancement in the PL intensity is observed after capping (fig.7.19(ii)). However for even longer post-growth annealing of 5 min the surface morphology changes drastically and a severe surface roughening have been observed. The surface exhibits a partial thermal desorption or segregation of the In$_x$Ga$_{1-x}$N layer (fig.7.19(iii)). The 2D islands are not found anymore, whereas large island-like features with a flat top surface are observed all over the surface. These structures appear with a larger size and the surface step-height also increases to about 1.5-2.5 nm, which is much higher as compared to the earlier 2D islands. As a consequence, the corresponding PL spectra after capping do not show QD-like light emission anymore as can be seen in fig. 7.19(iii).

The increase in PL intensity after 1 min of annealing without any change in surface morphology can be related as follows. Here we may speculate that during post-growth annealing the following process may occur: (i) In$_x$Ga$_{1-x}$N growth from the residual gas species in the reactor, (ii) improvement in crystalline quality of In$_x$Ga$_{1-x}$N adlayer due to surface diffusion processes and (c) temperature induced phase separation of In-rich emission centers. Whereas for 5 min annealing, a clear indication for thermally induced severe surface damage is found. Additionally, a plastic relaxation of the In$_x$Ga$_{1-x}$N layer may also occur which suppress the sharp peaks of PL light emission.

7.5 Conclusions

In conclusion, MOVPE grown In$_x$Ga$_{1-x}$N nano-islands were grown on GaN (0001) templates and investigated by STM with a special focus on their formation and morphology. A strong dependence of the island size, density and uniformity on the growth temperature, In partial pressure, growth rate and V:III material flux has been found. These results could be explained in terms of thermal activation of surface diffusion and the impact of the In surface concentration on the diffusion barriers as key factors which govern the surface morphology. A low temperature In$_x$Ga$_{1-x}$N growth at 600°C, with a reduced In partial pressure is required to achieve a high-density array of quantum dots. But the capping process at this low temperature exhibits severe problems which demand the In$_x$Ga$_{1-x}$N growth at higher temperatures. However, In$_x$Ga$_{1-x}$N growth at 700°C leads to the formation of 2D islands which after the capping process shows strong PL peaks indicative of single dot like emission.

Bibliography


Bibliography

Chapter 8

Summary and outlook

This thesis accompanied a research work related to the growth, structure and morphology of different self-assembled semiconductor nano-structures of great potential in optoelectronics. Both MBE and MOVPE grown samples have been studied using various characterization methods mostly with a VT-STM as well as with other analytical tools such as LEED, LEEM, XPS, ESCA-microscopy, TEM, PEEM, AES etc. Two types of semiconductor systems, Si- as well as GaN-based structures, have been investigated with a special focus on their surface characterization.

For Si-based nano-structures, Ga-induced surface reconstructions and nano-patterning of Si(111)-7×7 after submonolayer Ga deposition have been characterized. Substrate surface defects, i.e., steps and domain boundaries of Si(111)-7×7 highly influence the Ga nucleation process and finally lead to a 2D phase separation and nano-patterning. Depending on the Ga coverages, two types of phase separations between the Si(111)-7×7 domains and the step edge and domain boundary regions of the Si(111)-7×7 surface have been obtained for Ga/Si(111). Triangular Si(111)-7×7 reconstructed areas within the domain region surrounded by $\sqrt{3} \times \sqrt{3}$-Ga structures at the domain boundary and step edge regions have been observed for Ga coverages below than 1/3 ML. The shape and size of these $\sqrt{3} \times \sqrt{3}$-Ga domains can be tailored by proper choice of the surface miscuts. These nano-patterned substrates can highly influence subsequent Ge growth and offer an opportunity for a selective nucleation of 3D Ge islands along the initial $\sqrt{3} \times \sqrt{3}$-Ga decorated areas. In case of Ga coverages higher than 1/3 ML, however, $\sqrt{3} \times \sqrt{3}$-Ga reconstructed areas within the domain region are surrounded by $6.3 \times 6.3$-Ga structures at the domain boundary and step edge regions. All the findings have been explained in terms of surface stress, surface free energy, miscut direction, surface diffusion and energetics. To understand the growth mechanism of the self-assembled Ge islands in more details, further growth studies of Ge on other Ga or In nano-patterned Si(111) substrates are of high preference for future studies. Structural characterization of these Ge nano-islands such as surface reconstruction, shape and size of the island can make the growth mechanism more clear. To get the information regarding amount of Ge/Si composition, intermixing and the wetting layer thickness, a strain state analysis of the islands will be useful.
High quality Si₃N₄ and GaN films have successfully been grown on Si(111) substrates by N-plasma assisted MBE. For silicon nitride growth by exposure of Si(111) to active nitrogen at elevated temperatures, the surface morphology and the crystalline quality highly depend on the nitridation temperatures. For lower nitridation temperatures smooth silicon nitride films of poor crystallinity have been observed, whereas crystalline Si₃N₄ films are formed for a higher nitridation temperatures (>850°C) but at the same time the surface morphology becomes rough with insertion of holes and grooves. For nitridation temperatures up to 1000°C, a "8×8"-Si₃N₄ structure is found, whereas for higher temperature a 'quadruplet structure' of silicon nitride has been observed in LEED. Honeycomb-like "8×8" structures for Si₃N₄ film thickness below 2 ML and "8/3×8/3" superstructures for thicker films have atomically been resolved in STM. For GaN growth on Si(111) using silicon nitride as buffer layer, initial GaN nucleation only starts for a relatively low substrate temperature below 650°C. Introduction of the Si₃N₄ layer significantly improves the subsequently grown GaN layer film quality and well ordered GaN films of smooth surface morphology have been achieved for crystalline Si₃N₄ buffer grown at higher temperatures. An atomically resolved 3×3 surface reconstruction for a thin GaN film and a flat homogeneous surface consisting of triangular tile-like structures for thicker GaN films have been observed by STM. To correlate the morphological information to the film crystallinity of the GaN layer grown on Si₃N₄/Si(111) substrates, further structural investigations are carrying very much interest. For thicker GaN layer growth on Si(111), the optimization of the growth process is also an important followup.

