Ultra High Vacuum Low Temperature Scanning Tunneling Microscope for Single Atom Manipulation on Molecular Beam Epitaxy Grown Samples

A thesis presented to
the faculty of
the College of Arts and Sciences of Ohio University

In partial fulfillment
of the requirements of the degree
Master of Science

Kendal Clark
June 2005
This thesis entitled
Ultra High Vacuum Low Temperature Scanning Tunneling Microscope for
Single Atom Manipulation on Molecular Beam Epitaxy Grown Samples

By
Kendal Clark

has been approved for
the School of Physics and Astronomy
and the College of Arts and Sciences by

Saw-Wai Hla
Assistant Professor of Physics & Astronomy

Leslie A. Flemming
Dean, College of Arts and Sciences
An Ultra High Vacuum Low Temperature Scanning Tunneling Microscope (UHV_LTSTM) for single atom manipulation on Molecular Beam Epitaxy (MBE) grown nitride semiconductor samples has been designed and constructed. The operational capability of this STM is demonstrated on Ag(111) and GaN (000\(\bar{1}\)) surfaces at 6K and 80 K. On Ag(111) surface, individual silver atoms are repositioned by manipulating with the STM-tip. Conductance tunneling spectroscopy data acquired on this surface confirms the surface state onset at -63 meV. STM images of GaN (000\(\bar{1}\)) surface at 6 K shows novel low temperature reconstructed structures. STM images of this surface at 80 K reveals coexistence of 3x3, 6x4 and 6x6 regions and low temperature reconstructed structures.

Approved: Saw-Wai Hla

Assistant Professor of Physics & Astronomy
Dedications

This thesis is dedicated to my family who has always supported and encouraged me in everything that I have set out to accomplish, and to my wife, Tisha, who has always been beside me and has put up with the long hours spent with the machine.
Acknowledgments

First of all I would like to acknowledge and thank Dr. Saw-Wai Hla for giving me the opportunity to work in his laboratory and for his help during my studies here. I would also like to acknowledge my co-workers in the laboratory: Dandapani Acharya, Aparna Deshpande, Violeta Iancu, Joel Vaughn and Thy Vo without their help I could not have completed this work. I also want to acknowledge Dr. Art Smith and Muhammad Haider for the GaN samples. Finally, I would like to thank Randy Mulford and Roger Smith for all the machining work that they contributed to make this project possible.
# Table of Contents

Abstract ................................................................................................................. 3  
Dedications ............................................................................................................. 4  
Acknowledgments ................................................................................................. 5  
Table of Contents ................................................................................................. 6  
List of Figures ........................................................................................................ 8  

1. Introduction ..................................................................................................... 10  
   1.1 History of the Scanning Tunneling Microscope ........................................... 10  
   1.2 Operation Principle of the STM ................................................................. 11  
   1.3 STM Design and Experimental Setup ......................................................... 15  
   1.4 Images and Results .................................................................................... 24  

2. Interface Electronics and Spectroscopy ............................................................ 26  
   2.1 Design ......................................................................................................... 26  
   2.2 Construction ................................................................................................ 29  
   2.3 Results ......................................................................................................... 31  

3. Single Atom Manipulation ................................................................................ 33  
   3.1 Vertical Manipulation .................................................................................. 33  
   3.2 Lateral Manipulation ................................................................................... 34  
   3.3 Results ......................................................................................................... 35  

4. Gallium Nitride ................................................................................................. 37  
   4.1 Introduction to GaN Structure ..................................................................... 37
List of Figures

