Scanning Tunneling Microscopy Investigation of Rock-salt and
Zinc-blende Nitrides Grown by Molecular Beam Epitaxy

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This dissertation entitled

Scanning Tunneling Microscopy Investigation of Rock-salt and

Zinc-blende Nitrides Grown by Molecular Beam Epitaxy

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The surface and bulk properties of both scandium nitride and cubic gallium nitride, grown by radio frequency molecular beam epitaxy on MgO(001), are investigated.

The growth of both materials, ScN and c-GaN, leads to 001-oriented films. ScN(001) is found to have smooth growth under either nitrogen- or metal-rich growth conditions while metal-rich growth conditions are required to achieve such a growth mode for the case of c-GaN(001). For N-rich (Sc-rich) growth, ScN(001) surface consists of spiral pyramids and flat plateaus (spiral mounds). For the case of c-GaN(001), the film consists of rectangular-like domains, due to the 2-fold and 4-fold surface symmetries of c-GaN(001) and the substrate, MgO(001), respectively.

The surface of ScN(001) grown under Sc-rich conditions shows mainly 1×1 reconstruction, yet faint 2× is some times observed. The surface is found to be metallic. For the case of N-rich growth, the surface shows only 1×1 reconstruction with a surface gap of 0.9±0.1 eV. For c-GaN(001), the surface shows 1×1 during and after growth; however, the surface exhibits a disorder-order phase transition from 1×1 to c(4×16) (c(4×20)) for growth under Ga-rich conditions (more Ga-rich conditions) when the sample is let cool down to about 200 °C. The c(4×16) reconstruction is found to be metallic. After annealing the sample, c(4×16) transfers irreversibly to 4×1. This 4×1 is semiconducting with a surface gap of 1.3 eV.
The stoichiometry of ScN depends on the growth conditions: for N-rich growth the Sc/N bulk ratio is $1 \pm 0.02$, and for Sc-rich growth the bulk ratio of the compositions is similar to their flux ratio, leading to a film grown with N-vacancies. Nevertheless, no evidence is observed for a significantly sub-stoichiometric c-GaN film grown under Ga-rich conditions.

Approved: Arthur R. Smith
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Chapter 1

Introduction

Wurtzite group-III nitrides, such as AlN, GaN, and recently InN, have attracted and received intensive studies due to their electronic properties which show a large variation of the bandgap, $\sim 6.2 \text{ eV}$, $3.4 \text{ eV}$, and $0.9 \text{ eV}$ for AlN, GaN, and InN, respectively.[1] However, other group-III nitrides have not received that much attention and detailed exploration, for example group-III transition metal nitrides, ScN, YN, and LaN and zinc-blende group-III nitrides such as c-AlN, c-GaN, and c-InN.

In fact, a part of the exploration is to consider the effect of growth methods, growth conditions, substrate used, and processing, such as annealing, on the film properties. In this report, we study two materials grown by radio frequency molecular beam epitaxy on MgO(001): 1) the group-III transition metal nitride ScN and 2) the zinc-blende group-III nitride GaN. The outlines of our study in this thesis are shown in the following part.

The work this thesis contains is divided to two main parts. First part shows our investigation of the growth and the characterization of the rock-salt ScN grown by rf
MBE on MgO(001). In chapter three, we show the first growth of ScN on MgO(001) using rf MBE. The study shows the basic structural properties, bulk and surface.

In chapter four, comparisons between two different growth conditions, Sc-rich and N-rich, of ScN on MgO(001) are shown for bulk structure and stoichiometry, surface morphology and reconstruction, and optical properties.

Chapter five is dedicated for more investigation of ScN grown under Sc-rich conditions on MgO(001). In this chapter we address the issue of the N-vacancies in the bulk and on the surface.

Chapter six has intensive study of the ScN(001) surface. Both structural and electronic properties of the surface, which are also influenced by the bulk, are characterized by STM and STS. To insure certain observation, the indirect bandgap, optical spectroscopy of a 2.5 μm-thick film is presented and more discussion about this issue is addressed.

In chapter seven the growth of Mn-doped ScN is presented. The study contains two parts. In the first part, the effect of the growth temperature on the Mn incorporation and surface accumulation are addressed. In the second part, the effect of the Mn/(Mn+Sc) flux ratio on the Mn bulk incorporation as well as Mn incorporation effect on the lattice constants, both in-plane and out plane, are presented.

The second main part of the thesis shows our investigation of the growth of zinc-blende GaN on MgO(001). In chapter eight the study of bulk structure, surface morphology, and new surface reconstruction of cGaN(001)/MgO(001) grown under Ga-rich conditions are presented.
In the ninth chapter, more focus on the cGaN(001)-4×1 surface structure, which has been predicted to be semiconducting,[88] is presented; STM and STS results are employed to investigate this kind of reconstruction. Moreover, simulated STM images, calculated using SEISTA code by Nancy Sandler, are presented too to compare with the experimental STM images.

Chapter ten summarizes the work contained in this thesis. Three appendices are included for the paper contribution, contributed talks in conferences, and contributed posters.
Chapter 2

Instruments

2.1 Growth Methods

We grow our samples using radio frequency molecular beam epitaxy (rf MBE). A cryostat that uses $^4$He is attached to the growth chamber to achieve an ultra high vacuum (UHV), ultra low pressure, down to $\sim 10^{-11}$ torr. The growth chamber, which is home designed, consists of four ports as sources for the metal elements, such as Mn, Sc, Ga, and La. Effusion cells with ceramic crucibles, Fig. 2.1, are used to evaporate the materials. The flux of the elements is controlled by adjusting the temperature of the effusion cell read by the thermocouple [see Fig. 2.1], and the flux is determined by an in-situ crystal thickness monitor. Radio plasma is used as a source of ionized nitrogen with a valve attached to it to control the nitrogen pressure as an indication of nitrogen flux. Most of our growth have been performed at $0.9-1.1 \times 10^{-5}$ torr. The chamber pressure is monitored by an ion gauge, which functions in the range $10^{-3} - 10^{-11}$ torr.
2.1. Growth Methods

Figure 2.1: A schematic diagram of our home-designed and -built effusion cell used in the MBE growth chamber.

The substrate has a size of about $1 \times 1 \text{ cm}^2$ and is held by a sample holder made out of molybdenum. The *in-situ* transporting rods with *ex-situ* magnetic controllers are used to transfer the sample inside the chambers. The sample is introduced inside the growth chamber through a load-lock chamber with a base pressure of $10^{-7}$ torr, then the sample is transferred to the UHV analysis chamber through a gate valve between both chambers. An ion pump is used to pump on the analysis chamber as well as a titanium sublimation pump (TSP). Through a gate valve the sample is transferred to the growth chamber.

Prior, during, and after the growth, the sample is attached to a manipulatable growth stage; the manipulation allows the adjusting of the position of the sample in X, Y, and Z as well as both rotational angles, $\theta$ and $\phi$. Behind the sample place in the growth stage a graphite filament is used to set the desired temperature of annealing.
or growth. The sample temperature is determined using a thermocouple attached behind the filament and an ex-situ-optical pyrometer.

2.2 Reflection High Energy Diffraction

Reflection high energy electron diffraction (RHHED) is installed in the growth chamber to monitor the growth. A STAIB electron gun is used to send high energy electrons, usually 20 KeV, onto the sample surface with a small angle, 1-3°, then the diffraction patterns of the reflected beam is acquired by a CCD camera [see Fig. 2.2(a)]. Controlling the electron gun and displaying the diffraction are done using KSA 400 software produced by K-space Association [see Fig. 2.2(b)].

RHEED diffraction patterns is used to identified several structural properties of the sample surface, such as surface symmetry, surface smoothness, surface reconstruction, and in-plane lattice constant. Moreover, certain bulk properties can be sensed, yet not as much as the surface determination.

The way the in-plane lattice constant can be determined is by comparing the RHEED pattern of a known material, such as MgO(001) for our case, with the RHEED pattern of the grown film. The spacing between the main streaks of the RHEED patterns, d, is proportional to the inverse of the real space lattice constant, a. Therefore, if the lattice constants (streak spacing) of material A and material B are $a_A (d_A)$ and $a_B (d_B)$, respectively, then the following equation holds:
2.2. *Reflection High Energy Diffraction*

Figure 2.2: a) A schematic diagram of the RHHED system inside the growth chamber. b) KSA-400 software showing the RHHED patterns acquired by the CCD camera and the control bar of the electron gun.
2.3 Scanning Tunneling Microscopy

After finishing the growth and ensuring the smoothness of the surface, the sample is transferred to the analysis chamber to perform scanning tunneling microscopy (STM). STM imaging allows us to see the surface structure in real space rather than in K-space, seen by RHEED diffraction. STM images also allow us to explore the local geometrical and electronic structure of the surface.

As seen in Fig. 2.3, STM consists of a sharp tip, usually made of W, attached to a piezo tube to control the fine movement in X, Y, and Z directions. To approach the tip towards the sample surface inch-worms are used to move both the tip and the piezo tube until the tip senses the desired current at the set sample voltage within the limit of the fine movement. A feedback electronics controls the Z movement of the tip in order to maintain the same tunneling current, constant current mode. Plotting the Z position of the tip as a function of X and Y positions creates the surface image.

To explore the electronic structure at the surface, scanning tunneling spectroscopy (STS) is performed. The same setup of STM is used; however, the feedback electronics is disabled. Then variable sample voltage is applied and the tunneling current is acquired. The I-V curve is used to provide information about the existing filled and empty states at the surface. Hence, the surface band gap can be deduced.
2.4 Atomic Force Microscopy

For larger surface morphology studies, an *ex-situ* atomic force microscope (AFM), made by Park Scientific Instruments, is used. The AFM tip, attached to an optically reflecting cantilever, scans over the sample surface using piezo-electric effect applied to the sample. The tip experiences a force with the atoms on the sample surface, Van der walls force, and the cantilever deflects accordingly. The laser beam reflecting from the surface will change the reflection angle depending on the cantilever deflection[see Fig. 2.4]; the optical lens is used to adjust the laser beam on the cantilever. This change of the reflection angles will be acquired by two photo-detectors and the tip height is deduced. Hens, tip height as a function of X and Y is presented.
2.5 X-ray Diffraction

The bulk structure properties is mainly determined by X-ray diffraction (XRD). The XRD is taken with a Rigaku θ-2θ diffractometer using Cu Kα radiation with a wavelength, λ, of 1.54 Å. By determining the angle, 2θ, at which the spectrum shows a peak [see Fig. 2.5], the interplaner spacing, d, is determined using Bragg’s law

\[ \lambda_{hkl} = 2dsin(\theta) \]  \hspace{1cm} (2.2)

\[ \lambda_{hkl} = \frac{1}{((h/a)^2 + (k/b)^2 + (l/c)^2)^\frac{1}{2}} \]  \hspace{1cm} (2.3)
Figure 2.5: A schematic diagram of the XRD, showing the angle $\theta$ as well as how the sample is positioned between the X-ray source and detector.
Part I

The Investigation of Rocksalt

ScN(001)/MgO(001)
Chapter 3
Molecular Beam Epitaxial Growth of Atomically Smooth Scandium Nitride Films

3.1 Abstract

High quality scandium nitride films have been grown on magnesium oxide (001) substrates by molecular beam epitaxy using an RF plasma source for nitrogen. Both reflection high energy electron diffraction and X-ray diffraction confirm that these films have (001)-orientation. Atomic force microscopy reveals a surface morphology consisting of large plateaus and pyramids. The plateaus are found to be atomically smooth and have a 1×1 surface structure, as revealed by \textit{in-situ} scanning tunneling microscopy.
3.2 Introduction

The growth and surfaces of nitride semiconductors have been subjects of great interest recently.[2, 3, 4, 5] Most of the work has concentrated on group XIII Nitrides, and GaN in particular. Yet there are other nitrides with interesting properties, an example of which is scandium nitride, a group III transition metal nitride. For this unusual material, there is evidence that it is a semiconductor having a direct bandgap in the range 2.1-2.4 eV.[6, 7, 8, 9, 10, 11] Different from most conventional semiconductors, ScN is known to stabilize in the rock-salt crystal structure.[6, 8, 10] Due to the strong bonding between Sc and N, ScN is also thought to have a very high melting point of over 1500°C.[8, 12] Finally, ScN has a very small lattice parameter mismatch with GaN (< 0.3%), which might allow the growth of GaN/ScN heterostructures or ScGaN alloys.[7]

For a potentially useful electronic material, it is important to demonstrate that smooth epitaxial growth of singly-oriented films can be achieved. Dismukes et al. grew ScN using chemical vapor deposition on sapphire, resulting in (111)-oriented, but rough, films.[6] Moustakas grew ScN on sapphire(0001) using electron cyclotron resonance (ECR) molecular beam epitaxy (MBE), which also resulted in (111)-oriented, but rough, films.[10] Gall et al. grew ScN on MgO(001) using reactive magnetron sputtering, resulting in films having both (001) and (111) orientation.[8] A subsequent paper by Gall et al. reported that the use of a 20 V substrate bias during growth resulted in single (001) orientation but that these films were also rough.[9]
3.3. Experimental Procedure

In this chapter, we report the smooth growth of ScN using radio frequency (RF)-MBE. We find that RF-MBE growth results in well-oriented ScN films, having either (001), (110), or (111) orientation, depending on the starting substrate orientation. We find that (111) and (110) oriented ScN films grow in a 3-D growth mode with rough surfaces, but (001)-oriented ScN films can be grown in a 2-D growth mode, resulting in atomically smooth surfaces.

3.3 Experimental Procedure

The experiments are performed in a custom-designed vacuum system consisting of an MBE chamber coupled to a surface analysis chamber. The substrates are first cleaned with solvents, then loaded into the MBE chamber and heated up to \( \sim 1000 \, ^\circ\text{C} \) for 30 minutes (for growth on sapphire, the nitrogen plasma is also applied during this heating step). Then the sample temperature is lowered to \( \sim 800 \, ^\circ\text{C} \) prior to beginning the growth of ScN. The nitrogen flow rate is 1.1 sccm with the RF power set at 500 W. The effective Sc flux, estimated from the measured film thickness and the growth time, is in the range \( 4 \times 10^{13} - 3 \times 10^{14} / \text{cm}^2\text{s} \). The growth condition is monitored using reflection high energy electron diffraction (RHEED). Following growth, the sample is analyzed by \textit{in-situ} scanning tunneling microscopy (STM). After removal from the surface analysis chamber, the sample is analyzed using x-ray diffraction (XRD) and atomic force microscopy (AFM).
3.4 Results and Discussions

Initially, we grew ScN on sapphire (0001) substrates, resulting in (111)-oriented ScN. While the RHEED patterns during growth showed good ordering along the high symmetry directions, (1120) and (1100), the patterns were very spotty, indicating a rough growth surface. The roughness of these surfaces was later confirmed in AFM images, and XRD confirmed the (111) orientation. We also tried growth on MgO(110), and although the RHEED patterns showed good (110) orientation, they were also very spotty.

Evidently, ScN takes on the crystalline orientation of its substrate, but smooth growth is difficult (under our MBE conditions) for (110) and (111) orientations. This could be due to very small adatom diffusion lengths on surfaces with these orientations, as was suggested by Gall et al. in the case of (111) orientation.[8, 9]

If adatom diffusion lengths are larger for the (001) surface, then smooth growth may be possible. To grow (001)-oriented ScN, we use MgO(001) as a substrate. MgO also has rock-salt structure, and the lattice mismatch of ScN with MgO is 7.3%.

The RHEED patterns shown in Fig. 3.1 illustrate the stages of the growth process. Prior to heating, the as-loaded substrate has good crystalline quality, as seen in Fig. 3.1(a), which shows the RHEED patterns along the [100] and [110] azimuths. Clear diffraction spots are seen along both azimuths, as well as Kikuchi lines. However, the patterns are spotty, indicating some roughness.
3.4. Results and Discussions

Figure 3.1: Sequence of RHEED patterns for ScN growth process on MgO(001). a) as-loaded MgO surface prior to heating; b) MgO surface after 30 minutes of heating at 1000°C; c) ScN(001) surface during growth.
3.4. Results and Discussions

After heating the substrate to 1000 °C for 30 minutes, the diffraction spots elongate and sharpen into the distinct streaks shown in Fig. 3.1(b). These streaky patterns suggest that the MgO surface may be smoothened by the heating.

Scandium nitride growth is initiated on this smoothened MgO(001) surface. The RHEED patterns show good epitaxy from the very beginning. Figure 3.1(c) shows the RHEED patterns during growth for a ScN film of thickness about 1200 Å. These patterns are fairly streaky, indicating smooth growth. The ratio of the line spacing along [100] to the line spacing along [110] is close to $\sqrt{2}$, indicating 4-fold surface symmetry.

Detailed analysis of the RHEED patterns can be used to estimate the in-plane lattice constant of the film surface. This is done by dividing the spacing between the first-order diffraction lines for the ScN (Fig. 3.1(c)) by the spacing between the first-order lines for the MgO substrate (Fig. 3.1(b)). For the 1200 Å thick sample, we get a ratio of about 1.04, 2.5% less than the ratio of the expected bulk lattice constants for ScN and MgO at 800°C, 1.065.[6, 9] For thicker films (≥ 2000 Å and grown with higher Sc flux), we have measured ratios which are very close to the expected bulk ratio.

Fig. 3.2 shows XRD spectra for two films - one about 1200 Å thick and the other about 2400 Å thick. The two spectra have been normalized to the height of the ScN (002) peak which occurs near 40°. The peak in each spectrum near 43.1° is the MgO (002) peak. No ScN (111) peaks (which would be at 34.5°) are observed for these
3.4. Results and Discussions

Figure 3.2: 2θ x-ray diffraction spectra for two different ScN films grown on MgO(001). Neither film shows any (111) peaks.

or for any of our films grown on MgO(001). We conclude that RF-MBE growth on MgO(001) results in single oriented ScN(001).

By measuring the positions of the ScN (002) peaks in comparison to the MgO (002) peaks, we calculate the perpendicular lattice constants for these two films. In the case of the thinner film, we get a value of 4.48 Å, slightly smaller than the expected value of 4.501 Å. For the thicker film, the ScN(002) peak gets closer to 40.0°, giving a
perpendicular lattice constant of about 4.51 Å, slightly larger than the expected bulk value.

Atomic force microscopy images of the ScN(001) films clearly reveal a plateau-pyramid morphology, as shown in Fig. 3.3. For this 1 μm × 1 μm image, one observes numerous plateaus with square shapes as well as many pyramids which are 4-sided. The edges of these plateaus and pyramids are along \( h_{100} \) directions of the film which also coincide with the \( h_{100} \) directions of the substrate.

The pyramids have the same (001)-orientation as the plateaus. If they were \( (111) \)-oriented, we would expect to see three (001) facets and a (111) peak in XRD - but we do not. In fact, the sides are gently sloping, with typical apex angles of about 165°. Moreover, STM images reveal closely spaced steps on the sides of the pyramids. We believe the pyramids are centered on dislocations in the film. Assuming this, and counting the number of pyramids within the 1 μm\(^2\) image of Fig. 3.3, we estimate a dislocation density of \( \sim 10^9/\text{cm}^2 \).

As seen in Fig. 3.1(c), the RHEED patterns for ScN(001) show only 1×1 symmetry. This is expected since ScN has the rock-salt structure, and therefore the ionic character of the bonding will tend to suppress charge transfer, thus preventing reconstructions. Shown in Fig. 3.4 is an STM image of the ScN surface showing atomic resolution. The square 1×1 periodicity is clearly evident. The inset shows a magnification of the surface with a simple overlay for the rock-salt lattice. The larger square indicates the conventional surface unit cell, having an atom at the face center and sides along \( \langle 100 \rangle \). The smaller square inside, rotated by 45°, is the primitive
3.4. Results and Discussions

Figure 3.3: Atomic force microscopy image of ScN(001) grown on MgO, illustrating the plateau-pyramid morphology. The gray scale range is 89 Å.

Figure 3.3: Atomic force microscopy image of ScN(001) grown on MgO, illustrating the plateau-pyramid morphology. The gray scale range is 89 Å.
3.4. Results and Discussions

surface unit cell whose sides are aligned with the atomic rows observed in the image. Therefore, the atomic rows in the image are along \( \langle 110 \rangle \).

The two terraces in the image are separated by a single step. The measured height of this step is very close to 2.25 Å\(^2\), or half the lattice constant. By sighting along the dashed line crossing the step, one can see that the atomic rows on the lower terrace are shifted by half the row spacing along the [110] direction compared to the atomic rows on the upper terrace. This shift is due to the fact that adjacent (001) planes of the rock-salt lattice are offset by \( a/2 \) along the [100] direction.

A single (001) lattice plane of the rock-salt structure contains an equal number of N and Sc atoms. If we assume that the surface structure is similar to the bulk truncation, then our STM image should correspond to one of the two sub-lattices (Sc or N). Since the STM image of Fig. 3.4 was acquired with a sample bias of -0.5 V, one possibility is that we are imaging the N atoms (filled states). However, dual bias images obtained at +1 and -1 V showed only a small relative shift, much less than the expected \( a/2 \). More work is needed to clearly distinguish the two expected sub-lattices, [see chapter 6].

While this chapter has not presented data on the optical properties of these MBE-grown ScN films, from visual inspection, the films have a reddish or rusty color when white light is shined through them, consistent with an absorption near 2.2 eV. Optical measurements are presented in both chapters 4 and 6, giving detailed investigation of the optical properties.
Figure 3.4: Scanning tunneling microscopy image of plateau region on ScN(001). The image was acquired at a sample bias of -0.5 V and a tunneling current of 0.08 nA. The enhancement at the step edge is due to a local background subtraction. The inset is an expanded view of the surface acquired with a sample bias of -1.0 V and a tunneling current of 0.2 nA. A model of the rock-salt surface lattice is fit to the data.
3.5 Conclusion

In conclusion, we have investigated the growth of ScN by RF-MBE. We find that well-oriented ScN films can be grown which take on the orientation of their substrate. While (110) and (111) orientations have rough surfaces, (001)-oriented ScN can be grown smooth, which has been shown by RHEED, AFM, and STM data. For growth on MgO(001), we find only (001)-oriented ScN with a 1×1 surface reconstruction. We have shown atomically smooth terraces separated by single steps of height 2.25 Å, half the lattice constant of ScN.
Chapter 4

Molecular Beam Epitaxy Control of the Structural, Optical, and Electronic Properties of ScN(001)

4.1 Abstract

Scandium nitride (001) oriented layers have been grown on magnesium oxide (001) substrates by molecular beam epitaxy using a RF-plasma source and a scandium effusion cell. The Sc/N flux ratio is found to be critical in determining the structural, optical, and electronic properties of the grown epitaxial layers. A distinct transition occurs at the point where the Sc/N flux ratio equals one, which defines the line between N-rich and Sc-rich growth. Under N-rich conditions, the growth is epitaxial, and the surface morphology is characterized by a densely packed array of square-shaped plateaus and four-faced pyramids with the terraces between steps being atomically smooth. The films are stoichiometric and transparent with a direct optical transition at 2.15 eV. Under Sc-rich conditions, the growth is also epitaxial, but the morphology is dominated by spiral growth mounds. The morphology change
is consistent with increased surface diffusion due to a Sc-rich surface. Excess Sc leads to under-stoichiometric layers with N-vacancies which act as donors. The increased carrier density results in an optical reflection edge at 1 eV, absorption below the 2.15 eV band gap, and a drop in electrical resistivity.

