Growth and Scanning Tunneling Microscopy Studies of Magnetic Films on Semiconductors and Development of Molecular Beam Epitaxy/Pulsed Laser Deposition and Cryogenic Spin-Polarized Scanning Tunneling Microscopy System

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Doctor of Philosophy

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This dissertation titled
Growth and Scanning Tunneling Microscopy Studies of Magnetic Films
on Semiconductors and Development of Molecular Beam Epitaxy/Pulsed Laser
Deposition and Cryogenic Spin-Polarized Scanning Tunneling Microscopy System

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ABSTRACT

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Growth and Scanning Tunneling Microscopy Studies of Magnetic Films on Semiconductors and Development of Molecular Beam Epitaxy/Pulsed Laser Deposition and Cryogenic Spin-Polarized Scanning Tunneling Microscopy System (113 pp.)

Director of Dissertation: Arthur R. Smith

We not only perform growth and scanning tunneling microscopy studies of magnetic films on semiconductors using molecular beam epitaxy / scanning tunneling microscopy system in an existing lab, but we also carry out development of a novel molecular beam epitaxy/pulsed laser deposition and superconducting magnet cryogenic spin-polarized scanning tunneling microscopy system in a completely new lab.

We study the growth of iron nitride on gallium nitride using molecular beam epitaxy with Fe e-beam evaporation and radio frequency N-plasma growth. Thin iron nitride layers of thickness about 16 nm are grown and monitored in situ using reflection high energy electron diffraction. The samples following growth are analyzed ex situ using a variety of techniques including X-ray diffraction, Rutherford backscattering, and atomic force microscopy. The crystal phase and orientation with respect to the GaN substrate are deduced by monitoring the structure, morphology, and lattice constant evolution of the iron nitride film. The growth is discussed in terms of a 2-dimensional to 3-dimensional growth mode transition.

The investigation of the initial phase of sub-monolayer iron deposition on GaN(0001) pseudo-1×1-1 + 1/12 surface is carried out. To begin with, we verify an atomically smooth GaN growth surface with in situ reflection high energy electron diffraction. Scanning tunneling microscopy shows smooth terraces separated by single and double height bilayer atomic steps. About 0.42 ML iron is deposited on a smooth GaN surface, and the subsequent scanning tunneling microscopy images reveal waffle-like 2-dimensional islands
with a height of \( \sim 1.8-2.0 \, \text{Å} \), growing in a 2-dimensional mode outward from the GaN step edges of the pseudo-1 \( \times 1-1 + 1/12 \) surface. A clear 6 \( \times \) 6 structure is observed for the islands. The waffle-like islands also grow in the GaN spiral growth regions.

Studies of iron/Ga-rich N-polar GaN(000\(\bar{1}\)) reveal the formation of quantum spintronic nanostructures on N-polar GaN(000\(\bar{1}\)), formed by the deposition of iron onto the gallium-rich surface and investigated using scanning tunneling microscopy \textit{in situ}. The iron-induced islands are spontaneously formed after Fe deposition in the temperature range of 210–360 \( ^\circ \text{C} \). Higher deposition temperature leads to larger width islands with uniform quantum thickness. This thickness corresponds to about 3 (or 4) atomic layers. The islands also exhibit an atomically smooth surface with a zig-zag row structure having 4\(\times\)2 periodicity.

For the increasing need of nitride semiconductors and semiconductor based structures in electronic, optoelectronic and spintronic applications, and due to the powerful capabilities of scanning tunneling microscopy and spin-polarized scanning tunneling microscopy in probing structural, electronic, and even magnetic properties, we carry out the development of a nitrogen plasma assisted molecular beam epitaxy/pulsed laser epitaxy facility integrated with a cryogenic superconducting magnet scanning tunneling microscope system. The custom-designed molecular beam epitaxy growth system supports up to eight sources, including up to seven effusion cells plus a radio frequency plasma source, for growing a variety of complex materials, such as nitride semiconductors and magnetic materials, and incorporates \textit{in situ} reflection high energy electron diffraction and pulsed laser epitaxy. The custom-designed STM head has a modular design, consisting of an upper body and a lower body. The upper body contains the approach and scanning mechanism, as a key unit, while the lower body accepts molecular beam epitaxy/pulsed laser deposition grown samples using compression springs and sample skis. The design further enables tip exchange without removing the sample holder from the STM. The
modular design has the advantage of conveniently adapting the microscope to different applications and chamber systems in the future without changing the upper body design. A sample/tip handling system is designed and optimized for both the molecular beam epitaxy growth system and the scanning tunneling microscope system.

Approved:  

Arthur R. Smith  
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1 Introduction

Spintronics, spin-based electronics, is different from the traditional electronics for its use of spin degree of freedom of electrons. Spintronic devices could have advantages over conventional electronics, in terms of less power consumption, and faster data processing speed. [1] One example is the giant magneto-resistance (GMR), in which giant magnetoresistance was achieved by using spin-dependent transmission in multiple layer magnetic structure. [2, 3] The discovery leads to the successful use of the spin-valve reading heads for improving storage capacity of a magnetic hard drive by IBM. [4]

Besides metal based spintronics, such as GMR, semiconductor based spintronics is also a very promising field, as semiconductor devices are important in everyday life. The semiconductor-based spintronic applications are broad, covering spin-based field effect transistor, and spin-based light-emitting diode. It is crucial to create spin currents in semiconductors for semiconductor-based spintronic applications. By injecting currents from magnetic materials to semiconductors, spin polarized currents can be introduced in semiconductors.

Growths and properties of magnetic materials on semiconductors play important roles in the efficiency of spin injections, especially interface properties. Using ferromagnetic metal on semiconductor is one important approach for spin injection, such as iron on GaAs. However, there are concerns about spin injection efficiency. Theoretical calculations predicted that spin-polarization of the injected currents is limited to less than 0.1 %, in the diffusive transport regime. [5] It is not practical for applications with such low spin injection efficiency. The obstacle can be overcome with Schottky tunnel barrier between ferromagnetic metals and semiconductors; and efficient spin injections have been demonstrated. [6–9] Electron-spin polarization of 32% has been achieved by a reverse-biased Fe/AlGaAs Schottky contact. [7] Furthermore, it is also interesting to study the
magnetic materials on semiconductors for fundamental understanding of magnetism in such systems.

Compared with many studies carried out for Fe on conventional semiconductor GaAs, there are less studies for iron on wurtzite GaN, despite the fact that wurtzite GaN has increasing applications in both electronic and optoelectronic devices. [10–12] There are two polarities for c-plane GaN, namely, Ga-polar GaN(0001) and N-polar GaN(000\̅1), as shown in figure 1.1. The Ga to N bond is parallel to growth direction in Ga-polar GaN(0001), while the Ga to N bond is anti-parallel to growth direction in N-polar GaN(000\̅1). Under Ga-rich condition, there are 2 × 2, 5 × 5, 6 × 4 reconstructions of Ga-polar GaN surface, and 1 × 1, 3 × 3, 6 × 6, and c(6 × 12) reconstructions of N-polar GaN surface. [13, 14] Besides iron on wurtzite GaN, iron nitride on wurtzite GaN is also attractive due to corrosion and oxidation resistance of iron nitride. [15]

Molecular beam epitaxy (MBE) is a well known technique to achieve epitaxial growth with high control accuracy down to mono-layer (ML). The growth capability is enhanced with assistance of reflection high energy electron diffraction (RHEED). The properties of an MBE grown sample can then be investigated with in situ scanning tunneling microscopy (STM). STM is well known for its capabilities of probing structural, and electronic
properties with resolution down to nano-scale and atomic scale. Therefore, we carried
out studies of iron or iron nitride/wurtzite GaN with custom-designed MBE/STM facility
(lab one, Clippinger 151), in which the STM operates at room temperature. Many other
techniques have also been used ex situ to help analyzing samples, such as X-ray diffraction
(XRD), and atomic force microscopy (AFM).

The scientific research advances with the development of new instruments or
techniques. Besides regular scientific research, we have also carried out the development
of a new N-plasma assisted MBE/ pulsed laser deposition (PLD) and superconducting
magnet cryogenic SP-STM system. The new system is designed for new functionalities
that are not available in our current MBE/STM system. In terms of growth, the new
growth system supports up to eight cells, including seven effusion cells and one N-plasma
source, and pulsed laser deposition (PLD) or pulsed laser epitaxy (PLE). The cryogenic
superconducting magnetic field enhances the stability and power for STM investigations
of materials. The new system will deliver unique and strong capabilities of epitaxially
growing nitride semiconductors and a variety of materials with precise control down to
ML accuracy, and in situ probing local structural, electronic, and even magnetic properties
upon its completion. The sample/tip handling system enables in situ tip/sample transfer
and loading, and supports sample size from 1cm × 1cm up to 2” for MBE growth. The
1cm × 1cm sample can be transferred into STM head for in situ studies.

This project covers growth and scanning tunneling microscopy studies of magnetic
films on semiconductors by using our MBE/ room temperature STM (in lab one), and
development of MBE/PLD and superconducting magnet cryogenic SP-STM system in a
completely new lab (in lab two).

Chapter one is an introduction chapter for the work presented.

Chapter two covers the fundamentals of instruments or techniques used for the
research, in order to provide a brief technical background for understanding the research
carried out using these techniques.

In chapter three, we show the growth of iron nitride on wurtzite GaN(0001) by MBE, and discuss the epitaxial relationship between the film and the GaN (0001) substrate.

Chapter four studies initial phase of iron heteroepitaxy on Ga-polar GaN(0001) pseudo-1 × 1-1 + 1/12, in which STM studies were carried out on sub-ML iron deposition onto the GaN surface.

Chapter five shows STM studies of initial phase of iron heteroepitaxy on N-polar GaN(0001).

Chapter six describes the development of N-plasma assisted molecular beam epitaxy facility with cryogenic superconducting magnet spin-polarized scanning tunneling microscope, which mainly covers the custom-designed MBE/PLD growth system, the custom-designed STM head, and integration of the MBE/PLD growth system with the STM system in a custom-designed ultra-high-vacuum(UHV) multi-chamber system.

Chapter seven is an overall summary for the preceding chapters.

The appendix lists publications related to the work during my Ph.D. studies at Ohio University.
2 EXPERIMENTAL TECHNIQUES

2.1 Scanning Tunneling Microscopy

As illustrated in figure 2.1, with a bias voltage applied between a sample and a tip in STM, and the distance between the tip and the sample brought extremely close (less than 10 Å), there is a current tunneling through the tip and the sample. As the tip scans over the sample in a constant current mode, the tunneling current tends to deviate from a set point due to the height change over the sample surface. Based on the tiny offset, the feedback circuit will send a feedback signal to extend or retract the scanner, so that the tunneling current is constant at the set point during scanning. The amount of extending/retracting motion of the tip over the surface driven by the scanner, \( z(x,y) \), represents the surface contour of the sample surface in a simplified model.

An expression with spin-polarized tunneling effect considered for understanding STM images is shown below. [16, 17]

\[
I_t \sim \int g_V(E) \frac{1}{2} [n' n^s + m' m^s \cos \theta] dE
\]  

(2.1)

where the integral for the first term containing \( n' n^s \) is the contribution from normal electronic states, and the integral for the second term containing \( m' m^s \cos \theta \) is the contribution due to the spin effect. In the expression, \( g_V(E) = f(E - E_F) - f(E - E_F - eV) \) where \( V \) is applied bias voltage and \( f \) is the Fermi function.

The room temperature STM experiments on Fe/Ga-polar GaN (0001), and Fe/N-polar GaN (000\( \bar{1} \)) were carried out in lab 1 with the RHK SPM 100 controller. Software programs with data visualization and analysis capabilities, such as RHK XPMPro and Gwyddion, were often used when performing STM image processing and analysis, for example, performing drift corrections on STM images. [18, 19]
Figure 2.1: A schematic model of a scanning tunneling microscope in constant current mode. The tunneling current is amplified and converted to a voltage, and compared with the reference voltage corresponding to a set point. The difference is used by feedback electronics to generate a control voltage to either extend or retract the scanner such that the tunneling current is kept at a constant value.
2.2 Molecular Beam Epitaxy

Molecular beam epitaxy enables epitaxial growth on a substrate by using effusion cells or e-beam evaporators in a UHV chamber. In an effusion cell, as illustrated in figure 2.2, a source in the crucible is heated by a tantalum filament. A thermocouple detects the temperature of the cell. With a feedback loop, the heating power of the tantalum filament is set based on the difference between the temperature reading and the temperature set point, so that a constant effusion cell temperature is maintained. There is a shutter near the opening of the crucible to start or stop a growth. There are tantalum heat shields around the cell so that as much energy as possible is kept inside the effusion cell. There is also a water cooling jacket around the effusion cell to prevent the effusion cell from overheating the UHV chamber. The flux reaching the substrate depends on the effusion cell temperature. The equation below, provided in a book by H. Lüth, \[20\] illustrates the relationship between the flux and the cell temperature.

\[
F = \frac{P(T)a}{\pi L^2 \sqrt{2\pi mk_BT}} \tag{2.2}
\]

In the equation, \(P(T)\) is the equilibrium vapor pressure, \(a\) is the area of the cell aperture, \(L\) is the distance from the effusion cell to the substrate, \(m\) is the mass of the effusing species, \(k_B\) is the Boltzmann constant, and \(T\) is the effusion cell temperature. By adjusting \(T\), one can obtain desired flux.

By setting substrate temperature, flux, and growth time, epitaxial films with monolayer (ML) control precision can be achieved.
Figure 2.2: A schematic diagram of an effusion cell.
The MBE growths for iron nitride and iron in this project were carried out by using an iron e-beam evaporator or an iron effusion cell in our lab one, located in Clippinger 151. We initially used an iron e-beam evaporator, and later upgraded to an iron effusion cell.

2.3 X-ray Diffraction

The Bragg’s law,

\[ n\lambda = 2dsin\theta, \]

(2.3)
describes that the constructive interference forms when the phase shift is a multiple of \( \lambda \). In other words, the constructive interference happens when the path difference is a multiple of \( \lambda \), where \( n \) is an integer, \( \lambda \) is the wave length of X-ray, \( d \) is the spacing between atomic lattice planes, and \( \theta \) is the angle between the incident beam and the scattering plane. \( n\lambda \) on the left-hand side of the Bragg’s equation is a multiple of \( \lambda \), while \( 2dsin\theta \) is the path difference between two x-rays. In the schematic diagram in figure 2.3, the path difference should be \( AB + BC \), which equals \( 2dsin\theta \). If \( n\lambda = 2dsin\theta \), there is constructive interference.