1.1 Tunneling regions ........................................................................................................12
1.2 Electron tunneling between the tip and sample ...........................................................14
1.3 Cutaway of STM cryostat ............................................................................................17
1.4 Construction of STM system .......................................................................................19
1.5 UHV-LT-STM complete system .................................................................................20
1.6 Schematic of UHV complete system ...........................................................................21
1.7 STM scanner ................................................................................................................23
1.8 Ag (111) atomic resolution STM image .......................................................................25
1.9 Fast-Fourier-Transform of Ag(111) ............................................................................25
1.10 STM image of standing electron waves .....................................................................25
2.1 SR530 lock-in amplifier ...............................................................................................27
2.2 Schematic of AMP03 amplifier ..................................................................................28
2.3 Schematics of unity-gain amplifiers ..........................................................................28
2.4 Schematic of full spectroscopy circuit .........................................................................30
2.5 Picture of STM interface box .....................................................................................30
2.6 STM image of Spectroscopy location ........................................................................31
2.7 Graph of dI/dV vs. Voltage ......................................................................................32
3.1 Diagram of STM vertical manipulation .......................................................................34
3.2 Diagram of STM lateral manipulation .......................................................................35
3.3 Atomic manipulation images .....................................................................................36
4.1 Zinc-blende gallium nitride crystal structure ............................................................37
4.2 Wurtzite gallium nitride crystal structure ..............................................................38
4.3 Portable sample transfer chamber .......................................................................40
4.4 Sample transfer fork .............................................................................................40
4.5 STM image of GaN islands .....................................................................................42
4.6 GaN 6x4 and 6x6 reconstruction ...........................................................................42
4.7 STM image of buckled GaN structure ...................................................................43
4.8 STM image of row like GaN structure .................................................................43
4.9 STM image of both GaN regions ..........................................................................44
4.10 GaN buckled structure showing voltage dependence .........................................44
4.11 GaN row like structure showing voltage dependence .........................................44
Chapter 1

Introduction

1.1 History of the Scanning Tunneling Microscope

The Scanning Tunneling Microscope (STM) was invented in the early 1980’s by two physicists, Gerd Binnig and Heinrich Rohrer, who were at that time working at IBM Zurich Research Laboratories in Switzerland [1,2]. They used the quantum phenomena of electron tunneling through a vacuum barrier [3] to invent this novel instrument. The invention of STM opened up the door for imaging of conducting surfaces, in real space, with atomic resolution, which greatly revolutionized surface related sciences. The STM is not only used to image atomic landscapes of material surfaces but is also used to probe their electronic structures and, in some cases, vibrational modes by using a variety of tunneling spectroscopy techniques [4-9]. In 1986 Binnig and Rohrer received the Nobel Prize for the invention of the STM [2].

The STM has evolved during the late 1990’s with considerable work done on the manipulation of atoms and molecules [10-21]. The first manipulation example was demonstrated at IBM lab where the letters IBM were spelled with 35 xenon atoms on nickel (110) surface [13]. STM manipulation uses tip-surface interactions to move or to excite single atoms/molecules on surfaces. Single atoms can be either pulled or pushed with the STM tip by applying attractive or repulsive tip-atom interactions [11]. Depending on the atom manipulation path across a surface, the STM feedback signal will show unique signatures revealing the dynamics of the atom manipulation processes.
[11,17,18,21]. By combining a variety of manipulation procedures with complementary tunneling spectroscopy measurements, STM manipulation becomes the most influential and exciting technique of nanoscience.

At the initial part of this thesis, the fundamental quantum tunneling phenomenon is explained and the design, construction and operation principle of UHV-LT-STM system are described. The second part of the thesis focuses on the constructions of an electronic control system for the spectroscopy measurements, and a portable UHV system for transferring of MBE grown samples. The final part of the thesis is devoted to the test results and recent research achievements using this STM system on metal and semiconductor surfaces. These results include formation of a one dimensional atom array on Ag(111), tunneling spectroscopy data of Ag(111) surfaces, and novel reconstructed structures on GaN(0001) surface at low temperatures.

1.2 Operation Principle of the STM

The operation principle of the Scanning Tunneling Microscope relies on the Quantum Mechanical phenomena called tunneling [22]. From quantum mechanics we know that electrons have both particle and wave properties. This duality is what allows the electrons to tunnel, or pass through, a classical impenetrable barrier. If a quantum mechanical wave is incident on a barrier of finite width, then there is a finite probability that the wave will tunnel through the barrier and emerge on the other side. In the case of the STM, we consider the barrier to be the vacuum gap between the tip and sample. The electron can be considered as the wave that is incident on the vacuum gap barrier. Since
the tip and sample are metal, we will look at the simple case of two metal plates separated by a small distance. This distance (d) will be the tip sample distance.

Figure 1.1: Illustration of parallel plates (top), tip and sample (middle) and three tunneling regions (bottom).