4.2 Introduction

Transition metal nitrides are well known for their excellent physical properties including high hardness, mechanical strength, high temperature stability, and electronic transport properties that vary from semiconducting to metallic. Titanium nitride, the most studied transition metal nitride and which is used in optical and wear-resistant coatings, has a high hardness $H \sim 20$ GPa.\cite{9, 14, 15} However, only a limited number of papers have been published on the growth and properties of ScN, which is also hard, $H \sim 21$ GPa,\cite{9} and has a high melting point $T_m \sim 2600$ °C.\cite{17} Yet the major interest in ScN is for its electronic properties. While early theoretical work suggested that ScN might be a semimetal,\cite{18, 19} early experimental work by Dismukes and more recently by several other groups have all shown that ScN has a direct optical transition in the range 2.1–2.4 eV.\cite{6, 8, 9, 10, 16, 17} In addition, recent theoretical work has shown that ScN is a semiconductor with a direct transition at the $X$ point near 2.1 eV and a possible indirect transition from $\Gamma \rightarrow X$ at a lower energy in the range 0.9–1.6 eV.\cite{20, 21, 22}
4.2. Introduction

Further progress in understanding the properties of ScN requires detailed investigations of its crystal growth. The Sc-N bond is partially ionic,[23] which leads to its rocksalt crystal structure. In order to understand the growth of ScN, it is important to consider various possible crystalline orientations of the rocksalt structure. In the rocksalt structure, each Sc atom is bonded to six N atoms and each N atom is bonded to six Sc atoms with octahedral geometry. In the case of (111) oriented surfaces, each atom will have three dangling bonds pointing out of the surface. Indeed, while (111) oriented films have been reported by a number of groups, none have reported smooth growth, suggesting that a high surface diffusion barrier exists for (111) oriented surfaces.[6, 8, 10] By comparison, for the (001) bulk-terminated surface, each surface atom will be bonded to five neighbors, four in the surface layer and one in the second layer, thus leaving just a single dangling bond pointing out of the surface. There may therefore be a lower diffusion barrier on (001) compared to (111) oriented surfaces. Gall et al. reported (001) oriented ScN growth in the case of sputter deposition; however, in order to avoid the inclusion of (111) grains, it was necessary to apply a substrate bias resulting in incident N ions with energy about 20 eV.

Only two papers have reported the growth of ScN using molecular beam epitaxy (MBE).[10, 24] Moustakas et al. grew ScN on sapphire(0001) using ECR-MBE, resulting in polycrystalline films with highly preferred (111) orientation, consistent with the findings from other growth methods.[10] Recently, we reported the growth of ScN
4.2. Introduction

using RF-MBE.[24] For growth on sapphire (0001), we also obtained (111) orientation with a rough surface. Rough growth also occurred on MgO(110). For growth on MgO(001) on the other hand, we found that smooth, epitaxial films with (001) orientation were obtained, thus showing that the surface diffusion barrier on ScN(001) is indeed lower compared to ScN(111). Furthermore, since atomically smooth surfaces having terraces and well-defined step edges were obtained as shown by scanning tunneling microscopy (STM), the growth mode is evidently two-dimensional, indicating fairly large surface diffusion lengths at the growth temperature we used - about 800 °C.

Although epitaxial growth of ScN has now been achieved, it is still not known how the growth and properties of the ScN(001) depend on the growth conditions such as substrate temperature and Sc/N flux ratio. An advantage of MBE growth over other methods like reactive sputtering or chemical vapor deposition is that it allows to controllably vary the Sc-to-N flux ratio over a wide range. Thus, here we report the strong effects of the Sc/N flux ratio on the growth mode, surface morphology, and optical and electrical properties of ScN(001) films. When the Sc/N flux ratio is less than 1 (N-rich conditions), we find smooth epitaxial films, indicating substantial surface adatom mobility. Excess N atoms recombine and desorb as N$_2$; thus, the resulting stoichiometry is 1:1, and we observe a direct optical transition near 2.15 eV. As the Sc/N ratio exceeds 1 (Sc-rich conditions), a Sc-rich surface structure is formed. This changes the diffusion barrier, resulting in a net increase in the surface mobility. This increased surface mobility completely changes the surface
4.3. Experimental Procedure

morphology to a much smoother surface. However, since the Sc desorption rate from the surface is negligible, defects, most likely N-vacancies, are incorporated into the film, leading to under-stoichiometric films; these show degraded optical properties, including absorption below 2.15 eV and a reflection edge at 1 eV.

4.3 Experimental Procedure

The ScN layers are grown by MBE on MgO(001), using a radio frequency (RF) plasma source for nitrogen and an effusion cell for scandium. Substrate temperature is measured using a thermocouple located behind the substrate heater and also using an infrared pyrometer looking at the front side of the sample. The MgO(001) substrates are 1cm×1cm square and polished on the side where the ScN growth takes place. The samples are coated on the backside with titanium or molybdenum to absorb heat from the radiant substrate heater.

The growth procedure begins by cleaning the substrate using acetone and isopropanol. Then, after introducing the substrate into the growth chamber, it is heated at ∼ 950 °C with the nitrogen plasma source turned on. After 30 minutes, the substrate temperature is lowered to ∼ 800 °C, and the flow rate of nitrogen is set to 1.1 sccm. At this point, the MgO(001) substrates typically show streaky RHEED patterns along both (100) and (110) directions. Using such starting templates, ScN growth begins.
4.3. Experimental Procedure

To investigate how the growth depends on the flux ratio \( J_{Sc} / J_N \), samples are grown at different Sc flux in the range \( 0.3 - 4.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1} \) by adjusting the temperature of the scandium effusion cell. The flux is determined by measuring the thickness of the sample using a thickness profilometer and then computing the growth rate by dividing by the total growth time. Multiplying the growth rate in \( \text{Å s}^{-1} \) by the number density of Sc atoms in ScN (4.39 \( \times 10^{14} \text{ cm}^{-2} \text{ Å}^{-1} \)) yields the Sc flux in atoms cm\(^{-2} \) s\(^{-1} \). The obtained growth rate is in excellent agreement with the Sc deposition rate measured using a quartz crystal thickness monitor (XTM) located inside the growth chamber, and with the deposition rate as determined by measuring the sample thickness using optical methods.

For purposes of defining the Sc/N flux ratio, it is important to know the active nitrogen flux \( J_N \). In an effort to maintain the same effective N flux for this study, samples were grown using the same RF plasma power = 500 W. Background chamber pressure is set in the range \( 8 - 9 \times 10^{-6} \text{ Torr} \). It is difficult to measure directly the value of the active nitrogen flux at the sample position in the case of a nitrogen plasma source. Myoung et al., who reported a flux ratio dependent study of GaN growth by RF MBE, defined the effective nitrogen flux as the incorporated N flux at the highest growth rate in their system.[25] Such a procedure is possible in the case of GaN because of the unique kinetics of GaN growth in which excess Ga actually reduces the growth rate, as reported by Held and co-workers.[35] However, in the case of ScN growth, we have not observed such a maximum growth rate. Instead, when \( J_{Sc} \) exceeds \( J_N \), the growth rate continues to increase, resulting in non-stoichiometric
4.3. Experimental Procedure

growth. As we shall show, the value of $J_{Sc}$ at which this occurs becomes quite clear upon examining the film properties.

Therefore, we define the active nitrogen flux as that which gives the highest growth rate of ScN resulting in stoichiometric films as determined by Rutherford backscattering and by examining the film properties. The active N flux $J_N$ in our system is then the Sc flux at this transition point, which we refer to as $J_{Sc,t}$. In our system, this value of $J_{Sc,t}$ and thus the active N flux $J_N$ is $\sim 3.6 \times 10^{14}$ cm$^{-2}$ s$^{-1}$. The flux ratio $J_{Sc}/J_N$ is thus determined by dividing $J_{Sc}$ by $J_N$.

The growth process is monitored in real time using reflection high energy electron diffraction (RHEED). At the end of growth, the Sc shutter is closed and the N-plasma source is turned off at about the same time or shortly thereafter. After the sample cools down, it is transferred under ultra-high vacuum to an adjoining surface analysis chamber where it is analyzed using in-situ scanning tunneling microscopy (STM). Finally, the sample is removed from the vacuum chamber where it is analyzed using atomic force microscopy (AFM), X-ray diffraction (XRD), Rutherford backscattering (RBS), spectrophotometry, and four-point probe measurement of the room-temperature resistivity. The RUMP program is used to analyze the RBS data.[26]
4.4 Results and Discussion

4.4.1 Structural Properties

The crystalline orientation of the ScN films is determined using XRD. The x-ray wavelength is that of Cu $K\alpha$; since we usually do not resolve $K\alpha_1$ ($\lambda = 1.5405$ Å) vs. $K\alpha_2$ ($\lambda = 1.5443$ Å), we use an average value for $\lambda$ of 1.54 Å. Figure 4.1 shows a typical XRD spectrum for ScN grown on MgO(001) using MBE. In this case, the Sc flux was $2.9 \times 10^{14}$ cm$^{-2}$ s$^{-1}$, which equates to a Sc/N flux ratio of 0.80. A typical XRD rocking curve ($\omega$-scan profile) is shown in the inset. Similar XRD $2\theta$ spectra are observed over a wide range of Sc/N flux ratio from 0.13–1.17. A correction is applied to the XRD spectrum so that the 002 peak of MgO is shifted to 42.94°, in order to give the value found in tables for the MgO lattice constant of 4.213 Å.[27] Then for this sample we find the 002 peak of ScN at 39.84°, corresponding to a perpendicular lattice constant of $a_{\text{ScN,}\perp} = 4.526$ Å. The measured value is a little larger than the expected bulk relaxed value of 4.501 Å.[16] This indicates the layer may not be completely relaxed and/or there may be a small amount of compressive strain due to cooling from the growth temperature. Since 002 is the only significant ScN peak seen, we find that the ScN films grown on MgO(001) substrates have a single orientation which is (001). Thus, RF MBE growth of ScN on MgO(001) is a reliable method to obtain (001)-oriented ScN layers, in contrast to growth by reactive magnetron sputtering which yields to a mixture of (001)- and (111)-oriented grains.[8]
Figure 4.1: 2θ x-ray diffraction spectrum for ScN film grown on MgO(001); inset shows typical ω rocking curve profile for the same sample.
4.4. Results and Discussion

In Fig. 4.2 are shown RHEED patterns for the MgO(001) substrate and four different ScN(001) films grown on MgO(001) substrates at different flux ratios. The images on the left are acquired with the RHEED beam normal to the square sample edge, and it is known that the directions perpendicular to the sample edges are $\langle 100 \rangle$. The images on the right side of Fig. 4.2 are acquired with the sample rotated 45° in the azimuthal direction compared to the images on the left side, and are thus along $\langle 110 \rangle$. Because of the fcc structure, the spacing between the rows of Sc atoms along $\langle 100 \rangle$ is $\frac{a}{2}$, whereas the spacing between the rows of Sc atoms along $\langle 110 \rangle$ is $\frac{a}{\sqrt{2}}$. Therefore, in reciprocal space the spacing between the primary diffraction lines for $\langle 100 \rangle$ is $\sqrt{2}$ larger than the spacing along $\langle 110 \rangle$. Since we do not observe any fractional order lines, the surface structure is $1 \times 1$ both during and after growth. The RHEED patterns are also equivalent under 90° rotations. Therefore, these films have 4-fold symmetry as expected for the (001) face of the rocksalt structure and are thus epitaxial with the MgO(001) substrates with $[100]_{ScN} \parallel [100]_{MgO}$.

The Sc/N flux ratios for the films of Figs. 4.2(b), 4.2(c), 4.2(d), and 2(e) are 0.26, 0.8, 1.03, and 1.17, respectively. As seen in Fig. 4.2(b), for a flux ratio of only 0.26, the RHEED patterns along both directions are streaky but not totally smooth as seen by the nodes. While epitaxial growth occurs, the nodes correspond to some diffraction from the lattice perpendicular to the surface. This occurs when there exist some 3-dimensional surface features. Since the ScN rocksalt lattice is just fcc with a two atom basis (Sc and N), the reciprocal lattice is bcc with a possible intensity modulation of the spots. Therefore, the nodes seen along $\langle 100 \rangle$ correspond to reciprocal lattice
Figure 4.2: RHEED patterns for (a) MgO(001) substrate and (b)–(e) ScN(001) layers as a function of Sc/N flux ratio with $J_{\text{Sc}}/J_{N} = 0.26$, 0.80, 1.03, and 1.17.
points on the (100) face of the body-centered cube. Nodes seen along (110) correspond to reciprocal lattice points on the (110) plane of the body-centered cube which slices through the center of the cube.

For flux ratio $J_{\text{Sc}}/J_{\text{N}} = 0.8$, streaks are still present, but the nodes are brighter, indicating more 3-dimensional features under N-rich conditions. However, for Sc/N flux ratio = 1.03 (Sc-rich conditions), as seen in Fig. 4.2(d), the nodes are much weaker compared to Fig. 4.2(c). This shows that the 3-dimensional structures corresponding to the nodes are reduced in size or in number on the surface for slightly Sc-rich conditions. We thus find that Sc-rich conditions result in smoother surfaces.
4.4. Results and Discussion

Even for very Sc-rich conditions \( J_{\text{Sc}}/J_N = 1.17 \), the RHEED patterns are quite streaky as shown in Fig. 4.2(e).

To see how these RHEED patterns correlate with the surface morphology, we have performed AFM imaging on the same samples. Shown in Figs. 4.3(a), 4.3(b), 4.3(c), and 4.3(d) are AFM images of the same four ScN films grown using flux ratio \( J_{\text{Sc}}/J_N = 0.26, 0.80, 1.03, \) and 1.17, respectively. The size of each image is 2 \( \mu \text{m} \times 2 \mu \text{m} \), and the images are oriented with sides parallel to [100] and [010] directions.

As seen in the AFM image of Fig. 4.3(a), for the sample grown at \( J_{\text{Sc}}/J_N = 0.26 \) (very N-rich conditions), the surface is made up of many small mounds. While not all identical, close inspection reveals that many of these mounds have almost square shapes with flat tops; a typical flat-topped mound is outlined by a white square on the image. The square-shaped mounds have their sides along [100] and [010]. These square-shaped mounds are approximately 1200 \( \AA \times 1200 \AA \) in lateral size and about 74 \( \AA \) in maximum height (= gray scale range shown). The surface is thus very smooth (root-mean-square (RMS) roughness only 19 \( \AA \)), as also indicated by the streaky RHEED pattern shown in Fig. 4.2(b). Other mounds having a similar or slightly smaller size are pyramidal in shape. An example is indicated by P in the image. The pyramids are gently sloped, with apex angles of about 165°. The total density of both types of mounds is about 40 mounds \( \mu \text{m}^{-2} \) of which there are about 10 pyramids \( \mu \text{m}^{-2} \).

As seen in Fig. 4.3(b), for increased \( J_{\text{Sc}}/J_N = 0.80 \), we find a similar surface morphology composed of both flat-topped and pyramidal-shaped mounds. The mound
4.4. Results and Discussion

heights are very similar (gray scale range shown $= 86 \, \text{Å}$, RMS roughness $= 21 \, \text{Å}$); however, the mound densities are higher. The total density of flat-topped and pyramidal mounds is about 70 mounds $\mu\text{m}^{-2}$ of which there are about 30 pyramidal mounds $\mu\text{m}^{-2}$. This increased density of pyramidal mounds explains the increased node intensity seen in Fig. 4.2(c). Therefore, the nodes seen in the RHEED patterns for N-rich conditions [Figs. 4.2(b) and 4.2(c)] are a consequence of diffraction through the pyramidal-shaped mounds, which are the 3-dimensional surface structures. We thus observe increased pyramid density with increased Sc/N flux ratio in N-rich conditions.

As shown by the AFM image in Fig. 4.3(c), as the growth becomes Sc-rich ($J_{Sc}/J_{N} = 1.03$), we find distinctly different surface morphology. In place of the square and pyramidal-shaped mounds, the Sc-rich grown film shows smoother, rounded mounds; a typical rounded mound is outlined by a white circle on the image. These rounded mounds have typical diameters of 2000–3000 Å and have smaller height (gray scale range shown $= 52 \, \text{Å}$, RMS roughness $= 11 \, \text{Å}$). In addition, the mound density is only about 10 rounded mounds $\mu\text{m}^{-2}$. Compared to N-rich grown films, there are 4–7 times fewer mounds $\mu\text{m}^{-2}$ which are also nearly 2 times smaller in height. Fewer and shorter mounds correspond to a smoother surface which correlates with the streakier RHEED patterns shown in Fig. 4.2(d). Even at very high Sc/N flux ratio $= 1.17$, shown in Fig. 4.3(d), the surface morphology still consists of smooth rounded mounds.

To examine these surfaces with atomic-scale resolution, *in-situ* scanning tunneling microscopy (STM) has been performed. Shown in Fig. 4.4(a) is a STM image of a
4.4. Results and Discussion

Figure 4.3: AFM images of ScN films as a function of Sc/N flux ratio: (a) and (b) N-rich conditions; (c) and (d) Sc-rich conditions. Each image size is 2μm×2μm.
sample grown under N-rich conditions ($J_{Sc}/J_N = 0.46$). This image shows a zoom-in view of one of the square, flat-topped mounds $\sim 800 \text{ Å}$'s across and one of the pyramidal-shaped mounds. Individual atomic steps separating smooth terraces are observed. The atomic steps are generally along [100] and [010] directions. The terraces on the pyramidal mound are very narrow compared to those on the flat-topped mound but also along [100] and [010] directions. We attribute the pyramidal mounds to growth around screw-type dislocations in the film. Assuming one dislocation per pyramid, we estimate the dislocation density to be in the range $1 \times 10^9 - 3 \times 10^9 \text{ cm}^{-2}$ for our samples grown under N-rich conditions.

In Fig. 4.4(b) is shown a zoom-in STM image of a sample surface grown at $J_{Sc}/J_N = 1.03$. This image shows that these rounded mounds are in fact large growth spirals. The growth spirals completely dominate the ScN surface morphology under Sc-rich growth conditions. Two single bilayer height steps ($2.25 \text{ Å}$) emanate from the center of the spiral; therefore, the spiral is centered on a dislocation having a screw component of the Burger’s vector equal to 4.50 Å (the ScN lattice constant) and pointing in the [001] direction. Every mound on these surfaces has at least one dislocation at the center. In addition, we also find other dislocations not at the mound centers. Therefore the dislocation density calculated from the number of mounds is $1 \times 10^9 \text{ cm}^{-2}$, but including all dislocations, not just those at mound centers, we estimate from other STM images as many as $1 \times 10^{10} \text{ cm}^{-2}$ for the Sc-rich grown film.

We have shown that dislocations cause pyramid growth in the case of N-rich conditions and round spiral growth in the case of Sc-rich conditions. We now consider
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Figure 4.4: STM images of ScN(001) surfaces: (a) N-rich growth surface. STM sample bias = -2.0 V, tunnel current = 0.2 nA; (b) Sc-rich growth surface. Sample bias = 2.0 V, tunnel current = 0.2 nA.

the reason why we observe this difference. For a constant substrate temperature, there are three important factors affecting film morphology - deposition rate, desorption rate, and diffusion rate. As the AFM images of Fig. 4.3 illustrate, we observe a major change in the morphology with only a small change in the deposition rate. Moreover, as Sc/N flux increases, we observe a linearly increasing growth rate which suggests that there is very little desorption. Therefore, since the substrate temperature is held approximately constant, the most probable explanation for the change in morphology is a qualitative change in surface diffusion.

The ratio of the diffusion length under N-rich conditions, $L_{N-rich}$, to that under Sc-rich conditions, $L_{Sc-rich}$, can be estimated by comparing the terrace width for the pyramidal mound to that for the spiral mound. For the pyramidal mound shown in
4.4. Results and Discussion

Fig. 4.4(a), the terrace width is $\sim 30$ Å, whereas for the spiral mound of Fig. 4.4(b), the terrace width is $\sim 110$ Å. This is about a $4 \times$ increase in terrace width for Sc-rich conditions compared to N-rich conditions. Assuming that the diffusion length is proportional to the terrace width, the ratio $L_{\text{Sc-rich}}/L_{\text{N-rich}} \sim 4$. We attribute this increased diffusion length to a qualitative change in the Sc/N surface stoichiometry.

The well-ordered $1\times1$ reconstruction on one of the flat-topped mounds occurring under N-rich growth conditions has been atomically resolved by STM (shown in chapter 3).[24] Calculations by N. Takeuchi show that a slight relaxation of the surface atoms of the bulk-terminated surface occurs, with the Sc atoms being displaced downward by about 0.03 Å compared to the N atoms.[28] Therefore, under N-rich conditions, the stable surface is nearly bulk-like. Under Sc-rich growth conditions, RHEED, XRD, and RBS channeling all show that the NaCl-structure is maintained. Yet close inspection of the STM image of the ScN surface in Fig. 4.4(b) shows a qualitatively different surface in which we do not observe any well-ordered reconstruction as we do for N-rich surfaces. For these STM tunneling conditions, the surface appears mostly flat and featureless, aside from some nanometer-sized pit features. This weak contrast strongly suggests a surface with metallic character. We infer that it is likely the surface has much more than just a few percent additional Sc, which was recently shown by theoretical groups.[28, 29]

If such a Sc-rich surface structure exists, it could result in a decreased surface diffusion barrier due to weaker metallic Sc-Sc bonding. From our estimate of the
increase in surface diffusion length (above), we can calculate the approximate change in the surface diffusion barrier using the well-known Arrhenius law:

\[ N = \omega_A e^{-E_o/k_B T} \] (4.1)

where \( N \) is the average number of hops per unit time interval, \( \omega_A \) is the atomic oscillation frequency (attempt frequency), and \( E_o \) is the surface diffusion barrier. The diffusion length \( L \) is proportional to the square root of \( N \). Assuming that the diffusion hop length and the attempt frequency are independent of surface composition, we obtain the following expression for the difference in the diffusion barriers \( E_{N-rich} \) and \( E_{Sc-rich} \) for N- and Sc-rich conditions:

\[ E_{N-rich} - E_{Sc-rich} = 2k_B T \ln \frac{L_{Sc-rich}}{L_{N-rich}} \] (4.2)

For our typical growth temperature of 800 °C (1073 K), we thus calculate the difference in surface diffusion barriers to be about 0.26 eV.

