

Scanning Tunneling Spectroscopy Under Atmospheric Conditions to Characterize A Tungsten
Tip STM System For Use With Hydrogen Desorption

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Abstract

The electrical surface structure of (111) n-type silicon was investigated through the use of scanning tunneling spectroscopy (STS) to develop a model to determine oxide presence on a passivated silicon surface. I-V curves were obtained with a scanning tunneling microscope (STM) using a tungsten tip on various locations of passivated silicon while the passivation layer desorbed from the surface under standard atmospheric conditions. The derivative (dI/dV) of these curves then revealed the electronic structure of the surface of the sample. Through these scans, it was determined the system was operating in the same mode as a Shockley diode. The separation of the band energies between the tungsten tip and n-type silicon created a Shockley diode with a barrier height of 0.45 V that was verified with the dI/dV curves. The scans obtained showed a general shift in surface properties through a shift in the width and location of the conductance peaks as the scan time progressed. The shifts suggest an oxide growth due to the change in electrical structure or local density of states (LDOS) over time.

Introduction

The intentions of this project is to develop and explore scanning tunneling spectroscopy (STS) method as a means to measure oxide thickness on silicon wafers. The degree of success of the model is based on the ability to clearly define the difference between an oxide layer and passivated layer on the surface of the silicon. This project is a necessary step for the end goal of using the combination of passivation and a scanning tunneling microscope (STM) to manufacture nano scale patterns.

Passivation

Passivation of a surface is a process that can be used as a clean slate for manipulating the surface atoms. Passivation creates a layer of atoms on the surface which tends to be in a metastable state. For silicon immersed in hydrofluoric acid, hydrogen will be attached to the surface of the silicon to create a monoatomic coating of hydrogen on the

surface. The surface energy of the silicon hydrogen structure increases to turn the normally hydrophilic silicon into a slightly hydrophobic surface.

Desorption

The metastable silicon hydrogen surface allows for an energy source to selectively rip off or desorb the hydrogen from the surface and etch the pattern before all of the hydrogen will desorb from the surface. Once the hydrogen is desorbed from the surface in atmospheric conditions, an oxide layer will form. The resulting oxide layer that has been selectively placed on the silicon will then act as an etching mask. The process in which the oxide is formed in ambient conditions is shown in Figure 1. The moisture in the air acts as a source of oxygen to quickly form 20nm of native oxide¹ under the tip.

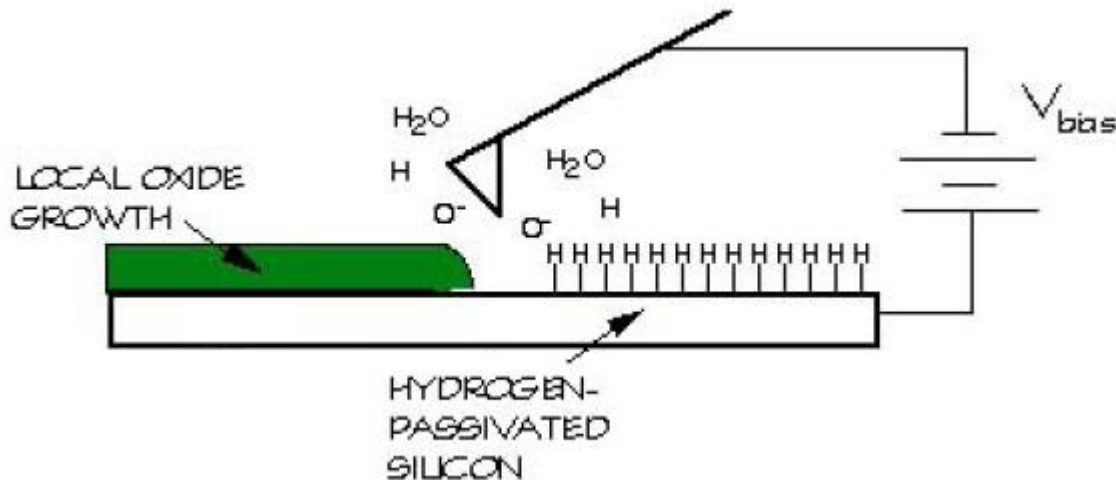


Figure 1: Typical Desorption process

Band Theory

The energies of materials are determined by solid state physics. The four aspects of band theory that will be utilized are the valence band, conduction band, Fermi energy level (E_F), and work function (Φ_s) and are shown in Figure 2. The valence band is range of energies in which the valence electrons will completely fill a shell. The conduction band is the range of energies in which the valence electrons will partially fill and will be able to exchange electrons with other atoms. For metals, the conduction and valence band are overlapping. For insulators, the gap in energy between the conduction and valence band is

large. In semiconductors, the gap between the conduction and valence band is small. The Fermi energy level is the energy in which no electrons will be found with greater energies near absolute zero temperatures. The Fermi energy is found somewhere in between the conduction band and the valence band. The work function is simply the energy required to remove an electron to a vacuum. When analyzing the interactions of different materials, the Fermi energies are aligned and the band gaps are superimposed on each other to show the electronic configuration.