The motion of the electron is determined by Schrödinger’s equation:

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + (V - E)\psi(x, t) = i\hbar \frac{\partial \psi}{\partial t} \quad [1]
\]

In this case, we will look at the time independent case and we will solve the Schrödinger equation in three regions:

Region I and III: \[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E \psi(x) \quad [2]\]

Region II: \[\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = (V - E)\psi(x) \quad [3]\]
Solutions to these equations are exponentials of the form:

\[ \psi (x) = Ae^{ikx} + Be^{-ikx} \quad [4] \]

We have 3 regions that have to match, region I: the tip, region II: the vacuum space and region III the sample (figure 1.1). This gives rise to three wave equations we must solve:

\[ \psi_1 (x) = A_1 e^{ik_1x} + B_1 e^{-ik_1x} \quad [5] \]

\[ \psi_{II} (x) = A_{II} e^{k_{II}x} + B_{II} e^{-k_{II}x} \quad [6] \]

\[ \psi_{III} (x) = A_{III} e^{ik_{III}x} + B_{III} e^{-ik_{III}x} \quad [7] \]

\[ k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad [8] \quad k_2 = \sqrt{\frac{2m(V - E)}{\hbar^2}} \quad [9] \]

\( k_1 \) and \( k_2 \) can be found from the time independent Schrödinger equation (Equation 2 and 3). Confining ourselves to only the region inside the barrier (region II) a simplified way to write the wavefunction in this region is:

\[ \psi_{II} (x) = \psi_{II} (0) e^{-k_2x} \quad [10] \]

The probability density that an electron will tunnel to the other side of the barrier is proportional to:

\[ \psi_{II} (x) \ast \psi_{II} (x) = |\psi_{II} (0)|^2 e^{-2k_2x} \quad [11] \]

What is measured in the laboratory using the STM is the tunneling current. To relate the tunneling current to the probability density we will look at energy diagram
representation of an electron tunneling between the tip and the sample shown in Figure 1.2. In the STM we apply a bias voltage (eV) to the sample. This process will either raise or lower the sample energy, depending on a positive or negative bias, from the Fermi energy ($E_F$). Here we assume that the work function ($\Phi$) of the tip and sample are the same, which is the case when the STM tip is formed by contacting the tip with the sample. With this assumption, we can then say the Fermi energy equals $-\Phi$ [22].

![Figure 1.2: Energy diagram of electron tunneling between the tip and sample.](image)

By interchanging the work function and the Fermi energy, and applying a small (eV<<$\Phi$) bias voltage, tunneling occurs. This tunneling can be thought of as the probability, $P$ that an electron in the nth energy state can tunnel through the barrier of width $d$:

$$P \propto |\psi_n(0)|^2 e^{-2kd}$$  \[12\]

$$k = \sqrt{\frac{2m\Phi}{\hbar^2}}$$  \[13\]
The tunneling current is directly proportional to the number of states on the surface within the energy interval eV. Summing over all the energy states in the interval eV the tunneling current becomes:

\[ I \propto \sum_{E_n=E_F-eV}^{E_F} \psi_n^*(0) e^{-2kd} \] [14]

This relation can be looked at in terms of the sample density of states \( \rho_s(x,E) \):

\[ \rho_s(x,E) \equiv \frac{1}{\varepsilon} \sum_{E_n=E-E_0}^{E} |\psi_n^*(x)| e^{-2kd} \] [15]

Then the current can be written as:

\[ I \propto V \rho_s(d,E_F) \] [16]

We now have the relationship that the current is proportional to the sample density of states at the Fermi energy and distance d, the tip height. This dependence of the current on the tip height is an exponential term so, it is exponentially sensitive to the tip sample distance [23, 24]. This sensitivity is what allows us to resolve atomic resolution images.

1.3 STM Design and Experimental Setup

The STM is housed within the Ultra-High Vacuum (UHV) chamber that operates at pressures in the \( 10^{-11} \) Torr range. A series of vacuum pumps are used to reach and maintain this pressure. The initial pump of the system is the rotary “roughing” pump that is capable of pressures down to \( 10^{-3} \) Torr. This pump is used to start the pumping of the vacuum chamber. The next pumping step is the turbo molecular pump, which is capable
of reaching a pressure of $10^{-9}$ Torr. When the pressure is below $10^{-6}$ Torr, the ion pump can be used. The ion pump is the main pump inside the chamber that is used to acquire and maintain the UHV pressure of $10^{-11}$ Torr. In conjunction with the ion pump and turbo pump, we also use a Titanium Sublimation Pump (TSP). This pump consists of a titanium filament that is heated to a point where it begins to sublime. The cryostat, located inside the chamber, also functions as a pump because it operates at low temperatures. Particles that hit the cold surface stick, this is what is known as a cryopump. The ion pump, TSP and cryopump are a good fit for the STM because they have no moving parts that can cause vibration.