**In-situ** cleaning of the MOVPE grown GaN/sapphire templates have been performed using N-plasma exposure at elevated substrate temperature. Plasma cleaning at low temperature is not able to remove the surface oxide completely, whereas cleaning at high temperature successfully removes the oxide but it results in a surface roughening. An efficient removal of surface oxide without degrading the surface morphology has been achieved by prolonged thermal degassing and subsequent plasma cleaning, starting at low substrate temperature followed by a short-period cleaning at high temperature. Various types of surface defects such as large screw pits and surface holes as well as small screw/threading dislocations and edge dislocations have been found on the GaN template surface. MBE growth of thin GaN layer on these templates indicates a defect induced GaN nucleation around the larger defects. However, for GaN templates containing only smaller defects, results in a smooth surface morphology for Ga-rich growth condition. A 4×4-surface reconstruction of high defect density is observed for GaN growth at 750°C, whereas for subsequent growth at 790°C, a 1D array (3 nm) of nano-clusters have been observed. For N-rich growth condition 3D growth dominates and a rather rough surface morphology with 3D islands formation has been found. To study the surface reconstructions of GaN based material, an in-situ characterization facility is required. This will help to optimize the GaN homo-epitaxy and makes it of high priority for future work. In addition, detailed studies of the 1D GaN nano-clusters concerning their orientation, structure is also required for a deeper understanding of the growth mechanism.

MOVPE grown self-assembled InₓGa₁₋ₓN nano-islands on GaN(0001) templates have been investigated with a special focus on their formation and morphology. The island size and shape, density and uniformity can highly be influenced by the MOVPE growth
parameters such as growth temperature, In$_x$Ga$_{1-x}$N deposit, growth rate, and III-V flux ratio. Using lower growth temperatures, reduces the In$_x$Ga$_{1-x}$N island size and enhances the homogeneity of the In$_x$Ga$_{1-x}$N surface. The In partial pressure has also a deep impact on the morphology by controlling the surface diffusion. For growth at 600°C with low In partial pressure, the homogeneous nucleation of small In$_x$Ga$_{1-x}$N islands with high density (10$^{12}$/cm$^2$) has been achieved. From the structural point of view, these islands are suitable for three-dimensional quantum confinement. However, due to severe problems during GaN capping at low temperature, these nano-islands do not show any QD-like photoluminescence. The heterogeneous nucleation of large islands is observed after growth at 650°C, leading to different complex island structures and shapes depending on the In partial pressure. Growth at a high In partial pressure results in the formation of spiral disc-like islands at substrate defects, whereas for reduced In partial pressure, a transition from a hexagonal islands with a flat top surface to a triangular pyramidal islands with side facets has been observed for increasing the island height. In case of growth at 700°C, two-dimensional (2D) islands with small granular structures on top have been observed. Sharp, spectral resolution limited photoluminescence (PL) emission lines indicative of single dot emission have been observed after a ‘novel’ capping of these 2D nano-islands. The findings have been explained in terms of surface diffusivity, thermal decomposition, selective In incorporation and sticking coefficients of the adsorbate species. Continuation of morphological studies will be performed to optimize the MOVPE and MBE growth conditions for In$_x$Ga$_{1-x}$N nano-structures as well as for the novel capping process. In this respect, an in-situ STM characterization would be a great benefit, especially for low temperature MBE capping. Furthermore cross-sectional STM investigations of In$_x$Ga$_{1-x}$N nano-structures are also planned. These studies are of particular interest for a thorough understanding of the processes occurring during cap layer growth.
List of publications

Related to this thesis


**Others**


First author conference contribution


- S. Gangopadhyay, Th. Schmidt, and J. Falta, N-plasma assisted MBE grown GaN films on Si(111), International Conference on Nitride Semiconductors (ICNS-6), Bremen, Germany (2005).


- S. Gangopadhyay, Th. Schmidt, and J. Falta, Annealing induced 2D nano-patterning of Ga/Si(111) studied by STM, Spring Meeting of the German Physical Society, Berlin, Germany (2005).


- S. Gangopadhyay, Th. Schmidt, and J. Falta, Temperature induced changes of Ga/Si(111) surface reconstruction studied by STM, Spring Meeting of the German Physical Society, Dresden, Germany (2003).
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