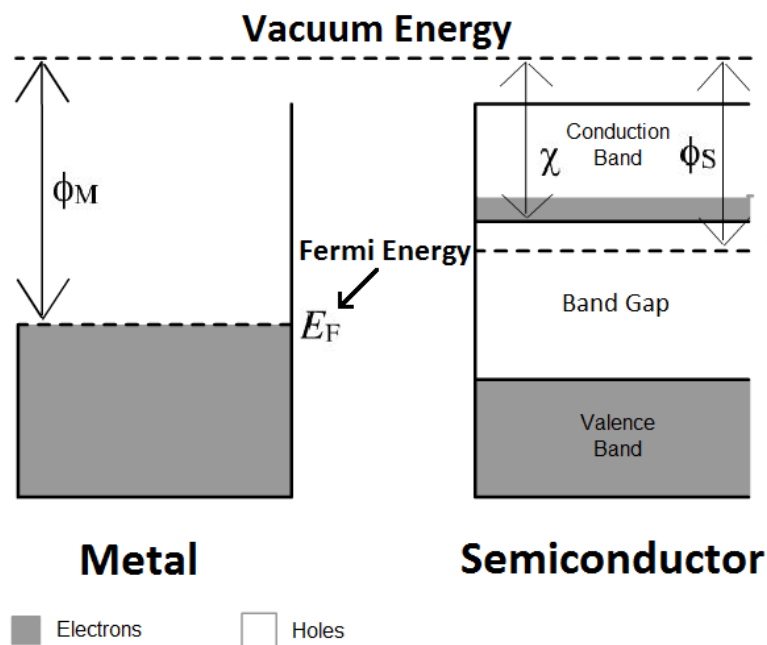


Figure 2: Energy diagram used to help in understanding the relationship between band gap structures

Tunneling

The STM utilizes tunneling theory from quantum mechanics. Tunneling in one dimension is derived from Schrodinger's equation and states that if two conductive materials are close enough together without touching, there is a probability that electrons will flow between the two conductors contrary to classical physics. This equation is shown schematically in Figure 3 and the derivation can be found in [6]. The probability function is exponentially sensitive to separation distance (z) as seen in Figure 3 that is utilized for STM.

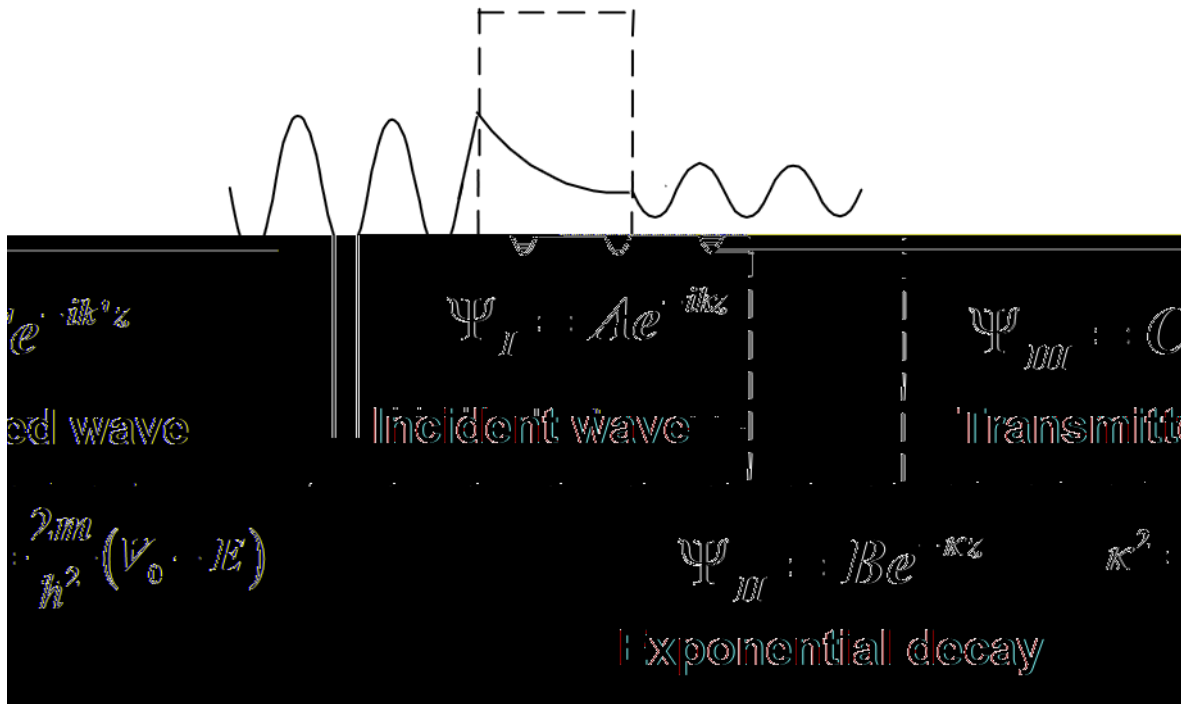


Figure 3: Schematic of tunneling effect showing the equations used to calculate tunneling probability

STM System

The STM system utilizes the tunneling effect by measuring the current developed between the tip and sample when in close proximity. The block diagram of an STM system is shown in Figure 4. The vertical sensitivity is in the range of picometers, and the horizontal sensitivity is typically in the range of tens of picometers. With such a high resolution, images can be taken of individual atoms. The tunneling current is in the range of pA to nA due to the small transmission probability of the tunneling current to the STM. The STM also controls the voltage applied to the tip. The control over the tip voltage allows for multiple modes of operation of the STM. The manipulation of the tip to find information about a single point electronic structure is referred to a scanning tunneling spectroscopy (STS).