To achieve the UHV pressures, i.e. below $10^{-9}$ Torr, it is required to bake the entire system. Baking the chamber is a procedure that heats the chamber up to a temperature above 100°C to boil and evaporate any water molecules that are attached to the chamber wall. Once the water and any other contamination are in the gaseous form they can easily be pumped out by the turbo and “roughing” pump.

The UHV chamber used for the STM system is a rolled stainless steel chamber that can be described in three sections. The first section of the system is the STM chamber that houses the STM and the cryostat (figure 1.3). The STM scanner is a modified Besoke-Beetle type and that is mounted to the cryostat via three suspension springs. The cryostat is a bath cryostat that has inner and outer coolant containers. The outer container is filled with liquid nitrogen, which also acts as a thermal radiation shield. The inner container is filled with either liquid nitrogen or liquid helium. When the cryostat is filled with liquid nitrogen we can obtain a sample temperature approximately
that of liquid nitrogen, which is 77K (-321°F). When the inner chamber is cooled with liquid helium the sample temperature approaches that of the liquid helium, which is 4.2K (-452°F).

Figure 1.3: Cutaway diagram of STM cryostat showing inner and outer containers.
The second section of the chamber is the preparation chamber (figure 1.5, 1.6). This is the part of the chamber where the sample is prepared before moving it into the STM. This is the largest part of the chamber and it houses the ion pump, UHV gauges, TSP, sputtering gun, sample storage unit and the manipulator. The preparation chamber is mainly used to prepare the samples by sputtering and annealing process as well as to deposit atoms/molecules on surfaces. For the metallic samples, the sample surfaces are cleaned by bombarding with high energy neon ions. The sputtering causes the sample surface to become rough because of the hitting of high energy Ne ions to remove undesired contaminations. To get a smooth surface after sputtering, the sample needs to be annealed. During the annealing stage, the sample is heated to a high temperature, which allows the atoms to diffuse across the surface and distribute evenly to smooth the sample.

The third part of the chamber is the load lock chamber. Located in the load-lock chamber is the turbo pump and a gate valve that opens into the preparation chamber. The main purpose of the load-lock is to allow samples and other tools to be placed inside the UHV chamber without venting of the entire chamber. The load-lock allows changes of tip, sample or the capability of small repairs without the need to vent the entire system. The load-lock is specialty designed to accept the portable UHV chamber that carries the MBE grown sample. By attaching the portable chamber to the load-lock the MBE sample is transfer into the STM under UHV conditions.
Image 1.4: STM construction pictures from top to bottom left to right; STM wiring, Manipulator, Chamber in frame, Load-lock attached, Ion pump inside of main chamber, graduate research assistants, Kendal Clark, Danda Acharya, Thy Vo and an undergraduate research assistant, Joel Vaughn, assembling the frame.
Figure 1.5: Complete UHV-LT-STM system. Labels are as follows: 1 – Cryostat, 2 – Preparation Chamber, 3 – Load-lock Chamber, 4 – STM Electronics, 5 – Manipulator Arm.
Figure 1.6: Schematic of UHV system and electronics rack. Figure shown with transfer chamber attached.
The STM is a modified Besocke-Beetle type scanner [25, 26], which incorporates three piezoelectric tubes that support the ramp and tip assembly (Figure 1.7). The three piezo tubes allow the tip to be coarsely approached to the sample. This approaching is achieved by the piezo tubes moving in a sequential order to rotate the ramp and approach the tip to the sample. This coarse tip approach can move the tip ~1mm closer to the sample. The three piezo tubes also allow the tip to be coarsely moved across the sample, and are used for the scanning the tip over a surface region during STM imaging. The tip assembly of the STM is made up of the ramp, the tip piezo and the tip. The ramp is the unit that allows for coarse adjustment of the tip to the sample. The tip piezo is directly attached to the ramp and has the tip attached to the other end. The tip piezo can be lengthened or shortened by the application of high voltage, unlike the three scanning piezo tubes, which move side to side depending on the voltage applied to them. This lengthening and shortening of the tip piezo allows us to have very fine adjustment, on the order of picometer scale, of the tip sample distance. The tip that is used in the STM is a tungsten wire that is electrochemically etched in a sodium hydroxide solution. There are other ways to prepare the tip, like cutting and pulling the tip with wire cutters to get a well-formed tip. This method is used mainly for tips made of other materials like Pt-Ir that cannot be electrochemically etched. A good STM tip has one atom at the apex of the tip. To achieve a stable and atomically sharp tip, we use in-situ tip-formation by gently touching the tip to the sample surface [20].
The STM is attached to the inner cryostat that is cooled to liquid helium temperatures for manipulation experiments. The tunneling current of the STM is on the order of nano-ampere ($10^{-9}$ A), so any noise that is present can overpower the signal coming in. In order for the STM to give atomic resolution and be able to perform atom manipulation all noise needs to be minimized. To minimize the noise we need to decouple the cause of the noise from the signal. The noise produced by mechanical vibration and other electrical noises are our main concern.