In a typical XRD experiment, the intensity of scattered x-ray is plotted against \( 2\theta \). At particular angles for a particular sample, the Bragg’s equation is satisfied, constructive interference forms, and peaks appear in the XRD pattern. Different crystal structures correspond to different \( d \) spacings, and different peak locations in the XRD pattern. Thus XRD can be used to determine the \( d \) spacing, and further the crystal structure for a sample.
2.4 Reflection High Energy Electron Diffraction

In reflection high energy electron diffraction (RHEED), accelerated electrons from a RHEED gun impinge on a sample surface at a small grazing angle, such as 1°. A diffraction pattern then forms on a RHEED screen. Because the grazing angle is small, RHEED is sensitive to surface. The applied high voltage for accelerating the electrons is usually 20 KV. RHEED is not only used to obtain information of sample lattice, but it is also used to monitor surface smoothness in real time during molecular beam epitaxial growth.

Suppose \( \mathbf{k} \) is the wave vector of incident electrons on an ideally flat surface, and \( \mathbf{k}' \) is the wave vector of outgoing electrons. According to Von Laue formulation of diffraction by a crystal, and assuming elastic scattering, the relationship between \( \mathbf{k} \) and \( \mathbf{k}' \) follows the equations below. [21]

\[
(k - k') \cdot r = 2m\pi \\
|k| = |k'|
\]
where \( \mathbf{r} \) is any vector of the surface crystal lattice in the case of a smooth surface, and \( m \) is an integer. One can decompose \( \mathbf{k} - \mathbf{k}' \) into \((\mathbf{k} - \mathbf{k}')_\parallel\) and \((\mathbf{k} - \mathbf{k}')_\perp\). \((\mathbf{k} - \mathbf{k}')_\parallel\) is parallel to the sample surface, and \((\mathbf{k} - \mathbf{k}')_\perp\) is perpendicular to the surface. Because \( \mathbf{r} \) is within the surface, it is always valid that

\[
(\mathbf{k} - \mathbf{k}')_\perp \cdot \mathbf{r} = 0,
\]  

(2.6)

Thus, equation 2.4 can be rewritten into

\[
(\mathbf{k} - \mathbf{k}')_\parallel \cdot \mathbf{r} = 2mn, 
\]  

(2.7)

To satisfy both equation 2.5 and equation 2.7, the tip of diffraction wave vector \( \mathbf{k}' \) should not only be on the same Ewald sphere as the tip of incident wave vector \( \mathbf{k} \), but also locate on the reciprocal rods. Here the Ewald sphere has a radius that is equal to \(|\mathbf{k}|\), with the center placed at the starting point of the incident wave vector. And the reciprocal rod 00 is placed at the tip of the incident wave vector. Thus the tip of diffraction wave vector \( \mathbf{k}' \) must be on the spots where rods and the Ewald sphere intersect, with the configuration shown in figure 2.4 (a) and (b). For RHEED experiments with fixed electron acceleration energy, which is usually 20 K eV, the radius of Ewald sphere is fixed. Locations of reciprocal rods determine the arrangement of RHEED spots on the RHEED screen.
Figure 2.4: Schematic diagrams of RHEED. 1. wave vector of incident electrons 2. sample 3. Ewald sphere 4. wave vector of outgoing electrons 5. reciprocal rod 6. RHEED pattern 7. RHEED screen.
For RHEED without considering broadening and assuming the reciprocal rods are infinitely thin, intersections of reciprocal lattice rods and the Ewald sphere will create maximum diffraction spots on the RHEED screen. In a real experiment, this is changed by the fact that there is device broadening and also the reciprocal rods have certain thickness. For atomically smooth terraces, intensity over a reciprocal rod is uniform along the axis, but the rod has thickness due to finite coherence length. Furthermore, the electron energy may not be perfectly sharp, which can turn the Ewald sphere into a spherical shell. Therefore, the intersections of rods and the spherical shell extend, and produce streaks on the RHEED screen, as shown in figure 2.5 (a). If the surface becomes rough in a real experiment, then the intensity over a reciprocal rod becomes less uniform and reciprocal rods change to reciprocal spots, leading to RHEED spots rather than RHEED streaks on the screen, as shown in figure 2.5 (b). The fact that a spotty RHEED pattern corresponds to a rough surface and a streaky RHEED pattern corresponds to a smooth surface is useful for achieving atomically smooth growth by MBE.
Figure 2.5: Schematic diagrams for the formation of a streaky pattern and a spotty pattern.
2.5 Atomic Force Microscopy

Atomic force microscopy images the sample surface by using interaction force between a sample and a tip.

As illustrated in figure 2.6 the laser reflects on the back of the cantilever and enters a position-sensitive photo-detector (PSPD). Responding to the force between the tip and the sample, the cantilever will bend and change the location of reflected laser light on the PSPD. The combination of the laser beam and PSPD can monitor the displacement of the cantilever, and thus the interaction force.

In the constant force mode, which we usually use, the location of the reflected laser light on the position sensitive detector is fixed. During scanning, once the interaction force and the location of the cantilever tends to change due to the surface morphology, a feedback signal will be sent to the electronic module and the computer. According to the feedback signal, the scanner will extend or retract to maintain a constant force between the sample and the tip. Thus the recorded amount that the scanner extends/retracts, \( z(x,y) \), represents the surface morphology of the sample, where \( z \) is the amount of vertical extending/retracting motion of the scanner for the tip at a lateral location \((x,y)\) of the sample surface. The sign of \( z(x,y) \) could be either same with or opposite to the surface morphology depending on the definition of the positive direction of \( z \) for the scanner.
Figure 2.6: AFM schematic diagram.
3 IRON NITRIDE ON WURTZITE GaN

3.1 Introduction

Iron is a well-known useful magnetic material; the corresponding nitride materials, iron nitrides, have many interesting properties. Iron nitrides, having various complex phases such as Fe$_{16}$N$_2$, Fe$_8$N, Fe$_4$N, Fe$_2$N, and FeN, are attractive for their high magnetic moments [22], corrosion and oxidation resistance [15], and many other attractive properties. Motivated by the potential attractive properties, there have been many attempts to achieve Fe-N films of various composition, and using various growth methods including sputtering [23–29], nitriding [30–34], ion implantation [35–38], and molecular beam epitaxy (MBE) [39–43].

Unfortunately, it is difficult to prepare Fe-N films having a single phase, which increases the difficulty of analyzing the properties of the separate phases. It is thus important and useful to explore growth of high quality single phase epitaxial Fe-N films [44]. While the more Fe-rich phases are expected, and have been found, to be magnetic, the phases closer to 1:1 stoichiometry are also very interesting for potential applications.

While zinc-blende FeN has not been reported to have high magnetic moment, it is possible that by growing on different types of substrates (forming strained layers), or by alloying with other nitrides, the material could become magnetic. For example, a theoretical paper has shown the existence of metastable magnetic states in zinc-blende FeN for unit cell volumes larger than the equilibrium value [45]. Therefore it is interesting to explore the growth of FeN in the zinc-blende phase.

In previous studies, Fe-N films have been grown on a wide range of conventional cubic structure substrates, such as MgO [25, 35], GaAs [39], InGaAs [40, 42], NaCl [27, 38], and Ge [46], but not hexagonal (wurtzite) GaN, a fast-developing semiconductor material with important technological applications. Wurtzite GaN is an attractive substrate due to
its wide band-gap (3.4 eV), ultra-violet light emitting characteristics, high hardness, and high-temperature stability.

It might be assumed to be difficult to combine a cubic material film with a hexagonal material substrate. However, as shown recently in our group [47], in some cases cubic structure films can match very well with hexagonal substrates, given a particular growth orientation.

We report successful epitaxial growth of high quality zinc-blende FeN on wurtzite GaN(0001), by employing e-beam evaporation in an ultra-high vacuum MBE chamber. (The contents in this chapter have been published in the reference [48]) The FeN films have a well-oriented epitaxial relationship with the substrate and grow smoothly for the first few monolayers.

3.2 Experimental

The experiments were performed in a custom-designed ultrahigh vacuum (UHV) MBE system with base pressure of low $10^{-10}$ Torr. Films were grown using an Fe e-beam evaporator and a radio-frequency (rf) nitrogen ($N_2$) plasma source. The Fe flux was calibrated using a quartz crystal thickness monitor. The N flux was set by the $N_2$ flow rate and plasma source power.

The substrates used were wurtzite GaN(0001) grown on sapphire(0001) using metal-organic chemical vapor deposition by a commercial vendor. Substrate surfaces were first cleaned with acetone and isopropyl alcohol, then loaded into the MBE chamber and either heated up to $\sim 650$-700 °C for 5 min, or else refreshed with a new layer of GaN by MBE growth.

During growth, reflection high energy electron diffraction (RHEED) using 20 keV electrons was used in-situ to monitor the surface structure and the in-plane lattice parameter. After removal of the grown sample from the chamber, ex situ X-ray diffraction
(XRD) using Cu $K_{\alpha}$ X-rays, was used to determine the crystal structure and out-of-plane lattice parameter. In addition, ex situ Rutherford backscattering (RBS), using incident He$^+$ ions of energy 5.6 or 2.2 MeV, was also carried out to investigate the film stoichiometry by our collaborator, Dr. David C. Ingram. Atomic force microscopy (AFM) was used to determine the surface morphology.

For the FeN film growth reported here, the substrate temperature was set to $\sim 210 ^\circ$C, the Fe flux was set to $\sim 2.3 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1}$, and the growth chamber pressure was set to $\sim 9.3 \times 10^{-6} \text{ Torr}$ with the rf N plasma forward power set to 500 W. The total growth time for the FeN layers discussed here was about 2 h. For the growth conditions used, the rate of FeN growth was $\sim 155 \text{ Å/2hr (± 4%)}$ based on the thickness (for 2-hour growth) estimated from RBS data which yields the sample total number of Fe atoms per unit area. Comparing to the growth rate expected based on the Fe flux rate measured, we find an effective Fe sticking coefficient $S$ during FeN growth of about 0.48.

### 3.3 Results and Discussion

#### 3.3.1 RHEED Evolution

Shown in Fig. 3.1(a) is the RHEED pattern of a wurtzite GaN(0001) substrate surface along $\langle 11\bar{2}0 \rangle$ taken before the start of FeN growth. The streaky pattern indicates a smooth starting substrate surface. Shown in figures 3.1(b - f) are RHEED pattern clips extracted from a 10 min movie that captured the very early stage of an iron nitride film growth on GaN. Each clip shows that the growth orientation of the FeN film conforms to that of the substrate. Later, we discuss the particular orientation and further deduce the crystal structure.

Figure 3.1(b) was captured at 30 s after the growth started, corresponding to about 1/4 monolayer (ML) of deposition. The slightly less streaky RHEED pattern suggests an initial 2-dimensional islanding growth mode. In Fig. 3.1(c), captured at 60 s or $\sim 1/2$ ML
deposition, the RHEED pattern continues to be similar. At 120 s corresponding to one ML deposition, we see that the pattern is more streaky, as seen in Fig. 3.1(d); this suggests that the first ML is very smooth. This could be due to the merging of islands to form a complete layer.

Figure 3.1: RHEED patterns for w-GaN(0001) substrate and FeN thin film surface during growth. (a) GaN surface before FeN growth, along \( \langle 11\bar{2}0 \rangle \); (b-f) initial stages of FeN growth, along \( \langle 110 \rangle \).

After 120 s, the RHEED pattern becomes increasingly less streaky. This can be seen at 240 s (2 ML) and 360 s (3 ML), as seen in Figs. 3.1(e) and 3.1(f). It is consistent
with a transition from a two-dimensional to three-dimensional growth. The initial stage of the growth was followed up to 600 s, about 5 ML, in which this trend continued. The roughening behavior seen between 120 s and beyond is consistent with growth past a critical thickness involving strain relaxation via the formation of three-dimensional islands, defects, and dislocations.

### 3.3.2 Lattice Spacing Evolution

The whole growth evolution for the first 5 ML appears to be consistent with a two-dimensional followed by three-dimensional mode, or the well-known Stranski-Krastanov (S-K) growth mode [49]. To further investigate this initial growth stage, we also measured, using the RHEED reciprocal streak spacing, the lattice spacing versus initial growth thickness for the duration of the 600 s period. This data is plotted in Fig. 3.2, which shows the atomic row spacing as a function of time.

We see that during the first two ML (up to about 240 s) there are some variations or oscillations in the lattice spacing, with an average trend of increasing, starting from the initial GaN inter-row spacing (2.76 Å). At about 2 ML and thicker, the trend is predominantly that the spacing steadily decreases. Below, we offer some possible explanations for the early variations in lattice spacing; such variations at the initial stage of growth differ somewhat from the classical pseudomorphic growth model, in which in the simplest case one expects a constant value up to the critical thickness. Nevertheless, after about 2 ML, the steady decreasing lattice parameter trend is quite consistent with well-known strain relaxation behavior. This is therefore suggestive of a critical thickness of about 2 ML (~ 5 Å).
Figure 3.2: In-plane inter-row spacing versus time, measured for the $\langle \bar{1}10 \rangle_{FeN} \parallel \langle 1\bar{1}20 \rangle_{GaN}$ azimuth, and at the growth temperature.
3.3.3 Crystal Structure Evolution at the Early Stage of Growth

Going back to Fig. 3.1, we notice an additional feature in the data not yet discussed. As the growing FeN film is not perfectly atomically flat, we observe modulations along the streak direction which are due to sampling of several ML’s deep into the surface (this can be due to few-ML height islands on the surface). As seen in Fig. 3.1(b), the top 3 highest intensity points are lined up horizontally, the same as for the GaN surface [Fig. 3.1(a)]. However, clearly visible by 60 s and always after that, we observe a trend of these spots becoming increasingly non-collinear (not lined up along the horizontal).