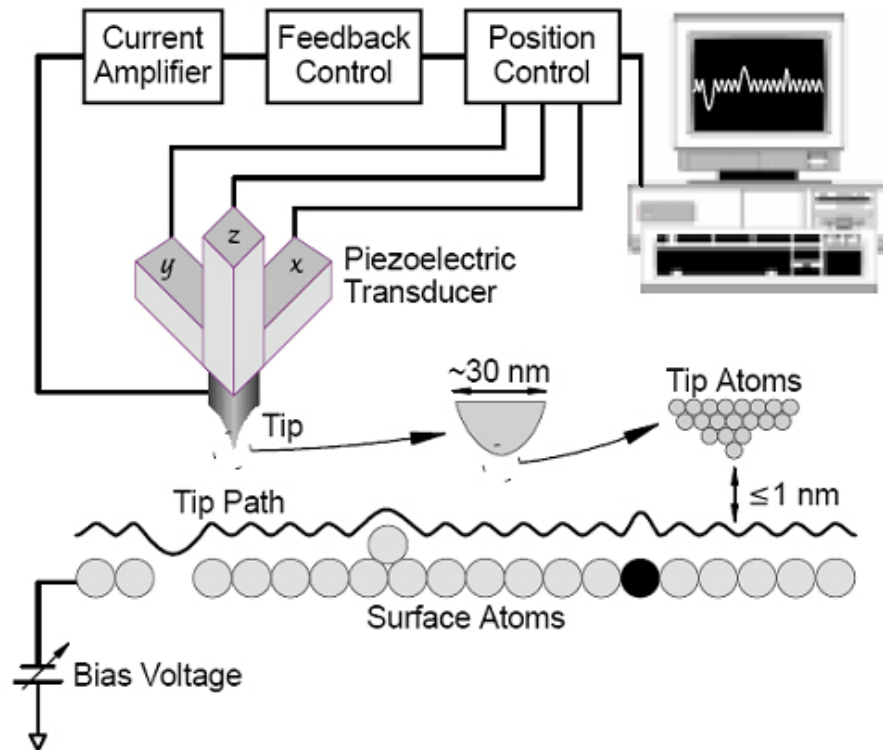


Figure 4: Diagram showing the operating components in an STM

Scanning Tunneling Spectroscopy

STS utilizes the STM by manipulating the normal scanning operation to obtain detailed information about the electronic structure. The most common use of STS is to find the function of local density of states (LDOS). The local density of states represents the distribution of electronically stable states for electrons to reside in that defines the electronic properties of a material. The LDOS is obtained by sweeping the voltage of the tip and measuring the resulting current or feedback displacement. The mode used in this study is the sweeping voltage method. The method produces current vs. voltage (I-V) curves. From the I-V curves, the change in current with the change in voltage (dI/dV) or conductance can be acquired. This derivative term plotted against voltage allows for a proportional read out of the LDOS represented by the areas under the curve. Finding the LDOS allows for the system being tested to be modeled using three dimensional quantum mechanics and solid state equations to more accurately describe the surface of the sample¹⁰. STS is being used as a surface analysis tool to test the presence of oxide on the surface through the change in the conductance graphs.

Experimental Procedures

Tip Etching

The STM system utilizes a tungsten tip that is sharpened to atomic sharpness using an electrochemical etch setup. The setup is seen in Figure 5 and utilizes KOH as an electrolyte to reduce tungsten to WO_3 and dissolve it into the solution. The drop method in which the tip is formed is a mechanical tip formation. The solution etches the wire on the surface of solution faster due to the higher concentrations of ions on the surface. As a result, a neck is formed on the wire that becomes so thin; the wire will fail mechanically and will tend to leave behind an atomically sharp tip. Then the current needs to be cut off before further etching of the tip occurs.

The STM tip etcher utilizes a Schmitt trigger cut off circuit to detect when the tip falls into KOH solution. The electrical schematic is shown in Figure 5. When the voltage falls below the threshold set inside the Schmitt trigger, the output will be driven to ground. The output is coupled with a MOSFET that controls the source of current from the gold counter electrode, and will shut off the current flow when the output is driven to ground. The circuit performs the cutoff procedure in <200 ns.

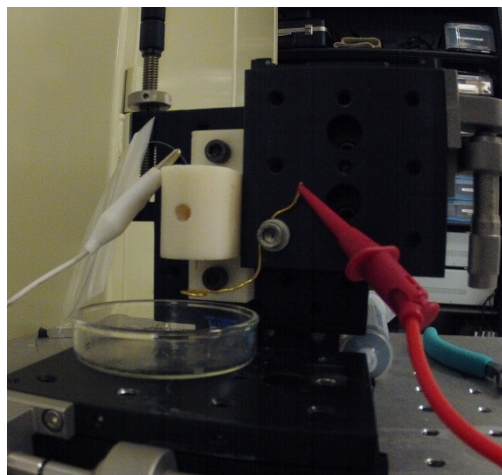
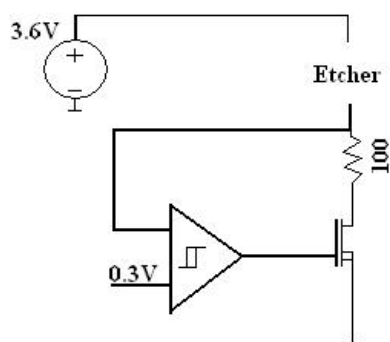


Figure 5: Schematic of cutoff circuit (left) along with the setup of the etcher (right)

To verify that the tip was suitable to measure the LDOS, the tip was tested with a sample of highly organized pyrolytic graphite (HOPG). A tip can be considered reasonably sharp if the atomic structure can be resolved. The tip used for spectroscopy was considered

to have a sharp enough point where each carbon atom able to be imaged (Figure 6). Along with verifying the sharpness of the tip, a test for double tips was performed. The double tip test was performed by measuring the distance between the carbon atoms to verify that the distance between atoms is 260pm.