The mechanical noise is usually a low frequency noise that couples when the STM is in physical contact with the surrounding cryostat. To eliminate this noise the STM is hung from three springs to isolate it from vibration. Also the use of Eddy currents, by way of magnets mounted to the base of the STM, damp lateral vibration of
the unit. Mechanical noise can also reach the STM if the entire UHV chamber is vibrating. To stop this, the chamber is isolated from the floor with air isolators.

Electrical noise is eliminated by shielding the wire carrying tunneling current. The STM electronic control system itself is another large cause of electronic noise. To reduce this cause of electrical noise all the STM electronics are shielded and grounded and the tip wire is kept to a minimum length. To prevent the room temperature electromagnetic radiation, the STM scanner is thermally shielded. The shielding is accomplished by the inner and outer cryostat shields that only have small view ports for sample transfer viewing. These view ports are covered when scanning. The main entrance to the STM is closed off by a large copper door on the outer cryostat and a stainless steel door on the inner cryostat.

1.4 Images and Results

After completion of the STM construction, test images were taken on a silver (111) single crystal sample. Atomic resolution images have been obtained and are shown in figure 1.8. The distance between two nearest neighbor silver atoms on the 111 surface is 2.89Å [17]. Corresponding FFT (Fast-Fourier-Transform) pattern of this surface clearly reveals hexagonal symmetry of the surface atomic arrangement (figure 1.9). At reduced biases below 100 mV close to the Fermi level (0V), we are able to image standing electron waves on the silver surface. These waves are produced by free surface state electrons scattered off of step edges, impurities or defects on the surface and they appear like water waves (figure 1.10) [16,17].
Figure 1.8: Atomic resolution STM image of Ag (111) surface showing hexagonal arrangement of silver atoms. Image size ~20Åx40Å. V=100mV I=2.2nA.

Figure 1.9: FFT pattern of Ag(111) surface showing hexagonal symmetry in momentum space.

Figure 1.10: Standing electron waves scattering from impurities and a step edge of Ag (111) surface. Image size ~400Åx600Å. Image parameters: V=70mV I=2.4nA.
Chapter 2

Spectroscopy and Interface Electronics

2.1 Design

One very powerful feature of the STM is its ability to perform spectroscopy on single atoms and molecules. The electronics that make this spectroscopy possible are the electronic interface box and the lock-in amplifier. The electronic interface box takes the digital signal, which controls all the movement of the STM ramp and tip, from the computer and interfaces it with BNC connectors so that a connection can be made to the STM. This allows the user at the computer to change the operating parameters of the STM from the computer interface. From the computer the parameters of the scanning can be adjusted to obtain the ideal image. Some of the parameters that can be changed are as follows: the bias voltage of the tip and sample, x and y offset of the tip, the tunneling current and the scanning size. The interface board allows these changes to be relayed to the STM, and it also relays information back to the computer so the STM program can store this information with each image. When an image is scanned and saved, the computer receives information about what parameters were used in the scanning. These parameters are the tip-sample bias, the tunneling current, x and y offset of the ramp and gain of the x, y and z high voltage amplifier.