This shift in the spot-pattern is consistent with a trend from wurtzite structure toward face-centered cubic structure (either rock-salt or zinc-blende) [50]. Such a structural transition is expected, since the structure of FeN is reported to be face-centered cubic, either rock-salt or zinc-blende [51]. The fact that we see evidence of a structural transition at such an early stage of the growth (well before the critical thickness is reached) may partly explain the lattice spacing variations also seen during this early stage. It is also possible that there could be some degree of intermixing of Ga and Fe at the interface which could also affect the lattice spacing in a complex way. Further experiments are underway to explore the latter possibility.

3.3.4 FeN on GaN Growth Beyond the Critical Thickness

For the remainder, we focus on the growth above the critical thickness (about 2 ML). As seen in Fig. 3.2, the lattice spacing above two ML steadily decreases, consistent with a relaxation phase. While the continuous RHEED acquisition ended at 600 s (about 5 ML), individual RHEED patterns were acquired up to the final growth thickness (63 ML) for several different samples.

For the data shown in Fig. 3.2, the in-plane inter-row spacing shows a change of already –0.05 Å starting from 240 s (near \( h_c = 2 \) ML) up to 600 s (5 ML); given that
the additional lattice spacing change from that point (5 ML, 2.735 Å in-plane inter-row spacing) up to the relaxed FeN thickness (2.66 Å in-plane inter-row spacing) is expected to be $-0.075\ \text{Å}$ ($= 2.66 - 2.735\ \text{Å}$), we estimate, using a linear extrapolation model, that the film surface layer will reach the fully relaxed FeN lattice constant at $\sim$ 10 ML total film thickness ($= 8\ \text{ML past } h_c$). Out of a total film thickness of 155 Å (63 ML), we expect therefore about 84% of the film to be fully relaxed.

Shown in Fig. 3.3(a) is the RHEED pattern along the same direction ([\bar{1}10]) as in Figs. 3.1(a-f), here taken at the end of a growth ($\sim$ 155 Å). Fig. 3.3(b) shows the RHEED pattern taken along \langle11\bar{2}\rangle. Neither of the RHEED pattern is streaky, suggesting a 3-D mode at the final stage of growth.

We also see [Fig. 3.3(a)] that the spot pattern has fully evolved to that of fcc. For comparison, the inset to Fig. 3.3(a) shows a reciprocal space map calculated from a superposition of structure factors for two inequivalent [111]-oriented fcc grains. The two inequivalent grains are rotated by 180° with respect to each other; if there was only one type of grain, the RHEED spot pattern would be left-right asymmetrical [50].

A bimodal distribution of grains is understandable, based on the fact that since fcc along [111] has 3-fold symmetry, it will tend to follow epitaxially upon a 3-fold symmetric substrate template. And, although the wurtzite structure has 3-fold bulk crystal symmetry about [0001], the bond directions rotate by 180° upon crossing any single (or odd multiple of single) monolayer step of the [0001] wurtzite surface, leading to A-type and B-type GaN steps and terraces. Therefore, since we expect as many A-type as B-type terraces, we can expect that both types of FeN grains will nucleate, consistent with the final RHEED pattern.

The in-plane lattice constants for several different FeN films at the end of the 155 Å growth were measured from RHEED patterns such as shown in Fig. 3.3. Thus the final layer in-plane spacing was found in the range 2.63 - 2.66 Å or $a = 4.29 - 4.34\ \text{Å}$.
Figure 3.3: RHEED patterns taken from the FeN layer after the growth. (a) $[\bar{1}10]$ azimuth; inset is the corresponding reciprocal space map calculated for two inequivalent [111]-oriented fcc grains; (b) [11$\bar{2}$] azimuth. Both RHEED patterns were taken at the growth temperature.
3.3.5 Epitaxial Orientation with GaN Substrate

The XRD pattern for a FeN film grown for 2 hours on GaN is shown in Fig. 3.4. The spectrum was calibrated using the wurtzite GaN peak as the reference peak. It should therefore locate at 34.60° assuming $c_{\text{GaN}} = 5.185$ Å and a Cu K$_\alpha$ mean wavelength = 1.5418 Å. Besides the large GaN peak, there are two other significant peaks at 36.45° and 77.25°. These peaks correspond to the FeN film; their small intensities are due to the very small FeN film thickness (about 155 Å) compared to the substrate.

![XRD 2θ spectra of FeN sample grown on Ga-polar w-GaN(0001). Measurement was made at room temperature.](image)

Assuming the two small peaks correspond to the first and second order for the FeN ((111) and (222) peaks), we calculate an FeN film average interplanar ($c$-direction) spacing of 4.27 Å. This value is in fairly good agreement with the lattice constant reported for zinc-blende type $\gamma$”-FeN, 4.33 Å [51].
As shown in Fig. 3.2, the in-plane lattice constant is stretched in the strained layer. By the volume conservation principle, the out-of-plane lattice constant is therefore expected to be contracted in the strained layer, compared to a relaxed layer. Thus it is reasonable that our measured XRD (out-of-plane) lattice constant \(a = 4.27 \text{ Å}\) should be slightly smaller than the true relaxed lattice constant, since it is the average of both strained and relaxed layers. In fact, it is slightly smaller than our in-plane lattice constant \(a = 4.29 \text{ Å} - 4.34 \text{ Å}\) at the end of growth measured by RHEED. Note that our RHEED value is very consistent with the reported zinc-blende value of 4.33 Å. [51]

The RHEED and XRD data are therefore quite consistent with each other, and both support the conclusion that the FeN film has a zinc-blende crystal structure with (111) orientation. Furthermore, our measured FeN lattice constant is certainly inconsistent with that reported for the rock-salt structure (4.50 Å) [51]. Thus, for our growth conditions, we find the epitaxial orientation with the GaN substrate to be \([111]_{ZB-FeN} \parallel [0001]_{w-GaN}\).

Using RBS data, our FeN film stoichiometry was measured, and the result was found to be iron fraction \(F_{Fe} = 55-58\%\) and corresponding N fraction \(F_N = 45-42\%\). This result is also consistent with previous experiments which found N fractions less than 50% [51]. Since our lattice constant values do not suggest metal interstitials, the RBS data therefore indicates N vacancies for our sample. N vacancies are in fact very common for transition metal nitrides, including ScN and MnN, [52, 53] which we have previously investigated. Therefore, we infer that the FeN film has a composition ratio of Fe:N in the range 1.0:0.82 - 1.0:0.72.

Now we discuss the in-plane orientation of the FeN film with respect to the GaN substrate. The FeN crystal vector directions for the RHEED patterns (shown for example in Figs. 3.3(a) and 3.3(b)) correspond to the substrate GaN \(\langle 11\bar{2}0 \rangle\) and \(\langle \bar{1}100 \rangle\), respectively. Thus, we also see that the azimuthal (in-plane) orientation of the film is lined up with that
of the substrate, and there is no rotation of the film with respect to the substrate. Thus we have the in-plane orientations \( \langle \bar{1}10 \rangle_{FeN} \parallel \langle 11\bar{2}0 \rangle_{GaN} \) and \( \langle 11\bar{2} \rangle \parallel \langle 1\bar{1}00 \rangle \).

In fact, this orientation was assumed already in displaying the calibration for Fig. 3.2 and the discussion of the lattice parameters of the FeN films, in which the inter-atomic spacing of Ga atoms, being 3.189 Å, leads to the inter-row spacing of the \( \langle 11\bar{2}0 \rangle \) direction equal to 2.76 Å. This spacing compares to the measured values for the relaxed FeN film of 2.63 - 2.66 Å, corresponding to an Fe-Fe inter-atomic spacing of 3.04 - 3.07 Å. The in-plane mismatch between the film and the substrate is therefore about \(-4.2\%\).

### 3.3.6 Film Topography and Epitaxial Growth Model

As seen in Fig. 3.5, the AFM image of the as-grown FeN film shows an array of uniformly distributed 3-D islands having lateral diameters of \( \sim 84 \) nm (valley-to-valley). These 3-D islands are spaced quite closely together, showing that they have merged to form a nearly continuous thin film. Analysis of the image shows that the root-mean-square(rms) roughness is 1.44 nm, but line profile measurements find islands having heights in the range \( \sim 1 - 8 \) nm. The larger island diameters (widths) compared to the much smaller island heights (width:height ratio = 10 - 84) shows that the surface, while not atomically flat, is still relatively smooth.

In Fig. 3.6, we show the structural model of the FeN (111) film growth on Ga-polar w-GaN(0001). The upward directions are [111] and [0001] for FeN and GaN, respectively. Their perpendicular directions are \( \langle \bar{1}10 \rangle \) for FeN and \( \langle 11\bar{2}0 \rangle \) for GaN. This model is based upon the conclusions drawn from the experimental data presented here. The film grows very smoothly with only small lattice spacing variations for the first about 2 ML, implying a strained initial layer. After this initial 2 ML, which corresponds to the critical thickness (about 5 Å), the film begins to relax during growth up to a layer thickness of at least 10 ML.
Figure 3.5: AFM image of a FeN film after 2-hour growth. The peak-valley height for the whole image area is $\sim 10$ nm, while the typical island height is 4-5 nm.

Figure 3.6: Structural model of FeN(111)/GaN(0001) in side view showing epitaxial relationship of FeN(111) to Ga-polar w-GaN(0001). Topography suggested is only qualitative.
= \sim 25 \text{ Å}. The relaxation process correlates with a change from 2-D to 3-D growth. Also, we observed that the crystal structure very quickly evolved from wurtzite to zinc-blende within as little as a few ML, and is fully evolved into zinc-blende by the end of the 155 \text{ Å} growth.

3.4 Conclusions

We demonstrated the growth of (111)-oriented FeN thin layers on GaN(0001) using molecular beam epitaxy using e-beam evaporation of Fe in combination with rf N-plasma with N\textsubscript{2} as the source gas. The results are that the FeN growth is consistent with a 2-D to 3-D (S-K) growth mode. The 2-D mode portion of the growth extends to about 2 ML. After this, the film began to relax, and we estimate an additional 8 ML (at least) of growth before reaching the fully relaxed lattice constant. The relaxation process correlates with a roughening of the film surface. Also, even from the very early stage of growth, the RHEED pattern shows signs of conversion from wurtzite structure at the FeN/GaN interface to face-centered cubic structure. Careful analysis of the RHEED and XRD data leads to the conclusion that the grown film has zinc-blende structure with relaxed lattice constant \( a \) in the range 4.29 - 4.34 Å. Furthermore, the RBS data finds that the FeN stoichiometry is Fe:N = 55:45 (1.0:0.82) up to 58:42 (1.0:0.72); the data suggests the existence of N vacancies. The film is epitaxial with the substrate, and the epitaxial orientation was determined to be \([111]_{\text{FeN}} \parallel [0001]_{\text{GaN}}\) and \(\langle \bar{1}10\rangle_{\text{FeN}} \parallel \langle 1\bar{1}20\rangle_{\text{GaN}}\) and \(\langle 11\bar{2}\rangle_{\text{FeN}} \parallel \langle 1\bar{1}00\rangle_{\text{GaN}}\), with two types of [111]-oriented FeN grains, 180° apart from each other.
4 Iron on Ga-Polar Wurtzite GaN

4.1 Introduction

Injection of spin-polarized current from ferromagnetic metals into semiconductors is an important approach to enable the use of spin degree of freedom in semiconductors. [1, 54] Efficient spin injection from ferromagnetic metals to semiconductors can be achieved with Schottky tunnel barrier at the interface between ferromagnetic metals and semiconductors. [6–9] There have been many studies of Fe on conventional semiconductor substrates, including GaAs. [55–61] Wide bandgap semiconductor GaN has increasing applications in electronic and optoelectronic devices. [10–12] Furthermore, it has been predicted that spin lifetime in pure GaN would be about three orders of magnitude longer than that in GaAs, [62] making GaN a promising semiconductor base besides conventional Si and GaAs.

A few groups have carried out studies of iron on Ga-polar wurtzite GaN grown with molecular beam epitaxy (MBE). [63–66] There are few studies focusing on initial heteroepitaxy phase of iron on wurtzite GaN by STM, especially for submonolayer Fe deposited on GaN surfaces. [66, 67] He, et al, reported STM studies of ultra-thin layers of iron on bulk-terminated GaN(0001)1×1 surface and iron on GaN pseudo- 1×1 surface; particularly, Fe induced √7 × √7 reconstruction was observed for 0.16 ML Fe on GaN pseudo-1 × 1 surface. [67] Despite of limited number of such studies, it is of great importance to investigate the initial phase of iron on wurtzite GaN, because the interface could significantly affect properties of ferromagnetic metals/semiconductors. Recent studies of interface over Fe/GaAs show that the composition and bonding at the interface affect spin injection more than the bulk properties of the Fe contact. [68]

Here we report our studies of initial phase of iron heteroepitaxy on atomically smooth GaN(0001) pseudo-1×1-1+1/12 surface. GaN(0001) pseudo- 1×1 surface is the most Ga-
rich structure on GaN(0001), and there is a Ga bilayer at the top of the surface according to the model proposed by Smith, et al. [14] One characteristic of pseudo-1 × 1 surface is the existence of additional so called 1 + 1/6 or 1 + 1/12 streaks at room temperature. In previous studies of Fe on GaN pseudo-1 × 1, the difference between pseudo-1 × 1-1 + 1/12 and pseudo-1 × 1-1 + 1/6 was not addressed for Fe deposition. These two surfaces could have different effects for iron deposition. Therefore it is useful to distinguish them for Fe deposition. In RHEED patterns, the distance between GaN main streak and 1 + 1/6 is about 1/6 of main streaks spacing, while the distance between GaN main streak and 1 + 1/12 is about 1/12 of main streaks spacing. GaN(0001) pseudo-1×1-1 + 1/12 is more Ga-rich than GaN(0001) pseudo-1×1-1+1/6. [14] We will focus on Fe/GaN(0001) pseudo-1×1-1+1/12 here.

We used both STM and in situ reflection high energy electron diffraction(RHEED) for comparative studies in real space and momentum space. STM images show iron induced 2-D islands growing from the step edge of GaN(0001) 1 × 1 − 1 + 1/12 surface, as well as the ordering on the 2-D islands.