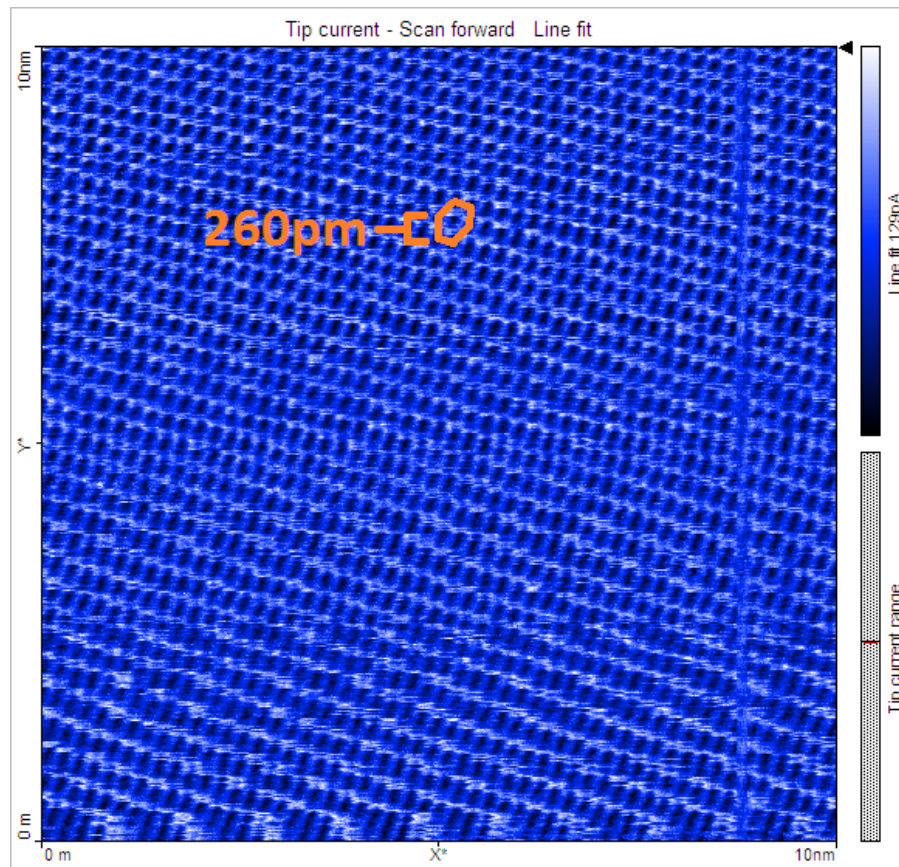


Figure 6: Atomically resolved HOPG with verification of atom spacing typical of a sharp tip

Passivation

Passivation of the wafer was performed in a simple three step process shown in Figure 7. First a 25mm, n type (111) wafer is cleaned with an evaporating solution cleaner (Novec 7100). Then the sample is dipped in buffered HF for 30 seconds. The sample was

rinsed in deionized water and blown dry with N₂ after being dipped in the HF. The samples were then imaged within 1 hour of passivation.

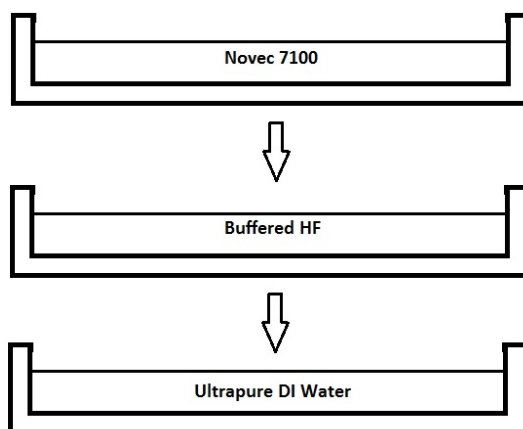


Figure 7: Passivation process

STM Spectroscopy

The samples were then diced to fit the STM and mounted on a magnetic sample holder with carbon tape to promote an electrical connection between the sample and tip. The STM system used was the Nanosurf Easyscan STM system on top of a TS150 active vibration isolation system. STS was performed by obtaining I-V graphs and converting them to conductance or dI/dV curves. The scan parameters used were a set point of -1V with a set current of 2nA. Scans were swept through the voltage range of -2 V to 0.7 V in 0.5 s. the average of 100 sweeps represents each of the scans shown in the following figures. Reverse voltage sweeps were also obtained after each forward scan. The dI/dV scans were obtained from the Nanosurf Easyscan software.

Results

I-V Curves

The I-V curves obtained reveal the electronic structure of the surface with the tip held statically above the surface. The averaging of the 100 I-V curves at each point helped reduce the amplitude of the noise by the square root of the samples averaged. Four scans of various locations within 100 nm of each other were obtained at different times. At the first

scan, the time is denoted as Time 1. The next three scans were performed after 8, 13 and 17 minutes respectively. Figure 8 shows the I-V curves of the scans superimposed to show the variance between each scan. What is evident between the scans is the increase in separation between the tips as shown by the reduced tunneling current. This separation can be facilitated by the growth of an oxide. The detailed scan features were distinguished by the taking the conductance curves which is the first derivative of these I-V curves.

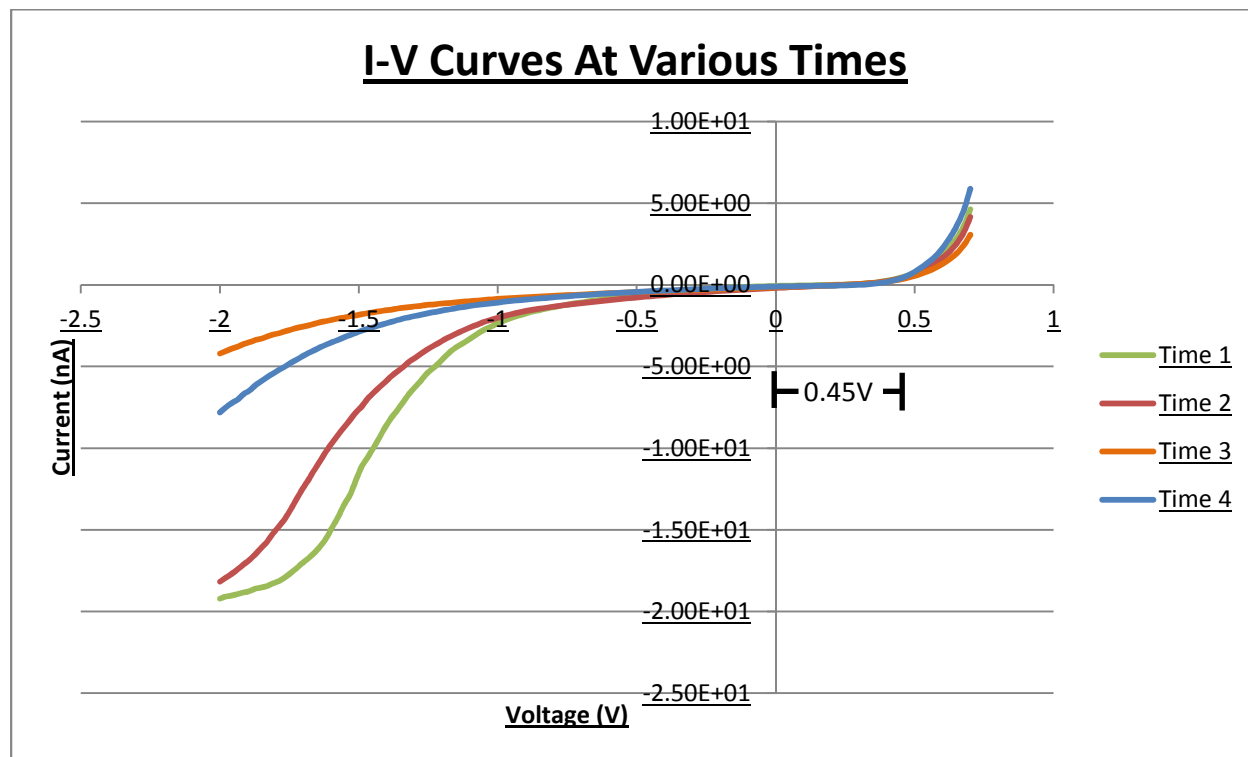


Figure 8: Superimposed I-V curves to compare the different

dI/dV Curves

The derivative of the I-V curves also represents the local density of states (LDOS) of the sample. Figure 9 shows the derivatives of the same series of I-V curves. There is a height reduction along with a shift in the LDOS at the different locations. The reductions of the peaks are due to the reduction of the current flow as shown in the I-V curves. The peak shifts indicate a change in electrical structure of the point being analyzed. The trend in

which the scans shift more as time progresses is worth noting as a possible influence from desorption of the hydrogen.

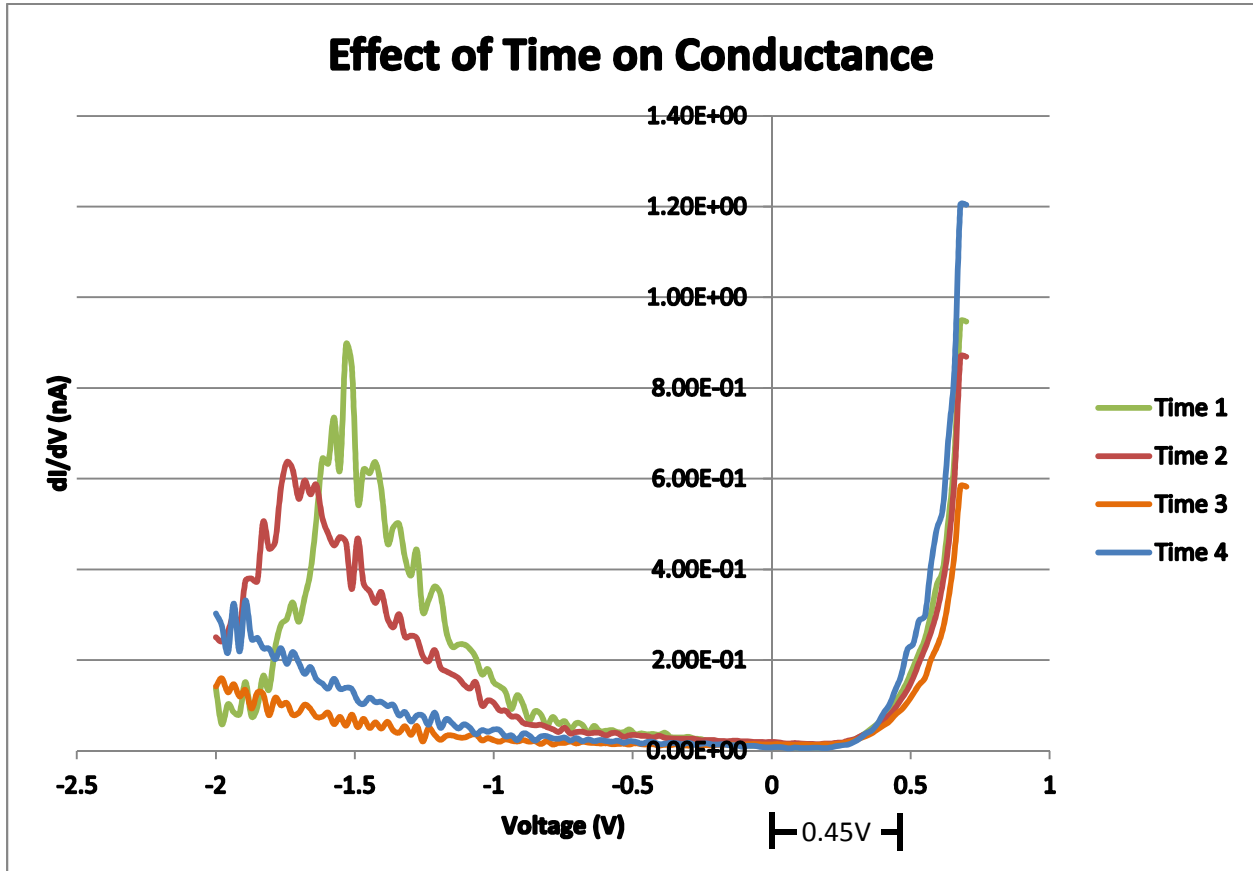


Figure 9: Conductance curve showing the LDOS of the sample

Capacitance Effects

While the STS graphs were being obtained, there was dependence on the sweep speed and data obtained. As shown in Figure 10, the forward sweep had a bump that does not match with the reverse sweep. This effect occurs when the voltage shifts from a negative to positive voltage applied, suggesting the effect is due to the discharge of a capacitor. The tunneling barrier can be thought of as capacitor due to the permittivity of free space. Because of the high impedance of the tunneling surface, little capacitance is needed to create a large RC cutoff. As a result of the product of the resistance of the system and capacitance of the system, the capacitance from an oxide layer will appear on the scan as

the bump in Figure 10. The reverse scan does not show the discharge of the capacitor since there was not enough time to fill the capacitor. As a result, there is no effect on the reverse sweep and the line does not have a hump.

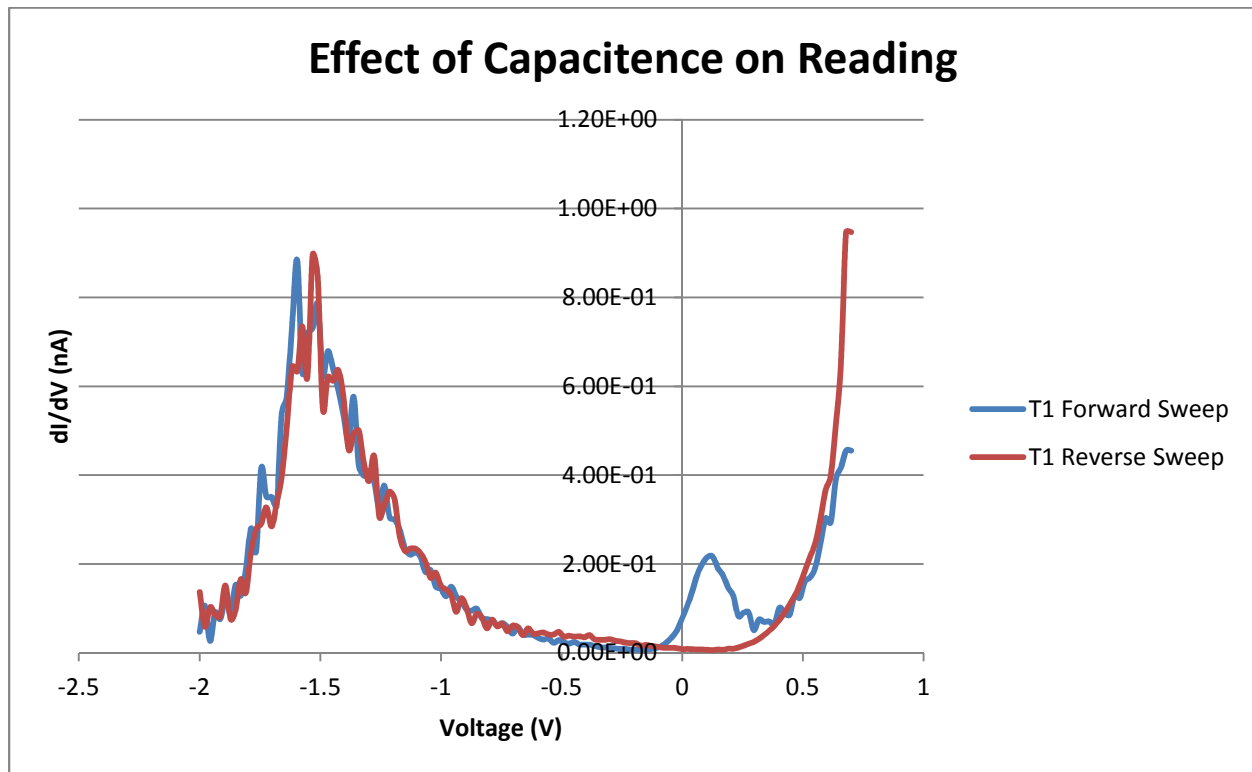


Figure 10: Forward and backward conductance curve showing the effects of capacitance

Discussion

Metal to Semiconductor Tunneling

When a metal and semiconductor transfer electrons to each other, there is a possibility for two types of junctions. The First is Ohmic, which follows Ohm's law where current and voltage will be directly proportional. The second is a Shockley junction where the Fermi energies of the semiconductor and metal differ greatly. As a result, a Shockley diode is formed that will have a nonlinear conducting profile.