The lock in amplifier is a key component in the acquisition of spectroscopy with the STM. Using the modulation from the lock-in amplifier the STM is able to detect very
An electronic circuit that works in conjunction with the lock-in amplifier is a precision unity-gain differential amplifier. Figure 2.2 shows the schematic of the amplifier intergraded circuit. Three integrated circuits are used in the making of the final circuit. Two of the intergraded circuits are used as precision unity-gain inverting amplifiers (figure 2.3). One unity-gain amplifier is used for the bias input voltage and the other is used for the modulation input voltage. The bias input is used for the tip-sample bias. The other unity-gain amplifier is used for the modulation input that comes from the sine output of the lock-in amplifier.

Figure 2.1: Stanford Research System SR530 lock-in amplifier [27].
When the modulation is turned off there is only an inverting of the bias voltage. When modulation is on, the sine wave, coming from the lock-in amplifier, is summed with the bias voltage. This summing is accomplished with the third unity-gain amplifier in the summing amplifier mode as shown in figure 2.3.

Figure 2.2: Schematic of AMP03 amplifier intergraded circuit [28].

Figure 2.3: Schematic of precision unity-gain inverting amplifier circuit (left) Schematic of unity-gain amplifier summing mode (right) [28].
2.2 Construction

The electron circuit (figure 2.4) that was built for the spectroscopy works in conjunction with the lock-in amplifier. The plus and minus fifteen volts were supplied to the circuits by a low noise DC power supply. The 0.1 uf capacitors used at the grounding points are decoupling capacitors, which eliminate any unwanted oscillations from the plus and minus fifteen volt power supply. Also, low pass filters were used on all the outputs to filter any unwanted frequencies. The modulation signal that comes from the lock-in amplifier is switched by a toggle that is mounted on the interface box. When spectroscopy is taken, the modulation is turned on and allowed to sum with the sample bias. A summing circuit alone could have been used without the gain-one inverting amplifiers. However, the gain-one amplifiers were incorporated to reduce noise and ensure accurate spectroscopy.

The front of the interface box houses the BNC connectors, the grounding block, the colored LEDs for signal traffic display, and the bias voltage display. The bias voltage is controlled by the computer and the bias voltage readout is displayed on the computer and saved with every image. The other bias voltage display gives confirmation that the selected bias is going to the sample. Figure 2.5 shows the interface box before and after mounting and installation in the electronics rack.
Figure 2.4: Schematic of full spectroscopy circuit diagram consisting of two inverting unity-gain amplifiers and one unity-gain summing amplifier.

Figure 2.5: Picture of interface box that contains the spectroscopy circuit before completion (right) and after installation (left).
2.3 Results

Using the lock-in amplifier and the specific electronics that are mentioned above, the spectroscopy of a single atom, molecule, or surface can be taken. When the spectrum is taken, the bias voltage is ramped from a starting value to an ending value and back again. During this ramping, a small amplitude of modulated voltage is added to the DC bias from the lock-in amplifier. Figure 2.6 shows a STM image of a flat silver terrace next to a step edge and the location where the spectroscopy was taken. The $\text{d}I/\text{d}V$ vs. voltage graph obtained directly from the lock-in is shown in figure 2.7. Here, the step like appearance of the $\text{d}I/\text{d}V$ curve near the Fermi level, is produced by the surface state of Ag(111). This graph matches with the inset graph, in figure 2.7, that was obtained from published results on Ag(111) surfaces [29].

Figure 2.6: STM image of Ag (111) surface. Dot indicates spectroscopy location.
Figure 2.7: Average spectroscopy of silver surface showing surface states around the Fermi level. Inset graph was obtained from reference 29 and is shown for comparison.
Chapter 3

Single Atom Manipulation

3.1 Vertical Manipulation

A very low thermal drift (usually <0.1 nm/hr) and very high stability of the low temperature STM constructed in this thesis work gives the capability to manipulate a single atom or molecule on a surface. One manipulation technique is vertical manipulation [4]. This technique can be used to improve the quality of the tip by contacting the tip with the sample. This contact forms the tip with atoms that are taken from the surface [20].