Increased diffusion length due to a change in surface structure under Sc-rich conditions would explain the crossover from plateau-pyramid to rounded spiral morphology. Another question is whether the excess Sc on the surface will desorb back into the vacuum or incorporate into the film. To check the Sc/N bulk composition ratio of our samples, we performed Rutherford backscattering on three samples grown at different flux ratios. The RBS spectra are then analyzed and simulated using the RUMP code. Figure 4.5 shows the results of the RBS RUMP computations of the incorporated
4.4. Results and Discussion

Sc/N ratios plotted vs. the incident flux ratios. As is seen, the incorporated ratio is equal to $1.00 \pm 0.02$ for $J_{Sc}/J_N = 0.26 \pm 0.03$. This indicates that excess N atoms are not incorporated under N-rich growth conditions. The RBS result also shows that $Sc/N = 1.00 \pm 0.02$ for $J_{Sc}/J_N = 1.03 \pm 0.03$ (slightly Sc-rich). Although we expect a slight deviation from 1:1 stoichiometry for this sample, this is near the limit of the RBS uncertainty. However, for incident flux ratio $J_{Sc}/J_N = 1.17 \pm 0.03$ (very Sc-rich), the RBS result shows that $Sc/N = 1.20 \pm 0.02$. We conclude that for Sc-rich conditions, the incorporated Sc/N ratio is equal to the incident Sc/N flux ratio (within uncertainty).

Since RHEED, XRD, and also RBS channeling (not presented) all show that ScN films grown under Sc-rich conditions are of high crystalline quality, the off-stoichiometry must be explained by the existence of various point defects. Possibilities could include Sc-on-N-site ($Sc_N$) antisite defects or Sc interstitials; however, since these could lead to local metallic bonding with different structure (i.e. Sc metal is hexagonal), we would expect substantial degradation of the NaCl crystal structure, which we do not see even for the highest flux ratio. We therefore think that a more plausible explanation is the formation of N-vacancies. NaCl-structure transition metal nitrides are known to exhibit large single phase fields; thus they can sustain large vacancy concentrations. For example, TiN is stable in the NaCl-structure for N/Ti ratios ranging from 0.6 to 1.2.[31]
4.4. Results and Discussion

Figure 4.5: Incorporated Sc/N concentration calculated from RBS data as a function of $J_{Sc}/J_N$.
4.4. Results and Discussion

4.4.2 Optical and Electrical Properties

As with the structural properties, the optical properties of ScN layers are found to be critically dependent on the Sc/N flux ratio. In this section, we describe how these properties vary with $J_{Sc}/J_N$. We find that although the films grown under Sc-rich conditions have smoother overall morphology, we also observe significant changes in the optical and electrical properties. In particular, we will show that the incorporated defects have a major effect on the reflection, transmission, and absorption coefficients of the film.

For samples grown under N-rich conditions, holding them up to a white light one observes an orange-red color, and the sample is very transparent. On the other hand, samples grown under Sc-rich conditions are darker in appearance. To make a quantitative comparison, we have measured the reflection and transmission coefficients, $R$ and $T$, for ScN layers grown using different Sc/N flux ratios using spectrophotometry. Then the absorption coefficient $\alpha$ was calculated from $R$ and $T$ using a method described elsewhere.[8] In Fig. 4.6 are shown representative sets of data.

For the sample seen in Fig. 4.6(a) which was grown under N-rich conditions ($J_{Sc}/J_N = 0.26$), $R$ and $T$ both show big oscillations due to multiple reflections at the interfaces. For $h\nu < 2.1$ eV, $R$ oscillates in the range 0.1–0.5, but then $R$ levels out to about 0.3 for $h\nu > 2.1$ eV. For $h\nu < 2.1$ eV, $T$ also oscillates in the range 0.4–0.8, but then $T$ drops off sharply for $h\nu$ near 2.1 eV. Similar behavior to that shown here is observed for all samples grown under N-rich conditions.
Figure 4.6: Transmission, reflection, and absorption coefficients for ScN(001) films as a function of photon energy for (a) a sample grown under N-rich conditions with (b) the corresponding graph of \((h\nu\alpha)^2\) vs. \(h\nu\); and (c) a sample grown under Sc-rich conditions [measurement by Daniel Gall].
Near $h\nu = 2.1$ eV, where $T$ drops off, we observe an increase in the absorption $\alpha$ up to about $3 \times 10^5$ cm$^{-1}$. Below 2.1 eV, $\alpha$ falls off to very small values and is essentially flat. If the absorption threshold near 2.1 eV corresponds to a direct band gap, the quantity $(h\nu\alpha)^2$ should be a linear function of $h\nu$. This plot is shown in Fig. 4.6(b) where it is seen that the data is indeed linear, strongly indicating that this threshold corresponds to a direct transition at the energy of 2.15 eV. No other absorption thresholds are observed down to 0.5 eV. If an indirect transition exists over the range of our measurement, it is below the sensitivity of our instrument.

The $R$ and $T$ spectra are substantially different for the films grown under Sc-rich conditions. As shown in Fig. 4.6(c) for the sample grown at a Sc/N flux = 1.17, $T$ is strongly reduced in the range 1–2 eV and shows almost no thickness oscillations. $R$ also shows a strong reduction in its oscillations in the range 1–2 eV, and it exhibits a sharp reflection edge at 1 eV, where it increases from 0.15 at 1 eV to 0.7 at 0.5 eV. The direct absorption at 2.15 eV is still observed, but sub-bandgap absorption is also observed at the level of $0.3–0.5 \times 10^5$ cm$^{-1}$. Very similar results are also obtained for the sample grown at $J_{\text{Sc}}/J_N = 1.03$.

We attribute the sharp reflection edge near 1 eV for the films grown under Sc-rich conditions to the existence of an increased number of free carriers compared to the samples grown under N-rich conditions. Several recent papers have described the calculation of carrier concentrations and mobility from infrared reflectivity measurements in the case of GaN.[32, 33] Fitting our ScN reflection spectrum with a Drude
free electron gas model via a method described elsewhere,[34] we estimate the carrier density to be about $2 \times 10^{21}$ cm$^{-3}$ for samples grown under Sc-rich conditions.

One possibility is that the free carriers are coming from the N-vacancies acting as donors. For the sample grown with $J_{Sc}/J_N = 1.03$, we would expect a carrier concentration of about $1.3 \times 10^{21}$ cm$^{-3}$, in reasonable agreement with the value estimated from the Drude model fit. If all defects were donors, the sample grown with $J_{Sc}/J_N = 1.17$ should have a carrier concentration of about $7.5 \times 10^{21}$ cm$^{-3}$. This is almost 4× higher than the value from the Drude model fit, indicating that some compensating defects may occur at this very high Sc-flux.

Finally, we have also measured room-temperature resistivity as a function of Sc/N flux ratio. The results of this study are plotted in Fig. 4.7. Under N-rich conditions ($J_{Sc}/J_N = 0.26$), the measured resistivity is $588 \pm 60$ $\mu\Omega$-cm. For $J_{Sc}/J_N = 0.8$, the resistivity decreases to $449 \pm 40$ $\mu\Omega$-cm. Then for Sc-rich conditions ($J_{Sc}/J_N = 1.17$), the resistivity drops significantly to $103 \pm 10$ $\mu\Omega$-cm. This large drop in resistivity is explained by the increased carrier concentration.

### 4.4.3 Discussion and Comparison to the Case of MBE Growth of GaN

In the N-rich growth regime, the growth rate of ScN is limited by the incident Sc flux since excess N atoms recombine and leave the surface as N$_2$. We have shown that such surfaces are still stable and that smooth, epitaxial, and stoichiometric films
4.4. Results and Discussion

Figure 4.7: Room temperature resistivity of several ScN(001) films as a function of $J_{\text{Sc}}/J_{\text{N}}$ [measurement by Daniel Gall].
are obtained under this condition. These films are transparent with a direct optical transition at 2.15 eV. In the Sc-rich growth regime, where the Sc flux exceeds the N flux, the growth rate is still determined by the Sc flux since desorption of Sc from the ScN surface back into the vacuum is negligible. However, the excess Sc does not degrade the crystal structure or lead to amorphous growth as seen by the RHEED pattern which remain clear and streaky under Sc-rich growth conditions. We also find a smoother surface morphology in AFM images and excellent single crystal structure by RBS channeling. Even for flux ratio as high as 1.17, we still obtain excellent crystallinity.

Comparing to the case of MBE growth of GaN, in the N-rich growth regime the growth rate of GaN is also limited by the Ga flux. N-rich conditions for GaN however lead to a spotty transmission pattern in RHEED, indicative of a rough surface. Several different groups have shown that Ga-rich growth conditions in MBE are favored for obtaining GaN with the smoothest surface. The reason for smooth growth of GaN under Ga-rich conditions is that GaN surfaces are stabilized by the presence of one or more layers of Ga at the surface. However, the excess Ga does not lead to non-stoichiometric growth. Held and coworkers showed that the excess Ga on the surface led to a Ga-rich surface layer but with the excess Ga re-evaporating back into the vacuum. Smith and co-workers showed that the stable surface reconstructions occurring on both polar faces of wurtzite GaN contained one or more layers of Ga. Tarsa and coworkers showed that Ga-rich conditions led to large round growth spirals, indicating that the diffusion length of adatoms is
increased under Ga-rich conditions. [84] If the excess Ga layers are removed however, the surface structure becomes unstable, resulting in rough growth.

We have shown that Sc-rich growth conditions also lead to large round growth spirals in the case of ScN growth. We have explained this is due to increased adatom diffusion length under Sc-rich conditions. However, since re-evaporation of Sc into the vacuum is negligible, Sc-rich conditions also lead to non-stoichiometric growth, unlike the case of GaN. A reason for this is the fact that the vapor pressure of Sc metal at the growth temperature of 800°C (3×10^{-8} Torr) is much lower than that of Ga metal at 800 °C (6×10^{-6} Torr). Since the rocksalt structure is maintained, N-vacancies are incorporated into the resulting film, and we observe a degradation of the optical properties, including sub-bandgap absorption, reduced transmission, and a reflection edge near 1 eV. Hence, while Ga-rich conditions may be preferable for GaN growth, N-rich conditions are clearly preferable for ScN growth by RF-MBE for the conditions described here.

4.5 Summary

We have grown ScN on MgO(001) substrates by RF-MBE and investigated how their structural, optical, and electrical properties depend on the Sc/N flux ratio during growth. We find (001) orientation for all flux ratios. RHEED patterns obtained during growth show that the surface is epitaxial under N-rich conditions and that the surface morphology is dominated by flat-topped and pyramidal shaped mounds.
4.5. Summary

For Sc-rich conditions, the growth is also epitaxial, but the surface morphology is distinctly smoother and is dominated by round spiral mounds. The transition to spiral mound growth morphology is explained by an increased diffusion length of adatoms when the surface becomes Sc-rich.

The XRD and RHEED observations correlate well with changes in the surface morphology as measured by in-situ STM and ex-situ AFM. The excess Sc flux during Sc-rich growth leads to an increased growth rate which involves most likely the incorporation of N-vacancies. This conclusion is supported by RBS measurements which show that the incorporated Sc/N ratio is equal to (within uncertainty) the incident Sc/N flux ratio for $J_{Sc} > J_N$. In addition, optical transmission and reflectivity measurements show very high reflectivity for photon energies in the range 0.5–1 eV and significant absorption below the bandgap in the range 1–2 eV, consistent with an increased carrier concentration.

On the other hand, for $J_{Sc} < J_N$, the incorporated Sc/N ratio measured by RBS is equal to 1. For these films, we find an optical absorption edge corresponding to a direct transition at 2.15 eV. ScN therefore attains its best structural and optical properties when grown under N-rich conditions.
Chapter 5

Phase Stability, Nitrogen Vacancies, Growth Mode, and Surface Structure of ScN(001) under Sc-rich Conditions

5.1 Abstract

Rock-salt structure scandium nitride films have been grown on magnesium oxide (001) substrates by molecular beam epitaxy using a rf plasma source for nitrogen. The case of Sc-rich growth conditions, which occurs when the scandium flux $J_{\text{Sc}}$ exceeds the nitrogen flux $J_{\text{N}}$, is discussed. Despite the excess Sc during growth, reflection high energy electron diffraction and x-ray diffraction shows that these films have only a single orientation which is (001), and ion channeling confirms the good crystallinity. Rutherford backscattering shows that these films are off-stoichiometric, and this is found to be directly related to variations in the nitrogen, not the scandium, content by secondary ion mass spectrometry. High-resolution x-ray diffraction reciprocal lattice mapping shows that these variations in the nitrogen content are related to the
existence of the N-vacancies. It is concluded that Sc-rich growth leads to the incorpora-
tion of N-vacancies into the crystal structure, the concentration of which depends
on the Sc/N flux ratio. Additionally, excess scandium conditions at the surface are
explored by in-situ scanning tunneling microscopy. The observed wider terrace widths
as compared to N-rich growth are due to an increased surface diffusion which is at-
tributed to a Sc-rich, metallic surface structure. Combined with the large dislocation
density, the enhanced diffusion results in a predominant spiral growth mode.

5.2 Introduction

Recently, there has been much interest in scandium nitride due to its electronic prop-
erties and possibility for combination with gallium nitride.[6, 8, 9, 10, 17, 21, 22, 41,
42, 43] Most reported ScN growth has been done using sputtering techniques or chem-
ical vapor deposition methods in which the flux ratio of Sc to N during the growth
is very difficult to control. An exception is Moustakas et al. who used ECR molec-
ular beam epitaxy (MBE) as the growth technique.[10] More recently, Al-Brithen et
al. reported the use of rf MBE to grow ScN; this allows the Sc:N flux ratio dur-
ing growth to be carefully controlled, permitting the study of the effects of N-rich
(Sc/N ratio < 1) up to Sc-rich (Sc/N ratio > 1) growth conditions.[24, 44] It was
found that N-rich growth conditions result in single oriented ScN (001) films with
smooth surfaces. Reflection high energy electron diffraction (RHEED) during growth
showed only 1×1 reconstruction. Scanning tunneling microscopy (STM) showed that
5.2. Introduction

the N-rich growth surface consists of plateaus and some pyramids (caused by spiral growth around dislocations) with a single atomic step height between terraces equal to half the lattice constant, 2.25 Å. It was also shown by Rutherford Backscattering that these films are stoichiometric (N/Sc = 1 to within the RBS accuracy ~ 2%).

The formation of non-stoichiometric transition metal nitrides has been a topic of great interest for many years. Titanium nitride, for example, is remarkable in that it can sustain a substantial range of composition variation while remaining single phase (rocksalt structure), thus implicating the existence of both N and Ti vacancies.[31]

In the case of ScN (also rocksalt structure) on the other hand, Porte reported the coexistence of two separate phases in under-stoichiometric sputtered ScN films which were prepared with lower N overpressures - ScN and Sc metal - as opposed to ScN_x with x less than 1.[43] It was argued that the absence of N-vacancies (not more than 0.5%) was due to their being energetically unfavorable. In our recent work, however, we have found a very different result - namely that growth of ScN by rf MBE results in quite high N-vacancy concentrations (up to 20%) if the Sc flux exceeds the N flux.[44]

Moreover, we have shown that such films are also smooth and highly crystalline; nevertheless, the N-vacancies do affect the electrical and optical properties. In this paper, we concentrate on the issue of off-stoichiometric ScN, presenting new data which confirms the stability of the rocksalt phase, the (001) orientation, and the existence of substantial concentrations of nitrogen vacancies. In addition, we also discuss the issue of surface structure and surface adatom diffusion and how these affect the smooth growth morphology of these off-stoichiometric ScN films.
5.3 Experimental Procedure

ScN layers are grown by MBE on MgO(001), using a radio frequency (RF) plasma source for nitrogen and an effusion cell for scandium. ScN growth takes place with the substrate set at ~ 800 °C and the base pressure of nitrogen set at $9 \times 10^{-6}$ torr with the N$_2$ flow rate of about 1.1 sccm.

The growth starts when the scandium shutter is opened. Scandium rich growth conditions occur when the Sc flux, $J_{Sc}$, exceeds the N flux, $J_N$. The average scandium flux $J_{Sc}$ is determined by measuring the final film thickness using a thickness profilometer; from this, and by knowing the growth time and Sc atomic density in ScN, the Sc flux $J_{Sc}$ is calculated. The effective N flux is determined to be $J_N \sim 3.6 \times 10^{14}$ cm$^{-2}$ s$^{-1}$ in our system for the stated conditions.[44] The flux ratio ($J_{Sc}/J_N$) can be adjusted by changing the scandium effusion cell temperature.

The growth is monitored in real time using RHEED. Following growth, samples can be transferred under vacuum to the scanning tunneling microscope for surface analysis. After taking the sample out of the chamber, it is analyzed using x-ray diffraction (XRD) with a Rigaku $\theta - 2\theta$ diffractometer having Cu $K\alpha$ radiation. Small pieces are also provided for analysis by Rutherford backscattering (RBS), ion channeling, XRD reciprocal lattice mapping, and secondary ion mass spectrometry (SIMS) [Charles Evans and Associates, Sunnyvale, CA].
5.4 Results and Discussion

5.4.1 Crystallinity and Orientation

In Fig. 5.1 is shown the XRD 2θ scan for a ScN film grown on MgO(001) under Sc-rich conditions ($J_{\text{Sc}}/J_{N} = 1.17$) displayed on log scale. The MgO 002 substrate peak appears at 42.94°, and the ScN 002 peak appears at 39.99°. The MgO 004 and ScN 004 peaks are also seen at 93.99° and 86.14°, respectively. As can be seen, no other peaks are observed. Therefore this sample, although grown under Sc-rich conditions, is highly crystalline with (001) orientation. From the positions of the peaks, the perpendicular lattice parameter for this sample is calculated to be $a_{\text{ScN}} = 4.509 \, \text{Å}$, slightly above the bulk relaxed value of stoichiometric ScN = 4.501 Å,[9] indicating mild compressive strain due to differential thermal contraction during cooling from growth temperature, 800°C, to room temperature. While this film has near ideal crystallinity, it will be shown below that it contains a large nitrogen deficiency.

Further evidence for the crystalline nature of these films is obtained from RBS, which has been performed for samples using a helium ion beam of incident energy of 2.189 MeV and a backscattering angle of 168°. Shown in Fig. 5.2(a) is a plot of the backscattering yield as a function of energy for a ScN film grown under slightly Sc-rich conditions ($J_{\text{Sc}}/J_{N} \sim 1.03$). Two results are shown - one for the sample [001]-direction randomly oriented with respect to the incident beam and the other for the sample [001]-direction aligned parallel to the incident beam. The scandium edge begins at $\sim 1.55 \, \text{MeV}$ (film surface) and ends at about 1.25 MeV (substrate-film
5.4. Results and Discussion

Figure 5.1: XRD 2θ scan for ScN film grown under scandium rich conditions.

$J_{Sc}/J_N = 1.17$
interface) while the N edge begins at \( \sim 0.7 \text{ MeV} \) (film surface) and ends at \( \sim 0.4 \text{ MeV} \) (substrate-film interface). The substrate edges for magnesium and oxygen begin at \( \sim 0.83 \) and \( 0.52 \text{ MeV} \), respectively.

It is clearly seen that the aligned spectrum has dramatically reduced backscattering yield compared to the non-aligned spectrum, showing that the channeling is extremely high along the [001] direction. The computed \( \chi_{\text{min}} \) for Sc, which is the ratio of the counts of the aligned spectrum to the counts of the non-aligned spectrum (at channel 210), is just 2.4%. Fig. 5.2(b) shows the 2-D ion channeling rocking scan. The Z-axis represents the total charge of the incident beam needed to produce a constant backscattered beam intensity while the X- and Y-axes represent the angular position of ScN[001] direction with respect to the incident beam. Therefore, orientations with higher channeling appear as higher points in the plot. The plot shows clearly the symmetry of the rocksalt lattice, with a strong central peak corresponding to channeling along [001] and clear ridges corresponding to 4-fold symmetry directions. These data further support the conclusion that the sample is a highly oriented, epitaxial, crystalline film.

### 5.4.2 Nitrogen Vacancies

RBS data is also used to determine the stoichiometry of the ScN films by fitting the RBS spectra using the RUMP simulation code.\[26\] The result gives the average Sc/N bulk composition ratio. This has been done for samples grown with various flux ratios. It was found that for a flux ratio \( J_{\text{Sc}}/J_{\text{N}} \) equal to 0.26 ± 0.03, RBS gives a...
Figure 5.2: (a) RBS channeling for ScN(001) film randomly aligned and well aligned with the incident beam. The film was grown under slightly Sc-rich conditions. (b) the RBS rocking scan for the same film [Measurement by David Ingram].
5.4. Results and Discussion

Sc/N composition ratio equal to 1.00 ± 0.02. For $J_{Sc}/J_{N} = 1.03 \pm 0.03$, RBS gives a composition ratio equal to 1.00 ± 0.02. Finally, for $J_{Sc}/J_{N} = 1.17 \pm 0.03$, RBS gives a composition ratio equal to 1.20 ± 0.02. This shows that N-rich conditions result in stoichiometric films (Sc/N = 1) while Sc-rich conditions result in non-stoichiometric films, and it shows that the bulk Sc/N composition ratio agrees well with the Sc/N flux ratio (within a few %) in the case of Sc-rich conditions.[44]

To determine variations in the composition ratio as a function of growth time, SIMS has been performed. In Fig. 5.3 is shown the SIMS depth profile for the non-stoichiometric ScN film having an average bulk composition ratio Sc/N of 1.20 ± 0.02, as determined from RBS. The total film thickness was about 6000 Å. Although there are no ScN standards to determine absolute concentrations of Sc and N from SIMS data, changes in the signals indicate variations in the bulk concentrations. As is seen, both Sc and N signals are nearly constant until ~ 2800 Å, indicating a fairly constant Sc/N bulk ratio. At 2800 Å, the Sc/N flux ratio was increased. What is seen is not an increase in the Sc signal but rather a decrease of about 4% in the N signal. Then, at 4900 Å, the Sc/N flux ratio was again increased, and again the N signal is observed to decrease, by about 2%. Throughout the entire growth, the scandium signal is nearly constant, independent of the Sc/N flux ratio, while the N signal changes several times.

Assuming that the sputtering rate is dependent on (e.g. inversely proportional to) the Sc density, it is understandable that the Sc signal should remain constant, independent of potential variations in the Sc density. In this case, it would be possible
5.4. Results and Discussion

to obtain false variations in the N signal. However, since the growth rate of ScN goes linearly proportional to the Sc flux (for N- or Sc-rich conditions), and since we do not observe the formation of Sc precipitates, it is more likely that the Sc density is in fact constant throughout the film, as the SIMS profile suggests. Moreover, if the changes in N signal were due only to variations in the sputtering rate, then corresponding changes should also have been observed at the same depths in the simultaneously measured C and O signals (not shown); such changes were not observed. Therefore, we conclude that changes in the N signal correspond directly to changes in the N density and thus that the N density varies with depth according to the Sc/N flux ratio in Sc-rich conditions, and attribute these changes in N density to variations in the number of N vacancies.

In order to confirm that the composition variations are actually due to N-vacancies and not for example related to antisite substitutions, we performed high-resolution x-ray diffraction reciprocal lattice mapping (HRRLM) on asymmetric 224 reflections in order to determine the relaxed lattice constant $a_0$ as a function of Sc/N flux ratio, following the procedure described elsewhere [Measurements by Daniel Gall].[45] Measured lattice constants perpendicular and parallel to the layer surface provide, together with the Poisson ratio $\nu_{ScN} = 0.20$,[16] values for $a_0 = 4.503 \pm 0.002$ Å, which were found to be independent of the Sc/N flux ratio. Thus, there is no detectable change in $a_0$ over the entire composition range $1.00 \leq \text{Sc}/\text{N} \leq 1.17$. Ab initio density functional calculations employing the generalized gradient approximation, periodic boundary conditions, and 16-atom supercells show that ScN$_x$ with x
Figure 5.3: SIMS profile as a function of distance from the substrate-film interface for a ScN(001) film grown under Sc-rich conditions and with changing flux ratio $J_{Sc}/J_N$ (measurements by Charles Evans and Associates).
5.4. Results and Discussion

= 0.88 has an $a_o$ which is almost identical (only 0.1 % smaller) to the stoichiometric ScN lattice constant if the N-deficiency is accounted for by N-vacancies. However, Sc on N antisite substitutions or Sc-interstitials result, for layers with $x = 0.88$, in a considerable increase of $a_o$ by 1.4% or 5.1%, respectively. Thus, the experimentally observed absence of a change in $a_o$ with Sc/N ratio is, within uncertainty, consistent with the presence of N-vacancies. In contrast, if the N deficiency in the layers grown with Sc/N > 1 would be due to antisite substitutions or Sc-interstitials, the change in $a_o$ would be clearly observable by our HRRLM experiments. Therefore, the reciprocal lattice mapping results show, in agreement with our SIMS data, that the deviations from stoichiometry for Sc/N > 1 are due to N-vacancies.

As discussed in the previous section, XRD and RBS channeling both show ideal crystallinity. Therefore, for rf MBE growth in Sc-rich conditions, the rocksalt crystal structure is apparently able to accommodate relatively high N-vacancy concentrations (up to 20%).[24, 44] Thus, Porte’s earlier work, which reported that sub-stoichiometric ScN films contain no N-vacancies but instead separated phases of ScN and Sc metal, seems not to be a general conclusion but rather a result specific to a certain growth technique (i.e. reactive sputtering followed by annealing).[43]

Recently, Stampfl et al., using density functional theory and a screened-exchange local density approximation (sX-LDA) method as well as the LDA, calculated the (neutral) bulk N-vacancy formation energy.[29] While this energy is quite high in the case of N-rich conditions (4.32 eV), it is much lower and in fact just slightly negative in the case of Sc-rich conditions (-0.42 eV). Therefore, while N-vacancies
are not easily formed under N-rich growth conditions, they can easily form under Sc-rich growth conditions. The same group also calculated the (neutral) bulk Sc-vacancy formation energies and found them to be very high for both Sc-rich and N-rich conditions, indicating that Sc-vacancies are energetically unfavorable which agrees with our experimental observations of constant Sc density.

5.4.3 Growth Mode and Surface Diffusion Barriers

Shown in Fig. 5.4 is a STM image of the surface of the ScN(001) film grown on MgO(001) at the flux ratio \( \frac{J_{Sc}}{J_N} = 1.03 \). The surface consists of big rounded spiral mounds, and smooth terraces are also observed, confirming that the growth is epitaxial. The step height between terraces is equal to \( a_{ScN}/2 = 2.25 \) Å, which is one atomic layer of ScN. The spiral mounds also contain pits which are seen near the mound centers; some other pits which are not at the mound centers are also observed, and these are correlated with the termination (or emanation) of one or more steps. It is therefore concluded that the pits at the mound centers or elsewhere are each correlated with the presence of a dislocation. Those dislocations near the mound centers evidently have a screw component of the Burgers vector while the others may have only edge components. By assuming one dislocation per pit, the total dislocation density is estimated to be \( \sim 1 \times 10^{10} \ cm^{-2} \). The slip line seen at lower left corner of Fig. 5.4 is attributed to thermal stress as the sample temperature was changed.

Spiral growth has also been observed under metal-rich conditions in the case of GaN(0001), as reported by several groups.[35, 40, 46, 47, 48, 49, 84] For example,
Figure 5.4: STM image of ScN(001) surface grown under scandium rich conditions. Sample bias = +2.0 V; tunneling current = 0.2 nA.
5.4. Results and Discussion

Tarsa et al. showed that the surface of GaN(0001) grown under Ga-rich conditions consists of spiraling hillocks as seen using atomic force microscopy.\cite{48, 84} Also, Smith et al., using \textit{in-situ} STM, observed growth spirals on the GaN(0001) surface for Ga-rich growth conditions.\cite{40} On the other hand, the GaN(0001) surface becomes rough under N-rich conditions which has been attributed to a kinetic accumulation of excess N on the surface combined with the fact that neither experiment nor theory finds an energetically stable N-terminated surface for GaN (0001) or (000$\bar{1}$), as noted by Feenstra et al.\cite{39, 49} The behavior is related to the strong Ga–N bonds formed at the surface under N-rich conditions which substantially increase the diffusion barriers for Ga adatoms; Ga–Ga bonds which predominate under Ga-rich conditions are weaker, and this leads to lower diffusion barriers. Zywietz et al. determined, based on density functional theory, the difference in diffusion barriers for Ga adatoms in Ga-rich conditions compared to N-rich conditions for both GaN (0001) and (000$\bar{1}$) surfaces, finding values of 1.4 eV and 0.8 eV, respectively.\cite{39}

The transition to a rounded spiral growth mode for these two systems (ScN and GaN) under metal-rich conditions suggests a common origin despite their very different crystal structures (rocksalt vs. wurzite). In the case of ScN, we recently estimated using STM measurements, the difference in surface diffusion barriers for Sc-rich conditions versus N-rich conditions to be about 0.26 eV, Sc-rich conditions having the lower barrier.\cite{44} We note that this is a much smaller difference compared to the case of GaN, consistent with the fact that atomically smooth and well-ordered surfaces of ScN(001) are also observed for N-rich conditions.\cite{24} Since we do not observe a
If a Sc-rich surface structure exists for ScN(001), the decrease in the surface diffusion barrier in going to Sc-rich conditions may also be a consequence of weaker metallic Sc–Sc bonding as compared with Sc–N bonding at the surface. From the CRC table of diatomic bond strengths,[53] the metallic Sc–Sc bond strength is 1.69 ± 0.22 eV which is weaker than the Sc–N bond strength which is 4.87 ± 0.87 eV. These numbers are comparable to the case of GaN. From the CRC table, the bond strength of Ga-Ga is 1.43 ± 0.22 eV, slightly weaker than Sc-Sc. This is interesting since the melting point of Ga (303 K) is so much lower than that of Sc (1812 K); however, the dissociation energies are similar (e.g. to reach a common vapor pressure of $2 \times 10^{-4}$ torr, we need $T_{Ga} = 1223$ K and $T_{Sc} = 1423$ K). Finally, while the Sc–N bond has more ionic character than the Ga–N bond (due to a larger electronegativity difference), the Sc–N bond has about the same strength as the Ga–N bond. For example, the melting point of ScN was reported to be 2873 ± 50 K,[50] whereas the melting point of GaN was theoretically estimated to be 2791 K.[51] Thus, the common origin of the growth behavior between ScN and GaN may be related to the similarity in their bonding energies.

5.4.4 Scandium Rich Surface Structure

The drop in surface diffusion barrier upon crossing into Sc-rich conditions suggests a corresponding qualitative change in the surface structure. In the case of GaN(0001),
5.4. Results and Discussion

It was found that the surface structure which forms under Ga-rich conditions has approximately two additional monolayers of Ga on top of the Ga-terminated bilayer whereas these monolayers disappear under N-rich conditions.[40, 49, 54] In the case of ScN, Stampfl et al. have recently calculated various surface structural models, including ideal-relaxed (bulk terminated), Sc-terminated, 2Sc-terminated and N-vacancy models.[29] They found that the ideal-relaxed 1×1 model is energetically most favorable over a wide range of nitrogen chemical potential, including the N-rich end of the range. This result was also obtained via first-principles calculations by Takeuchi.[28]

For Sc-rich conditions, Stampfl et al. calculated that a 2×1 N-vacancy model would be energetically most favorable within a small range of chemical potential on the Sc-rich side.[29] Their 2×1 N-vacancy model consists of rows of surface N-vacancies running along [110]. In addition, their 1×1 Sc-terminated model was also found to be lower in energy than the ideal surface under Sc-rich conditions but a little higher in energy than the 2×1. Both the 2×1, in which half the surface N-sites are vacancies, and the 1×1 Sc-terminated models, in which all N-sites are vacancies, have substantial metallic bonding character.[29] This is consistent with our tunneling spectroscopy experiments on ScN(001) grown under Sc-rich conditions where we find metallic surface states [see chapter 6].[52]

Displayed in Fig. 5.5 are STM images at higher resolution of a ScN(001) surface acquired following growth under Sc-rich conditions. Dashed lines in each image enclose the identical surface region for comparison. At a sample bias of +2.0 V, as shown in Fig. 5.5(a), smooth terraces are observed with meandering steps; the minimum step
Results and Discussion

height between terraces is a single atomic layer or half the lattice constant of ScN = 2.25 Å. Aside from some tiny dark pocks, very little structure is seen on the terraces, consistent with a metallic surface. More detail can be seen at a lower sample bias of +1.0 V, as shown in Fig. 5.5(b). Here one observes a random-looking distribution of nanometer-sized protrusions. These protrusions are numerous, appearing to occupy a large fraction of the surface area. As a result, the step edges are somewhat less distinct but still visible.

While no well-ordered surface reconstruction is evident, the structure of the surface grown under Sc-rich conditions is clearly very different compared to that grown under N-rich conditions. In addition, the fact that the surface is very smooth with well defined step edges implies that the growth follows the step-flow mode; therefore, the protrusions seen in the STM images of Fig. 5.5(b) are not nucleation centers (i.e. new ScN islands) but rather are related to the intrinsic structure of the terrace. And since the surface exhibits metallic conductivity, we conclude that the top layer contains an excess of Sc metal. It is thus likely that the tiny protrusions correspond to scandium-rich clusters which are similar in structure to the Sc-terminated reconstruction - namely that they are deficient in N atoms. The clustering could be related to the instability of the Sc-terminated reconstruction and could provide a mechanism for lowering the surface energy. The regions between the protrusions most likely correspond to the more bulk-like second layer.
Figure 5.5: STM images of ScN(001) surface grown under scandium-rich conditions. a) sample voltage = +2.0 V, tunneling current = 0.2 nA; b) sample voltage = +1.0 V, tunneling current = 0.2 nA. The areas between the dashed lines in the two images correspond to the same surface region.
5.4. Results and Discussion

Shown in Fig. 5.6 are schematic side-view models of the ScN(001) surface in (a) N-rich conditions and (b) Sc-rich conditions. For N-rich conditions, the surface is stoichiometric and the step edge is distinct. For Sc-rich conditions, the excess Sc atoms in the top layer make the step edge appear less distinct, consistent with the STM image of Fig. 5.5(b). Such a Sc-terminated surface would have metallic character, could be established during Sc-rich growth, and is qualitatively consistent with the Sc-rich surface models proposed by Stampfl et al. Note that the surface stoichiometry is independent of the bulk stoichiometry. For example, the top layer could contain 100% N vacancies while the bulk contained only a few % N vacancies (depending on the flux ratio).

Further evidence that the Sc-rich surface top-layer contains mainly Sc has recently been obtained. The RHEED patterns for Sc-rich growth always show clear first-order streaks, as we have previously reported.[24, 44] However, some very weak half-order streaks are occasionally observed along [110], as shown in the RHEED pattern in Fig. 5.7(a). These are more clearly evident in the averaged line profile shown in Fig. 5.7(b). Weak half-order streaks are consistent with a small amount of ordering of surface atoms into the 2×1 N-vacancy reconstruction predicted by Stampfl et al.[29]. In this case the top layer would contain some nitrogen atoms. However, we have so far not observed any well-ordered 2×1 regions by STM.

To explore the 2×1 seen in RHEED further, another experiment was performed. The ScN growth was initiated on MgO(001) under Sc-rich conditions, and the RHEED pattern showed a weak 2× from the very beginning. Later during the growth, the
Figure 5.6: Schematic side-view atomic models of (a) ScN(001) under N-rich conditions having bulk-like top layer and (b) ScN(001) under Sc-rich conditions having Sc-clusters as the top layer.
Figure 5.7: (a) RHEED pattern along [110] for ScN(001) under Sc-rich conditions, and (b) the averaged horizontal line profile showing the existence of 2x.
Sc/N flux ratio was reduced. Surprisingly, the 2\times pattern remained. Even for very low Sc/N flux ratio, the weak half-order streaks did not disappear. This suggests that surface N-vacancy ordering may lead to bulk ordering. Bulk ordering of N-vacancies is prevalent in manganese nitride, as we have observed in our recent studies of that material.\[55\] However, the 2\times streaks seen in Fig. 5.7 are not always observed, and we have seen no other evidence for bulk N-vacancy ordering in ScN. Thus, the basic rock-salt structure is very stable, even with the presence of significant quantities of N-vacancies.

5.5 Summary

We have studied the epitaxial growth of ScN on MgO(001) substrates under Sc-rich conditions using rf MBE. XRD and RBS confirm that the rocksalt phase is maintained and that the films have good crystallinity with (001) orientation. SIMS shows that only the N density changes when the flux ratio $J_{Sc}/J_N$ is changed; the Sc density remains constant which indicates that the film has a N vacancy concentration which depends on the Sc/N flux ratio under Sc-rich conditions. The relaxed lattice parameter remains constant with changing Sc/N flux ratio, confirming that the N-deficiency in layers grown under Sc-rich conditions is due to N-vacancies. Large-scale STM images show that Sc-rich growth conditions result in the spiral growth mode with large mounds and smooth terraces. The increased terrace widths compared to N-rich growth conditions indicate increased surface adatom diffusion. Detailed STM images
5.5. Summary

of the surface strongly suggest a metal-rich, metallic surface layer. The spiraling growth mode can therefore be attributed to enhanced surface diffusion due to weaker Sc-Sc bonding. The RHEED pattern for Sc-rich conditions occasionally shows weak half-order streaks along [110], indicating a small degree of surface ordering which may be related to the 2×1 N-vacancy reconstruction predicted by Stampfl et al. Note the resulting bulk stoichiometry will be directly related to the flux ratio, not the surface stoichiometry. Lastly, while Sc-rich conditions result in lower diffusion barriers, the excess Sc results in N-vacancies which have detrimental effects on the bulk optical properties, as shown in chapter 4.[44]
Chapter 6

Surface and Bulk Electronic Structure of ScN(001) Investigated by STM, STS and Optical Absorption Spectroscopy

6.1 Abstract

ScN(001) 1×1 surfaces have been prepared by growing ScN on MgO(001) using radio frequency molecular beam epitaxy. *In-situ* ultra-high vacuum scanning tunneling spectroscopy indicates that the Fermi level at the surface lies slightly above the Sc 3d conduction band edge, which is attributed to a downward band bending at the surface. *In-situ* scanning tunneling microscopy is used to image the Sc and N atom sublattices. While only one atom (Sc) appears at small negative bias, both atoms (Sc and N) appear at certain positive sample biases due to the partially ionic nature of the bonding. Charge accumulation near ionized sub-surface donors is evident from the long range topographic distortions at the surface. The combination of tunneling
spectroscopy and optical absorption results show that ScN has an indirect bandgap of $0.9 \pm 0.1$ eV and a direct transition at 2.15 eV.

6.2 introduction

Transition metal nitrides (TMNs) have been receiving a lot of interest for their unique physical properties including high hardness, high temperature stability, mechanical strength, off-stoichiometry, magnetic properties, and electronic transport properties that vary from semiconducting to metallic.[8, 9, 16, 20, 22, 31, 44, 55, 56, 57, 58, 59, 60, 61] One TMN of great interest, due to its unique properties and potential applications, is ScN. Scandium can be combined with nitrogen to form a rocksalt compound with lattice constant $a_{\text{ScN}} = 4.501 \, \text{Å}$, hardness $H \sim 21$ GPa, and melting point $T_m \sim 2600 \, ^\circ\text{C}$.[8, 17, 24, 44, 58, 59, 62] A very small mismatch in the lattice constants between ScN and c-GaN suggests the interesting possibility of forming either ScN/GaN heterojunctions or ScGaN alloys.[7, 41, 42] The rocksalt structure of ScN is attributed to the bonding between Sc and N being partially ionic.[63] Early theoretical work reported that ScN had a semimetallic electronic structure.[18, 64, 65] However, new theoretical work concludes that ScN is instead a semiconductor with a direct optical transition at the X point between 2 and 2.9 eV. An indirect transition from $\Gamma \rightarrow X$ below the direct one is also expected in the range 0.9-1.6 eV.[20, 21, 22] Experimental reports have determined that a direct transition lies in the range 2.1-2.4 eV.[6, 7, 8, 10, 17, 44]
6.2. introduction

The possible indirect transition and other issues regarding ScN have been difficult to address experimentally due to various complications in growing the films, such as the difficulty to grow ScN having a specific crystalline orientation, and the difficulty to obtain a film having a smooth surface. Bai et al. grew ScN using a variety of growth methods, such as reactive sputtering from a Sc-metal target in a pure nitrogen atmosphere. This resulted in ScN films having various crystal orientations, depending on the growth method used and the type of substrate.[17] Gall et al. showed that the growth of ScN on MgO(001) using ultra-high-vacuum reactive magnetron sputter deposition resulted in an epitaxial single crystal ScN(001) film if a specific substrate bias or a TiN buffer layer was applied; otherwise, ScN(111) would also form.[9, 8, 16]

Shortly after this, Al-Brithen et al. showed that the growth of ScN on MgO(001) using rf MBE resulted in an epitaxial film having very high crystalline quality, single (001) orientation, and atomically smooth surface terraces.[24] The stoichiometry of the ScN(001) grown film using rf MBE was later shown to depend on the flux ratio, $J_{Sc}/J_N$, during growth.[44] If the growth is under scandium rich conditions, the bulk Sc/N ratio (measured as high as 1.00:0.83) approximately equals the flux ratio $J_{Sc}/J_N$ during growth, but the rocksalt structure is maintained, resulting in growth with nitrogen vacancies.[44, 58] If the growth is under nitrogen rich conditions, N-vacancies are suppressed and the material is close to stoichiometric (1:1).

In prior work, Al-Brithen et al. succeeded in imaging one of the surface atom sublattices of ScN(001) $1\times1$ but did not determine if those atoms were Sc or N.[24] Subsequent theoretical work by Takeuchi et al. and also Stampfl et al. found that
the energetically most stable surface structure of ScN(001) in N-rich conditions is the ideal, bulk-like surface; they also presented simulated STM images showing Sc and N atoms at different biases.[28, 29] To compare with experiments, however, it is essential to know the actual surface bandgap and Fermi level position. Therefore, it remains to be shown experimentally what atom on the ideal ScN(001) 1×1 surface is imaged in STM and how that relates to the electronic structure.

In this chapter, in-situ ultra-high vacuum (UHV) STM and scanning tunneling spectroscopy (STS) are combined with optical absorption spectroscopy to study the surface and bulk electronic structure of ScN(001), identify the surface atoms imaged in STM as a function of sample bias voltage. As well, we address the indirect bandgap issue.

6.3 Experimental Procedure

ScN layers are grown by molecular beam epitaxy (MBE) on MgO(001), using a radio frequency (RF) plasma source for nitrogen and an effusion cell for scandium. Details of the MBE growth setup and substrate cleaning procedure are described in chapter 3. ScN growth takes place with the substrate set at ~ 800 °C and the base pressure of nitrogen and plasma source power set at 9 × 10^{-6} torr and 500 Watts, respectively.

The growth starts when the scandium shutter is opened. Scandium (nitrogen) rich growth conditions occur when the Sc flux, \( J_{\text{Sc}} \), (N flux, \( J_N \)) exceeds the N flux, \( J_N(\text{Sc flux, } J_{\text{Sc}}).[44, 58] \) The average scandium flux \( J_{\text{Sc}} \) is determined by measuring
the final film thickness using a thickness profilometer; from this, and by knowing the growth time and Sc atomic density in ScN, the Sc flux $J_{\text{Sc}}$ is calculated. The effective N flux is determined to be $J_N \sim 3.6 \times 10^{14}$ cm$^{-2}$ s$^{-1}$ in our system for the stated conditions.[58, 44] The flux ratio ($J_{\text{Sc}}/J_N$) can be adjusted by changing the scandium effusion cell temperature.

The growth is monitored in real time using RHEED. Following growth, samples are transferred under vacuum to the scanning tunneling microscope chamber for in-situ surface analysis. STM tips are prepared by electrochemical etching in a NaOH solution followed by dipping in H$_2$O to remove residual hydroxides. After loading into the STM chamber, electron beam heating using a tip bias of +160 V and an emission current of $\sim 1.5$ mA for a period of about 20 minutes is used to clean the tips prior to use.

After removing the sample from the chamber, the metal backing of the substrate is removed, leaving just the ScN film on the MgO (bandgap $\sim 8$ eV) substrate. Optical analysis was performed using a Varian CARY UV-VIS-NIR two-beam spectrometer with a wavelength range from 176 to 3300 nm. Transmission spectra were obtained by placing the sample directly in the beam while reflection data was acquired in a W-geometry, using an Al-mirror which was calibrated with the identical beam path and measurement settings as used for the reflection measurements. The overall uncertainty in the reflection and transmission spectra is less than 2% and is primarily due to sample positioning errors and diffuse scattering from the back surface of the MgO substrate.
6.4 Results and Discussion

6.4.1 Scanning Tunneling Microscopy of Ideal, Bulk-like ScN(001) 1×1

It is widely known that, in the case of covalent compound semiconductor surfaces, the anion is imaged at negative sample biases (filled states) while the cation is imaged at positive sample biases (empty states). This principle of atom selective imaging was demonstrated conclusively by Feenstra et al. in the case of the GaAs(110) surface.[66] Following this rule in the present case of ScN(001) 1×1, the majority band of states in the valence band (VB) should be the N 2p states, while the majority band of states in the conduction band (CB) should be the Sc 3d states. However, as has been shown by several recent theoretical works, since the bonding is partially ionic, there is a minority band of Sc 3d states in the VB and also a minority band of N 2p states in the CB.[20, 22, 28] For example, the N atoms have also some empty character, and the Sc atoms have also some filled character. Since for our sample the Fermi level is close the CB (as will be shown by the STS results), STM images are expected to show mainly the cations (Sc atoms) but possibly also the anions (N atoms).

We note that density functional calculations predict that the N atoms of this surface are buckled upward by $\sim 0.02$ Å compared to the Sc atoms, resulting in a relaxed but unreconstructed surface.[28, 29] However, 0.02 Å is a small difference,
and electronic effects may totally dominate geometrical effects in STM images. The proof of the chemical identification will therefore require the results of STS.

6.4.1.1 Bias Dependence of Sublattice Protrusions

Figure 6.1 shows STM images of the ScN(001) 1×1 surface grown under N-rich conditions as a function of sample bias voltage. All images belong to the same terrace, but not exactly the same area due to thermal drift effects.

As seen in Figs. 6.1(a)-(h), the images are mainly composed of a square array of prominent protrusions which are clear at all displayed sample biases, from $V_S = -0.8$ V to $+0.6$ V. The spacing of these protrusions is $\sim 3.2$ Å, corresponding to the spacing along [110] between atoms of the same type on a bulk-like ScN(001) 1×1 surface. The minimum observed step height between adjacent terraces was previously determined to agree with the ScN(001) interplanar spacing.[24] Upon crossing a single monolayer height step, the atomic rows shift by one-half the row spacing, as expected if the prominent atomic row directions are along $(\frac{1}{2}, \frac{1}{2}, 0)$, as shown in Fig. 6.1(a). It will be shown below that these most prominent protrusions correspond to the Sc atoms.

As $V_S$ increases above $\sim +0.3$ V, Figs. 6.1(g) and 6.1(h), within the same image a second array of smaller protrusions begins to appear in addition to the primary protrusions. These smaller protrusions, mainly visible in Fig. 6.1(h) at $V_S = +0.6$ V, clearly correspond to the sublattice opposite to that of the prominent protrusions, and it will be shown below that these lesser protrusions correspond to the N atoms.
Figure 6.1: STM images of a ScN(001) 1×1 surface grown under N-rich conditions acquired at different sample biases. The gray scale ranges are (a) 0.7, (b) 0.35, (c) 0.38, (d) 0.38, (e) 0.38, (f) 0.27, (g) 0.31, and (h) 0.31 Å, respectively. The tunneling current was set at 0.1 nA. Crosses are marked at the centers of the S features.
6.4. Results and Discussion

At higher sample biases $V_S > +0.6$ V, the atomic corrugation of the STM images (not shown) becomes increasingly weaker due to increased tip-sample separation.

At $V_S = -0.8$ V, we observe the appearance of several bright spots in the STM image, denoted S, which are centered on the smaller protrusion sublattice (N) sites, as seen in Fig. 6.1(a); these localized features extend over approximately 4 neighboring prominent protrusion (Sc) sites. We have not seen these features at other sample biases. One possibility is that they are O or CO adsorbates which attach to the four neighboring Sc atoms. In Fig. 6.1(a) we count 6 S sites out of about 340 surface sublattice sites, so the coverage is $\sim 1.8\%$.

As seen in Fig. 6.2, simultaneous dual-bias imaging was also performed on an identical surface area at bias voltages of $V_S = +0.1$ V [Fig. 6.2(a)] and $V_S = +0.5$ V [Fig. 6.2(b)] with tunneling current set at $I_T = 0.1$ nA. This ScN(001) surface was prepared under N-rich conditions, similarly to that of Fig. 6.1. At $V_S = +0.1$ V, the sublattice of prominent atomic (Sc) protrusions, whose row directions are along $h_{\bar{1}10}$, is clearly visible. At $V_S = +0.5$ V, these prominent atomic (Sc) protrusions appear reduced in size compared to those at $+0.1$ V, likely due to the increased tip-sample separation, while the opposite sublattice of smaller (N) protrusions appears clearly. The Sc-N-Sc-N chain directions of the rocksalt structure are along $\langle 100 \rangle$.

Dual-bias images acquired at $V_S = -0.3$ V and $+0.3$ V are also displayed in Figs. 6.2(c) and 6.2(d), respectively. Here it is clearly seen that there is no shift in the position of the prominent atomic protrusion between these two biases. These main
6.4. Results and Discussion

Figure 6.2: Dual bias STM images of ScN(001) $1\times1$ surface grown under N-rich conditions. a) $V_S = +0.1$ V; b) $V_S = +0.5$ V; c) $V_S = -0.3$ V; (d) $V_S = +0.3$ V. Tunneling currents for (a)-(d) are 0.1 nA. The gray scale ranges are 0.28 Å, 0.13 Å, 0.32 Å, and 0.23 Å for (a)-(d), respectively.

protrusions correspond to the Sc atomic sites. At +0.3 V in Fig. 6.2(d), the N-sites are faintly visible.

6.4.1.2 Charge Accumulation

It is also noticed in most of the images of Fig. 6.1(a) some areas which are brighter compared to the surrounding area. These bright areas are seen at all displayed sample biases, several of which are labeled in Fig. 6.1 as LTD (long-range topographic distortion). Similar effects have been seen in STM images of GaAs(110) surfaces by
Strosco et al., Zheng et al., and Chao et al. in the case of n-type, n-type, and p-type samples, respectively.[67, 68, 69] It has been shown that for GaAs(110) surfaces that these LTD’s, as they have been referred to, are due to the presence of either ionized dopant impurities within the top 5 or 6 atomic layers[68, 69] or to charged surface adsorbates.[67] Zheng et al. and Chao et al. even categorized the apparent brightness according to which subsurface layer the ionized dopant occupies.[68, 69]

In the present case of rocksalt ScN(001), also a non-polar, relaxed surface, we give a similar interpretation to the observed bright patches. It will be shown (below) from the spectroscopy measurements that the sample is highly n-type ($4.8 \times 10^{18} \text{ cm}^{-3}$). This high n-type conductivity is attributed to O$_N$’s and/or nitrogen vacancies (V$_N$’s), both of which can act as donors in ScN.[21, 42, 44, 70] Although for N-rich growth, Stampfl et al. found that the V$_N$ formation energy for N-rich conditions is very high (4.32 eV),[29] growth kinetic limitations might still result in some V$_N$’s. Moreover, O$_N$’s could occur; one source of oxygen could be diffusion from the substrate, MgO. Another possibility could be trace oxygen impurities from the sources. Whether from V$_N$’s or O$_N$’s, the bright patches seen in Fig. 6.1 are attributed to the effects of ionized subsurface donors. Since these ionized donors are positively charged, they attract to their vicinity free conduction electrons, resulting in local accumulation of electron density which appears in the STM images as the bright patches. The spectroscopy (next section) suggests that this accumulation is accompanied by a downward band bending of a few tenths of an eV.
6.4. Results and Discussion

6.4.2 Scanning Tunneling Spectroscopy of ScN(001) Surfaces

In this section, the tunneling spectroscopy of ScN(001) surfaces acquired under UHV conditions is discussed, first for the N-rich case. This is followed by a discussion of dopant-induced band bending, then by the identification of the surface atoms seen in STM images for the ideal 1×1 surface. After that, the tunneling spectroscopy is discussed for the N-deficient surface. In Figs. 6.3 and 6.4, the upper panels [Figs. 3(a) and 4(a)] display measured current vs. voltage, (I-V) curves while the lower panels [Figs. 6.3(b) and 6.4(b)] display the normalized conductance, \( \frac{dI/dV}{I/V} \) vs. voltage, (NC-V) curves, numerically calculated from the I-V data of the upper panels. Normalized conductance (NC) is in general well known to be proportional to the surface local density of states (LDOS), and here we calculate it following the method described by Feenstra.[71] The bar over the I/V indicates broadened I/V values are used to avoid divergences near the band edges.[71] The horizontal dashed lines in the NC-V panels indicate where NC equals zero and unity. All sets of spectra were acquired using tungsten tips with a fixed tip-sample separation for each spectrum. Graphs 3(a) and 4(a) are the results of averaging over 16 and 10 STS spectra, respectively.

6.4.2.1 Tunneling Spectroscopy of Ideal, Bulk-like ScN(001) 1×1 Surface

Figure 6.3 shows the I-V and NC-V curves for a stoichiometric ScN(001) surface grown under N-rich conditions having an atomically well-ordered surface structure similar to the ones shown in Figs. 6.1 and 6.2. In Fig. 6.3(a), the current on the negative sample
bias side slowly becomes more negative over a range of about one volt and then turns sharply down, whereas on the positive sample bias side it increases exponentially from near zero volts. Since positive sample bias corresponds to electrons tunneling into the sample, thus into the empty or conduction band (CB) states, the I-V behavior is consistent with a semiconductor where the Fermi level \( E_F \) is close to the CB. This indicates that the sample is highly \( n \)-type \( (n = 4.8 \times 10^{18} \text{ cm}^{-3}) \), see optical absorption analysis, below), and it has important consequences for determining which atoms (Sc or N) are imaged in STM.

As seen in Fig. 6.3(b), the NC is close to zero at its minimum (point A which occurs near \( V_S = -0.1 \text{ V} \)), which suggests that this surface is a semiconductor (Note: in absence of band bending this minimum would occur at \( E_F \)). As \( V_S \) increases over the range -0.1 to +0.75 V [point A to point E], the NC increases approximately linearly with \( V_S \). Such linear behavior is in excellent agreement with bulk calculations which find a linearly increasing DOS with energy for the Sc 3d states in the lower part of the CB near the X point.[20] Also, surface calculations show the same linear behavior for the Sc 3d 1×1 surface LDOS.[28] Thus, the linear relation of the NC-V curve in the bias range from \( \sim -0.1 \text{ V} \) to +0.75 V is attributed to the Sc 3d states with the conduction band minimum (CBM) at the X-point 0.1 eV below \( E_F \).

At the point E \( (V_S = +0.7 \text{ V}) \), there is another turn-on leading to the peak C2. We associate this peak with a Sc derived surface state (actually a surface resonance since it lies within the bulk CB).
Figure 6.3: Averaged tunneling spectroscopy results for the ideal, bulk-like ScN(001) surface grown under N-rich conditions: (a) current vs. voltage; (b) normalized conductivity vs. voltage. Inset is a band diagram showing Fermi level position relative to conduction band and band bending near the surface.
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As $V_S$ decreases from -0.1 V, we find a hump at the point D. Since the position of this D feature with respect to the CB edge varies with position on the surface, it is evidently not an intrinsic ScN state. While it could be an extrinsic state, similar features have been seen by Feenstra for the clean, non-polar surfaces of several III-V semiconductors.[71] In those cases of $n$-type conductivity, the "dopant-induced" features are due to electrons tunneling out of filled states near the bottom of the CB into empty states of the tip. This tunneling occurs even for very small negative sample biases, giving the appearance of a very small energy gap. Feenstra reported that observation of the dopant-induced component is an indicator of high surface quality.[71] In the case of the non-polar ScN(001) 1×1 surface which is heavily $n$-type, substantial dopant-induced tunneling is possible. The D feature can therefore be attributed to this effect.

At $V_S \sim -1.0$ V in Fig. 6.3(b), a strong onset appears at the point B. In other sets of data (not shown), while the position of the CBM varies by 0.1-0.2 eV, we find that the voltage difference from point A to point B is constant, indicating an intrinsic ScN bandgap with the point B at the valence band maximum (VBM). Therefore, we find an energy gap at the surface $\Delta E_{g,\text{min}} = e(V_A-V_B) \sim 0.9$ eV. The value of $\Delta E_{g,\text{min}}$ is much smaller than the measured direct gap of ScN (2.1-2.4 eV)[6, 7, 8, 10, 17, 44]; however, it is within the range of the predicted indirect gap for ScN (0.9–1.6 eV)[20, 21, 22] suggesting that the point B corresponds to the theoretically predicted VBM at the $\Gamma$ point. Below the B onset lies a peak at $C_1$. This peak can be interpreted as a
N derived surface state (surface resonance). For Fig. 6.3, the data range does not extend far enough to reach the onset of the VBM at the X point.

6.4.2.2 Origin of Long-Range Topographic Distortion: Band Bending on ScN(001)

Spectroscopy from different surface areas shows that the Sc 3d states extend below E_F by 0.1-0.3 eV. One possible explanation is that the Sc 3d surface LDOS is shifted to lower energies compared to the bulk. Yet, according to Takeuchi et al., the surface LDOS is very similar to that of the bulk, and surface relaxation results in only a small energy gain of 0.03 eV/1×1 cell compared to the non-relaxed surface.\cite{28} Moreover, Stampfl et al.’s calculations indicate that the ScN(001) surface has no states inside the band gap.\cite{29}

Estimating from the theoretical electron band effective mass $m^* = 0.281 m_e$,\cite{72} and experimental dielectric constant $\varepsilon \sim 7.2$,\cite{20} we calculate a donor ionization energy of approximately 74 meV using the hydrogenic model. From the results of our optical studies (below) we get a carrier concentration of $4.8 \times 10^{18}$ cm$^{-3}$, but we do not know the (unintentional) dopant concentration. However, since the material is high $n$-type, $E_F$ should lie close to the CB in the bulk, as indicated schematically in the inset of Fig. 6.3(a). Moreover, the absorption spectrum (discussed below) indicates that the material is semiconducting, so the Fermi level should lie below the CB edge in the bulk. The STS spectroscopy on the other hand shows that $E_F$ at the surface
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is 100-300 meV above the CBM. This can be explained by a downward band bending at the surface.

A downward band bending in the vicinity of the bright LTD’s seen in Fig. 6.1 is also expected. These LTD’s, corresponding to electron accumulation, can be explained as due to a lowering of the band edge caused by the Coulomb field of the subsurface ionized donors, as was explained for the case of $n$-type GaAs(110).[68] We also find that the amount of band bending varies from spectrum to spectrum as it should since it depends on where on the surface the spectrum was acquired. We further note that observing the LTD’s as raised features at both positive and negative sample biases is due to $E_F$ being inside the CB at the surface in the vicinity of those features. For either positive or negative sample bias, the greater band bending near the LTD regions results in a larger integrated LDOS compared to the surrounding area. For a constant current image, this results in the tip retracting slightly, causing the bright areas in Fig. 6.1.

6.4.2.3 Identification of Sublattice Atoms for Ideal, Bulk-like ScN(001) 1×1 Surface

The STM image is determined by the integral over those states between $E_F$ and $E_F + e \times \text{(applied bias voltage)}$. Since for the ideal 1×1 surface with high $n$-type doping there are Sc 3d states both above and below $E_F$ as has been shown, for any small sample bias either positive or negative, the tunneling current will contain a large contribution from the Sc 3d states. Even for bias voltages $<-0.1$ V, the
tunneling current will still include the Sc 3d contribution, and only the dopant induced contribution begins to be added (states labeled D in Fig. 6.3). Thus, within the sample bias voltage range -0.8 to +0.6 V, the primary protrusions must be the Sc atoms.

At sufficient positive sample bias (> +0.3 V), the N sublattice begins to appear [see Figs. 6.1(h) and 6.2(b)]. This indicates that N derived states exist within the Sc 3d CB, as has been predicted by Takeuchi et al. who also showed both Sc and N atoms in their gray plots of the LDOS at $V_S = +1.0$ V.[28]

According to Takeuchi et al.’s LDOS calculations, the upper part of the VB is composed primarily of N 2p derived states but also a small contribution of Sc 3d states. Those authors therefore showed gray plots at negative sample bias, finding both Sc and N atoms at $V_S \sim -0.5$ V and primarily N atoms at $V_S \sim -1.0$ V. But this was assuming almost no surface gap (underestimated). As seen in the NC-V spectrum of Figs. 6.3(b), the N 2p states only begin to appear for $V_S < -1.0$ V. In chapter 3,[24] we reported that only a small relative shift, much less than the expected $a/2$, was observed in dual bias images recorded at sample biases of +1.0 V and -1.0 V. This is now understood since the Sc 3d states are dominant for our $n$-type sample over the range -1.0 to +1.0 V.

Stampfl et al. also made simulated STM images for sample bias voltages of -2.0 V and +2.0 V, which showed N atoms and Sc atoms, respectively, but not both types of atoms at the same bias. They also found a surface gap using a screened-exchange LDA approach, with surface states outside the bulk gap. We cannot make direct
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comparison to their simulated images since we did not achieve atomic resolution images at such large magnitudes of voltage.

6.4.2.4 Tunneling Spectroscopy of N-deficient ScN(001) Surface

The N-deficient ScN(001) surface is prepared by growth under Sc-rich conditions. The resulting bulk structure is composed of a complete Sc sublattice but a N sublattice having $V_N$’s in proportion to the excess Sc flux during growth.[44] The crystal structure remains rocksalt, and the bulk $V_N$’s make the film highly $n$-type with carrier densities on the order of $10^{21} \text{ cm}^{-3}$.[44] Concerning the surface from calculations, Stampf et al. found that a $2 \times 1$ N-vacancy structure was energetically most favorable under Sc-rich conditions; also the Sc-terminated structure was not too much higher in energy.[29] There are many states in the bulk gap, making the surface metallic. Takeuchi et al. also found a metallic surface structure with new surface states close to $E_F$.

Our STM images of the Sc-rich grown surface show qualitative good agreement with the calculations, although no well-ordered surface structure is observed; however, smooth terraces and single atomic height steps are clearly visible.[58] This surface also shows a clearly lower surface adatom diffusion barrier (by 0.26 eV) compared to the stoichiometric surface, which is attributed to the weaker Sc-Sc bonding (metallic) compared to Sc-N bonding (covalent/ionic).[58, 44] It was concluded that this surface contains an excess of Sc metal, with up to 100% N vacancies.[58]
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The main advantage of doing tunneling spectroscopy on this surface is that, because of the Sc-rich (N-deficient) surface structure, the N derived surface state should be absent. This may allow to isolate the bulk projected valence band states. Figure 6.4 shows the tunneling spectroscopy results for ScN(001) grown under Sc-rich conditions. Figure 6.4(a) shows that the current increases exponentially with positive sample voltage from near the Fermi level. Figure 6.4(b) shows that the derived normalized conductance has the expected CB linear relation with voltage starting at $V_S = 0$ V up to at least $\pm 0.4$ V, similar to the stoichiometric case [Fig. 6.3(b)]. The value of the NC at $E_F$ is close to unity, consistent with a metallic surface. The peak near $V_S = +0.7$ V is attributed to a Sc derived surface peak.

The turn-on of states near the Fermi level indicates that the X point CB onset is near $E_F$, as indicated in the band diagram shown in the inset of Fig. 6.4. The valley of states between $V_S = 0$ and -0.9 V is attributed to metallic or defect states within the bandgap. It can also be noticed that the N derived surface state peak $C_1$ seen for the stoichiometric surface [Fig. 6.3(b)] is absent for the N-deficient surface [Fig. 6.4(b)]. A band onset, consistent with the theoretically predicted VBM at the $\Gamma$-point, is observed at $V_S \sim -0.95$ V, and therefore, we find a bandgap $E_g$ of $\sim 0.95$ eV. Another band onset, consistent with the theoretically predicted VBM at the X point, is observed near $V_S \sim -2.2$ V. With the CBM near 0 V, the energy difference between the onset and the CBM is consistent with reported values for the direct transition at the X point in the range 2.1-2.4 eV and in excellent agreement with our own measured value of 2.15 eV.[6, 7, 8, 10, 17, 28, 29, 44]
Figure 6.4: Averaged tunneling spectroscopy results for the Sc-rich ScN(001) surface grown under Sc-rich conditions: (a) current vs. voltage; (b) normalized conductivity vs. voltage. Inset is a band diagram showing Fermi level position relative to conduction band.
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6.4.3 Optical Absorption Measurement

The primary goal of the optical measurements presented here is to find evidence for the indirect gap of ScN, predicted to be between 0.9 and 1.6 eV.\cite{20, 21, 22} This has not been attempted previously primarily because the optical absorption due to an indirect transition is several orders of magnitudes smaller than that of the direct transition and it is therefore hard to observe experimentally. In order to increase the measurement accuracy in the present investigation, in particular in the low-absorption wavelength range, we have grown a rather thick epitaxial ScN layer on MgO(001) with a thickness of 2.5 $\mu$m.

Fig. 6.5(a) shows the measured transmission $T(h\nu)$ and reflection $R(h\nu)$ spectra in the energy range from 0.38 to 3 eV. The oscillation in the spectra are interference fringes due to multiple reflections from the layer surface and the layer-substrate interface and indicate considerable transparency in the interval between 0.5 and 2 eV. This is perfectly consistent with the transmission data, showing a steep increase of $T(h\nu)$ around 0.5 eV and a steep decrease around 2 eV, which can be accounted for by the free carrier absorption at $h\nu < 0.5$ eV and direct interband transitions with an onset energy of 2.15 eV, respectively.\cite{44} The reflectivity increases slightly as a function of photon energy in the transparent wavelength range and exhibits a broad peak around 2.2 eV. This is due to a small increase in the refractive index below the direct bandgap and a resonance just above the onset of interband transitions,
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as expected from basic oscillator theory and in agreement with previously reported optical properties of ScN.[20]

The transmission and reflection spectra were fit simultaneously using an iterative procedure which accounts for an infinite set of multiple reflections on layer surface, layer-substrate interface, and substrate back-surface. The optical properties of the MgO substrate were taken from *Handbook of Optical Constants of Solids II.*[73] Good convergence of the fit was achieved by calculating the reflection coefficients in the transparent range, 0.4 - 2.1 eV, without accounting for the extinction coefficient k. That is, during the iterative fitting procedure the reflection coefficients at the surfaces and interfaces were calculated using a constant k = 0, while a variable k ≥ 0 was used to calculate the absorption within the layer. With this approach, the extinction coefficient and consequently also the absorption coefficient are determined solely from the intensity loss during the travel of the light through the bulk of the layer and are only to second order affected by possible surface irregularities including surface roughness or oxides. This method adds a small error of less than 0.5% to the determination of the absorption coefficient in the transparent region (hν < 2 eV), but removes all possible systematic errors due to a wrong treatment of surface effects. The fit provides values for the refractive index of ScN in the transparent range of n = 2.7-2.9, in good agreement with the previously reported range from 2.6 to 2.8.[20]

Fig. 6.5(b) shows the obtained absorption coefficient α as a function of photon energy hν in the energy range 0.38 < hν < 2.5 eV. α decreases with increasing photon energy down to a minimum of 8× 10² cm⁻¹ at 0.85 eV. It then increases, first slowly
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Figure 6.5: (a) Reflection and transmission coefficients $R$ and $T$ as a function of photon energy $h\nu$ acquired for a 2.5 $\mu$m thick ScN film grown under N-rich conditions; (b) corresponding, calculated absorption coefficient $\alpha$ as a function of photon energy $h\nu$. Dotted line is the fitted Drude free electron model curve, and inset shows square root of $(\alpha - \alpha_{Drude})$ versus $h\nu$[Measurements by Daniel Gall].
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and then steeply, as the photon energy approaches the direct transition at 2.15 eV and reaches $\sim 10^5 \text{ cm}^{-1}$ (outside the shown range) at 2.2 eV. The absorption minimum, $8 \times 10^2 \text{ cm}^{-1}$, is 1-2 orders of magnitudes lower than previously published values ranging from $6 \times 10^3 \text{ cm}^{-1}$ to $3 \times 10^4 \text{ cm}^{-1}$ indicating the high crystalline quality of the samples used in our study.\cite{6, 20, 44, 64} More importantly, by acquiring optical transmission data from a rather thick layer, as described above, the accuracy of the present data in the low-absorption regime is considerably higher.

The absorption in the low photon energy range ($h\nu < 0.5$ eV) is primarily due to intraband transitions, i.e. absorption from free carriers in the conduction band. The optical properties in this energy range can be described by the Drude model, providing the following expression for the complex dielectric function $\varepsilon(\omega)$:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)}$$  \hspace{1cm} (6.1)

Here $\omega_p$ is the plasma frequency and $\gamma = 1/\tau$ is the Drude damping term with $\tau$ being the free electron relaxation time. $\varepsilon_{\infty}$ is a constant accounting for all interband transitions as well as the core electrons. The dashed line in Fig. 6.5(b) is obtained by fitting the experimental data for $h\nu < 0.75$ eV with the expression in Eq. 6.1. The fit provides a value for plasma frequency of $2.9 \times 10^{14} \text{ s}^{-1}$, which can be used to determine the free carrier concentration $N$ using

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m^*}.$$  \hspace{1cm} (6.2)
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Using an optical effective mass \( m^* \) equal to 0.178\( m_e \), results in a value for \( N \) of \( 4.8 \times 10^{18} \text{cm}^{-3} \). We attribute the charge carriers to electrons in the conduction band due to \( V_N \)’s or \( O_N \)’s which act as donors. The carrier relaxation time, also obtained from the Drude-fit, is \( 7.7 \times 10^{-15} \text{s} \). This gives, using a density of states effective mass \( m^* = 0.281m_e \), a value for the room-temperature mobility = 48 \( \text{cm}^2/\text{Vs} \).

In order to investigate interband transitions and detect a possible indirect gap, we subtract the absorption \( \alpha_D \) due to the Drude free carriers (dashed line in Fig. 6.5(b)) from the measured absorption \( \alpha \). This difference corresponds to the absorption \( \alpha_t \) due to interband transitions. The square root of the absorption due to an indirect transition is expected to increase linearly with photon energy. We therefore plot in the inset of Fig. 6.5(b) \( \sqrt{\alpha_t} \) vs \( h\nu \). \( \alpha_t \) is zero for \( h\nu = 0.8 \text{eV} \) and increases above this value, indicating an onset for interband transitions. The \( \sqrt{\alpha_t} \) plot exhibits a linear range between 0.9 to 1.7 eV consistent with an indirect transition. The extrapolation to zero intensity occurs at about 0.6 eV. The exact onset energy for the indirect transition is strongly dependent on the fitting parameters of the Drude-model, and therefore contains a relatively large uncertainty also due to possible contributions of mid-bandgap defect states. Nevertheless, the optical absorption data indicates that there is an indirect transition within the interval of 0.6-1.1 eV. This is consistent with our STS results showing that the minimum gap in ScN is in the range 0.9-0.95 eV.
6.5 Conclusions

It has been experimentally shown that both atoms, Sc and N, of ScN(001) grown smoothly under N-rich conditions are resolved using STM. Based on scanning tunneling spectroscopy results, it is determined that the most prominent atom observed at low bias voltages (both positive and negative) for highly $n$-type ScN(001) 1×1 is the Sc atom due to the Fermi level at the surface being inside the Sc 3d band. The N atom also appears at positive sample biases due to a minority band of N 2p states in the CB. We also observe long range topographic distortions at the surface which are attributed to the effect of charge accumulation around sub-surface positively ionized dopants.

STS of the stoichiometric ScN films also shows a bandgap of $\sim 0.9$ eV, while STS of N-deficient ScN films shows a similar bandgap of $\sim 0.95$ eV as well as the second onset at $\sim 2.2$ eV. The ideal 1×1 surface is concluded to be semiconducting although the presence of additional conductance, which is attributed to the high density of electrons in the conduction band, makes the apparent gap very small. The N-deficient surface, on the other hand, is metallic. Optical absorption results for a 2.5 $\mu$m thick ScN film grown under N-rich conditions indicate indirect absorption in the range 0.9 to 1.7 eV. These results give new experimental evidence for an indirect gap in ScN of $0.9 \pm 0.1$ eV and the direct transition at 2.15 eV.
Chapter 7

Incorporation of Manganese into Semiconducting ScN Using Radio Frequency Molecular Beam Epitaxy

7.1 Abstract

The alloy incorporation of manganese into semiconducting ScN, using radio frequency molecular beam epitaxy, has been investigated. The x-ray diffraction and reflection high energy electron diffraction measurements show the face-centered tetragonal rocksalt type of the crystal structure with Sc and Mn atoms in the cation lattice sites and the N atoms in the anion lattice sites. In addition to the alloy incorporation, which is clear from the positions of the diffraction peaks, AFM images show that the surface of the alloy grown at $T_S \leq 518 \, ^\circ\text{C}$ contains dot-like features, indicating some surface accumulation. The dot aerial density is found to reduce as the growth temperature increases, whereas the alloy incorporation increases at 518 °C. This behavior is suggestive of a thermally-activated process, and it is well explained by an Arrhenius
law, giving an activation energy (diffusion barrier) of 0.67 eV. Moreover, increasing the growth temperature to 612 °C leads to an increased desorption-rate, resulting in small Mn incorporation. It has been found that the growth is nearly optimized at \( T_S = 518 \) °C for high Mn incorporation, smooth growth, and small accumulate density. The alloy is found to have lattice parameters which depend on the Mn/(Mn+Sc) bulk ratio. The alloy lattice constants follow Vegard’s law depending on the Mn bulk fraction and the lattice constants of ScN and \( \theta \)-phase MnN. The Mn incorporation and Mn incorporation coefficient for films grown at \( T_S = 518 \) °C increase as the Mn/(Mn+Sc) flux ratio increases.

### 7.2 Introduction

It is currently of great interest to dope III-V semiconductors, such as GaAs and GaN, with transition metal magnetic dopants, such as Mn and Cr, for the purpose of forming a dilute magnetic semiconductor. The GaN system in particular became of high interest due to the prediction of a \( T_C \) in MnGaN above 300 K.[74] However, transition metals, including Mn and Cr, commonly adopt octahedral bonding configurations with N rather than tetrahedral.[56, 57, 61] This dissimilarity may contribute to problems with growth, including difficulties with incorporation and also precipitation of Mn or Mn\(_x\)N\(_y\) phases in MnGaN. As a characteristic of the dissimilar bonding configurations (non-isocry stallinity) MnGaN does not clearly follow Vegard’s law.[75]
It is therefore of interest to find a semiconductor system which is octahedral and which may therefore be easily doped with Mn. One such possibility is ScN.

Transition metal nitrides (TMNs) such as ScN have been receiving a lot of interest in recent years for their unique physical properties including high hardness, high temperature stability, mechanical strength, off-stoichiometry, magnetic properties, and electronic transport properties that vary from semiconducting to metallic. [8, 9, 16, 20, 21, 22, 31, 44, 55, 56, 57, 58, 59, 60, 61, 76, 77, 78]

ScN itself is expected to have novel applications of its own. ScN stabilizes in a rocksalt structure, having octahedral bonding, with a lattice constant $a_{\text{ScN}}=4.503$ Å, hardness $H=21$ GPa, and melting point $T_m\approx 2600$ °C. Moreover, ScN exhibits an optical gap at $E_g \approx 2.15$ eV and a lower energy gap at $\sim 0.9$ eV.[6, 8, 17, 21, 22, 24, 41, 44, 52, 58, 59, 62] The smooth and epitaxial growth of ScN(001) on MgO(001) was achieved at temperature ($T_S$) of 800 °C by radio frequency molecular beam epitaxy (rf MBE).[24, 44, 58]

MnN forms a face-centered tetragonal (fct) structure exhibiting an anti-ferromagnetic behavior at room temperature.[56, 77] Yang et al. reported the growth of MnN using rf MBE at $T_S$ over the range of 250-450 °C, showing the lattice constants of this material to be $a_{\text{MnN}} = b_{\text{MnN}} = 4.22$ Å and $c_{\text{MnN}} = 4.12$ Å.[57] The reported reflection high electron energy diffraction (RHEED), by the same group, of MnN(001) grown at $T_S = 450$ °C indicates the growth is smooth.

It is well known for MBE growth that the growth temperature of the ternary alloys and the species flux ratios affect the incorporation, precipitation, and adatom
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desorption even in the case of an isocrystalline alloy system.[75, 79, 80] For example, for the case of doping GaN with Mg, increasing the growth temperature over the range 600-700 °C results in an exponential reduction of Mg incorporation.[81] As another example, incorporation of several percent Mn in GaAs must be done at low temperature to avoid precipitation of MnAs. In the case of GaMnAs a low growth temperature allows one to incorporate several percent of Mn, but usually a lot of interstitial Mn is present, i.e. not all Mn is incorporated for Ga. At higher growth temperature the maximum Mn content, before precipitation sets in, is lower, but usually interstitial Mn is avoided. There is clearly a balance of rates which takes place, which must include incident flux rate \( R_f \), incorporation rate \( R_i \), surface desorption rate \( R_d \), and surface accumulation rate \( R_a \). Atoms which diffuse on the surface can either incorporate in a lattice site, desorb from the surface, or accumulate on the surface. Incorporation into defect sites can also occur. Hence, the equation \( R_f = R_i + R_d + R_a \) holds. Clearly, it is necessary to determine the growth conditions for a given system which optimize the properties of interest. Therefore, it is important to investigate the structure of the bulk and the surface of the alloy as a function of those growth conditions in order to engineer the structural, magnetic, and electronic properties of the alloy.

In this chapter, we report the growth of MnScN on ScN(001)/MgO(001) by rf MBE. Since no study has been reported about this alloy, our study is mainly oriented towards the investigation of the structural properties and growth mechanisms. In the first section, the Mn incorporation and the crystalline symmetry are discussed,
as well as the surface smoothness, accumulation, and desorption as a function of the sample growth temperature ($T_S$). In the second section, alloy lattice parameters and Mn incorporation as a function of Mn/(Mn+Sc) flux ratio ($R$) are presented. Accordingly, the measured lattice constants of the alloy vs. Mn/(Mn+Sc) bulk ratio ($x$) are also presented. Moreover, optical absorption measurements as a function of $x$ are shown.

### 7.3 Experimental Procedure

MnScN layers are grown by rf MBE on ScN(001)/MgO(001), using a radio frequency plasma source for nitrogen and effusion cells for both scandium and manganese. MgO(001) substrates are first cleaned with solvents, then loaded into the MBE chamber and heated up to $\sim 1000$ °C for 30 min with nitrogen plasma applied.[24, 44]

Prior to the growth of MnScN, growth of a ScN(001) buffer layer, under N-rich conditions, on MgO(001) takes place with $T_S \sim 800$ °C and the base pressure of nitrogen and plasma source power set at $1.1 \times 10^{-5}$ torr and 500 Watt, respectively; the effective N flux for the stated conditions is $\sim 3.6 \times 10^{14}$ cm$^{-2}$ s$^{-1}$.[24, 44] The Sc flux, determined using a crystal thickness monitor, is $1.14 \times 10^{14}$ /cm$^2$sec, and the growth time of the buffer layer is 40-45 min.

After the growth of ScN(001)/MgO(001), $T_S$ is reduced to the growth temperature of MnScN. Having set $T_S$, both Sc and Mn shutters are opened, starting the growth of the MnScN alloy. Sc flux and nitrogen pressure and power are kept the same, as
in the buffer layer growth. Two types of growth parameter studies were performed. First, MnScN films were grown with the same Mn/(Mn+Sc) flux ratio (R= 19%), each having a different T_s. Second, MnScN films were grown at the same temperature (T_s = 518 °C), each using a different R. The growth time for both sets of the MnScN films is about 120 min, resulting in MnScN layer thicknesses in the range 1700-2000 Å.

The growth is monitored in real time using RHEED with electron energy = 20 keV. After taking the sample out of the chamber, x-ray diffraction (XRD) measurements, using Cu Kα x-rays, and atomic force microscopy (AFM) imaging are performed. Peak-fitting is used to determine the XRD peak positions and RHEED pattern streak spacings. The XRD, RHEED, and AFM results are employed to study the alloy crystal symmetry, surface smoothness and morphology, and alloy lattice constants.

7.4 Results and Discussion

7.4.1 MnScN Alloys Grown At Different Temperatures With The Same Mn/(Mn+Sc) Flux Ratio

Figure 7.1 shows the XRD spectrum of the MnScN film grown at T_s = 330 °C and the alloy peak position as a function of the growth temperature for R= 19%. In Fig. 7.1(a), three peaks are seen at 2θ = 39.98°, 40.56°, and 42.95°. The first and third peaks are attributed to ScN 002 and MgO 002, respectively, for the following
three reasons. First, their positions do not vary with the change of the growth parameters. Second, the peak intensities agree with the thickness of each film, small for the buffer layer ScN 002 and very high for the substrate MgO 002. Third, the corresponding lattice constants from their peak positions (4.512 Å for ScN and 4.213 Å for MgO) agree well with the known values of 4.503 Å and 4.213 Å, respectively (Note spectrum is calibrated to MgO 002).[6, 24, 44, 58] The middle peak has not been seen in ScN(001)/MgO(001) films which we have reported.[24, 44, 58] Consequently, the middle peak in Fig. 7.1(a), at 2θ = 40.56°, is attributed to the MnScN alloy.

Similar MnScN spectra have been observed for MnScN grown at T_s = 424 °C, 518 °C, and 612 °C. Since XRD of each film shows only one peak for the alloy (plus the higher orders, not shown), this indicates that MnScN forms a crystalline layer with 001 orientation. Variations of the alloy peak position corresponds to a variation of the lattice parameter for each alloy layer, and the difference of the lattice constants indicates different Mn incorporation.

Figure 7.1(b) shows the XRD peak position of the alloy, 2θ, as a function of T_s. What can be seen is that for the 2 lowest values of T_s, the position of the alloy peak (thus the alloy incorporation) is about the same. At T_s = 518 °C, the alloy peak is shifted further away from that of ScN 002, indicating a slight increase in alloy incorporation. Finally, at T_s = 612 °C, the alloy peak partially overlaps the ScN 002 peak, and thus the alloy incorporation is considerably reduced.

The symmetry of the alloy surface structures has been examined by RHEED. Figure 7.2 presents the RHEED patterns of MnScN grown at different temperatures.
Figure 7.1: a) XRD spectrum of MnScN on ScN(001)/MgO(001) grown at 330°C; b) The alloy MnScN observed XRD peak position as a function of the growth temperature.
The left and right panels show RHEED of the MnScN(001) acquired along [010] and [110] of ScN(001).

The patterns of all films show 4-fold $1 \times 1$ surface symmetry with no reconstruction. Moreover, the patterns of the MnScN(001) alloy are similar to the RHEED patterns of ScN(001),\cite{9, 24, 44} indicating the rocksalt type of the alloy surface unit cell. This means that the alloy has a fct crystal structure having $[010]_{MnScN} || [010]_{ScN}$ and $[110]_{MnScN} || [110]_{ScN}$. Therefore, the MnScN(001) alloy grows epitaxially on ScN(001).

The fact that the alloy lattice constants get smaller compared with ScN shows that the Mn atoms are not in defect sites; i.e. interstitial sites. Rather, they are on the Sc sites. Therefore, this suggests that in the MnScN films Mn and Sc atoms will be at the cation sites while the N atom is at the anion site of the lattice.

The rf MBE growth of ScN(001) under N-rich conditions requires a high growth temperature, $T_S = 800$ °C, in order to achieve a film with a smooth surface;\cite{24, 44} however, attaining 2-dimensional growth of fct MnN(001) can be achieved at $T_S = 450$ °C, as determined by RHEED.\cite{57} This indicates that adatoms on the MnN surface have smaller surface diffusion barrier comparing with adatoms on ScN(001). It is interesting that for the alloy, fairly streaky RHEED patterns are obtained at temperatures comparable to those used for MnN.

Although RHEED of all films, shown in Fig. 7.2, is generally streaky, spots and rings are observed. For the film grown at $T_S = 330$ °C, the RHEED patterns show segmented streaks and spots, which indicates some roughness on the surface. RHEED patterns of the film grown at $T_S = 424$ °C are streakier, exhibiting smaller spots and
Figure 7.2: RHEED patterns of MnScN films grown at different sample temperatures ($T_s$) acquired along both [010] and [110] directions of ScN(001).
some faint rings. The reduction of the spot size indicates improved surface smoothness although the rings are indicative of some polycrystalline structure existing on the surface (Note: This is only due to the surface accumulation, to be discussed). For the case of the growth at $T_S = 518 \, ^\circ C$, RHEED shows streakier patterns, and rings are hardly visible. Increasing the growth temperature to $T_S = 612 \, ^\circ C$, the surface of the MnScN shows only segmented streaks, indicating increased surface roughness.

In order to investigate the surface structure in real space, AFM imaging has been performed. Figure 7.3 shows AFM images of MnScN surfaces grown at different growth temperature. The size of each image is $5\mu m \times 5\mu m$.

In Fig. 7.3(a-c) the AFM images of the alloys show that the surface is covered with a certain density of sub-micrometer-sized dot-like structures. These features are suggestive of surface accumulation although their structural and chemical nature are not identified. Quantitatively, these features (in Fig. 7.3(a)) occupy a total volume of $1.3 \times 10^{10} \, \text{Å}^3/\mu \text{m}^2$ compared to the MnScN layer volume of $2 \times 10^{11} \, \text{Å}^3/\mu \text{m}^2$; namely, the accumulation volume is less than 7% of the total MnScN film volume. Interestingly, their aerial density ($\sigma$) is reduced considerably as the growth temperature is increased. This trend is consistent with the RHEED, which shows the most streaky pattern at 518$^\circ C$. The rings and spots in the RHEED patterns of Figs. 7.2(a) and 7.2(b) are therefore attributed to these dot-like features. For the case of growth at $T_S = 330 \, ^\circ C$, the dot density is very large, yet the size of each dot is small. At $T_S = 424 \, ^\circ C$, the dot density is smaller but the dot size is larger, resulting in the largest r.m.s. roughness of the 4 surfaces shown. For growth at $T_S = 518 \, ^\circ C$, the dot density
is reduced further, but the sizes are similar to the case of 424 °C. This is attributed to increased evaporation. Negligible dot density is observed for growth at \( T_S = 612 \) °C, but the surface shows an r.m.s. roughness of 9.9 Å, consistent with ScN(001) layers grown at low temperature.

This behavior is consistent with a thermally-activated process. For example, at low \( T_S \), the diffusion length and surface desorption are limited, which results in more numerous, but smaller dots (accumulates). At higher \( T_S \), the diffusion length is increased, leading to the formation of fewer, but large, dots (accumulates). The thermally-activated process of the surface diffusion is described by an Arrhenius law

\[
N = \omega_A e^{-E_B/k_B T},
\]

where \( N \) is the average number of hops per unit time interval, \( \omega_A \) is the atomic oscillation frequency (attempt frequency), and \( E_B \) is the surface diffusion barrier. The diffusion length \( L \) is proportional to the square root of \( N \). Accordingly, \( L \) increases as the temperature increases, leading to a reduction of the aerial dot density, an increase of the dot size, and an improvement in the surface smoothness. Smaller incorporation at \( T_S = 612 \) °C is really due to increased desorption.

Since the Mn incorporations in the MnScN alloys grown at \( T_S \leq 518 \) °C are similar to each other, as indicated by the XRD measurement, it suggests their surfaces have similar surface diffusion barriers (\( E_B \)). Assuming the aerial dot density (\( \sigma \)) is
7.4. Results and Discussion

Figure 7.3: AFM images of MnScN films as a function of the growth temperature. Each image size is 5\(\mu\)m\(\times\)5\(\mu\)m. The gray scale of the images shown in Fig. 7.3(a), 7.3(b), 7.3(c), and 7.3(d) are 135 Å, 150 Å, 80 Å, and 40 Å, respectively; moreover, the root mean square (r.m.s.) roughness of the surfaces are 40 Å, 50 Å, 15 Å, and 10 Å, respectively. Note: dark horizontal bands in the images are due to a line-by-line background subtraction.
7.4. Results and Discussion

inversely proportional to the square of the diffusion length, \( L^2 \), which is as mentioned proportional to the average number of hops per unit time (\( N \)), the following relation is obtained

\[
\ln(\sigma) = C + \frac{E_B}{k_B T_s},
\]

where \( C \) is a constant.

In Fig. 7.4, the natural logarithm of the number of accumulates per 100 \( \mu m^2 \) vs. the inverse of the growth temperature is plotted. As can be seen, the relation is quite linear. The slope of the fitted line is \( \frac{E_B}{k_B} \), according to Eq. 7.2. From this, the calculated diffusion barrier is about 0.67 eV. This value compares well with values of diffusion barriers on other nitride surfaces. For example, in the case of GaN, the diffusion barriers of the Ga adatom on N-terminated (Ga-terminated) GaN(0001) and GaN(0001) are 1.8 (0.4) and 1.0 (0.2) eV, respectively.[39] Therefore, the diffusion barrier of 0.67 eV for the non-polar surface, MnScN(001), has an intermediate value between the Ga- and N-terminated wurtzite GaN\{0001\} surfaces, which are polar.

Growth of MnScN(001) is approximately optimized at \( T_s = 518 ^\circ C \) to achieve high Mn incorporation, smooth surface, and low density of accumulates, as indicated by XRD, RHEED, and AFM, respectively. In the next section, the growth of MnScN at \( T_s = 518 ^\circ C \) with different R for each film is presented.
Figure 7.4: The natural logarithm of the dot aerial density as a function of the inverse growth temperature.
7.4. Results and Discussion

7.4.2 Epitaxial Growth Of MnScN With Different Mn/(Mn+Sc) Flux Ratios

Figure 7.5 shows the XRD spectra of MnScN grown on ScN(001) at $T_S = 518 \degree C$ with different R. The Mn/(Mn+Sc) flux ratios for films of Fig. 5(a), 5(b), and 5(c) are 10 %, 19 %, and 26 %, respectively. The three peaks ScN 002, MgO 002, and MnScN 002 are clearly evident. For R= 10%, the alloy peak overlaps with the ScN peak. At higher flux ratios, the alloy peak is shifted further to the right of the ScN peak.

The increase of the angle of MnScN 002 peak with increasing R indicates a reduction of the alloy vertical lattice constant ($c_{alloy}$), indicating increased Mn incorporation when R increases.

The surface structure of MnScN(001) has been investigated by RHEED. Figures 7.6(a-c) show the RHEED patterns along [010] of MnScN(001) grown at $T_S = 518 \degree C$; R of each surface is given. Furthermore, Fig. 7.6(d) shows the plot of the averaged-line profiles of the right streak of each figure as a function of the distance from the corresponding left streak.

RHEED of all films shown in Fig. 7.6 shows 4-fold symmetry of the surfaces and streaky patterns, consistent with our observation in the previous section. No reconstruction besides $1\times1$ is seen for any surface. It is seen from Fig. 7.6(d) that the spacing between the streaks increases as Mn flux is increased, corresponding to a decrease in the in-plane lattice constants, ($a_{alloy}$ and $b_{alloy}$). The reduction of the
### 7.4. Results and Discussion

#### Figure 7.5: XRD spectra of MnScN grown at $T_s = 518 \, ^\circ\text{C}$ at different Mn/(Mn+Sc) flux ratios: (a) 10%; (b) 19%; and (c) 26%.

<table>
<thead>
<tr>
<th>Alloy XRD</th>
<th>Arbitrary Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) MnScN 002</td>
<td>R = 10%</td>
</tr>
<tr>
<td>ScN 002</td>
<td>MgO 002</td>
</tr>
<tr>
<td>(b) MnScN 002</td>
<td>R = 19%</td>
</tr>
<tr>
<td>ScN 002</td>
<td>MgO 002</td>
</tr>
<tr>
<td>(c) MnScN 002</td>
<td>R = 26%</td>
</tr>
<tr>
<td>ScN 002</td>
<td>MgO 002</td>
</tr>
</tbody>
</table>

$2\theta$ (°) range: 38 to 45
lattice parameters as R increases is indicated by XRD, as mentioned, and is also attributed to the increased Mn bulk fraction.

To calculate $c_{\text{alloy}}$, we use Bragg’s law. For the calculation of $a_{\text{alloy}}$, the spacing between the main streaks of the alloy RHEED patterns along [010] ($d_{\text{alloy}}$) is compared with the spacing between the main streaks of ScN(001) along the same direction ($d_{\text{ScN}}$). As is well known, $d_{\text{alloy}}$ and $d_{\text{ScN}}$ are proportional to the reciprocal lattice constants of the alloy and ScN, respectively; therefore, the ratio of streak spacings ($d_{\text{alloy}}/d_{\text{ScN}}$) is equal to the reciprocal ratio of the real lattice constants, $a_{\text{alloy}} = \frac{d_{\text{ScN}}}{d_{\text{alloy}}}$.

As a result, $a_{\text{alloy}}$ is extracted.[82]

Applying Vegard’s law considering the known lattice constants of ScN and $\theta$-phase MnN as well as the measured lattice parameters of the alloy, the Mn/(Mn+Sc) bulk ratio, $x$, is calculated. In fact, both the in-plane and vertical lattice constants of the MnScN alloy, $a_{\text{alloy}}$ and $c_{\text{alloy}}$, are used to calculate the Mn fraction in the bulk $x_a$ and $x_c$, respectively, as:

$$x_a = \frac{(a_{\text{ScN}} - a_{\text{alloy}})}{(a_{\text{ScN}} - a_{\text{MnN}})}, \quad (7.3)$$

$$x_c = \frac{(c_{\text{ScN}} - c_{\text{alloy}})}{(c_{\text{ScN}} - c_{\text{MnN}})}, \quad (7.4)$$

Figure 7.7(a) shows the Mn bulk incorporation as a function of R. The data represented by the diamond symbol is the incorporation calculated from lateral spacing, $a_{\text{alloy}}$, using $a_{\text{ScN}} = 4.503 \text{ Å}$, as reported by Dismukes et al., and $a_{\text{MnN}} = 4.22 \text{ Å}$, as
Figure 7.6: a-c) RHEED patterns of MnScN alloys grown at $T_S = 518 \, ^\circ\text{C}$ at different Mn/(Mn+Sc) flux ratios; d) the average line profiles of the right (1 0) streak as a function of the distance from the corresponding left (-1 0) streak. The solid, dashed, and dotted lines are for RHEED patterns shown in (a), (b), and (c), respectively.
reported by Yang et al.\cite{6, 57} Moreover, the data represented by the square symbol is the incorporation calculated from the vertical lattice constant of the alloy, $c_{\text{alloy}}$, using the same lattice constant of ScN, $a_{\text{ScN}} = c_{\text{ScN}},[6]$ and $c_{\text{MnN}} = 4.1287 \text{ Å}$.\cite{57}

As noticed, both $x_a$ and $x_c$, calculated by RHEED and XRD, agree with each other within a small difference, less than 2.3%. Therefore, this shows that the alloy forms a continuous fct Mn$_x$Sc$_{1-x}$N phase.

In fact, applying Vegard's law, assuming the lattice constants of $\eta$-Mn$_3$N$_2$, $a_{\text{Mn$_3$N$_2$}} = 4.21 \text{ Å}$ and $c/3_{\text{Mn$_3$N$_2$}} = 4.04 \text{ Å},[57]$ has been examined; however, there is a large difference between $x_c$ and $x_a$ in that case. For example, for the film grown at R = 19%, the difference between calculated $x_a$ and $x_c$ is about 12%. This implies that the lattice constants of $\eta$ phase, Mn$_3$N$_2$, are not the right parameters to calculate the Mn bulk fraction in MnScN grown under the stated conditions.

The Mn incorporation coefficient, $x/R$, for films grown with $R = 10\%, 19\%$, and $26\%$ are 0.54, 0.89, and 0.95, respectively. In fact, as seen in Fig. 7.7(a), both $x$ and $x/R$ increase as $R$ increases.

Due to the fact that Mn/(Mn+Sc) bulk ratio $x$, is always less than Mn/(Mn+Sc) flux ratio $R$, it suggests that the accumulates mainly consist of Mn or MnN. However, for growth at $T_S = 330 ^\circ C$, the accumulates may also contain Sc due to the reduced surface diffusion and possibility of increased surface metal intermixing.

Figure 7.7(b) shows the alloy lattice constants, $a$ and $c$, as a function of the Mn bulk incorporation, $x$. The lattice constants at $x= 0$ and 100 % are the values known for ScN and $\theta$-phase MnN, respectively. The data points are the lattice constants
measured for the films, so the interpolation, the dashed line, indicates the expected lattice constants of Mn_xSc_{1-x}N for 0.25 < x < 1.

Qualitatively, the samples show a gradual darkening with increasing Mn incorporation, x. Furthermore, using a hot probe measurement, all films show n-type behavior, as does ScN grown using similar growth method in our system.[83]

7.5 Summary

MnScN(001) alloys have been grown by rf MBE on ScN(001)/MgO(001) substrates. Structural measurements combined together, XRD and RHEED, show that MnScN alloy has a fct structure having $a_{alloy} = b_{alloy} \neq c_{alloy}$. The growth is nearly optimized at $T_S = 518$ °C for high Mn incorporation coefficient, as indicated by XRD, and smooth surface having fewer dot-like structures, as indicated by RHEED and AFM. The lattice parameters reduce as x increases. The alloy MnScN lattice constants follow Vegard’s law in both a and c directions considering the lattice constants of ScN and $\theta$-phase MnN. Mn incorporation as well as Mn incorporation coefficient at $T_S = 518$ °C increases as Mn/(Mn+Sc) flux ratio increases.
Figure 7.7: a) Mn bulk fraction in the alloy, $x_a$ and $x_c$, calculated from Eq. 7.3 and Eq. 7.4 as a function of Mn/(Mn+Sc) flux ratio; b) The lateral and vertical lattice constants, $a$ and $c$ respectively, of MnScN alloy as a function of the Mn bulk fraction; the dashed line is the extrapolation of our experimental results which gives the expected lattice constants of the alloy for any Mn bulk concentration.
Part II

The investigation of Zincblende

GaN(001)/MgO(001)
Chapter 8

Surface Reconstruction of Cubic GaN(001) surface Grown by rf MBE under Ga-rich Growth Conditions

8.1 Abstract

GaN has been grown using rf MBE on MgO(001) under Ga-rich conditions. XRD indicates that the film is cubic GaN(001). AFM shows that c-GaN(001)/MgO(001) surface consists of rectangular-like domains perpendicular to each others. RHEED indicates the smoothness of both the substrate and the grown film. c-GaN(001) shows 2×8 reconstruction if T_s is below 200 °C and 1×1 above that. After annealing the film, RHEED shows 4× patterns. STM images shows that the 2×8 RHEED pattern corresponds to c(4×16) surface reconstruction. STS plots suggest 2×8, c(4×16), has a metallic state. Similar behavior of c-GaN(001) surface grown under more Ga-rich conditions is observed; however, the surface exhibits a c(4×20) reconstruction instead of c(4×16) as in the case of growth under Ga-rich conditions.
8.2 Introduction

The surface of GaN, in general, has attracted and received a lot of studies due to the importance of this material properties such as the direct band gap and the tetrahedral bonding structure, which could lead to the growth of GaN alloys and heterostructure with the other tetrahedral semiconductors. [2, 35, 39, 40, 47, 48, 49, 54, 84, 85, 86, 87, 88] While the surface of the wurtzite GaN has been studied intensively, the surface of the cubic GaN (c-GaN) is still unexplored as much. The surface reconstruction of c-GaN(001) has shown different reconstructions depending on the growth conditions and the substrate used. For the growth of c-GaN on GaAs(001), the surface shows $1 \times 1$, $2 \times 2$, and $c(2 \times 2)$ reconstructions.[89, 90, 91, 92] Moreover, $\sqrt{10} \times \sqrt{10} - R18.4^\circ$ reconstruction also has been reported as a Ga-dimer vacancy structure derived from $c(2 \times 2)$.[86, 87] The growth of c-GaN on SiC/Si(001), in contrast, shows that c-GaN(001) surface has $1 \times 1$ and $4 \times 1$, and these reconstructions are correlated with the sample temperature and the Ga flux during growth.[91, 92, 93, 94, 95] However, when an arsenic background is applied, the surface shows $2 \times 2$, and $c(2 \times 2)$ for the case of $4 \times 1$ and $1 \times 1$, respectively.[94] A recent study by Kim et al. has shown that the growth of GaN on GaP(001) leads to a single crystal c-GaN(001) with $2 \times 2$ reconstruction under Ga-rich growth conditions; however, under N-rich growth conditions the film will preferentially result in a wurtzite GaN layer.[96] While all previously mentioned results are about GaN grown on zincblende(001) substrates, Kikuchi et al. also reported the growth of the GaN on MgO(001), and they have shown that the
8.2. Introduction

surface has a 1×1 reconstruction.[91] Moreover, Powell et al. reported that the surface of c-GaN on MgO(001) has a two-domain 4×1 reconstruction when the growth temperature is above 600 °C; the two-domain structure is due to the fact that the substrate has 4-fold surface symmetry, yet c-GaN has 2-fold surface symmetry.[97]

Neugebauer et al., employing first principles total energy calculations, reported that 4×1, consisting of linear Ga tetramers, is found to be an intrinsic reconstruction; however, 2×2 is not understood as an intrinsic reconstruction of c-GaN(001).[88] In fact, Neugebauer et al. found that 2×2 is understood if the reconstruction of c-GaN(001) surface involves As atoms, and similar behavior is expected for the other group V , in agreement with the reconstruction reported for c-GaN grown on GaAs(001) and GaP(001) or for the case of having the As background.

In this chapter, we present the growth of GaN(001) by radio frequency molecular beam epitaxy (rf MBE) on MgO(001) under Ga-rich and more Ga-rich growth conditions. X-ray Diffraction (XRD) and atomic force microscopy (AFM) results are reported to show the structural properties of the grown GaN/MgO(001) films in the first part of the results and discussion section. In the second part, reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) data are presented to show the reconstructions of the c-GaN(001) surface. In the third part, both STM and scanning tunneling spectroscopy (STS) have been employed to determine the electronic state of the surface reconstruction. In the last part, RHEED patterns and STM imaging are shown for the special case of c-GaN(001) grown under more Ga-rich conditions, and they are compared with the other results.
8.3 Experimental Procedure

Cubic GaN layers are grown by rf MBE on MgO(001), using a radio frequency (RF) plasma source for nitrogen and an effusion cell for Gallium. Details of the MBE growth setup and substrate cleaning procedure are described in chapter 3.[44, 24] GaN growth takes place with the substrate set in the range $550-700 \, ^\circ\text{C}$ and the base pressure of nitrogen and plasma source power set at $0.9-1.1 \times 10^{-5}$ torr and 500 Watt respectively.

The growth starts when the Gallium shutter is opened. Gallium rich growth conditions occur when the Ga flux exceeds the N flux. The growth is under Ga-rich growth conditions when the Ga flux $\sim 2.1-2.7 \times 10^{14} / cm^2 sec$ and under more Ga-rich conditions when the Ga flux $\sim 3.3 \times 10^{14} / cm^2 sec$. The growth is ended by closing the Gallium shutter and turning off the plasma power at the same time. The Ga flux has been determined by a thickness crystal monitor at room temperature.

The growth is monitored in real time using RHEED. Following growth, samples can be transferred under vacuum to the scanning tunneling microscope chamber for surface analysis. Then the sample is taken out the chamber for XRD using Cu K$\alpha$ and AFM studies for more surface and structural studies.
8.4. Results and Discussion

8.4.1 Bulk Structure

Figure 8.1 shows the XRD of GaN/MgO(001). Apparently, there are two peaks beside the substrate peaks in the spectrum. First peak at 39.84° corresponds to the spacing \(d \approx 2.26\,\text{Å}\), and the other peak is at \( \approx 85.89° \) corresponding to the spacing \(d \approx 1.13\,\text{Å}\). No other significant peaks have been seen in the spectrum.

Clearly, both film’s peaks represent the second and the forth order of c-GaN(001) with a lattice constant = 4.52 Å, in close agreement with the measured and predicted values reported by many experimental and theoretical groups. [92, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107] This shows that the film is (001)-oriented following the orientation of the substrate, MgO(001). The inset in Fig. 8.1 shows the rocking curve (\(\omega\)) of c-GaN002 peak. The Full Width at Half Maximum (FWHM) is about 58°, which falls in the range of FWHM, reported for c-GaN(001).[92]

Figure 8.2 shows the AFM images of c-GaN(001)/MgO(001). Figs. 8.2(a), (b), and (c) are 10\(\mu\)m \(\times\) 10\(\mu\)m, 5\(\mu\)m \(\times\) 5\(\mu\)m, and 2\(\mu\)m \(\times\) 2\(\mu\)m AFM images, respectively. The sides of the figures are parallel to \(\langle 010 \rangle\) directions of the substrate, as indicated. As can be seen in Fig. 8.2 the surface consists of rectangular-like domains rotated about each other by 90°; nevertheless, all domains have (001) orientation as indicated by XRD. The sides of these domains are along \(\langle 110 \rangle\) directions of the substrate. Moreover, no domains with hexagonal symmetry have been seen, consistent with the XRD. Clearly, the surface smoothness of the domains can be seen, especially in
Figure 8.1: $2\theta$ x-ray diffraction spectrum for GaN film grown on MgO(001). The inset shows the rocking curve of c-GaN002 peak.
Fig. 8.2(c). The assignment of determining the lateral orientation of these domains needs more surface study which will be presented in the next section.

8.4.2 Surface Structure

Figure 8.3 shows the RHEED patterns of the substrate and the Ga-rich-grown film surfaces along [110] direction of MgO(001). Figure 8.3(a) shows the RHEED patterns of the substrate prior the growth showing streaky diffraction patterns. Figure 8.3(b) shows RHEED of the grown film during the growth, and even after growth same patterns are observed, not shown. Figure 8.3(c) shows RHEED of the surface after the film let cool down at $T_s < 200 \, ^\circ C$ with the horizontal line profile attached underneath. Figure 8.3(d) is the RHEED patterns of the same film after annealing at $T_s = 740 \, ^\circ C$. In fact, RHEED in all Fig. 8.3 show 4-fold symmetry.

RHEED patterns of the substrate indicate the smoothness of the surface, suggesting that our prior growth methods of substrate preparation, nitridation and annealing, are relevant. In Fig. 8.3(b), RHEED patterns of c-GaN grown under Ga-rich conditions show that the surface is grown smoothly with $1\times1$ reconstruction. After-growth RHEED also shows similar reconstruction for $T_s > 200 \, ^\circ C$. The ratio of the spacing between the main streaks for MgO(001), Fig. 8.3(a), to c-GaN(001), Fig. 8.3(b), equals the inverse ratio of their lattice constants, $(a_{MgO}/a_{c-GaN})^{-1}$. Since spacing between streaks in RHEED is proportional to the inverse of the lattice constants; thus, this indicates that $(110)$ of c-GaN(001) are parallel to $(110)$ of MgO(001). As
8.4. Results and Discussion

Figure 8.2: AFM images of c-GaN(001)/MgO(001). The gray scale and the root mean square roughness of a, b, and c are 345 Å and 64.8 Å, 345 Å and 66.1 Å, and 289 Å and 53.1 Å, respectively.
8.4. Results and Discussion

Figure 8.3: RHEED patterns for (a) MgO(001) prior growth, (b) c-GaN(001) during growth, (c) c-GaN(001) after growth below 200 °C with a horizontal line profile attached underneath, and (d) c-GaN(001) after annealing at 740 °C.

A result, the sides of the rectangular-like domains seen in Fig.2 are parallel to (110) of c-GaN(001).

After the sample is let cool below 200 °C, RHEED patterns of c-GaN(001) show 2× reconstruction (Fig.3 (c)). Also 8× reconstruction is observed, as can be seen in the line profile of Fig. 8.3(c). In fact, if the sample temperature is raised above 200 °C, RHEED will show 1× again with reversibility. Since the film consists of
8.4. Results and Discussion

domains rotated by 90° about each other; therefore, 2× and 8× can be the recon-
structions along two directions perpendicular to each other. For example, if domain
A (Fig. 8.2(c)) shows 2× along the short side, then domain B (Fig. 8.2(c)) will show
8× along the long side, which is parallel to the short side of domain A. Therefore,
RHEED will exhibit both reconstruction along the same direction as in Fig. 3(c). As
a result, c-GaN(001) has 2×8 reconstruction as indicated by RHEED when grown
under Ga-rich conditions.

In fact, this new 2× reconstruction (N2×), is different from previously reported
2× reconstruction (P2×), when using GaAs(001) or GaP(001), or when having an As
background for SiC(001) substrate, [86, 87, 90, 92, 94, 96] for three reasons. First,
MgO(001) is used as a substrate which does not have As or P, and our chamber is
free of group V elements or compounds except N. Second, N2× dose not occur during
the growth or even at sample temperature higher than 200 °C while P2× does occur
even during growth. Third, N2× observed below 200 °C is accompanied with 8×;
however, P2× dose not accompanied with 8×. Therefore, this is the first time, up to
our knowledge, to observe such an intrinsic 2×8 reconstruction for c-GaN(001).

Due to the large surface unit cell of 2×8, it is hard to perform a theoretical
calculation to understand the nature of this reconstruction. However, comparison
with another GaN surface reconstructions can be useful.

Smith et al. reported the formation of Ga adatom 3×3 on 1×1 Ga adlayer for
wurtzite GaN(0001) grown by rf MBE under Ga-rich growth conditions.[2] 3×3 is
formed with reversibility at T ≤ 300 °C, and it is associated with an order-disorder
transition of the Ga adatoms atop 1×1 Ga adlayer. Even higher order reconstructions with order-disorder transitions have been reported by the same group for the same surface, such as 6×6. This reversible order-disorder transition is attributed to the weak Ga-Ga bonding, between Ga adatoms and Ga adlayer, comparing with the strength of Ga-N bonding.

Since c-GaN(001) has been grown under Ga-rich conditions, it is expected to have Ga excess on the surface, Ga adatoms. Moreover, due to the order-disorder transition observed at $T_s \sim 200$ °C for c-GaN(001)-2×8 reconstruction, this infers that Ga adatoms form 2×8 reconstruction on Ga-truncated c-GaN(001), similar to the case of 3×3 formed on GaN(0001)-1×1 reported by Smith et al. One more thing that supports this conclusion is that if Ga adatoms form 2×8 on N-truncated c-GaN(001), this will lead to have 4×1 reconstruction observed and predicted by several groups as an intrinsic reconstruction of Ga-truncated c-GaN(001).[88, 92, 94, 95, 97]

Fig. 8.3(d) shows RHEED patterns of the same film in Figs. 8.3 (b) and (c) after annealing at $T_s = 740$ °C. Clearly, 4× reconstruction is apparent in consistence with the fact that RHEED is acquired along $\langle 110 \rangle$ of c-GaN(001). In fact, it is impossible to observe 1× alone since, as demonstrated by AFM (Fig. 8.2), the rectangular-like domains will show 4× along all $\langle 110 \rangle$ directions of MgO(001), similar to the case of observing 2× and 8× at the same time.
8.4. Results and Discussion

Having 4× after annealing at a temperature higher than the one used during growth suggests that 2×8 is formed because of the Ga adatoms on the surface, similar to the case of GaN(000\bar{1})-3×3 that GaN(000\bar{1})-1×1 is the only reconstruction observed after annealing,[2] in agreement with our previous conclusion.

Figure 8.4 shows the STM images of c-Ga(001), exhibiting 2×8 in RHEED, acquired at different sample biases and tunneling currents using Fe-coated W tip. The sides of the images are parallel to \((110)\) of MgO(001). The sample biases of STM images in Figs. 8.4 (a), (b), and (c) are 0.5 V, 0.1 V, and -1.0 V, respectively; moreover, the tunneling currents are 0.6 nA, 0.9 nA, and 0.2 nA, respectively. A schematic model is presented in Fig. 8.4(d). The dashed circles determine the same point in each Figure.

In Fig. 8.4(a), the STM image shows that the surface of c-GaN(001) consists of strips of Ga adatoms along Y axis with wavy sides. The periodicity of strips, along X axis, is about 25.6 Å, which is eight times the spacing between two adjacent Ga atoms on a bulk-truncated, unreconstructed c-GaN(001) surface (d_{Ga–Ga}), 3.2 Å. Moreover, also each strip consists of trimmed rows along X axis. The spacing between two adjacent rows belonging to the same strip, along Y axis, equals 6.4 Å, which equals 2d_{Ga–Ga}. As is noticed in Fig. 8.4(a), if the length of the row is shrunk, then the length of both adjacent rows in the adjacent strips, at the same Y level, will be expanded.

Clearly, this ordering of the strips and rows forms a surface symmetry with periodicity 2d_{Ga–Ga} along Y direction and 8d_{Ga–Ga} along X direction, resulting in a 2×8
8.4. Results and Discussion

Indeed, this agrees with our conclusion from the RHEED patterns that 2× and 8× seen in Fig. 8.3(c) are not parallel to each other in a single domain (see Fig. 8.2), yet they are along perpendicular directions.

As can be seen in Fig. 8.4(b), each strip consists of rows of atomic protrusions, and the number of protrusions in the rows belonging to the same strip alternates 4-3-4-3 with a shift in the atomic position by half the spacing between the protrusions in the same row. The spacing between two protrusions in the same row is 6.4Å, which equals 2d$_{Ga-Ga}$. Similarly, their number in each row along X axis alternates 4-3-4-3. This alternating in Ga adatoms number explains the nature of the wavy sides of the strips, seen in Fig. 8.4(a). The spacing between the last protrusion in one strip and the first one in the adjacent strip along X axis is 9.6 Å, which equals 3d$_{Ga-Ga}$.

From the symmetry of the atomic protrusion arrangement, the conventional unit cell is presented in the schematic model, Fig. 8.4(d). The conventional unit cell of the surface reconstruction is c(4×16) which is observed as 2×8 reconstruction by RHEED. The density of protrusions is 14 per c(4×16) unit cell; therefore, if each protrusion represents a Ga adatom, the coverage of Ga adatoms is 21.875 % of one monolayer (ML).

In the STM image of c-GaN(001)-c(4×16) acquired at $V_s$ = -1.0 V, Fig. 8.4(c), the appearance of the protrusions looks different depending on the place of the atom. As is seen, protrusions at the edge of the rows, especially the rows with 4 atoms, appear more distinct than the others. This variation of the appearance is related to the chemical nature of the bonds between Ga-adatoms and Ga atoms at the
Figure 8.4: STM images of c-GaN grown under Ga-rich conditions acquired with Fe-coated W tip at different sample biases and tunneling currents: (a) $V_s = +0.5 \, \text{V}$, $I_t = 0.6 \, \text{nA}$; (b) $V_s = +0.1 \, \text{V}$, $I_t = 0.9 \, \text{nA}$; and (c) $V_s = -1.0 \, \text{V}$, $I_t = 0.2 \, \text{nA}$. The gray scales of a, b, and c are 0.82 Å, 0.96 Å, and 1.43 Å, respectively.
surface as well as the bonds between Ga adatoms themselves, which is related to the surface structure. Different bonding natures change the local electronic structure leading to variation of local density of states (LDOS). Therefore, the change of LDOS changes the local corrugation of the STM images. Since the edge adatoms appear more distinct, this means that they have more integrated LDOS between -1.0 eV and the Fermi level than the ones in the middle of the strip.

### 8.4.3 Surface State

In Fig. 8.5, STM images of c-GaN(001)-c(4×16) acquired with W tip are presented. STS performed on the surface with the same tip is also presented.

The sample biases of STM images in Figs. 8.5(a) and (b) are +0.3 V and -0.3 V, respectively. The tunneling current for both images is the same, $I_t = 0.08$ nA. The strips are along Y direction while rows are along X direction.

As can be seen in both Figs. 8.5(a) and (b), the images show similar appearance of the atoms. All features are similar to the ones acquired with Fe-coated W tip (see Fig. 8.4) with small variation in the appearance due to the differences of acquisition parameters, sample bias and tunneling current, and the kinds of tip, W or Fe-coated W.

Being able to image the surface at small sample biases, $V_s = +0.3$ V and -0.3 V, suggests that the surface has a narrow bandgap, $E_g < 0.6$ eV, or even zero gap. Moreover, the qualitative similarities of the local corrugation in both STM images indicates that Ga adatoms forming c(4×16) reconstruction do not have completely
8.4. Results and Discussion

filled or empty states, yet the states of all adatoms are partially occupied, indicating zero gap.

STM images with $V_s = +0.3$ V and -0.3 V cannot be conclusive to determine the state of the surface reconstruction since other parameters, such as the tip kind, can play a role for the surface appearance. However, series of images with a continuous variation of sample bias from negative to positive values, or vice versa, is useful to confirm the state of the surface. Instead, STS also can provide the information about whether the surface is metallic or semiconducting.

Figure 8.5(c) shows the Tunneling current vs. voltage (I-V) curve, and Fig. 8.5(d) displays the normalized conductance $(dI/dV)/(I/V)$ vs. Voltage V, (NC-V) curve, numerically calculated from the I-V data in Fig. 8.5(c). The (+) symbol determines where the origin of the graph is. The horizontal dashed lines in the NC-V panel indicate where NC equals zero and unity. The bar over the $I/V$ indicates broadened I/V values are used to avoid divergence near the band edges.[71] Both I-V and NC-V are the average of 16 spectra.

I-V curve, in Fig. 8.5(c) shows a smoothly continuous variation of the tunneling current with changing the sample bias. Even in the range between $V_s = +0.3$ V and -0.3 V, the plot shows non-zero values of the current, but in the vicinity of $V_s = 0$ V it is hard to visualize the current values. The plot in Fig. 8.5(d), NC-V, dose not go to zero in the vicinity of $V_s = 0$. Moreover, NC passes through unity at zero voltage.

Clear non-zero current in the I-V curve, except the vicinity of the zero-voltage, indicates that the surface has states in all energies. NC-V plot shows also non-zero
Figure 8.5: STM and STS of c-GaN(001)-c(4×16) acquired with W tip: (a) and (b) STM images acquired at $V_s = +0.3$ V and -0.3 V, respectively, with the same tunneling current, $I_t = 0.08$ nA, (c) and (d) tunneling current vs. voltage, I-V, curve and normalized tunneling current, NC-V, curve, respectively.
density of state for all energies confirming the observation of the I-V plot. Moreover, even at the vicinity of zero-voltage the density of state is not zero indicating metallic surface. The metallic surface is also indicated by that NC passes through unity at zero voltage. Therefore, it is concluded that c(4×16) has a metallic surface.

### 8.4.4 Surface Reconstruction of c-GaN(001) Grown under More Ga-rich Conditions

Figure 8.6 shows the surface study by RHEED and STM of GaN(001) grown under more Ga-rich conditions. In Fig. 6(a) the RHEED pattern of the surface at $T_S < 200 ^\circ C$. During and after the growth RHEED patterns are similar to the case of growth under Ga-rich conditions. Moreover, a disorder-order surface-structure transition occurs at about 200 °C. Clearly, 2$\times$ reconstruction is apparent; however, 8$\times$ is not observed. Thus, this is an indication of a change of the strip width, which causes the 8$\times$ RHEED streaks for the case of Ga-rich growth. Moreover, the similarity of the order-disorder surface transition temperature with the case of Ga-rich growth indicates that the 2$\times$ reconstructions, for both cases, have similar structures.

To verify the surface structure in real space, STM imaging has been performed. Figure 8.6(b) shows the STM image of c-GaN(001) grown under more Ga-rich conditions; Fig. 8.6(c) shows a schematic diagram of the STM image, and the dashed circles denote the same position. The STM image shows that the surface is constructed of strips, and each strip consists of atomic rows, the small gray circles are
8.4. Results and Discussion

Figure 8.6: a) RHEED pattern of GaN(001) grown under more Ga-rich conditions after the growth; RHEED was acquired at $T_S < 200 \, ^\circ C$. b) The STM image of the surface acquired at $V_S = +0.7 \, V$ with $I_T = 0.8 \, nA$. c) A schematic diagram of the atomic protrusions shown in (b).
atop the atomic protrusions of the rows. The spacing between two adjacent rows in the same strip is $2d_{Ga-Ga}$, which explains the $2\times$ reconstruction seen in the RHEED. In contrast to the case of the Ga-rich growth, the number of atomic protrusions on each row belonging to the same strip alternates 4-5-4-5 as seen in the figure; thus, RHEED patterns does not show $8\times$. The distance between two adjacent protrusions on adjacent strips along the atomic rows is 9.6 Å, leading to a strip periodicity of 32 Å; hence, the surface reconstruction is $c(4\times20)$, which is a higher order surface reconstruction than the case of Ga-rich growth.

8.5 Summary

Cubic GaN(001) has been grown smoothly under Ga-rich conditions on MgO(001) using rf MBE. The growth of a zinc-blende crystal on a rock-salt substrate leads to formation of dual domains, oriented 90 ° about each other as revealed by AFM. The surface of c-GaN(001) shows $2\times8$, $c(4\times16)$, as an intrinsic reconstruction, indicated by RHEED and STM. STM and STS suggested that c-GaN(001)-$c(4\times16)$ is metallic. Growth of c-GaN(001) under more Ga-rich conditions leads to $2\times$ RHEED patterns, yet $8\times$ does not appear. STM imaging shows that this $2\times$ is actually $c(4\times20)$. 
Chapter 9

Scanning Tunneling Microscopy of Ga-tetramer Rows on Cubic GaN(001)-4×1

9.1 Abstract

Cubic GaN(001)-4×1 has been studied by scanning tunneling microscopy and spectroscopy. Scanning tunneling microscopy imaging acquired at both negative and positive sample biases shows that the surface consists of rows aligned along [110] with a periodicity along [110] of 12.8 Å. Dual-bias imaging shows a shift of the corrugation maximum position by ~6.4 Å as the sample bias changes from a negative to a positive voltage, and vice versa. The experimental images are in good agreement with the simulated images of the surface reconstruction calculated by SIESTA code. The scanning tunneling spectroscopy indicates the semiconducting nature of the 4×1 having a surface gap of 1.3 eV, in good agreement with the surface gap predicted by Neugebauer et al., of 1.2 eV.
9.2 Introduction

The surface of GaN, in general, has attracted and received a lot of studies due to the importance of this material properties such as the direct band gap and the tetrahedral bonding structure, which could lead to the growth of GaN alloys and heterostructure with the other tetrahedral semiconductors. [2, 35, 39, 40, 47, 48, 49, 54, 84, 85, 86, 87, 88] While the surface of the wurtzite GaN has been studied intensively, the surface of the cubic GaN (c-GaN) is not as much explored.

All reported scanning tunneling microscopy of c-GaN(001) have been reported for growth on GaAs(001).[86, 108, 109] Moreover, in the last chapter we have shown intrinsic surface reconstruction of c-GaN(001). So far no reports, up to our knowledge, have been about the observing of c-GaN(001)-4\times1 surface structure in real space.

Feuillet et al., has shown experimentally that 4\times1 is an intrinsic surface reconstructions of c-GaN(001). Moreover, Neugebauer et al., employing first principles total energy calculations, reported that 4\times1, consisting of linear Ga tetramers, is found to be an intrinsic reconstruction of c-GaN(001); moreover, the surface is predicted to be semiconducting having a surface gap of 1.2 eV.[88] Furthermore, the tetramer structure on cubic group III-nitrides is also predicted for the case of cubic AlN(001);[110] nevertheless, the tetramer structure on either cubic GaN(001) or cubic AlN(001) has not been verified in real space by all means. In chapter 8, we show other surface reconstructions; moreover, we show, by RHEED, that 4\times1 is the surface
9.3. Experimental Procedure

reconstruction after removing the Ga-adatoms from the surface. However, we do not
show the STM results.

In this chapter, we present the STM imaging and scanning tunneling spectroscopy
(STS) of c-GaN(001)-4×1. Moreover, the experimental data is compared with the
theoretical simulation performed by SIESTA code, by Nancy Sandler.

9.3 Experimental Procedure

Cubic GaN layers are grown by rf MBE on MgO(001), using a radio frequency plasma
source for nitrogen and an effusion cell for Gallium. GaN growth takes place with the
substrate temperature ($T_S$) set at $\sim 580$ °C, measured by an optical pyrometer with
emissivity set to be 0.7, and the base pressure of nitrogen and plasma source power
set at $9 \times 10^{-6}$ torr and 500 Watt respectively.

The growth is under Ga-rich conditions with a Ga flux $\sim 2.3 \times 10^{14} \text{ /cm}^2\text{sec}$. The
growth is ended by closing the Gallium shutter and turning off the plasma power at
the same time. The Ga flux is determined by an in situ crystal thickness monitor at
room temperature. After the growth is ended the film is annealed at $T_S = 700$ °C
until reflection high energy electron diffraction (RHEED) shows 4×.

The growth is monitored in real time using RHEED. Following growth, samples
can be transferred under vacuum to the scanning tunneling microscope chamber for
surface analysis.
9.4 Results and Discussion

Figure 1 shows RHEED patterns of c-GaN(001). Figure 1(a) shows RHEED of the surface at $T_S$ of 490 °C after the growth; similar patterns during growth, not shown, are observed. As clearly seen, c-GaN(001) grown under Ga-rich conditions exhibits only 1×1 reconstruction. Figure 1(b) is the RHEED patterns of the surface acquired at room temperature. Clearly, 2× and 8× reconstructions are evident, which are related to the excess Ga on the surface as described in chapter 8. Figure 1(c) shows RHEED patterns of the GaN(001) at room temperature after annealing at $T_S = 700$ °C. The patterns are streaky, confirming a smooth surface. The surface clearly, from RHEED, exhibits a 4× reconstruction, which is known to be an intrinsic reconstruction for c-GaN(001).[88, 94] No other reconstruction have been noticed on this surface after annealing, which indicates an impurity-free surface. In fact, it is found that after depositing 0.15 monolayer of Ga on the surface, 2× reconstruction appears again and 4× disappears. Thus, 2× surface structure is more energetically favorable when there exists an excess of Ga atoms on the surface.

Figure 9.2 shows the STM images, acquired at different sample biases, of c-GaN(001) after annealing and their averaged line profiles. Both Figs. 9.2(a) and (b) show that the surface consists of rows aligned along [110] with a periodicity along [110] of 12.8 Å, in consistent with the tetramer spacing.

The filled-states line profile, Fig. 9.2(c), has almost a sinusoidal shape with corrugation amplitude of $\sim 0.9$ Å. The line profile of the empty state, Fig. 9.2(d), has a
9.4. Results and Discussion

Figure 9.1: RHEED patterns of c-GaN(001): a) and b) after growth; and c) after annealing at $T_S = 700$ °C. $T_S$'s during RHEED acquisition are 490 °C for (a) and room-temperature for (b) and (c).
rounded saw-tooth shape with corrugation amplitude of $\sim 0.45$ Å; the asymmetry is attributed to the STM tip.

According to the model of Neugebauer et al., the tetramer consists of 4 Ga atoms held together by 3 linear bounds; as each Ga atom has 2 back-bonds, the end-atoms each has one dangling bond.[88] Since electron counting holds for the $4\times1$, these dangling bonds are empty, while the 3 intra-tetramer bonds are filled. Thus, we expect that the peak of the filled state corrugation should correspond to the center of the tetramer, and the peak of the empty state corrugation should correspond to the midpoint between tetramers.

In order to verify this expectation, we performed dual-bias STM imaging on the same surface, Fig. 9.3(a). The STM image consists of three regions in which the sample bias ($V_S$) is different. $V_S$ of the upper, middle, and lower areas of the STM are +1.2 V, -1.2 V, and +1.2 V, respectively, and the tunneling current is the same for all. The alternating $V_S$ during the acquisition of the STM image shows the difference between the empty and filled states. As clearly seen, the positions of the rows in the empty state, are shifted with respect to the positions of the rows in the filled state.

Figure 9.3(b) shows the averaged line-profiles $lp_1$, $lp_2$, and $lp_3$ of the areas A, B, and C, respectively, with the linear Ga tetramer model, proposed by Neugebauer et al., imposed.[88] The empty states line profiles look identical, indicating no artificial effect occurs due to voltage switching. The filled state line profile, $lp_2$, looks similar to the line profile of the filled state in Fig. 9.2(a) with similar corrugation amplitude even though the sample voltage is different, indicating no states existing in the range $V_S$
9.4. Results and Discussion

V = -2.0 V, \( I = 0.04 \text{ nA} \)

V = +1.2 V, \( I = 0.04 \text{ nA} \)

Figure 9.2: a) and b) show the STM images of GaN(001)-4\times1 surface acquired at \( V_S = -2.0 \) V and +1.2 V, respectively. c) and d) are the averaged line profiles of the dashed rectangles in (a) and (b), respectively.
9.4. Results and Discussion

Figure 9.3: a) Dual bias STM image on c-GaN(001); and b) line-profiles of the dual bias image with the tetramer model proposed by Neugebauer *et al.*
9.5. Comparison with the Simulated STM Images

-2.0 V– -1.2 V. This agrees with the reported surface band structure of c-GaN(001)-4×1 that the three filled surface bands are close to each other since the STM image spans all the states located between the Fermi level and the sample bias.

From the line profiles, lp1 and lp2, clearly the maximum of the empty state corresponds to the minimum of the filled state, which agrees with our expectation from the separate STM images, Figs. 9.2(a), and (b) [see the tetramer model in Fig. 9.3].

Neugebauer calculation of c-GaN(001)-4×1 surface band structure shows that the surface is semiconducting with a surface gap of 1.2 eV, so in order to verify this prediction we performed STS on the row structure. Figure 9.4 shows the STS spectrum acquired on the surface of c-GaN(001). The plot shows zero I_t in the V_S range of -0.5 V–+0.8 V, indicating a surface gap of 1.3 eV. This gap is in closed agreement with the predicted gap. The tunneling from the filled band shows a more rapid increase comparing with tunneling into the empty band. This is consistent with the band structure calculated by Neugebauer et al., in which they show that the filled surface bands are almost dispersionless and close to each other, yet the empty surface bands are much more dispersive.

9.5 Comparison with the Simulated STM Images

Figure 9.5 shows the simulated STM images, performed using SIESTA code by Nancy Sandler. In Figs. 9.5(a) and (b) the images show the topographic electronic density of the filled and empty states, respectively, as a function of the space. Both images
9.5. Comparison with the Simulated STM Images

Figure 9.4: STS plot showing \((I_t-V_s)\) characteristics of the surface; the plot is the average of 16 spectra.
show that the surface consists of rows along [110] with a periodicity along [1\bar{1}0] of 12.8 Å, consistent with the STM observation. For the filled state STM image, the protrusions seen are located in between the atoms in the same tetramer; moreover, the dark region is located in between the tetramers, where the empty dangling bonds are located. On the other hand, the protrusions seen for the empty state image are close to be above the atoms in the tetramer. Further more, the bright protrusions are centered between tetramers, and the dark ones are atop the two middle atoms in the same tetramer. The shift of middle part of the bright protrusions by half the tetramer periodicity is consistent with the observed shift of the peak positions, seen in Fig. 9.3.

Figure 9.5(c) and (d) are the filtered simulated STM (fs-STM) images, averaged over certain range, which can be practically compared with the experimental STM images since the sharpness of the tip is not ideal which quite often averages over the features on the probed surface. As is seen, the fs-STM shows only rows along [110] with a shift of the bright protrusions by half the tetramer periodicity; moreover, the corrugation along [110] is not resolved, in good agreement with the real STM images shown in both Figs. 9.2 and 9.3.

9.6 Conclusion

STM and STS have been performed on c-GaN(001)-4\times1 surface. STM images of both the empty and filled states have shown that the surface consists of rows along
Figure 9.5: Simulated STM images of: a) filled state; b) empty state; c) filtered filled state; and d) filtered empty state.

[110] with periodicity of 12.8 Å along the perpendicular direction. Line profiles of the dual bias STM images, along [110] show a phase shift of the rows periodic structure between the filled and empty states by 180°. STS spectrum indicates the surface is semiconducting with a surface gap of 1.3 eV. The STM images are found to be consistent with the simulated STM images, calculated using SIESTA code by Nancy Sandler.
Chapter 10

Conclusion

ScN and c-GaN are grown by rf MBE on MgO(001). Both ScN and GaN result in 001-oriented films. For the case of ScN(001) the smooth surface is achieved by either growth under Sc-rich or N-rich conditions. For growth under Sc-rich the ScN surface consists of spiral mounds centered on screw-type dislocations. The surface shows mainly $1\times1$ reconstruction, yet faint $2\times$ is some times observed. The surface is metallic. The surface of ScN grown under N-rich conditions consists of spiral pyramids and flat plateaus. The surface shows only $1\times1$ reconstruction. The surface is semiconducting with a surface gap of $0.9 \pm 0.1$ eV.

The growth under Sc-rich leads to N-vacancies incorporated in the film; however, growth under N-rich conditions leads to Sc/N bulk ratio of $1\pm0.02$. Both growth conditions show that the film has an optical bandgap of 2.15 eV; however, for growth under Sc-rich conditions the film shows a sub-bandgap absorption.

For the case of c-GaN(001) only growth under Ga-rich conditions leads to smooth growth. The surface of c-GaN(001) consists of rectangular-like flat domains oriented about each other by $90^\circ$, due to the fact c-GaN(001) has 2-fold surface symmetry yet
MgO(001) has 4-fold surface symmetry. The surface shows 1×1 reconstruction during and after the growth. However, after the sample is let cool down to about 200 °C the surface shows a disorder-order phase transition from 1×1 to c(4×16) for growth under Ga-rich conditions and c(4×20) for growth under more Ga-rich conditions. Both c(4×16) and c(4×20) reconstructions are formed by the Ga-adatoms on the Ga-adlayer. c(4×16) is found to be metallic.

Removing the Ga-adatoms by annealing the surface at 700 °C-800°C leads to the known 4×1 surface reconstruction. The surface consists of rows aligned along [110] with a periodicity along [1̅0] of 12.8 Å. The surface is found to be semiconducting with a surface gap of 1.3 eV.
References


[11] Whether ScN also has an indirect band gap at lower energy is currently an issue under investigation.


[13] We calibrated the z-scale of our STM by measuring single steps heights on GaN(0001) grown on sapphire, which are known to have a height of 2.59 Å.


[23] We calculated ScN to be $\sim$ 18% ionic by setting a linear combination of ionic and covalent radii equal to the known lattice constant of ScN, 4.501 Å.


[27] The value for $a_{\text{MgO}} = 4.213$ Å is from the Inorganic Index to Powder Diffraction (Joint Committee on Powder Diffraction Standards, International Center for
Powder Diffraction Data, Swarthmore, PA, 1997): MgO (Card No. 04-0820). In the last chapter, we had used 4.195 Å for $a_{MgO}$; using 4.213 Å in that chapter, calculated values for $a_{ScN,\perp}$ would increase by about 0.02 Å.


[52] H. Al-Brithen et al., submitted to Phys. Rev. B.


[72] These values are obtained from Professor W. R. L. Lambrecht’s calculations, who finds at the X-point CBM a longitudinal effective mass $m_l = 1.441m_e$ and a transverse effective mass $m_t = 0.124m_e$. For the optical effective mass, we use $3/m_{opt} = 1/m_l + 2/m_t$, while for the DOS effective mass, we use $m_{DOS}^3 = m_t^2m_l$.


[82] RHEED for both ScN and MnScN was acquired at the growth temperature of the alloy, $T_g = 518 \ ^\circ C$, and room-temperature ScN lattice constant is used to extract the in-plane room-temperature MnScN lattice constant assuming a very small difference between the thermal expansion coefficients of ScN and MnScN.


Appendix A

List of Publications


- *Surface and Bulk Electronic Structure of ScN(001) Investigated by Scanning Tunneling Microscopy/Spectroscopy and Optical Absorption Spectroscopy*, Hamad A. AL-Brithen, Arthur Smith, and Daniel Gall, Accepted in Phys. Rev. B.


- *Ga/N flux ratio influence on Mn incorporation, surface morphology, and lattice polarity during radio frequency molecular beam epitaxy of (Ga,Mn)N*, MB.


Appendix B

List of contributed Talks in Conferences

B.1 I was the presenter

- *Scanning Tunneling Microscopy Study of the Surface Reconstructions of Cubic GaN Grown by rf MBE on MgO(001)*, Hamad A. H. AL-Brithen, and Arthur R. Smith, 2003 March Meeting of the American Physical Society, Austin, TX.


B.2. I was a co-author


B.2 I was a co-author


- *Growth Regimes of (Ga,Mn)N during rf MBE and their effects on the Alloy Formation*, Muhammad B. Haider, Costel Constantin, Hamad A. H. AL-Brithen, Haiqiang Yang, Arthur R. Smith, Eugen Trifan, David C. Ingram, C. V. Kelly, and Yumi Ijiri, 2003 March Meeting of the American Physical Society, Austin, TX.
B.2. I was a co-author


Appendix C

List of contributed Posters in Conferences

C.1 I was the presenter


C.2 I was a co-author