4.2 Experimental

We performed the experiments in a custom-designed MBE/STM system. We grew fresh GaN(0001) pseudo-1 × 1-1 + 1/12 using a Ga effusion cell and a radio-frequency (rf) nitrogen (N₂) plasma source, on commercially available GaN (0001) substrates, and deposited Fe using an Fe effusion cell. We calibrated Fe and Ga fluxes using a quartz crystal thickness monitor and set the N-plasma flux by setting the growth chamber pressure and the plasma source power.

A commercially available GaN (0001) substrate was loaded into the UHV growth chamber after solvent cleaned. The substrate was heated at the temperature of ~ 720 °C under N-plasma for 20 - 30 minutes. Growth of fresh GaN(0001) pseudo-1 × 1-1 + 1/12
was carried out at the temperature of $\sim 670-690$ °C, with Ga flux of about $4.8 \text{ atoms} \times 10^{14} /\text{cm}^2 \text{ s}$, growth chamber pressure set to $\sim 2.1 \times 10^{-5}$ Torr and rf N-plasma forward power set to 500 W. During growth, RHEED was used to monitor the surface smoothness. After an atomically smooth surface was established, the sample was cooled to room temperature to verify the existence of $1 + 1/12$ streaks of GaN(0001) pseudo-1 × 1-1 + 1/12 surface. Fe was deposited on GaN(0001) pseudo-1 × 1-1 + 1/12 at the temperature of $\sim 360$ °C. The amount of Fe deposition was about $4.8 \times 10^{14} \text{ atoms/cm}^2$, $\sim 0.42$ ML (based on GaN lattice, $11.35 \times 10^{14} \text{ atoms/cm}^2$ for 1 ML). STM experiments were performed in the UHV analysis chamber adjacent to the growth chamber.

4.3 Results and Discussion

Figure 4.1: RHEED patterns for Fe on GaN(0001) pseudo-1 × 1-1 + 1/12 taken along GaN $\langle 11\bar{2}0 \rangle$ (left side) and $\langle 1\bar{1}00 \rangle$ (right side). (a/b) the GaN surface at room temperature before Fe deposition; (c/d) the GaN surface at the growth temperature before Fe deposition; (e/f) Fe/GaN surface at the growth temperature; (g/h) Fe/GaN surface at the room temperature.
The RHEED patterns before iron deposition in figure 4.1 (a)(b) at room temperature and (c)(d) at the growth temperature, indicate an atomically smooth GaN(0001) pseudo-1 × 1-1 + 1/12 surface. The streaky RHEED patterns after sub-ML iron deposition in figure 4.1 (e)(f) at the growth temperature and (g)(h) at room temperature, indicate that the surface is still atomically smooth. Additional 1/3 and 2/3 order streaks appeared in the RHEED pattern taken along ⟨1̅100⟩ after the iron deposition, indicating new surface structure. After the sample is cooled down to room temperature, RHEED patterns change significantly. 6×6 streaks appear along GaN ⟨11̅20⟩ and ⟨1̅100⟩. In the 6× streaks along ⟨1̅100⟩, some streaks have different intensity against the other streaks, as illustrated in figure 4.1-(h). The RHEED patterns suggest a distinct surface structure with sub-ML iron onto GaN(0001) pseudo-1 × 1-1 + 1/12.

Figure 4.2-(a) displays atomically smooth steps on a GaN(0001) pseudo-1×1-1+1/12 surface. Figure 4.2-(b) shows novel waffle-like 2-dimensional (2-D) islands on the surface of sub-ML iron/GaN(0001) pseudo-1 × 1-1 + 1/12. Some just started the growth, so the lateral size is rather small; while others have developed larger lateral size. The 2-D islands from the lower sides of step edges have V-shape, and round shape. The islands always grow outward from the GaN step edges in 2-dimensional growth mode. This can be explained in term of Ehrlich-Schwoebel barrier. [69–71] As illustrated in figure 4.3-(a), as atoms approach the higher side of the step edge, their direction will change due to the energy barrier at the higher side of the step edge. At the lower side of the step edge, the energy is lower, which serves as a trap for atoms approaching. Therefore, they would tend to stay and result in the growth from the lower side of the step edge, as shown in figure 4.3-(b). As illustrated in the line profile (figure 4.2-(c)), the heights of the 2-dimensional islands are about 1.8-2.0 Å. Furthermore, no matter growing from a lower side of step edge of a single step or a double step, the 2-D island heights are same. The parallelogram-shaped label in
Figure 4.2: (a) STM image of a GaN(0001) pseudo-1×1-1+1/12, $V_S = -1.75$ V, $I_t = 0.10$ nA; (b) STM image of the waffle-like feature of iron deposited on a GaN(0001) pseudo-1×1-1+1/12 surface, $V_S = -1.75$ V, $I_t = 0.10$ nA, in (b), the image is applied extra plane subtraction for displaying purpose only; (c) Line profile over the feature with GaN steps oriented horizontally.
Figure 4.2-(b) marks a $6 \times 6$ cell on the waffle-like island. The waffle-like islands also grow in a spiral growth region of the GaN surface, as illustrated in figure 4.4. The curved arrows indicate the spiral growth of the GaN surface. Clearly, the waffle-like islands grow from the GaN edge, despite of the curved shape of spiral growth.

Figure 4.3: (a) Atoms approaching the higher side of a step edge reverse their direction due to the energy barrier, and atoms approaching the lower side tend to stay near the lower side of the step edge due to the energy trap; (b) atoms grow from the lower side of the step edge.
Figure 4.4: STM image of the waffle-like feature on the spiral growth region of a GaN(0001) pseudo-1 $\times$ 1-1 + 1/12 surface, after iron deposition, $V_S = -1.75$ V, $I_T = 0.10$ nA. The two arrows indicate spiral growth of the GaN.
We construct models for the Fe-induced 2-D islands on GaN(0001) pseudo-1 \times 1-1 + 1/12, based on GaN(0001) pseudo-1 \times 1 model proposed by Smith et al. \cite{14}. Figure 4.5-(a) displays the top view of Ga-polar bulk GaN(0001). The smaller parallelogram-shaped mark represents a 1 \times 1 surface unit cell for top Ga layer of GaN(0001), and the larger parallelogram-shaped label represents a 6 \times 6 cell. Figure 4.5-(b) displays the side view of Ga-polar bulk GaN(0001) for the region within the rectangle mark in figure 4.5-(a), in which Ga to N bond is pointing upward, along growth direction. As illustrated in figure 4.5-(c/d), there are two Ga layers on the top of the bulk GaN for GaN(0001) pseudo-1 \times 1-1 + 1/12. In the first layer, Ga atoms follow 1 \times 1 lattice. In the second layer, 7 \times 7 of Ga atoms are packed into a 6 \times 6 cell on the surface for GaN(0001) pseudo-1 \times 1-1 + 1/12. The top Ga layer has fluid-like nature, given the low melting temperature of Ga, 303 K, which is near room temperature.

As iron atoms are deposited onto GaN(0001) pseudo-1 \times 1-1 + 1/12, iron atoms are likely to sink into Ga bilayer, pushing some Ga atoms to the top. \cite{72} Corresponding to the model in figure 4.6-(a/b), when deposited onto the GaN surface at the growth temperature, iron atoms sink into Ga bilayer at \sqrt{3} \times \sqrt{3} – R30° locations, and some Ga atoms are driven to the top surface. Because the top Ga atoms from Ga bilayer are very mobile, the key contributions to RHEED patterns from the 2-D islands are coming from \sqrt{3} \times \sqrt{3} – R30° lattice of Fe atoms. We simulate RHEED profile for 2-D island by plugging \sqrt{3} \times \sqrt{3} – R30° lattice of Fe into a RHEED simulation program. \cite{73} Simulated RHEED profiles for the surface are shown in figure 4.6-(c/d), which are in good agreement with experimental RHEED profiles in 4.6-(e/f). There are \frac{1}{3}-order and \frac{2}{3}-order streaks for \langle 1 \bar{1} 00 \rangle in both simulated and experimental RHEED profiles, as indicated by arrows.
Figure 4.5: Model for bulk GaN(0001) (a/b, top view/cut view); model for GaN(0001) pseudo-1 × 1-1 + 1/12 (c/d, top view/cut view).
Figure 4.6: Model for iron/GaN(0001) pseudo-1 × 1-1 + 1/12 at the growth temperature, iron atoms sink into Ga adlayer, with Ga atoms driven out, top view (a), cut view (b); simulated RHEED profile for the sample at the growth temperature with beam along GaN \langle 1\bar{1}20 \rangle (c), and along GaN \langle 1\bar{1}00 \rangle (d); experimental RHEED profiles for beam along GaN \langle 1\bar{1}20 \rangle (e), and along GaN \langle 1\bar{1}00 \rangle (f), after background subtraction and normalization by central peak height.
After the sample is cooled down to room temperature, Ga atoms at the top of the 2-D islands become less energetic, resulting in a change in surface structure. It is not a surprise that these Ga atoms could form $6 \times 6$ lattice, given that in the aforementioned model for GaN(0001) pseudo-$1 \times 1 - 1 + 1/12$, $7 \times 7$ Ga atoms are packed into a $6 \times 6$ cell. Figure 4.7-(a) is a zoomed in image of a 2-D island, showing that half region in the $6 \times 6$ cell is more filled than the other half region in the cell, and atoms at corners stay at slightly higher level than those inside the marked cell. A possible model is shown in figure 4.7-(b) and figure 4.8-(a/b). In figure 4.7-(b), only Ga atoms at the top are shown for convenient comparison with the STM image. There are more Ga atoms filling in the half region(BCD) than the other half region(ABD) in the model, consistent with the STM image.

![Figure 4.7](image.png)

Figure 4.7: (a) Zoomed in STM image of a waffle-like 2-D islands; (b) model for iron/GaN(0001) pseudo-$1 \times 1 - 1 + 1/12$ after cooling down to the room temperature, top view for Ga atoms at the top only.

Figure 4.8 (a/b) displays the model for the iron/GaN(0001) pseudo-$1 \times 1 - 1 + 1/12$ at room temperature with multiple layers. The level for Ga atoms within the cell is slightly lower (0.5 Å) than that for Ga atoms at the corners of the cell. By the aforementioned RHEED simulation program, we again use the Ga arrangement on the top layer and the $\sqrt{3} \times \sqrt{3} - R30^\circ$ Fe ordering to simulate RHEED profile for 2-D island regions. The form factor ratio of Ga form to Fe atom is set to $1 : 0.84$ according to the form factors corresponding to 20 Kev electron beam energy ($31.37 : 26.38 = 1 : 0.84$), available
in the national institute of standards and technology (NIST) X-ray attenuation databases. [74] The simulated RHEED profile are shown in figure 4.8-(c)\((\langle 11\bar{2}0\rangle)\) and figure 4.8-(d)\((\langle 1\bar{1}00\rangle)\). For \(\langle 11\bar{2}0\rangle\), there are five fractional streaks at \(\frac{1}{6}\), \(\frac{2}{6}\), \(\frac{3}{6}\), \(\frac{4}{6}\), and \(\frac{5}{6}\)-order, in good agreement with the experimental RHEED profile(figure 4.8-(e)). For \(\langle 1\bar{1}00\rangle\), \(\frac{2}{5}\), \(\frac{4}{5}\)-order streaks have higher intensity over \(\frac{1}{6}\), \(\frac{3}{6}\) and \(\frac{5}{6}\)-order streaks, also in good agreement with RHEED profile(figure 4.8-(f)). The 2-D waffle-like islands coverage fraction \((f_{\text{island}})\) on the surface is about 1/3 of the surface (0.34 based on a survey of STM images). In the aforementioned model, the iron contained in the 2-D island is 1/3 ML. Therefore, the iron amount on the surface is \((1/3 \text{ ML}) \times (1/3) = 1/9 \text{ ML}\). The estimated ratio of the amount of iron that remained on the surface to the amount deposited is \((1/9\text{ML})/(0.42\text{ML}) = 0.26\).

### 4.4 Conclusions

We investigated \(\sim 0.42 \text{ ML}\) iron deposition on GaN pseudo-\(1 \times 1-1 + 1/12\) surface. With Fe deposition, 2-D islands grow outward from step edge of the GaN surface. Room temperature STM reveals a clear \(6 \times 6\) structure of the 2-D islands, consistent with RHEED patterns taken at room temperature. The island heights are about 1.8 to 2.0 Å. We have constructed models for the two different surface structures at the growth temperature and room temperature. The two different surface structures are reversible as illustrated using RHEED experiments. The simulated RHEED profiles based on the models agree well with experimental RHEED profiles, and STM results at room temperature.
Figure 4.8: Model for iron/GaN(0001) pseudo-1 \times 1-1 + 1/12 after cooling down to room temperature, top view (a), cut view (b); simulated RHEED profile for beam along GaN $\langle 1\overline{1}20 \rangle$ (c), and along GaN $\langle 1\overline{1}00 \rangle$ (d); experimental RHEED profiles for beam along GaN $\langle 1\overline{1}20 \rangle$ (e), and along GaN $\langle 1\overline{1}00 \rangle$ (f), after background subtraction and normalization by central peak height.
5 Iron on N-polar Wurtzite GaN

5.1 Introduction

As a wide band gap semiconductor, wurtzite GaN is a promising material for spintronics. One important application is ferromagnetic metal/semiconductor structures for spin injection. It was predicted by S. Krishnamurthya et al. that spin lifetime in pure GaN would be longer than that in the conventional semiconductor GaAs. [62] The longer spin lifetime makes GaN an attractive alternative to more traditional semiconductors for potential spintronic applications.

A few studies of Fe growth on Ga-polar GaN(0001) have been reported; [64, 66, 67] but for the N-polar GaN(000̅1) surface, there have been almost no studies with the exception of a recent paper by Gao et al. [75] In their paper, they reported epitaxial orientations of Fe on GaN(000̅1) for thin film samples consisting of 30 nm Fe deposited onto high temperature annealed GaN.