Along with tip forming, the vertical manipulation technique can be used to deposit or remove atoms, or clusters of atoms, from the sample surface. In order for an atom to transfer from the surface to the tip, the tip must come close enough to the sample so the energy gap separating the two energy wells of the tip and the sample surface is reduced [4]. It can be said that at this point the atom is bound to the tip as well as the sample. When this is achieved, the tip is retracted and the bond between the atom and the surface is broken. The atom now resides on the tip and can be placed elsewhere on the sample.
3.2 Lateral Manipulation

Considerable amounts of work have been done dealing with lateral manipulation of atoms on surfaces [4, 10, 11, 13, 15, 17, 18, 20, 21]. With this STM, we are able to laterally manipulate single atoms and molecules on surfaces. The tip-atom interaction increases when the tip is approached close to the manipulated atom [4]. When the tip is moved parallel to the surface with this close-distance, the tip-atom interaction drives the atom to move along with the tip. Depending on the attractive or repulsive nature of interaction, two different manipulation modes, “pulling” and “pushing” of atom, can be performed [11, 18, 21]. In the “pulling” mode, the atom follows the tip in a discontinuous manner due to the attractive interaction. This tip-atom attraction is originated from the overlapping of the electronic wave-functions between the manipulated atom and the tip-apex atom. In “pushing” mode, the atom is moved in front of the tip due to a repulsive interaction [11]. Generally, the repulsive interaction is originated from the electrostatic interaction between the tip-apex and the manipulated atom. In most cases, “pulling” is the
main manipulation mode for manipulation of a metallic atom on a metal surface. If the atom is temporarily bound to or trapped under the tip, then “sliding” mode manipulation can be observed [11,21]. During “sliding”, both the manipulated atom and the tip-apex move together smoothly across the surface potential landscape [4,11].

![Figure 3.2: Schematic of lateral manipulation of a single atom along the sample surface.](image)

3.3 Results

Controlled single atom manipulation has been achieved with this UHV-LT STM. Single silver atoms have successfully been moved to form a line of 4 atoms on a Ag(111) surface, shown in figure 3.3. The atoms were extracted from a silver cluster created by a tip-sample contact.
Figure 3.3: A Series of 5 images where individual silver atoms have been moved to form a line. Tunneling parameters $V=70\text{mV}$ $I=1.1\text{nA}$.

Click to View Atom Manipulation Movie.
Chapter 4

Gallium Nitride

4.1 Introduction to GaN Structure

Gallium Nitride (GaN) is a wide-gap semiconductor that has become popular to study in recent years because it can be used in short wavelength (blue to violet) light emitting diodes (LEDs) [30,31]. Gallium Nitride can form two types of crystal structures, zinc-blende (figure 4.1) or wurtzite (figure 4.2). The zinc-blende structure has a lattice constant $a = 4.52 \, \text{Å}$ and an energy bandgap of 3.2-3.3 eV at 300 K. The zinc-blende structure is not favorable to grow, but can be grown under the correct conditions [32]. The wurtzite structure is a hexagonal structure with lattice constant $a = 3.189 \, \text{Å}$ and $c = 5.185 \, \text{Å}$. Wurtzite GaN has a bandgap of 3.44 eV at 300 K. Wurtzite GaN is a direct bandgap semiconductor, which makes it possible for lasers and LEDs to be made from this structure [33]. Wurtzite GaN can be grown either nitrogen terminated, (GaN (000$\bar{1}$)) or gallium terminated, (GaN (0001)).

![Figure 4.1 Crystal structure of zinc-blende gallium nitride.](image)
Figure 4.2: Crystal structure of wurtzite gallium nitride showing both gallium and nitrogen faces (left). Diagram showing C axis of wurtzite gallium nitride (right).
4.2 Sample Transfer

The GaN sample, which is studied in the STM, is grown in a MBE growth chamber by the group of Prof. A. Smith at Ohio University. The MBE chamber is not attached to this STM so the sample must be transferred to the STM under an ultra-high-vacuum environment to avoid contamination. For this purpose, we have successfully developed a portable sample transfer chamber (figure 4.3). A battery powered ion pump maintains a pressure of $10^{-10}$ Torr in this portable chamber. Because the surface of GaN is very reactive, this pressure is necessary to keep the GaN sample clean. Once the chamber is attached to the STM, the load lock is pumped out using the rotary and turbo pumps. Once the pressure is equalized between the two chambers, the gate valves are opened and the sample can be transferred into the preparation chamber. The manipulator arm then grabs the sample off of the MBE sample holder with the sample transfer fork (figure 4.4) and moves it to the STM sample holder. Finally the manipulator places the sample inside the STM. Once the sample is cooled to the desired temperature, scanning can begin.
Figure 4.3: Sample transfer chamber that is used to transfer the MBE grown sample to the UHV-LT-STM.