The Shockley diode created in this application was from the interactions of the Fermi energy levels of the n-type silicon and the tungsten tip. As a result, the I-V scans represent the operating conditions of the Shockley diode created. The barrier difference between the n-type silicon and the tungsten was calculated to be 0.45 V^8 . This separation of barriers distorts the band structure of the n-type silicon (Figure 11). The distortion is caused when the Fermi energies of the two materials try to balance to be equal. The effect of the distortion is the creation of a depletion layer that acts as an insulator or extension to the tunneling gap. The tunneling gap is widened or shortened based on the applied voltage, affecting the measurements on the LDOS of the system being analyzed.

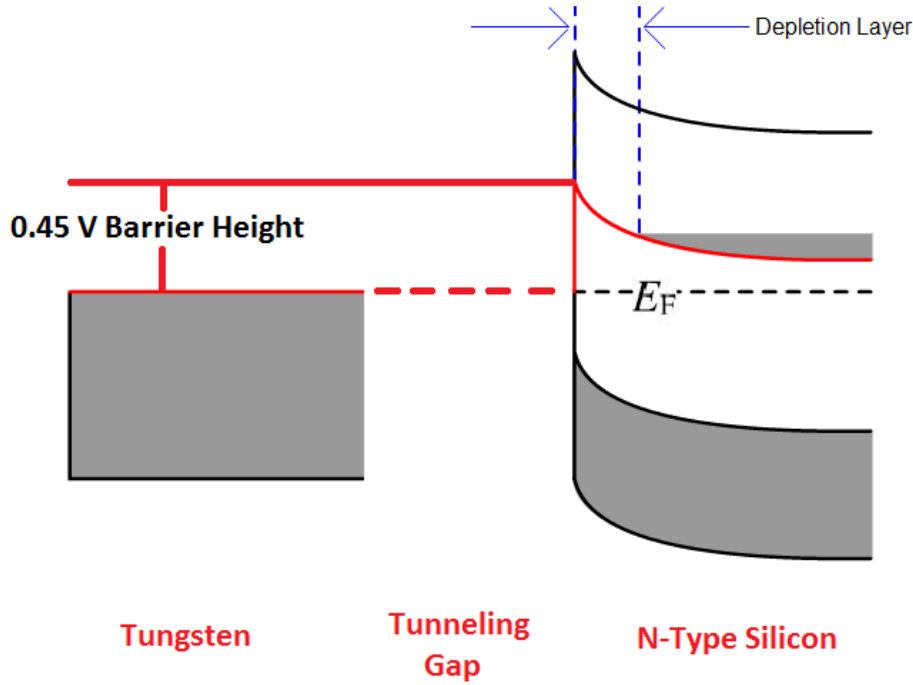


Figure 11: Schematic of Shockley diode created

Forward Bias

When a positive voltage is applied to the tip, the shift of the depletion layer decreases the tunneling distance, exponentially increasing the conductivity of the sample (Figure 12). This exponential function is clearly seen in the conductance curves in the positive bias region. The

barrier difference of 0.45V was also seen as the point when the current begins to rise exponentially due to the decrease of the depletion layer. The conduction masked the LDOS measurement by superimposing the exponential function on top of the LDOS, making it impossible to distinguish the different states.

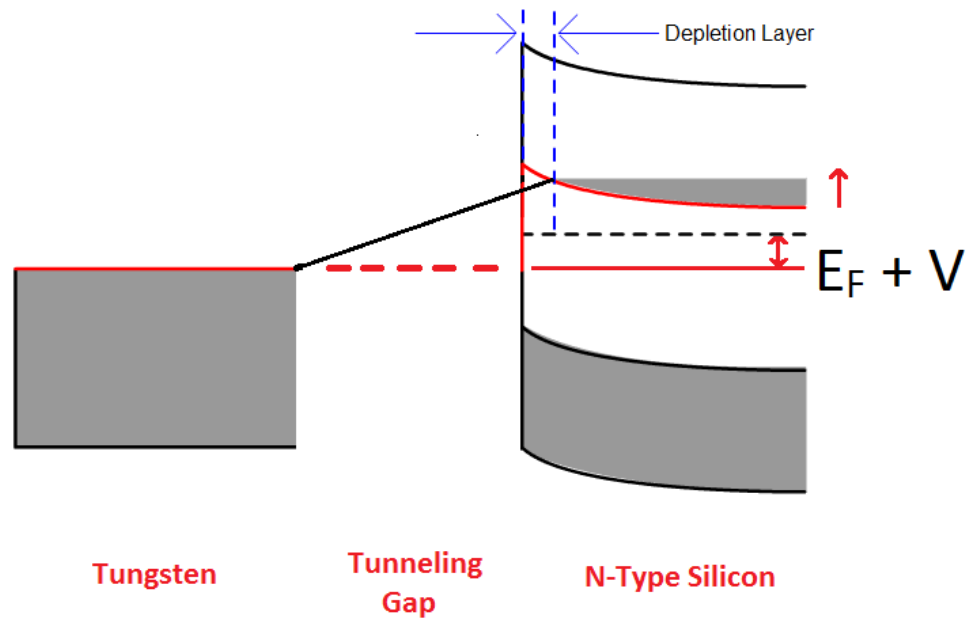


Figure 12: Forward Bias Shockley diode with tunneling

Reverse Bias

When a negative voltage is applied to the tip, the shift of the depletion layer increases the tunneling distance (Figure 13). As a result, the current is severely reduced because of the exponential decay of current with time. When the negative tip voltage is enough to match with the Fermi energy of the sample, the current flowing through the sample drops to zero. Current from additional voltage now flows from the tip to the sample, giving the negative current seen in Figure 8. The shift in tunneling distance as a function of applied voltage creates a distortion of the LDOS results that would cancel some peaks completely. The shifts in the LDOS between scans may be due to the tip location, but there is no data to confirm the location of each scan, leaving insufficient information to analyze the peak shifts.

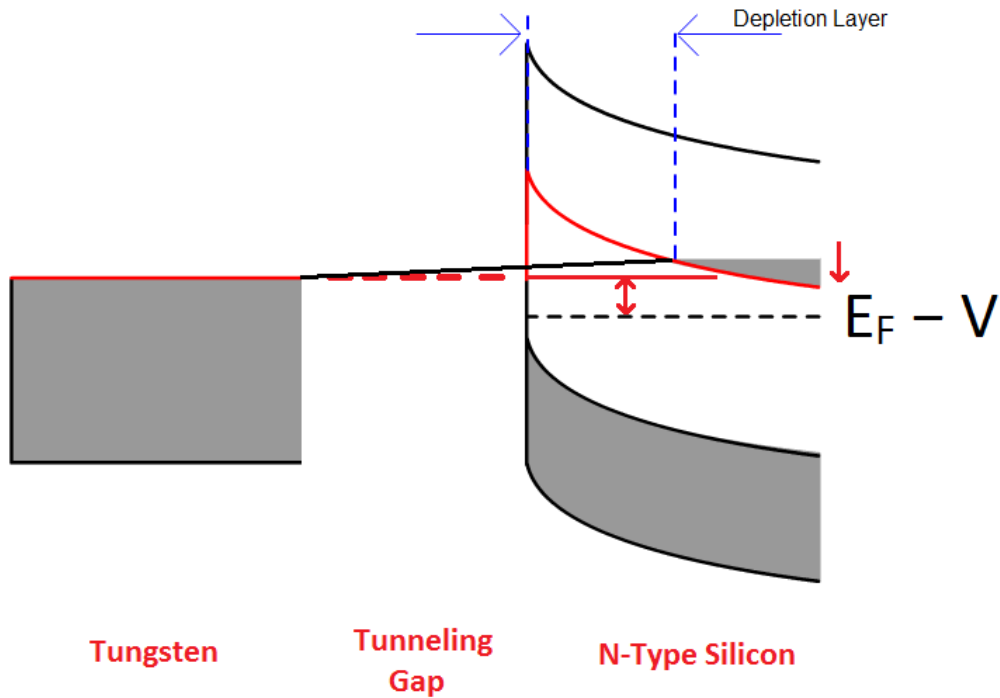


Figure 13: Reverse Bias Shockley diode with tunneling

Capacitance of the Oxide

The capacitance of the oxide yields an interesting opportunity. If the RC constant of the system can be measured, the capacitance of the tunneling gap can be found. Because of the permittivity of free space, the capacitance can be thought of as a composite of a known capacitor through free space in series with the capacitance of an insulator on the surface of the conductor. Thus the thickness of the oxide may be able to be calculated from a capacitance meter that can measure the change in capacitance from the surface.

Due to the fact that tungsten tips were used for the spectroscopy, there is a concern about the oxide on the tip. Tungsten forms WO_3 in the presence of atmospheric conditions. This oxide layer will eventually form on the tip of the STM probe, affecting the model used. The thickness of the oxide can reach up to 20 nm⁷ that would render the tip inoperable due to the reduction of current. Due to the large work function values of insulators, the model is not changed much, but instead affects the ability to obtain quality STS between the tip and silicon. As a result of this oxide, many scans were not able to show the LDOS with an acceptable signal to noise ratio.

Model Considerations

The STS scans of the sample obtained were noisy and unstable. By considering some of the complications of the basic band gap theory, the sources of noise will be considered for a more complete model concept. The sources of noise ranged from the STM system to material considerations.

Some of the instability between spectrums can be due to the passing of molecules such as air or water between the tip and the sample. The air or water will act as an insulator that will perform the same masking that an oxide would do, so variations in the measurement will appear as high frequency noise as molecules pass through the tunneling gap. Further analysis can use an STM under ultra-high vacuum can confirm these interactions.

Thermal drift between the sample and tip causes changes in the tip sample distance and location. Change in tip sample distance affects the spectroscopy greatly by exponentially affecting the current flow to the sample. Since the tip is locked into place while the spectroscopy is running, tests that take minutes to average out the noise may have inaccuracies due to the drift of the sample away or towards the sample. While the drift may be slow and small, the noise it can contribute can reduce the sensitivity to the point where the LDOS can be overrun with noise. Also the horizontal shift in location can shift the density of states slightly. This is due to the atom on the tip progressing from taking a spectroscopy of the top of an atom to the location in between the atoms, leading to different energy states present.

The last consideration for increasing the stability of the scan is to use a white led light to offset the Shockley band shifting effect⁴. This shift can offset the LDOS of the sample, making acquisition of the LDOS difficult. One way to mitigate this effect that was not able to be implemented yet is to expose the surface of the sample to a wavelength of light greater than the work function. As a result of this test, more information about the LDOS of the valence band can be obtained.

Conclusion

STS data revealed the operational mode of the STM interaction with the sample to be a combination of modes of a Shockley diode and a tunneling diode. As a result, the initial intention of finding the LDOS was impeded by the characteristics of the Shockley diode. Upon discovery of the modes of operation, improvements to the system were suggested to facilitate a properly functioning system. Ultimately the development of a reliable model will allow for the STM system that was characterized to be used in desorption of hydrogen from silicon to form nanometer thick layers of oxide to be used as an etch mask.

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