Epitaxial growth of compound semiconductors typically depends sensitively on the III/V (cation/anion) ratio, and this is often related to the relative stability of different surface structures. In particular, it is desirable for device injection efficiency to have a well-ordered semiconductor surface. Growth of ferromagnetic material on compound semiconductor surfaces therefore must consider the stoichiometry of the surface which, after combining with the ferromagnetic material, can influence the resultant magnetic properties especially taking into account the possibility of formation of interfacial compounds. For example, growth of Fe on GaAs surfaces has been studied by Schultz et al., in which a thin interface layer consisting of Fe₃Ga was reportedly formed. [68]

In the case of GaN growth, the well-ordered surface is frequently grown under Ga-rich conditions, and stable surface structures (including 1 × 1, 3 × 3, 6 × 6, and c(6 × 12)) [13] are all relatively Ga-rich. Removing too much Ga from the surface by annealing can lead
to a disordered surface, particularly if the 1×1 Ga adlayer is decomposed, which can easily happen in high-temperature annealing. Therefore, it is desirable to explore Fe growth on the well-ordered, Ga-rich GaN growth surface and also to examine the dependence of the Fe growth on the surface stoichiometry.

By depositing sub-monolayer Fe onto the atomically smooth GaN surface at ∼210 °C containing both Ga-rich and less-Ga-rich regions, we have found that the Fe selectively grows in the Ga-rich regions. Furthermore, after depositing Fe onto a Ga-rich atomically smooth GaN surface at ∼210 °C, we annealed the sample to higher temperature (∼360 °C) and observed significant improvement in the ordering of the Fe island structures. Intrigued by that, we then directly grew Fe on a Ga-rich GaN surface at the higher temperature (∼360 °C) and obtained further improvements in Fe layer quality. We will present here the scanning tunneling microscopy and reflection high energy electron diffraction studies in which these effects are observed.

5.2 Experimental

The experiments were carried out in a custom-designed ultra-high vacuum (UHV) molecular beam epitaxy/scanning tunneling microscopy (MBE/STM) system. In the MBE chamber, GaN was grown using a radio-frequency (rf) nitrogen plasma source and a gallium effusion cell; Fe was deposited using an Fe effusion cell. In the adjoining analysis chamber, the STM studies were performed on samples transferred directly from the MBE chamber.

In detail, sapphire substrates were solvent-cleaned in acetone and isopropanol before being loaded into the system. After being heated under N-plasma for about one hour at ∼800 °C, a GaN buffer layer was first grown at ∼620 °C followed by the main GaN layer which was grown at ∼690-730 °C. During growth, the N-plasma power was set at 500 W, and the MBE chamber pressure was set to ∼1.9 ×10⁻⁵ Torr. A smooth Ga-rich, N-polar GaN surface was then achieved. The surface structure was monitored during growth
using *in-situ* reflection high energy electron diffraction (RHEED). The surface showed a streaky RHEED pattern after growth. Such surfaces exhibit well-ordered, atomically-smooth terraces in STM. On the smooth GaN surface, sub-monolayer (sub-ML) Fe was deposited mainly at two different temperatures (∼ 210 and ∼ 360 °C). The iron deposition amount is $4.8 - 5.0 \text{ atoms} \times 10^{14}/\text{cm}^2$, ∼ 0.43 ML if we count it based on GaN lattice (11.35 × 10^{14} \text{ atoms/cm}^2 for 1 ML).

### 5.3 Results and Discussion

The amount of gallium on the gallium nitride (000$\bar{1}$) surface in the form of gallium adatoms is a key parameter in the formation of iron-based structures at the surface of GaN layers. Therefore, it is important to explore the dependence on gallium coverage in these experiments. In addition, it is important to explore the substrate temperature dependence of the Fe-deposited surface. As shown in table 5.1, one may consider the four different types of surface preparation procedures which we have explored in this study. All four types involve GaN growth under Ga-rich conditions as the starting point, in order to create an atomically smooth GaN surface. For Type I, additional annealing is performed at $T_{Sub} \sim 650\text{-}700 \, ^\circ\text{C}$ after the completion of growth (after turning off the N plasma source) in order to create a Ga-poor GaN surface, on which Fe is subsequently deposited at $T_{Sub} \sim 210 \, ^\circ\text{C}$. For purposes of this chapter, we use the term Ga-poor to mean a surface which consists on average of only the Ga adlayer + additional very small quantities of Ga adatoms, i.e. < 0.1 ML Ga adatoms; although overall the surface is mostly 1×1, locally there can still be some Ga-rich regions. For Type II, Fe is directly deposited onto the as-grown GaN surface (no additional annealing) at $T_{Sub} \sim 210 \, ^\circ\text{C}$. For Type III, Fe is directly deposited at $T_{Sub} \sim 210 \, ^\circ\text{C}$ onto the as-grown surface, followed by annealing up to ∼ 360 °C. And finally for Type IV, Fe is directly deposited onto the as-grown surface at $T_{Sub} \sim 360 \, ^\circ\text{C}$. 
Table 5.1: Types of Fe/GaN (000\bar{1}) samples studied as a function of starting surface and Fe deposition/annealing temperatures.

<table>
<thead>
<tr>
<th>Type</th>
<th>Starting surface</th>
<th>Deposition and annealing temperatures</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>Ga-poor GaN</td>
<td>Fe deposition at ( \sim 210^\circ C )</td>
</tr>
<tr>
<td>II</td>
<td>Ga-rich GaN</td>
<td>Fe deposition at ( \sim 210^\circ C )</td>
</tr>
<tr>
<td>III</td>
<td>Ga-rich GaN</td>
<td>Fe deposition at ( \sim 210^\circ C ) + annealing at ( \sim 360^\circ C )</td>
</tr>
<tr>
<td>IV</td>
<td>Ga-rich GaN</td>
<td>Fe deposition at ( \sim 360^\circ C )</td>
</tr>
</tbody>
</table>

Next, we consider in detail the results for the Type I surface. The starting Ga-poor surface is atomically smooth as indicated by the streaky RHEED patterns in figure 5.1(a) and (b). After depositing \( \sim 0.43 \text{ ML} \) iron onto this Ga-poor surface, the RHEED pattern is still streaky, as seen in Fig. 5.1(c) and (d) but contains some very weak \( \frac{1}{4} \)-order lines along \( \langle 11\bar{2}0 \rangle \) and some weak \( \frac{1}{2} \)-order lines along \( \langle 1\bar{1}00 \rangle \); this suggests the existence of a new ordered Fe-induced structure at the surface.
Figure 5.1: RHEED patterns for Fe on N-polar GaN (000\bar{1}) taken along GaN \langle11\bar{2}0\rangle (left side) and \langle\bar{1}00\rangle (right side). (a/b) Ga-poor GaN surface before Fe; (c/d) Type I Fe/GaN surface; (e/f) Ga-rich GaN surface before Fe; (g/h) Type II Fe/GaN surface; (i/j) Type III (annealed) Fe/GaN surface; (k/l) Type IV Fe/GaN surface. All taken at growth/annealing temperature.

Shown in Fig. 5.2 are STM images of the Type I Fe/GaN surface. As seen in Fig. 5.2(a), the Type I surface shows regions of 1\times1 which appear featureless without excess Ga
adatoms (A regions) and regions containing island structures (B regions). The featureless A regions correspond to the 1×1 Ga adlayer structure. The island-like B regions appear to contain excess gallium in the regions between the islands, suggesting that the islands tend to grow in the local Ga-rich regions. A line profile across the image at the location of the dashed line is displayed in Fig. 5.2(b). The profile shows the existence of GaN bilayer steps with height \( c/2 = 0.26 \) nm along with islands of height \(~ 0.51\) nm and width \(~ 10\) nm. The shapes of the islands vary from rounded to square-like. We also see a pit on the 1×1 step region in the image (Fig. 5.2(a)) and line profile (Fig. 5.2(b)). This is due to the dissociation of GaN during high temperature annealing.
As shown in figure 5.2(c) taken within an island-containing B region, we resolved ordering on the islands as well as within the regions between the islands. The islands themselves exhibit different types of ordering. As seen in the lower left island, a row-like reconstruction is observed; whereas, the island at middle right of the image shows an oblique-type ordering with the lattice oriented at $\sim 30^\circ$ with respect to the rows of the other island. A zoom-in view of this island structure is shown in Fig. 5.2(d) where we see that the island surface consists of atomic-like protrusions with a spacing of $\sim 1.0$ nm. Further work is on-going to determine if this regular array corresponds to a reconstruction or to a bulk-like periodicity of one of several possible Fe-Ga phases.

As for the areas surrounding the islands, we see the reconstruction is similar to the well-known c(6×12) although not as well-ordered. [13] Such features are frequently found for the Fe/GaN samples presented here. Ga-rich surfaces prior to Fe deposition were also studied by STM during these experiments, and some similar structures were found on those surfaces as well, and sometimes co-existed with c(6×12) reconstruction. The disordered is likely due to the presence of Fe impurities, and similar effects in the case of Mn impurities have also be observed in our group. [76]

Based on the results for the Type I sample, it is clear that the Fe islands have a strong tendency to nucleate within the Ga-rich regions (B regions). This tendency can be explained in terms of island nucleation probabilities. At $\sim 210^\circ$ C, Ga adatoms can move freely on the Ga adlayer (A regions), as is clear from many previous RHEED and STM experiments. This can be understood since Ga is a liquid already near room temperature (melting pt. 303 K). Iron has a much higher melting point on the other hand (1808 K). Iron atoms landing on the A regions encounter a potential energy landscape where it is relatively easy to move around at $\sim 210^\circ$ C. In comparison, Fe atoms landing on regions containing additional Ga adatoms (B regions) have a much higher probability of encountering other unbound Ga adatoms and forming Fe-Ga dimers. Dimer diffusion would be expected to be much slower,
Figure 5.2: STM images of Type I Fe/GaN(000$\bar{1}$) surface. The island width is typically about 10 nm; island height is typically about 6 Å. The ellipse marks the dissociated region on the GaN(000$\bar{1}$) $1 \times 1$ step. a) Area including both Type A and Type B regions, $V_S = 1.75$ V, $I_t = 0.10$ nA; the steps shown in the image(a) are tilted by applying plane subtraction for convenient viewing only; b) line section at the location marked in (a); c) zoom-in of Type B-region, $V_S = 1.00$ V, $I_t = 0.15$ nA; the arrow indicates the row direction of a 2-dimensional (2-D) island having row-like structure (marked by star); the ellipse marks GaN-like reconstruction; d) atomic-resolution zoom-in of another 2-D island having oblique lattice, $V_S = 1.00$ V, $I_t = 0.15$ nA; e) line section at the location marked in (c).
thus leading to island nucleation within the Ga-rich B regions. Fast diffusion of Fe within the Ga-poor A regions will lead accumulation of adatoms within the adjacent Ga-rich B regions, as evident from the STM images of Fig. 5.2.

Referring back to Fig. 5.2(c), we also notice a tendency for the islands to have similar heights. This is seen in the line section displayed in Fig. 5.2(e), which shows that the two islands have heights of \( \sim 0.6 \) nm and \( 0.7 \) nm measured from the GaN-like region; the difference is therefore only \( \sim 1 \) Å. The GaN-like areas have a height of \( \sim 1.8 \) Å (in range of 1-2 Å) relative to the 1×1 Ga adlayer level, base on a survey on the samples presented here. The islands have heights of \( \sim 0.78 \) nm and \( 0.88 \) nm relative to the 1×1 Ga adlayer level. As it is known in many other systems that uniform height islands can be the result of energetic mechanisms, it is therefore possible that an energetic mechanism may also be at play in this case to result in the formation of uniform-height islands.

To further explore the growth of Fe islands within Ga-rich areas of the N-polar GaN surface, we have studied the Type II sample in which growth under Ga-rich conditions was followed without any annealing, leaving the sample in a Ga-rich state over the entire surface. RHEED patterns for the Type II sample prior to Fe deposition are shown in figure 5.1(e) and (f) in which a 3×3 reconstruction in RHEED patterns is clearly observed after cooling the sample to room temperature. However, after \( \sim 0.43 \) ML iron deposition, the 3× streaks have almost completely disappeared, as seen in Fig.5.1.(g) and (h). Nor are any new 2× streaks seen after Fe deposition for the Type II sample.

STM measurements of the Type II sample with Fe are shown in Fig. 5.3(a); here it is seen that the surface consists of a high density of islands similar to what was observed on the Type I sample in the B regions [see Fig.5.2(a)]. However, the island features for the Type II sample do not reveal any particular reconstructions or ordering, consistent with the lack of Fe-induced reconstruction streaks [see Fig.5.1(g) or (h)]. A line profile across the
Figure 5.3: a) STM image of Type II Fe/GaN(000\bar{1}) surface showing Type B region, $V_S = -3.00$ V, $I_t = 0.15$ nA; b) line section at the location marked in (a); c) STM image of Type III Fe/GaN(000\bar{1}) surface showing 3-fold rotated domains of row-structured islands, $V_S = -1.75$ V, $I_t = 0.10$ nA; d) line section at the location marked in (c). Arrows indicate GaN \langle 11\bar{2}0 \rangle directions.
island features, as presented in Fig. 5.3(b), reveals a variety of island heights and shapes, but similar to the case of the Type I sample, the maximum height is about 0.6-0.7 nm.

In order to improve the structure of the islands, the Type II sample was annealed at (∼360°C) for one hour (which is referred to as the Type III sample). As seen in Fig. 5.1(i) and (j), annealing leads to a clear 4×2 pattern in RHEED. After cooling down to room temperature, the 4×2 pattern remained.

As shown in Fig. 5.3(c), STM images show that the Type III (annealed) sample exhibits 2-dimensional, row-reconstructed islands having 3 different crystalline directions at 120° from each other. The row orientations therefore correspond to the 3-fold symmetry of the GaN substrate surface and in particular to the ⟨1120⟩ directions of the GaN substrate surface. We also see that the row-reconstructed islands appear to sit on a broader featureless plateau, which is likely due to tip effect. Surrounding the plateau regions can clearly be observed areas of GaN-like reconstruction exhibiting the disordering which is also apparent between the islands in the Type I sample (Fig. 5.2(c)). Again taking a line section of the height data reveals that the row-reconstructed islands have heights of 0.6 nm with respect to the disordered GaN-like regions, 0.7-0.8 nm with respect to the 1×1 Ga adlayer level.
Based on the successfulness of the annealing in producing a surface with more consistent island domains, Fe was directly deposited onto a Ga-rich GaN surface at higher temperature, namely at $\sim 360^\circ C$ which is referred to as sample Type IV. As can be seen from the RHEED patterns in Fig.5.1(k) and (l), higher temperature deposition leads immediately to the $4\times2$ reconstruction pattern.

As can be seem from the STM image in Fig. 5.4(a), the Type IV sample surface contains large area islands exhibiting the same row-like reconstruction pattern as seen for the Type III (annealed) sample (Fig. 5.3(c)). The sizes of these islands can be 50 nm or more in width. Outside of the islands are regions of GaN-like reconstruction. Clearly, direct iron deposition at $\sim 360 ^\circ C$ leads to significantly improved Fe-induced island structures compared to deposition at $\sim 210 ^\circ C$.

This temperature dependence can be explained in terms of island nucleation density. At lower Fe deposition temperatures, Fe has less mobility within the Ga-rich surface region due to some of the Ga adatoms being frozen out (e.g. the Ga adatom $3\times3$ orders below $\sim 300 ^\circ C$) [77]; this leads to the nucleation of a larger number of small islands. Whereas, at $\sim 360 ^\circ C$ (well above the surface disordering temperature for Ga $3\times3$), Ga adatoms are highly mobile on the surface, and the Fe adatoms are able to move around with larger diffusion length. This leads to a smaller probability of island nucleation and thus to fewer numbers of Fe-induced islands nucleating. Once an Fe-induced island has nucleated, however, it can freely grow in size thus reaching the large island sizes observed for the Type IV sample.

Coming back to the point of a preferred island thickness, shown in Fig. 5.4(b) are two line sections: (profile 1) across an island edge boundary and (profile 2) across an intra-island vacancy island. Several points can be made from these line sections. First, they reveal an atomically smooth island surface. Second, from line profile 1 we observe a step height of 0.6 nm, similar to the island heights observed for Type I, Type II, and Type III
Figure 5.4: STM images of Type IV Fe/GaN(000\bar{1}) surface. a) Fe-induced 4\times2 large-area island together with partially disordered GaN-like reconstructed area, $V_S = -1.75$ V, $I_t = 0.10$ nA; b) line sections at the locations marked in (a), with the portions corresponding to the 2-D island surface aligned at a same level; c) zoom-in atomic-resolution image of the 4\times2 zig-zag row-structured island, $V_S = -1.00$ V, $I_t = 0.10$ nA. Arrows indicate GaN \langle11\bar{2}0\rangle directions. The ellipse marks vacancy region.
Figure 5.5: a/b) top view / side view model for epitaxial relationship between 2-D zig-zag island and GaN surface; c) simulated RHEED profile for ⟨1120⟩; d) simulated RHEED profile for ⟨1100⟩; e) experimental RHEED profile for ⟨1120⟩ normalized by central peak height; f) experimental RHEED profile for ⟨1100⟩ normalized by central peak height.
samples. Thus the islands have heights of 0.7-0.8 nm with respect to the 1×1 Ga adlayer level, taking into account an adatom layer thickness of ∼ 0.18 nm. Considering line profile 2 which shows a vacancy island feature, the depth of this feature is apparently limited by the tip sharpness, since we see at the edge of the Fe-induced island an intermediate step at the upper side with the same step height as the vacancy island depth. This is concluded to be a tip effect, thus we only gauge the island thickness by comparing to the level well away from the island edge (thus to avoid the tip effect). Therefore, we conclude that the 4×2 structured island has a specific, quantum thickness which is preferred for Fe/N-polar GaN.

The detailed atomically resolved structure of the large area Fe-induced islands of the Type IV sample is presented in Fig.5.4(c). It is seen that the row structures consist of zig-zag chains of atoms (or possibly atom clusters). The 4×2 unit cell is shown as well in the image. One can notice a few missing atoms or vacancy sites in this otherwise nearly perfect 4×2 reconstructed island surface.

Based on all of these observations, we present a model of the 4×2 island structure in Fig. 5.5(a/b). This schematic model shows 3-layer structure on GaN(000¯1) 1 × 1. It starts with a layer adjacent to the substrate consisting of both Fe and Ga atoms following the GaN hexagonal lattice. The next layer is an iron layer following the GaN hexagonal lattice. The Fe atoms at the top layer follow 4×2 lattice, marked in the surface unit cell. There is an additional iron atom within the unit cell at the top layer, which is ∼ 0.15 Å lower than the other iron atoms. Fe layer positions for the zig-zag atoms (or clusters) are located at alternating adatom sites at the top surface, with the zig-zag row direction being along [11̅20]. In this model, we propose that there are iron atoms at the top of the 2-D island, because 4×2 RHEED patterns remain the same as the temperature changes between room temperature and the growth temperature. If Ga atoms are at the top of the islands, we expect
RHEED patterns to change as the temperature changes between room temperature and the growth temperature.

The spacing $D$ between zig-zag atoms is equal to $\sqrt{(a^2 + (2l)^2)}$ with $l = 1.84$ Å; therefore we get the spacing $D = 4.87$ Å. To explore the accuracy of the zig-zag model, we have carried out RHEED simulations based on the model. We use a program to simulate RHEED profiles by entering atom ordering on sample surfaces, [73] in which broadening parameter of peaks can be manually set. Furthermore, form factor parameters can be set to account for different form factors of different elements if there are more than one element in the unit cell.

Because RHEED is sensitive to the surface, we plug the atom arrangement at the top of the 2-D island into the simulation program to simulate corresponding profile, and superimpose it with the RHEED profile for GaN, for the region without 2-D Fe-induced islands. Given the 2-D islands coverage about 1/4 of the surface (0.27 based on a survey of STM images), area ratio of region without 2-D island to region with 2-D island is 3:1. Therefore we scale the central peak height of simulated GaN profile to be 3 times of that of simulated 2-D island profile before adding them together. The simulated RHEED profiles are displayed in Fig. 5.5(c) (⟨11̅20⟩) and 5.5(d) (⟨1 ̅00⟩). Along ⟨11̅20⟩, three fractional streaks occur at the $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ positions, with the $\frac{1}{2}$-order streak having the highest intensity, in very good agreement with the experimental RHEED profile [Fig. 5.5(e)]. Along ⟨1̅00⟩, a single fractional streak occurs at the $\frac{1}{2}$-order position, also in very good agreement with the experimental RHEED profile [Fig. 5.5(f)]. The agreement between simulation and experiment suggests that the proposed surface model is schematically correct and suitable as a guide for future theoretical calculations.

Next we consider the island height measurements. Since throughout this investigation we have never observed the 4×2-reconstructed islands with a different thickness, we conclude that the islands have a preferred, quantum thickness which is related to their
energy of formation. Clearly, the 0.7-0.8 nm thickness corresponds to a thickness of approximately 3-4 atomic layers.

We can further make some estimates of the island composition, based on only a few assumptions about the amount of Ga on the starting surface \((\theta_{\text{Ga}})\), the quantity of Fe deposited \((\theta_{\text{Fe}})\), and the island coverage fraction on the surface \((f_{\text{island}})\).

We estimate \(\theta_{\text{Ga}}\) to be \(2/9\). The Fe deposited was \(\theta_{\text{Fe}} = 0.43\) ML. We also estimate, based on a survey of the STM images, that \(f_{\text{island}} = 0.27\). Therefore, we calculate the Fe contained in the islands as \(\theta_{\text{Fe}}/f_{\text{island}} = (0.43\ \text{ML})/(0.27) = 1.5\) ML. Assuming that the amount of Ga within the islands is the same as the average Ga coverage, we then calculate an Fe/Ga ratio for the islands \(Fe : Ga_{\text{island}} = (1.5\ \text{ML})/(2/9\ \text{ML}) = 6.75\).

While the uncertainty is appreciable, because the sticking coefficient for iron is usually less than one, and the amount of Ga within the islands is not necessarily the same as the average Ga coverage on the surface as we assume. Nevertheless, the estimate suggests that the observed islands could have high Fe content, and therefore could be ferromagnetic based on the fact that Fe-Ga phases with Fe:Ga > 3:1 are already ferromagnetic. Further work will be necessary to investigate with greater accuracy the chemical content of these Fe-induced islands.

5.4 Conclusions

Molecular beam epitaxy and scanning tunneling microscopy measurements reveal the growth of Fe-induced island structures on the N-polar GaN(000̅1) surface. It is found that the Fe-induced islands nucleate within Ga-rich regions of the surface. Higher deposition temperature leads to larger sized islands. The larger-sized Fe-induced islands exhibit a \(4\times2\) zig-zag structure with the rows oriented along the \(\langle 11\bar{2}0 \rangle\) directions of the GaN substrate surface. Stoichiometry estimates suggest that the islands could have a high Fe:Ga ratio about 7. Furthermore, the atomically smooth islands clearly have a preferred thickness of
3 (or 4) ML. These results indicate a route to the formation of Fe/GaN spintronic device structures at the surface of N-polar GaN(000\(\bar{1}\)) and may be useful for future spin-injection devices.
6 New System Development

6.1 Introduction

Scanning tunneling microscopy (STM) enables direct imaging of material structures down to the nanoscale and atomic scale in real space. Together with characterization techniques in momentum space, scanning tunneling microscopy and scanning tunneling spectroscopy provide insightful understanding of structural and electronic properties. Due to the strong capability of spin-polarized STM (SP-STM) for probing local magnetic properties, [78] there have been many reports of the development of SP-STM systems in cryogenic superconducting magnetic fields. [79, 80]

Semiconductors and semiconductor based structures play crucial roles in electronic, optoelectronic, and spintronic applications. For example, ferromagnet/semiconductor structures are useful for injection of spin-polarized currents into semiconductors. Efficient spin injection has been achieved for Fe/GaAs structures. [6] The need for nitride semiconductor and semiconductor-based structures is increasing rapidly. One example is the rising importance of GaN, in optoelectronic applications. As basic research can often have huge impacts on progress of applications, it is advantageous to develop a system that is not only capable of growing high quality semiconductors and semiconductor-based structures epitaxially with real time film quality monitoring, but also able to investigate the structural, electronic, and magnetic properties down to the nanoscale or even atomic scale.

Therefore, we have carried out the development of a N-plasma assisted molecular beam epitaxy/pulsed laser deposition facility with cryogenic superconducting magnet spin-polarized scanning tunneling microscope integrated in a UHV system. The N-plasma assisted molecular beam epitaxy growth system is capable of growing nitride semiconductors and nitride semiconductor-based structures, and a variety of materials, with up to eight ports for MBE effusion cells and N-plasma source. In situ STM studies
on the MBE grown sample are carried out after the sample is transferred to the analysis chamber. For developing such a system, it is necessary to properly address challenges of integrating a N-plasma assisted MBE growth system with an SP-STM system; for example, a sample handling system should be designed and optimized for both custom-designed N-plasma assisted MBE growth and the scanning tunneling microscope. Whitman, et al. reported a sample handling system for integrating a modified commercial STM to an MBE facility. [81] In our case, the tip and sample handling system should be designed for in-situ tip/sample transfer and exchange for both MBE and SP-STM in an integrated UHV system.

Furthermore, the design requirements from the N-plasma assisted MBE and cryogenic superconducting magnet SP-STM are often competing. For example, it is preferable to grow a larger wafer from the point of view of general sample growth, whereas a small sample is desirable for the STM head, both for the purpose of achieving a high-Q STM and also due to the dimensional constraints owing to the use of a split-coil superconducting magnet with limited central bore size. Our sample handling system not only supports up to a 2” O.D. wafer solely for MBE growth, but also a 1cm × 1cm small sample that can be inserted into the limited space of the cryogenic superconducting-magnet STM.

6.2 Instruments

6.2.1 Overall System Layout

As illustrated in figures 6.1-(a/b/c), the system has four custom-designed chambers: 1) growth chamber (GC); 2) analysis chamber (AC); 3) central distribution chamber (CDC); and 4) load lock chamber (LLC). The GC, AC, CDC, and LLC are all interconnected chambers. All are UHV chambers except for the LLC (high vacuum) which has a viton-sealed entry door for quick loading of samples/tips into the UHV systems and only requires turbomolecular pumping. The CDC has eight ports positioned in a radial layout. Three of the eight ports on the CDC are used to join the GC, AC, and LLC via gate valves. The other
five ports are for visual access or to provide expansion capabilities in the future for adding new chambers or components. The entire system rests on a custom-designed robust floating base. Four isolators are used to float the system including the base and the chambers during scanning tunneling microscopy (STM) experiments, to reduce noise transmission from the floor to the STM (figure 6.1-(a) and (b)).

There are ion pump (IP) and titanium sublimation pump (TSP) systems for each of the CDC and AC, a cryopump (CP) for the GC (figure 6.1-(c)), and a turbomolecular pump (TMP) backed by a scroll pump (SP) (not shown) for the LLC. Through either indirect connection (via the LLC to the CDC) or via additional vacuum line connections (to the GC and AC, not shown), the TMP/SP system also provides for initial pump-down from air, in order to reach the cross-over pressures for turning on the IP’s and/or the CP. There is a vibration damper located in between the TMP and the LLC, to reduce noise transmission into the STM system during STM operation.
6.2.2 Sample Handling System

The sample handling system should meet requirements of both the N-plasma assisted MBE system and the SP-STM system. The sample holder should not only be compatible with both MBE growth experiments and SP-STM experiments, but also be able to be transferred \textit{in situ} between the two systems. In this case, we use a commercially available sample holder design which has the capability of handling an up to 2-inch O.D. semiconductor wafer, and allows the wafer to be transferred to a growth stage for MBE growth. [82]

The sample holder is designed as follows. There are six slots at the perimeter of the sample holder, including a lock position and a release position within each slot. By turning the sample holder in the proper direction, a sample holder is transferred from one transporter to another transporter as explained in following steps. As seen in Fig. 6.2-(a), clip set 1 installed on transporter A is grabbing the sample holder with spring force at the lock positions of slots 1, 3, and 5. Next, as seen in Fig. 6.2-(b), clip set 2 on transporter B is inserted into the release positions of slots 2, 4, and 6. Due to the larger space at the release positions than at the lock positions, there is no or negligible spring force between the sample holder and clip set 2. Turning clip set 2 counter-clockwise forces clip set 2 into lock positions. At the same time, the sample holder also turns counter-clockwise, releasing clip set 1 from lock positions into release positions. Now retracting transporter B, the exchange of the sample holder from transporter A to transporter B is now completed. The sample can also be transferred from transporter B back to transporter A by reversing the aforementioned steps.

While the sample holder depicted in Figs. 6.2(a-c), is designed for use with the MBE growth stage, by itself it is not directly compatible with SP-STM sample stage. For the purpose of adapting to the SP-STM system, the sample holder is modified by reducing the size of the central opening and adding several tapped holes (0-80) and Ta leaf springs, so
Figure 6.1: Overall system layout. (a) top view of system showing chambers and support structure; (b) illustration of table floating geometry; (c) 3-dimensional (3-D) model of the system, 1. cryogenic superconducting magnet STM, 2. ion pump with titanium sublimation pump 3. cryopump 4. sample transfer and storage center installed onto a 12” O.D. CF port of the central distribution chamber.
that it becomes an STM sample holder carrier (Fig. 6.2-(d)) for carrying a custom-designed STM sample holder (Figs. 6.2-(e-f)). The custom-designed STM sample holder is called the MBE/STM sample holder since it is compatible with, and optimized for, both STM and MBE. The MBE/STM holder is able to carry a $1cm \times 1cm$ sample for both MBE and STM studies. The MBE/STM sample holder is held in the sample holder carrier using the leaf springs, as shown in Fig. 6.2-(d).

By using the transfer system described above, a sample/sample holder (sample on sample holder) may be loaded from atmosphere into the LLC, transferred to the CDC, picked up by the CDC Z-drive transporter, moved into the GC by the GC transporter, and finally transferred onto the growth stage. After a fresh sample is grown on the substrate, the sample/sample holder is transferred back to the CDC where it can be picked up by the AC transporter and moved into the AC. At that point, the MBE/STM sample holder can be removed from the sample holder carrier and inserted into the STM sample stage, using a wobble stick manipulator.

Furthermore, the CDC is not only the sample/sample holder transfer center but also the sample/sample holder storage center. A rotating platter can hold up to 4 sample holders at one time, any of which is accessible for use in the MBE or SP-STM. A sample is transferred first to the CDC from the LLC and then either stored on the platter or transferred to one of the other chambers connected to the CDC.
Figure 6.2: MBE/STM sample holder. a-c) illustrate the sample holder slots including lock and release positions for sample holder transfer; d) photograph of composite MBE/STM sample holder integrated onto the regular MBE sample holder; e) zoom-in view of MBE/STM sample holder; f) perspective view of MBE/STM sample holder.
6.2.3 N-Plasma Assisted Molecular Beam Epitaxy Growth System

The custom-designed, nitrogen plasma assisted molecular beam epitaxy (PAMBE) growth system is capable of growing a variety of materials with controlled accuracy down to single mono-layers including, but not limited to, nitride semiconductors and magnetic materials. The MBE system also integrates reflection high energy electron diffraction (RHEED), the custom growth stage, the N-Plasma source, our home-designed, home-built effusion cells, and a unique home-designed, home-built pulsed laser epitaxy (PLE) system.

The epitaxial growth facility is therefore a hybrid system, containing both MBE and PLE - which may be used simultaneously or separately. The GC has totally 31 UHV ports which are used for viewports, an ionization gauge, flux sensors, growth components, and future applications.

For PLE, as illustrated in the cutout view of the growth system shown in Fig. 6.3(a) and (b), the pulsed, high energy laser beam enters the entry port and impinges at an angle of ~ 45 degrees upon one of up to 9 different targets installed on a unique target carousel. The target carousel system is installed from the GC bottom port. The laser spot creates a plume which impinges on the downward facing sample, leading to pulsed laser epitaxial growth.

For MBE, there are eight effusion cell ports, one being used for the N-plasma source, leaving 7 ports for different elemental evaporators. Each of the eight ports is oriented 50 degrees away from the central vertical axis of the chamber. During an MBE growth experiment, a sample substrate placed on the growth stage faces downward at the center of the GC. The geometry of the effusion cells and laser target system is illustrated in Fig. 6.3(b).
Figure 6.3: N-plasma MBE/PLE growth system. a) cut-away view of growth chamber; b) illustration of the MBE and PLE source geometries with respect to the sample holder.
MBE growth starts after setting the sample substrate to the desired sample growth temperature either by the use of the growth stage heater for high temperatures, or in the case of low temperatures by the use of the built-in liquid nitrogen cooling on the growth stage. After the substrate temperature is set, one or more effusion cell shutters are opened, the elemental flux rates having been previously set to the desired values, and in the case of nitride growth, with the nitrogen plasma source active.

The in-situ RHEED system enables monitoring of the growth in real time, a crucial capability for optimizing the growth parameters to achieve films of specified or optimized properties. The port for the RHEED gun, and the port for an 8 inch phosphor-coated RHEED screen are both oriented one degree below the horizontal plane, at opposite sides of the chamber. The growth stage has the capability to heat samples from up to \( \sim 800 - 1000 \) \( ^\circ \text{C} \) and to cool samples down to \( \sim -80 \) \( ^\circ \text{C} \) by use of flowing L-N\(_2\). The combination of RHEED with the sample cooling ability is also useful for investigation of surface reconstructions and surface phase changes which occur at low temperatures. Such information may be compared with LT STM data on the same sample.

6.2.4 Cryogenic Scanning Tunneling Microscope System and Integration of MBE and STM Systems

6.2.4.1 STM in Cryogenic Superconducting Magnet Cryostat

The cryogenic superconducting magnet cryostat has a liquid nitrogen reservoir and a liquid helium reservoir. The superconducting magnet is inside the liquid helium reservoir. There is a bore opening at the center of the cryostat, allowing the installation of a flow cryostat insert from the top of the helium reservoir cryostat.

The LT STM system was designed to operate in two different configurations: 1) configured as an LT-STM (\( \sim 4.2 \) \( ^\circ \text{K} \)) in direct contact with the base of the liquid helium reservoir cryostat; and 2) configured as a variable temperature (VT) STM in the range 4.2 -
300 K (by direct connection to the tip of the flow cryostat). It was chosen to first try the LT configuration since this would not require the further complications of having to adjust the helium flow rate nor to be concerned about temperature stabilization as one must in the VT configuration. But in order to make it easy later to change to the VT configuration, it was decided that the electrical connections should come from the top and wind down around the flow cryostat body.

Therefore, this decision necessitated a way to support the body of the STM at the tip of the flow cryostat for insertion into the liquid helium reservoir cryostat, followed by a way to decouple the STM mechanically from the flow cryostat while at the same time being able to make a firm connection with the base of the magnet cryostat and also maintain the electrical connections coming down from the top.

Here we describe the method of achieving these requirements. The method involved designing 1) a coupling device to be located in between the STM body and the flow cryostat in which, by a simple rotation, it is possible to either couple or decouple the STM body; and 2) a pedestal device to be located in between the STM body and the base of the magnet reservoir. These designs are shown schematically in Fig. 6.4.

As can be seen, the coupling device consists of two parts: 1) Part A is connected to the tip of the flow cryostat by a screw; and 2) Part B is connected to the STM body by screws. Part A and Part B interlock at a certain range of angles to allow insertion of the flow cryostat into the reservoir cryostat bore (Fig. 6.4(a)), but at another range of angles become decoupled; at that point, it would be possible for the STM body to rise by $\sim \frac{1}{8}$-inch (it can never fall). There is then a position in which Part B will be physically not in contact with Part A (decoupled, see Fig. 6.4(b)). Whereas, the electrical connections will remain intact since the wires are designed to have some flexibility.

As can also be seen from Fig. 6.4, the pedestal device also consists of two parts: 1) Part C which is a long support pedestal section physically bolted to the STM body; and 2)
Part D which is a small support flange to be used for bolting to the base of the flow cryostat and also to the long pedestal section. As the support pedestal is lowered into the magnet cryostat bore initially along with the STM body (Fig. 6.4(a)), the support flange is then connected to the pedestal by screws, pushed up slightly, rotated to decouple the coupling device at top of the STM body, and then bolted to the base of the magnet cryostat (Fig. 6.4(b)). At this point, the STM should be mechanically and electrically decoupled from the flow cryostat and mechanically and thermally coupled to the magnet cryostat in the LT-STM configuration.

It should also be pointed out however, that while the support pedestal is mechanically tightened to the STM body at the bottom of the STM body via bolts and washers, it is electrically isolated from the STM body using a sapphire plate and washers painted with insulating epoxy.
Figure 6.4: Illustration of the installation of the STM into the cryogenic superconducting magnet cryostat. (a) STM with pedestal and coupling device on the cryostat insert loaded from the top; (b) STM and pedestal pushed up by the small flange and mechanically coupled to the bottom of L-He magnet cryostat; 1. tip of the flow cryostat, 2. coupling device between tip of the flow cryostat and the STM body 3. STM body, 4. support pedestal, 5. support flange.
6.2.4.2 Modular Design in STM Head

The microscope has been designed to be modular; it consists of an upper body and a lower body, which are attached together through three sets of bolts and nuts as seen in Fig. 6.5(a)(one set is not visible from the current viewing direction). The upper body is mainly for coarse approach and scanning, while the lower body is mainly for accepting an MBE-grown sample or a tip shuttle. The modular design of the STM head allows us to change the lower body easily to accommodate different sample geometries for different chamber systems/applications in the future without affecting the design of the upper body. Such upper body can be conveniently adapted to fit a new MBE chamber system or even a new application beyond studying MBE-grown samples, by changing the lower body independently. To enable such a modular design, two removable bridge beams have been designed and used in the upper body. Such removable bridge beams allow the installation of 4-40 screws to attach upper body and lower body together. Furthermore, we use detachable shear piezo stack bundles, in which the shear piezo stacks for coarse approach are sitting on Macor/phosphor bronze plates. In this way, the detachable bundles can be tighten to or removed from the upper body by using 2-56 tapped holes on the upper body and 2-56 clearance holes on the plates. Such a detachable bundle design makes it very convenient to detach the piezo stack bundles for service or modification without affecting the main upper body. The removable bridge beams allow a screw driver to conveniently tighten/loose the detachable shear piezo stack bundles to/from the upper body. The removable bridge beams allow easy access to and the use of the detachable shear piezo stack bundles. Two sets of such modular designed STM heads have been machined. One has been used to replace the original STM head in a double-stage spring suspension system with eddy current damping in our lab 1 (Clippinger 151), in which atomic-resolution images are easily and regularly obtained with such modular designed head. The implementation of such a modular STM
head to the double-stage spring suspension system in the lab 1 is a separate project, and is done by another student, Kangkang Wang.

Figure 6.5: (a) Model for modular STM design including upper and lower body; (b) top section view model of upper body; (c) side section view model of upper body showing prism and shear piezos; 1. sapphire prism, 2. scanner support, 3. tube scanner, 4. Macor bushing, 5. tip holder receptacle, 6. tip holder, 7. tip, 8. shear piezo stack on a plate, 9. upper body main frame, 10. bridge beam, 11. ball for pressing piezo stacks onto sapphire prism, 12. molybdenum leaf spring.
The upper body uses the well-known S.H. Pan style stick-slip inertial motor for tip coarse approach. [83] Such an approach mechanism has been used successfully in STM heads intended for spin-polarized STM studies. [79, 80] One end of the scanner is glued to a Macor support, which is glued into the inner bore of a 6-sided sapphire prism. The opposite end of the scanner supports the tip receptacle via a Macor bushing. The Macor bushing electrically separates the tip receptacle from the scanner (Fig. 6.5(b,c)). The sapphire prism is clamped by 6 sets of shear piezo stacks, with two sets applying pressure on one of 3 different sides located 120 degrees apart. Each pair of shear piezos are attached to a plate. Two of three plates are tightened to the upper body. The third plate is pressed at its midpoint towards the sapphire prism by a small ball which is pushed by a molybdenum leaf spring. The plates are made of Macor/phosphor bronze.

Operation of the inertial motor is illustrated in Fig. 6.6. Coarse approach of the tip in the downward direction is shown in Fig. 6.6(a). At time $t_a$, the shear piezo begins to shear gradually downward (under sticking conditions) by applying gradually increasing voltage to the piezo, moving the tip from height $H_a$ at time $t_a$ to height $H_b$ at time $t_b$. At time $t_b$, the tip is at level $H_b$, with the shear piezo offset downward. At that point, a rapid voltage drop pulls the shear piezo upward quickly (under slipping conditions), leaving the sapphire prism, scanner, and tip at their current locations. At time $t_c$, the tip remains at level $H_b$, a fraction of a micron lower than position $H_a$ at time $t_a$; whereas, the shear piezo has returned to its previous location at time $t_a$. Repeating this process between times $t_a$ and $t_c$ results in moving the STM tip downward by macroscopic amounts.

An upward coarse motion of the tip is accomplished by reversing the downward motion process, as illustrated in Fig. 6.6(b) in which the sense of the applied voltage signals is reversed. For example, between time $t_e$ and time $t_f$, the shear piezo voltage is reduced gradually from a maximum positive value to a minimum value, moving the tip gradually upward (under sticking conditions) from position $H_e$ to position $H_f$ - a fraction of a micron
above the original position. Next, the rapid increase of the voltage from time $t_f$ to time $t_g$ results in the shear piezo returning to its original position (under slipping conditions) while leaving the sapphire prism and tip unmoved. Repeating this cycle results in macroscopic movement of the tip in the upward direction.

Figure 6.6: (a) Illustration of downward motion of STM tip during a coarse tip approach; (b) illustration of upward motion of STM tip during a coarse tip retraction.
6.2.4.3 Integration of N-plasma Assisted MBE with STM

The lower body is designed to accept MBE/PLE sample holders and tip shuttles carrying tip holders. Tip holders can be loaded into the STM scanner receptacle without removing the sample holder from the sample stage. As illustrated in figure 6.7(a), the sample stage is mechanically coupled to the lower body frame and electrically decoupled from the lower body frame via a sapphire plate, bolts, nuts, and washers painted with insulating epoxy. The sample stage consists of three parts - part 3.1, 3.2, and 3.3 - which are integrated together and enable sample loading using compression springs (Fig. 6.7(b)). Screws pass through vertical holes and compression springs in part 3.1 and 3.3, and then tighten into a sample ski. The holes only allow the screws to pass through, and hold compression springs against the skis. This therefore allows the sample holder to be held in place between the stationary slots above the sample holder and the skis below the sample holder. Also, the front ends of the skis are rounded to ensure smooth insertion of the sample holder into the sample stage.
Figure 6.7: Model of lower body. 1. lower body frame, 2. sapphire plate, 3. sample stage, 3.1, 3.2 and 3.3 are three pieces of sample stage which are tightened together, 4. sample holder, 5. sample ski, 6. compression spring, 7. tip shuttle loading slot, 8. sets of screws (8.1), Macor tubes (8.2), washers painted with insulating epoxy (8.3), and nuts (8.4) for mechanically coupling the sample stage and the lower body frame. 9. screws, 10. opening in 3.2 for passing screw, 11. custom screw to tighten sample ski, 12. compression spring, 13. 0-80 tapped hole with vent hole in the sample ski.
It is crucial to properly address the conductivity issues that is due to use of semiconductor samples (as opposed to all-metallic samples), since a key purpose of the MBE/STM system is to study nitride semiconductor-based structures. It is common that nitride semiconductors are grown on insulating substrates - for instance gallium nitride growth on sapphire substrate. First of all, the substrate is commonly held in place using metal wire clips which look round in cross-section and also carry the electrical contact to the STM sample bias. Figure 6.8(a) illustrates the shadow formed on the substrate due to MBE growth in the vicinity of one of the sample clips; as can be seen, in this case there will not be any contact between the sample clip and the freshly grown film. And in the case of non-conducting or poorly conducting substrates, the fresh film will therefore be floating relative to the sample bias, leading to no possibility of having a stable tunneling current. This problem will also easily cause a tip crash during tip approach. Thus it is essential to have a way to make contact between the sample clip and the film subsequent to growth.

The solution generally is to shift the sample/sample clip contact location after MBE growth. Figures 6.8(b,c) illustrate one method in our system to achieve a good contact point between the sample and the sample clip. As seen in Fig. 6.8(b), a wobble stick approaches the sample holder, and a small rod installed on a wobble stick pushes the sample so that the sample clip is shifted away from the shadow area on the sample surface. After this, the sample holder is ready for loading into STM sample stage. Figures 6.8(d,e) illustrate a second method used in our system to achieve good electrical contact to the sample. This method makes the contact automatically as the sample is loaded into STM head. This is achieved by employing an additional wire clip as shown in Fig. 6.8(d). This additional clip is attached to the sample holder; as the sample holder is inserted into the STM sample stage, a bar on the sample stage forces the contact wire to bend and shift away from shadow area to a new point. Because the shifting is done simultaneously during sample loading into STM sample stage, this second method is called the load-and-shift method.
Figure 6.8: (a) Illustration of shadow formed around sample clip area; (b/c) before/after shifting sample in sample holder by shifting the sample with a wobble stick; (d/e) before and after shifting sample clip on sample surface by using bending and shifting contact wire on sample surface; 1.1 substrate, often non conducting, 1.2 in-situ MBE grown layers, 3. shadow due to sample clip, 4. sample clip, 5. MBE/STM sample holder, 6. Molybdenum screw, 7. W or Ta sample clip, 8. tapped hole, 9. guiding slot for sample shifting, 10. wobble stick, 11. rod installed on the wobble stick, 12. additional contact wire, 13. shadow area on sample surface touched by the contact wire during MBE growth, 14. new area away from shadow on the sample area that the contact wire touches after shifting, 15. stopper part in the sample stage.
Figure 6.9: Independent tip loading. (a/b) tip shuttle with tip holder; (c) tip shuttle loaded into STM without removing sample holder. 1. tip holder, 2. leaf spring, 3. pan head screw, 4. washer and lock spring set, 5. tip shuttle legs, 6. handling tab, 7. guiding slot, 8. reference surface, 9. sample holder.
There are independent slots in the sample stage for loading an STM tip shuttle (carrying an STM tip holder); therefore, new tips can be loaded into the STM without removing the sample from the STM sample stage. The tip shuttle has a V-shaped opening on its top plate, allowing easy retracting of the tip shuttle after the tip is picked up by the scanner. The bottom plate has a larger opening for the coating and annealing of the tip which points downward. The bottom legs of the tip shuttle, as seen in Fig. 6.9(a), can slide into the dedicated slots on the sample stage.

One key point is to make very good alignment of the tip holder with the tip holder receptacle attached to the scanner, and also have enough flexibility to insert tip shuttle into the STM head when transferring a tip. To achieve this, there is a leaf spring attached to the left side of the tip shuttle and a lock spring and screws attached to the right neck of the tip shuttle. The screws are tightened on the tip shuttle with a washer and lock spring set. The leaf spring not only ensures smooth tip shuttle loading, but also pushes the screw heads on the tip shuttle against a reference surface. The lateral offset of the screw heads from the tip can be adjusted by changing the number of washers and lock springs and fine adjusted by the degree of tightening. By presetting the lateral offset of the screw heads, the lateral location of the tip shuttle in the STM head can be well defined. The use of the reference screws on one side and the leaf spring on the other side then enables convenient alignment of the tip holder with the tip holder receptacle and flexibility during tip transfer. This then enables reproducible, reliable tip transfers.

6.3 System Performance

Figure 6.10 shows the system after setting up, in which the analysis system with cryogenic superconducting magnet SP-STM and the central distribution chamber are displayed in figure 6.10-(a), and the MBE/PLE growth system is displayed in figure 6.10-(b). The system is capable of growing semiconductor-based materials. Figure 6.11(a)
shows the *in situ* RHEED pattern taken along $\langle 11\bar{2}0 \rangle$ of an MBE-grown GaN in the system. Clear first order streaks are observed. Also, $1/3$ and $2/3$ order streaks indicate a Ga-rich surface. Ga-rich GaN surfaces have been studied by Smith *et al.* previously. [14] Then we tested the transfer of the GaN sample from GC to AC for *in situ* STM scanning. The successful transfer enabled us to perform STM scanning on the GaN surface. The large-scale STM image in Fig. 6.11(b) shows epitaxial growth terraces on GaN, with a typical lateral size of about 500 nm. Figure 6.12(a) shows an STM image of an HOPG surface. The line profile in Fig. 6.12(b) shows that it is a double atomic-height step of $\sim 0.67$ nm.

![Figure 6.10: System after setting up (a) 1. analysis system with cryogenic superconducting magnet SP-STM, 2. central distribution chamber; (b) 3. MBE/PLE growth system.](image)
In Fig. 6.12(b), we see that the existence of noise level in the range of 50 pm to 100 pm makes it hard to further zoom in for atomic resolution image, because typically a noise level below 5 pm is required for atomic resolution imaging. Such initial testing results are not unexpected. We had anticipated the possibility of noise level higher than 5 pm before the initial testing, because the room for the lab 2 system is super noisy with a huge pipe passing through the lab room, carrying air needed for air handling system for the whole building and there are various pumps and chillers running in the building. We know the modular STM head is rigid enough for atomic-resolution imaging, which is already demonstrated by atomic resolution images obtained in lab 1 with a double-stage spring suspension system with eddy current damping. In lab 2, the STM head is mechanically connected to the cryostat without a double-stage spring suspension system with eddy current damping, which will increase noise transmission to the head. However, we have intended to do this, because we will use the STM head in a cryogenic superconducting magnetic field up to ~4.5 T, in which a spring suspension system with eddy current damping is not preferable because the magnet for the eddy current damping would conflict with the superconducting magnet. Therefore, we have intended not to use a spring suspension system with eddy current damping, but rather to reduce noise transmission by other means. Further STM testing will be needed to verify atomic resolution imaging, subsequent to an ongoing effort (not part of this dissertation project) to reduce the noise transmission from the building into the STM.
Figure 6.11: (a) RHEED pattern on MBE-grown wurtzite GaN(000\bar{1}) surface taken along GaN(11\bar{2}0); (b) STM image of GaN surface, $V_s = -2.63$ V, $I_t = 0.16$ nA.
Figure 6.12: (a) STM image of HOPG, $V_s = +0.11$ V, $I_T = 0.3$ nA; (b) line profile across the step.
6.4 Summary and Outlook

We have carried out the development of a nitride MBE/PLE growth system integrated with a cryogenic superconducting magnet spin-polarized scanning tunneling microscope system. Integrated in a custom-designed UHV multi-chamber system, the MBE/PLE growth system supports up to eight MBE sources, including seven effusion cells and a N-plasma source. The custom-designed STM head has a modular design, with the advantage of conveniently adapting the microscope to different applications and chamber systems in the future without changing the design for the upper body, which is a key unit as it contains approach and scanning mechanism. A sample/tip handling system is designed and optimized for both the molecular beam epitaxy growth system and the scanning tunneling microscope system. The MBE growth system and the sample/tip handling system are proven functional. Initial tests of the STM on GaN and HOPG surfaces have been performed. Terraces of GaN surfaces and a double atomic-height step on the HOPG surface have been imaged successfully. Further work and STM testing will be needed for atomic resolution imaging, subsequent to an ongoing effort (not part of this dissertation project) to reduce the noise transmission from the building into the STM head.
7 Summary

The project covers growth and scanning tunneling microscopy studies of magnetic films on semiconductors using MBE/STM system in an existing lab, and development of a novel MBE/PLD and Superconducting Magnet Cryogenic SP-STM System in a completely new lab.

The growth of (111)-oriented FeN thin layers on GaN(0001) was investigated using molecular beam epitaxy assisted with rf N-plasma. From the very early stage of growth, the RHEED pattern shows signs of conversion from wurtzite structure at the FeN/GaN interface to face-centered cubic structure. In addition, the FeN growth agrees with a 2-D to 3-D (S-K) growth mode. Analysis of the RHEED and XRD data leads to the conclusion that the grown film has zinc-blende structure with relaxed lattice constant $a$ in the range 4.29 - 4.34 Å. The epitaxial relationship between the film and the substrate was determined to be $[111]_{FeN} \parallel [0001]_{GaN}$ and $\langle \bar{1}0\bar{1} \rangle_{FeN} \parallel \langle 11\bar{2}\bar{0} \rangle_{GaN}$ and $\langle 11\bar{2} \rangle_{FeN} \parallel \langle 1\bar{1}00 \rangle_{GaN}$, with two types of [111]-oriented FeN grains, 180° apart from each other.

We studied the initial phase of $\sim 0.42$ ML iron deposition onto GaN pseudo-$1 \times 1-1 + 1/12$ surface. We observe that 2-D iron-induced islands grow outward from step edges of the GaN surface. Room temperature STM studies reveal a clear $6 \times 6$ structure of the 2-D islands, with heights of about 1.8 to 2.0 Å. This agrees with RHEED patterns taken at room temperature. Furthermore, zoomed-in STM images show that the half region inside the unit cell is more filled than the other half region. In addition, we observe different surface structures as temperature changes between room temperature and the growth temperature as illustrated using RHEED experiments and the change is reversible. Models for the two different surface structures at the growth temperature and room temperature have been constructed. The models agree with room temperature STM images. Also the simulated RHEED profiles based on the models are consistent with experimental RHEED profiles.
Molecular beam epitaxy and scanning tunneling microscopy measurements reveal the growth of Fe-induced island structures on the N-polar GaN(0001) surface. Fe-induced islands nucleate within Ga-rich regions of the surface for sub-ML iron deposition. Higher deposition temperature leads to larger sized islands, which exhibit a $4\times2$ zig-zag structure with the rows oriented along the $(11\bar{2}0)$ directions of the GaN substrate surface. Moreover, the atomically smooth islands clearly have a preferred thickness of 3 (or 4) ML. These results indicate a route to the formation of identical thickness 2-D iron-induced islands, which may have potential uses for spin injection devices.

In comparison, we observe significant difference of initial phase of iron deposition due to the different polarities of GaN substrates, namely N-polar GaN(0001), and Ga-polar GaN(0001). $4\times2$ 2-D islands occur for Fe/Ga-rich N-polar GaN (0001), while $6\times6$ 2-D islands occur for Fe/Ga-rich Ga-polar GaN(0001) after samples are cooled down to room temperature. The stability of the structures is also different. The $4\times2$ structure remains at the growth temperature, while $6\times6$ changes into another structure as illustrated by RHEED experiments. The fact that $6\times6$ changes easily into a different surface structure when heated supports the model with Ga adatoms on the top layer of 2-D islands, because similar behaviors of surface structure change during heating have also be observed for both Ga-rich Ga-polar GaN (0001) and Ga-rich N-polar GaN (0001) surfaces with Ga adatoms at the top.

We have carried out the development of a nitride MBE/PLE growth system integrated with a cryogenic superconducting magnet spin-polarized scanning tunneling microscope system. The MBE/PLE system not only supports up to eight MBE sources, including 7 effusion cells and a N-plasma source, but also has in situ RHEED and sample heating/cooling capabilities. For convenient adaption to different applications and chamber systems in the future, the custom-designed STM head has a modular design, consisting of an upper body and a lower body; and the upper body contains the approach and scanning
mechanism as a key unit. The capability of transferring an STM tip from atmosphere to the STM head in an ultra-high-vacuum chamber without the need for opening and subsequently baking the UHV chamber is crucial for scanning tunneling microscopy experiments on semiconductor-based structures. During the initial tests, terraces of the GaN surface and a double atomic-height step on the HOPG surface have been imaged successfully. Further work and STM testing will be needed for atomic resolution imaging, subsequent to an ongoing effort (not part of this dissertation project) to reduce the noise transmission from the building into the STM head.
REFERENCES


[18] Gwyddion is a free scanning probe microscopy data analysis software program (http://www.gwyddion.net).


APPENDIX: LIST OF PUBLICATIONS

Publications in peer-reviewed journals:


* A Modular Designed Ultra-High-Vacuum Spin-Polarized Scanning Tunneling Microscope with Controllable Magnetic Fields for Investigating Epitaxial Thin Films, Kangkang Wang †, Wenzhi Lin †, Abhijit V. Chinchore, Yinghao Liu, and Arthur R. Smith, in press, Review of Scientific Instruments. [† Wenzhi Lin is one of the two co-first authors.]


* Epitaxial Growth of Ferromagnetic δ-phase Manganese Gallium on Semiconducting Scandium Nitride (001), Kangkang Wang, Abhijit Chinchore, Wenzhi Lin, David C. Ingram, Arthur R. Smith, Adam J. Hauser, and Fengyuan Yang, J. Crystal Growth 311,
2265 (2009).