Figure 4.4: Sample transfer fork preparing to remove the gallium nitride MBE sample from the sample holder.
4.3 Results

Nitrogen terminated GaN (000\(\bar{1}\)) samples have been grown with the MBE system and studied in this STM. The RHEED patterns during the final stages of growth of the samples reveal well known GaN (000\(\bar{1}\)) with 3x3 Ga added reconstruction [34-37]. The STM images have been taken on GaN sample surface at both liquid nitrogen and liquid helium temperatures. At both temperatures, atomic resolution images have been obtained and novel structures have been observed. Figure 4.5 shows a STM image at liquid nitrogen temperature showing large islands of GaN. Here, a hexagonal arrangement of surface Ga atoms, a known 3x3 Ga added structure can be seen. Other known GaN reconstructions, like 6x4 and 6x6, were also observe and are shown in figure 4.6. At liquid helium temperatures, the STM images provide four distinct novel structures. Two of which are, a buckled hexagonal structure (figure 4.7) and a row-like structure (figure 4.8). The buckled hexagonal structure was most frequently observed on the sample. The difference between the bucked and row like structures was easy to determine from large scanning areas. The buckled structure would show up very light in the STM image. Since light and dark regions in STM images correspond to the higher and lower tunneling probability, the observed light region indicates a high conductance. The row like structure appears darker, indicating a low conductance. This contrast between light and dark STM images (figure 4.9) of GaN was seen throughout all the scanned areas. The two structures showed a voltage dependence that drastically complicated the STM image as the bias voltage was lowered (figure 4.10 and 4.11). Complete analyses of the physical structures along with the electronic properties are in the process of being published.
Figure 4.5: STM image of GaN showing large GaN islands. Image size ~400Åx400Å. Scanning parameters: Temp~80K V=2.1V I=0.48nA.

Figure 4.6: Known GaN reconstruction. Left image is 6x4 GaN reconstruction, Image size ~80Åx80Å. Right image is 6x6 GaN reconstruction, Image size ~150Åx150Å. Scanning temperature is ~80K.
Figure 4.7: STM image of GaN showing buckled hexagonal structure. Image size ~100Åx100Å. Scanning parameters: Temp~6K V=1.0V I=1.1nA.

Figure 4.8: STM image of row-like structure. Image size ~40Åx40Å. Scanning parameters: Temp~6K V=700mV I=1.1nA.
Figure 4.9: STM image of both regions. 1 – Buckled region and 2 – Row like region. Image size ~300Åx500Å. Scanning parameters Temp~6K V=1V I=1.1nA.

Figure 4.10: Voltage dependence of buckled GaN structure. Left STM image taken at I=1.1nA V=1V Right image of same area taken at I=1.1nA V=400mV.

Figure 4.11: Voltage dependence of row-like GaN structure. Left STM image taken at I=1.1nA V=700mV Right image of same area taken at I=1.1nA V=200mV.
Chapter 5

Conclusion

An Ultra High Vacuum Low temperature Scanning Tunneling Microscope has been constructed and controlled single atom manipulation has been achieved. A history of the scanning tunneling microscope has been given and the operating principle of STM using tunneling theory has been explained. The electronics used for tunneling spectroscopy measurements have been constructed and presented. The atomic manipulation capability of the STM is demonstrated by constructing an array of four single atoms on Ag(111) surface at liquid helium temperature. A brief description of the gallium nitride sample has been given and the sample transport method has been explained. The UHV-LT-STM has the ability to scan on MBE grown nitride samples and results of scanning on GaN has been presented showing novel new structures at low temperatures.

With the ability of the STM to image, manipulate and perform spectroscopy on single atoms and molecules the STM has become a necessary tool in the building of novel nanostructures and probing of new physical phenomena. The added capability of this UHV-LT-STM to image and manipulate MBE grown nitride samples makes it a very unique instrument for nanoscale spintronic research. These added capabilities open up multiple opportunities for imaging and manipulating on samples that have never been studied under these conditions before.
Bibliography:


