

## LAB UNIT 5: Scanning Tunneling Microscopy

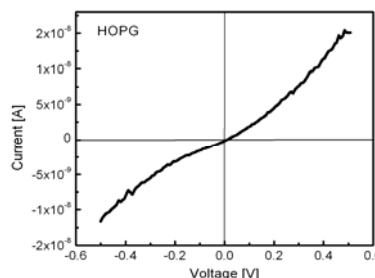
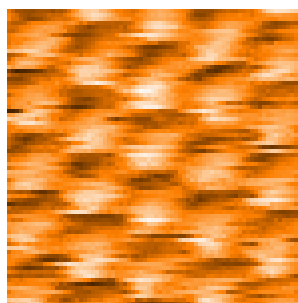
### Specific Assignment: STM study of HOPG and Gold films

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**Objective** This lab unit introduces scanning tunneling microscopy (STM) technique, used to obtain real space atomic resolution images of conductive surfaces. The tunneling spectroscopy mode of STM is employed to examine local density of state (LDOS) of the surface.

**Outcome** Learn about the basic principles of scanning tunneling microscopy, including a short introduction of the tunneling phenomena, and learn how the STM images can be correctly interpreted. Attain STM images and the local density of state of a HOPG (highly ordered pyrolytic graphite) and gold (Au) sample in ambient atmosphere.

**Synopsis** The STM provides real space atomic resolution images through tunneling current between a conductive tip and a conductive/semiconductive surface. In this lab unit, we employ two STM modes, i.e., constant current imaging mode and tunneling spectroscopy mode, to study HOPG (graphite) and gold (Au). HOPG is one of well studied materials and serves as a standard for STM technique, and the interpretation of the STM images as well as the spectroscopic analysis are debated actively in literatures. Here, taking into consideration of artifacts such as thermal drift, students will determine the lattice constant and the atom-to-atom distances of HOPG. The contrasting spectroscopic data of the HOPG and Au will illustrate the difference in electronic structure between semi-metals and metallic systems.



**A STM image (Left, 9 Å x 9 Å ) and a voltage dependent tunneling spectroscopy curve (Right) of HOPG**

**Materials** Highly Ordered Pyrolytic Graphite (HOPG) and Gold (Au) film

**Technique** STM in imaging mode and tunneling spectroscopy mode

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## 1. Assignment

The assignment is to study the layered structure of HOPG and Au films. Specifically, the lattice constant and the atom-to-atom distances of HOPG will be determined from the STM images. Conductivity, i.e., band structure, of HOPG and Au are also discussed by analyzing the tunneling spectroscopy data. The steps are outlined here:

1. Familiarize yourself with the background information provided in Section 4.
2. Test your background knowledge with the provided Quiz in Section 2.
3. Conduct the STM experiments in Section 3. Follow the experimental step-by-step procedure.
4. Process images and analyze the spectroscopy data as described in Section 3
5. Finally, provide a report with the following information:
  - (i) Result section: In this section you show your data and discuss instrumental details (i.e., limitations) and the quality of your data (error analysis).
  - (ii) Discussion section: In this section you discuss and analyze your data in the light of the provided background information.  
It is also appropriate to discuss section (i) and (ii) together.
  - (iii) Summary and outlook: Here you summarize your findings and provide an outlook on how one could proceed.

The report is evaluated based on the quality of the discussion and the integration of your experimental data and the provided theory. You are encouraged to discuss results that are unexpected. It is important to include discussions on the causes for discrepancies and inconsistencies in the data.

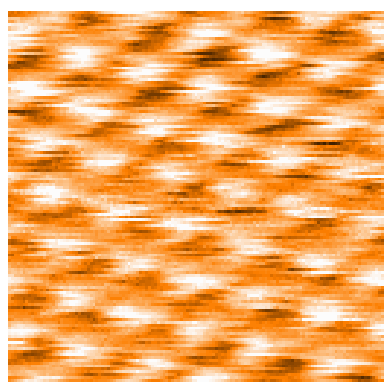
## 2. Quiz – Preparation for the Experiment

### Theoretical Questions

- (1) Sketch the tunneling phenomena between a metallic STM tip and a metallic sample surface at (a) no bias voltage, (b) positive voltage, and (c) negative voltage.
- (2) How does a contamination of a STM tip, with organic molecules for example, influence the tunneling current, i.e., the tunneling barrier? Discuss.
- (3) Sketch the electronic structures and I-V curves of tunneling spectroscopy of the four systems; metallic, semi-metallic, semiconductive, and non-conductive.
- (4) What is “three-fold-hexagon” of HOPG? Explain.

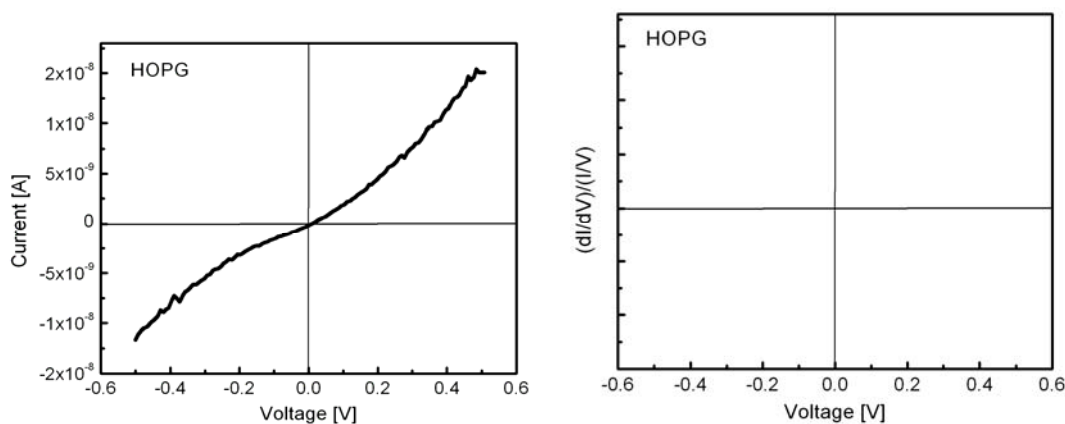
### Prelab Quiz

- (1) (6pt) The STM image (below) of a HOPG shows honeycomb structure, known as “three-fold-hexagon” pattern. Determine the lattice constant and the atom-to-atom distance of HOPG of the STM image below.



(1.4 nm x 1.4 nm)

- (2) (2pt) An actual I-V curve of a HOPG sample is shown below. Sketch the differential conductance  $(dI/dV)/(I/V)$  of this I-V curve in the given space.



- (3) (2pt) List the reasons why the atomic structure of gold sample is difficult (or impossible for our lab) to obtain?

### 3. Experimental Assignment

#### Goal

Following the step-by-step instruction below, obtain the STM images and determine the characteristic lattice constant of HOPG. Analyze the tunneling spectroscopy data to determine the conductivity of the systems. Analyze and discuss the data with the background information provided in Section 4. Provide a written report of this experiment.

#### *Specifically provide answers to the following questions:*

- (1) According to the analysis, what were the lattice constant and the atom-to-atom distance of the HOPG?
- (2) Compare the values obtained in (1) with the literature values. How closely does your result agree/disagree that of the literature values? Discuss your findings.
- (3) Show the STM images that were obtained at different bias voltage. Discuss how and why they are different/ indistinguishable.
- (4) According to the spectroscopic analysis, what type of system is HOPG? How about Au? Explain your conclusion.
- (5) STM has been applied to image DNA and other biological macromolecules, which are in general not conductive. How would you image a single biological molecule placed on a gold substrate?

#### Safety

- Wear safety glasses.
- Refer to the General rules in the AFM lab.
- Wear gloves when handling ethanol.

#### Instrumental Setup

- Easy Scan 2 STM system with 0.25nm (diameter) Pt/Ir wire (STM tip)
- STM granite vibration isolation platform

#### Materials

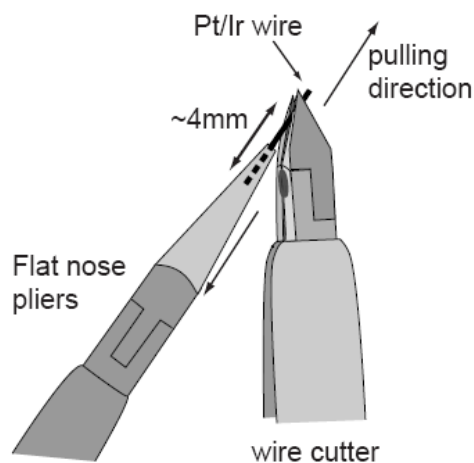
- Samples: Highly Ordered Pyrolytic Graphite (HOPG) and a gold film. Samples are kept in designated containers when they are not used to avoid contamination.
- Ethanol in squeeze bottle and cotton swabs for cleaning.
- Scotch tape for cleaving the HOPG layers.

#### Experimental Procedure

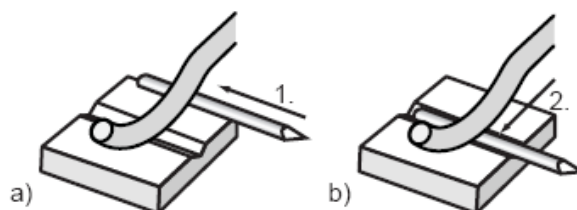
Read carefully the instructions below and follow them closely. They will provide you with information about (i) preparation of the experiment, (ii) the procedure for attaining the STM images, (iii) attaining the tunneling spectroscopy data, (iv) the procedure for closing the experiment, and (v) on how to process/analyze the STM images and to process spectroscopy data.

**(i) Preparation of the experiment**

- (1) *Wear gloves whenever handling any part of the STM system. Also never talk/breathe to any part of the STM systems. Your breath contains billions of organic substances.*
- (2) Make the STM tip: (This part will be performed with a TA)
  - a. Make sure everybody is wearing gloves, again.
  - b. Clean the wire cutter, the flat nose pliers, pointed tweezers, and rounded tweezers with ethanol. Place them on a Kimwipe. Make sure they are dry. These are the only tools that can come in contact with Pt/Ir wire.
  - c. Cut out 1 ~ 2 cm of the Pt/Ir wire with the wire cutter.
  - d. Hold the end of the wire firmly with the pliers. (Figure 3.1) Try not to bend (forming a kink) the wire.
  - e. Place the wire cutter as obliquely as possible (Figure 3.1). Close the cutters until you can feel the wire, but do not cut the wire.
  - f. Pull the cutters in the direction shown in the figure. The tip is torn off, rather than cut through, to create a sharp tip.
  - g. *Do not touch the newly created tip with anything, including the cleaned tools and Kimwipe.*
  - h. Hold the tip wire at just behind the tip using the pointed tweezers. Release the flat nose pliers.
  - i. Cut the wire so that the total length of the tip wire is ~ 4mm.
- (3) Install the tip into the STM head.
  - a. Put the tip wire on the tip holder parallel to the groove in the tip holder so that it crosses below the tip clamp. (Figure 3.2(a))
  - b. Move the tip wire sideways until it is in the groove in the tip holder. (Figure 3.2(b))



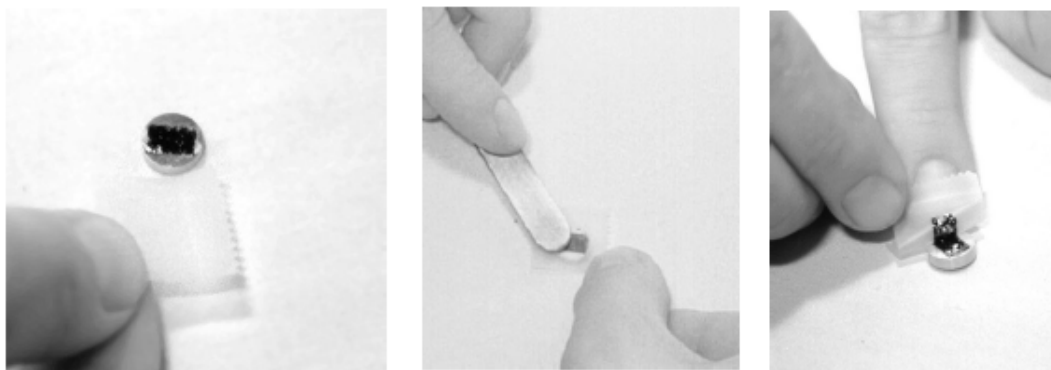
**Figure 3.1:** Creating a sharp STM tip.



**Figure 3.2:** Installing the tip into the STM head.

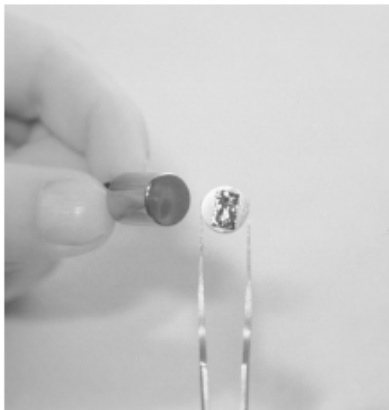
(4) Install the sample.

- a. Remove the sample holder from the storage container by holding the black plastic part. **DO NOT TOUCH** the metal part.
- b. Check for any contamination (dust, fingerprint) on the metal part. If cleaning is necessary, follow the cleaning procedure.
  - i. Moisten a cotton swab with ethanol and gently clean the surface.
  - ii. Allow the alcohol to completely dry.
- c. Place it on the sample holder guide bar of the STM head. Make sure it does not touch the tip.
- d. Cleave the HOPG (graphite) sample. (Figure 3.3)
  - i. Stick a piece of scotch tape gently to the graphite and then gently press with the back, flat part of the tweezers.
  - ii. Pull the tape off. The topmost layer of the sample should stick to the tape, leaving a freshly exposed graphite surface.
  - iii. Remove any loose flakes with the part of tweezers.



**Figure 3.3:** Cleaving the graphite sample.

- e. Using a tweezers, hold the graphite sample at the magnetic pak.
- f. Take the sample holder (handle at the black plastic part), and place the graphite sample on the magnet.
- g. Place the sample holder back on the STM head. Make sure it does not touch the tip.

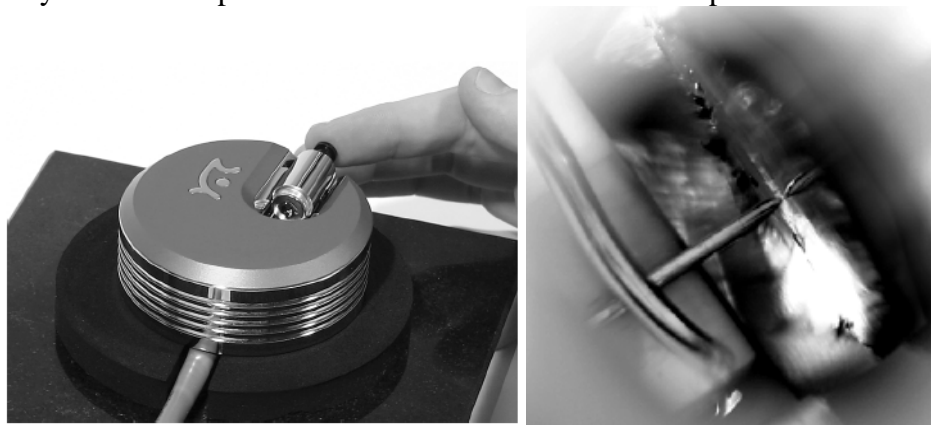


**Figure 3.4:** Placing the sample on the sample holder.

- (5) Turn on the Controller main power switch.
- (6) Open the Easy Scan 2 control software.
- (7) In the operation mode panel, select STM.

**(ii) Procedure for attaining the STM images**

- (1) Coming in contact.
  - a. Push the sample holder carefully to within 1mm of the tip. The tip should not touch the sample.
  - b. Look into the graphite surface. There should be a small gap between the very end of the tip and the reflection of the end of the tip.



**Figure 3.5:** Coarse approach.

- c. Open the Positioning window.
- d. Through the magnifier, watch the distance between the tip and sample as click Advance in the approach panel. The tip should be within a fraction of a millimeter to the surface (i.e., the reflection of the tip).
- e. Set control parameters in Z-control panel: Set point 1nA, P-gain 10000, I-gain 1000, Tip voltage 50 mV.
- f. Click Approach.

- g. If the approach was finished successfully, the probe status light changes from blinking to green and automatically start to scan. If not, retract and try again.
- (2) Adjust imaging parameters (scan speed, scan direction, tilt, P-gain and I-gain) as the same manner as for AFM imaging. Set the resolution to 256. For attaining atomic resolution,
  - a. For STM, faster scan speed is better for reducing the thermal drift.
  - b. Image ~ 500 nm area to find a flat location. Zoom into the flat area.
  - c. The atomic resolution images will be ~ 4nm scan size.
  - d. If the image does not show atomic features, try different scan direction, reduce the gains.
  - e. If none of above work, come out of contact, re-approach. Consult your teaching assistants for further suggestions.
- (3) For storing images click Photo in the imaging window. Name files accordingly.
- (4) Take images at the bias voltage (tip voltage) of 50mV, 250 mV, -50 mV, and -250 mV. Take at least two STM images for each bias voltage.

### (iii) Attain the tunneling spectroscopy data

- (1) Stop scanning.
- (2) Open the spectroscopy window.
- (3) Set parameters: Modulated output is tip voltage, start value -0.5V, end value 0.5 V, modulation time 1s, data point 128, and average 1.
- (4) Reset the Z-control parameters in z-control window: set-point 1nA and voltage 50mV.
- (5) Click *+Point*, and select a location in the image. Click *Start*.
- (6) The obtained I-V curve will appear as a dual line graph.
- (7) Save the curve.
  - a. Click the I-V curve.
  - b. Click Photo from the imaging window tool bar. The STM image and I-V curve appears as a separate window.
  - c. From File, select Export, current chart as..., (X, Y, Z)-Points (\*.csv). Name accordingly.
- (8) Take 3 I-V curves at different locations.
- (9) Change the modulated output to Z-axis, start value 1nm, and end value 36 fm.
- (10) Select a point and start. Save the data. Attain three I-z curves.

*Do the same for GOLD film.*

- a. Au film can't be cleaned, so handle with extra care not to contaminate.
- b. Atomic resolution of Au is very hard to attain. For this lab, it is sufficient to image the surface of Au and I-V curves.

### (iv) Procedure for the closing experiment

- (1) Wear gloves.
- (2) Retract the STM tip as far as possible by auto-positioning.
- (3) Close the Easy Scan 2 software window.
- (4) Leave the STM tip on the head.

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- (5) Take the sample off of the sample holder. Place the sample in its case.
- (6) Clean the sample holder with ethanol and a cotton swab. Let it dry.
- (7) Place the sample holder in the case. Close the cap tightly.
- (8) Place the STM cover over the STM head.
- (9) Turn off the controller power switch.

### (v) Instruction for data analysis

- (1) Open the Easy Scan 2 program to process images. Save the images with scale bar.
- (2) The Report program is also used to measure the lattice distance and the atom-to-atom distance of HOPG sample. It will be helpful to also to show the images with the measuring lines, etc. in your final report. So save images as you take measurements (to be imported to your report).
- (3) Open the spectroscopy files with Excel.
- (4) Generate columns:  $\ln(I)$ ,  $\ln(V)$ , and  $d(\ln(I))/d(\ln(V))$ . Calculate  $\ln |I|$  and  $\ln |V|$ .
- (5) Create two plots of  $\ln(I)$  vs  $\ln(V)$ , one for  $V_{\text{bias}} < 0\text{V}$  and one for  $V_{\text{bias}} > 0\text{V}$ .
- (6) Using *Add trendline* function, obtain the fit curves for the  $\ln(I)$  vs  $\ln(V)$  curves separately for  $V_{\text{bias}} < 0\text{V}$  and one for  $V_{\text{bias}} > 0\text{V}$ . Use either 2nd order or 3rd order polynomial, whichever gives a better fit.
- (7) Differentiate the fit curve that is equal to  $d(\ln(I))/d(\ln(V))$ . Type the derivative equation in the cells of the  $d(\ln(I))/d(\ln(V))$  column.
- (8) Create a plot of  $I$  vs  $V$  (current as a function of voltage, raw data), and differential conductance  $((dI/dV)/(I/V) = d(\ln(I))/d(\ln(V)))$  as a function of voltage.
- (9) Also Plot  $I$ - $z$  curve, i.e. current as a function of the  $z$  distance in semi-log scale.
- (10) According to Equation 2,

$$\log(I) = -A\sqrt{\phi} \cdot z + C$$

determine the barrier height  $\phi$ .

## 4. Background: Scanning Tunneling Microscopy and Spectroscopy

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### Motivation

With the development of quantum mechanics in the early 20<sup>th</sup> century, mankind's perception of nature was stretched to a great degree leading to new axioms, and the recognition of the particle-wave dualism. It was found that particles with small masses such as electrons could interchangeably be described as waves or as corpuscular objects. With the wave character of matter, particles exhibit a probability of existence at places, where they can classically not exist. One of these phenomena is the tunnel effect, which describes the ability of an electron to tunnel through a vacuum barrier from one electrode to the other. Since 1960 tunneling has been extensively studied experimentally. This led in 1981 to the first microscopic tool with which atoms could be observed in real space – the scanning tunneling microscopy. In addition to the atomic resolution imaging capability of STM, tunnel currents could be studied with this tool in a spectroscopy manner providing insight into the local density of state (LDOS) of material surfaces.

### Scanning Tunneling Microscopy

While vacuum tunneling was theoretically predicted by Folwer and Nordheim 1928,<sup>1</sup> it was not until 1981 with G Binnig and H. Rohrer's introduction of the scanning tunneling microscope (STM) that provided the first observation of vacuum tunneling between a sharp tip and a platinum surface.

#### Wavefunction Overlap, Electron Probability

STM is based on a quantum mechanical phenomenon, called tunneling. In quantum mechanics, small particles like electrons exhibit *wave-like* properties, allowing them to “penetrate” potential barriers, a quantum mechanical probability process that is based on classical Newtonian mechanics impossible.\* In general, STM involves a very sharp conductive tip that is brought within tunneling distance (sub-nanometer) of a conductive sample surface, thereby creating a metal-insulator-metal (MIM) configuration. In the representation of one-dimensional tunneling (Figure 4.1), the tunneling wave of the sample electrons,  $\psi_s$ , and the wave of a STM tip electrons,  $\psi_t$ , overlap in the insulating gap, allowing a current to flow.

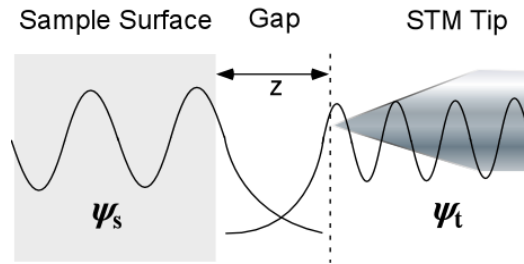
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\* A more detailed discussion on barrier tunneling is provided in a later section of this text.

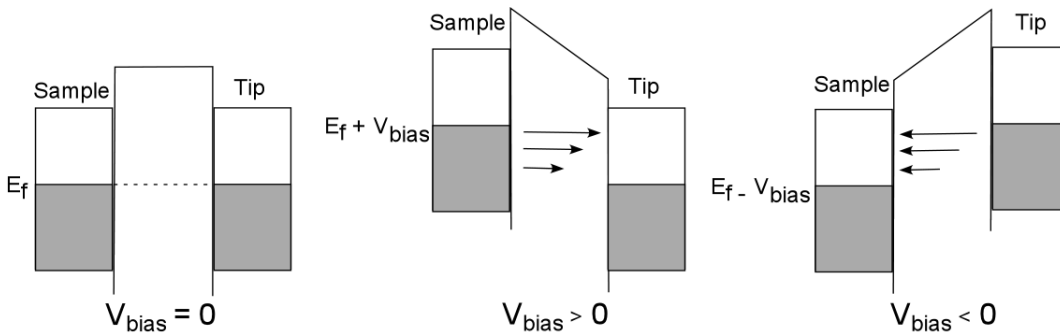
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To achieve some understanding of the physical meaning of the wave function  $\psi$ , we consider the square magnitude of it, which represents the probability of finding an electron at a given location. Generally, this is visualized with electron clouds for atoms or molecules, or for condensed phases with energy levels, as illustrated with the gray shaded areas in Figure 4.2. In metals, electrons fill the continuous energy levels up to the Fermi level,  $E_F$ , which defines an upper boundary, similar to the sea level. Above  $E_F$  we find electrons that are activated (e.g., thermally). We can raise the Fermi level (e.g., of the sample) in regards to a second material (e.g., tip) by applying a voltage.

Thus, to observe the tunneling current  $I$  of electrons through the vacuum gap between the sample and the tip, a bias voltage,  $V_{bias}$ , is applied, as shown in Figure 4.2. At  $V_{bias} = 0$ , the electrons cannot flow in either direction since the Fermi level,  $E_f$ , of both the tip and the sample is equal, i.e., the gradient is zero. When  $V_{bias} > 0$  (positive bias), the Fermi level of the sample is raised by  $V_{bias}$ , and the electrons in the occupied state (filled with electrons) of the sample can tunnel into the unoccupied state of the tip. Similarly, when  $V_{bias} < 0$  (negative bias), the electrons in the occupied state of the tip tunnel into the unoccupied state of the sample.



**Figure 4.1:** Schematic of STM one-dimensional tunneling configuration.



**Figure 4.2:** Schematic of a metal-insulator-metal tunneling junction. The grey area represents electron filled states (occupied level) and the white area is empty states, ready to accept electrons (unoccupied level).

STM images represent the local magnitude of the tunneling current in the x-y plane. As the tunneling current strongly depends on the tip-sample distance (i.e., the width of the vacuum gap or insulator air gap) the convoluted information it provides are composed of (a) topographical changes and (b) surface electronic anisotropy.

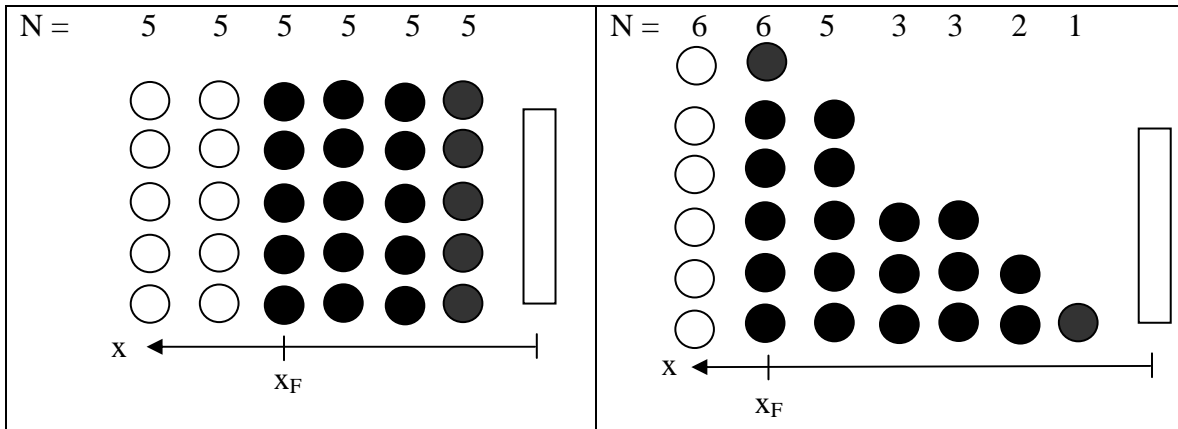
Tunnel Current, Vacuum Gap Size and Density of States

The tunneling current decays exponentially with the distance gap distance  $z$ , and is strongly affected by the density of states (DOS) of the sample at the Fermi level,  $\rho_s(E_f)^2$ ; i.e.,

$$I \propto V_{bias} \rho_s(E_F) \exp\left[-2\sqrt{\frac{2m(\phi - E)z}{\hbar}}\right] \propto V_{bias} \rho_s(E_F) \exp(-1.025\sqrt{\phi} \cdot z), \quad (1)$$

where  $m$  is the mass of electron and  $\hbar$  is the Planck's constant.

An electronic state describes a specific configuration, an electron can possess. For instance, it can have either a spin up or spin down, or a particular magnetic momentum etc. A state is described by a set of quantum mechanical numbers. Each state can only be filled by one electron. Consider a classroom of  $X$  chairs with  $Y < X$  students. The chairs represent the states and the students the electrons. Let us assume, it is hard to read the board, and the students are all very interested in the subject. Consequently the chairs will be filled up towards the front with some empty seats in the back. This situation is illustrated in Figure 4.3. The chairs in each row are represented by circles. Filled circles represent student occupied chairs. The distance from the board is indicated with  $x$ . The number of chairs per row represents the density of states (DOS) for a particular classroom. Two distinctly different classrooms are shown in Figure 4.3. In the second classroom  $N$  is a function of the  $x$ . The last row that is filled is identified by  $x_F$ . Returning to electrons in metals;  $x_F$  corresponds to the Fermi energy  $E_f$ ,  $N$  to  $\rho_s$  and  $N(x_F)$  to  $\rho_s(E_f)$ . In the case of the free electron model for s-/p-metals at zero Kelvin,  $\rho_s(E)$  is proportional to the square root of the energy.

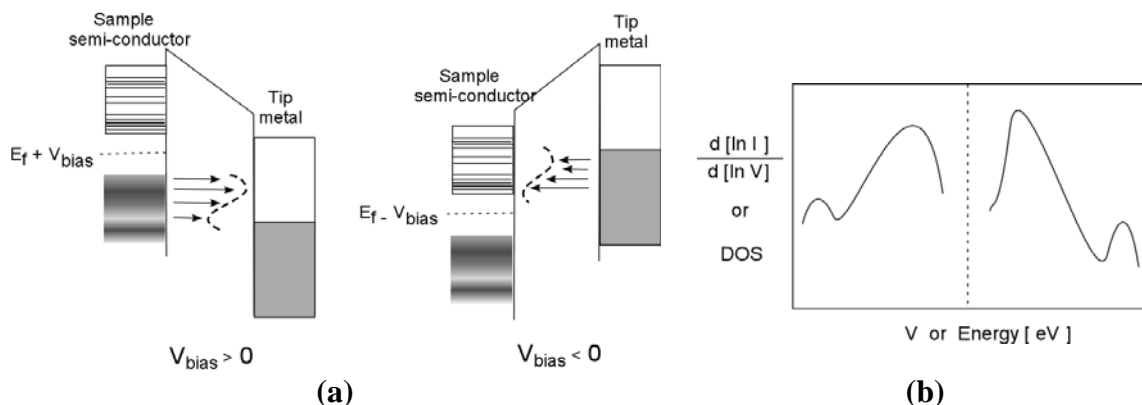


**Figure 4.3:** Density of state (DOS),  $N$ , and Fermi energy  $x_F$  in two classroom settings. (left)  $N$  is constant. (right)  $N(x)$ .

Many physical properties are affected or depend on the number of states within an energy range (i.e., the energy density of states). While in metals and semi-metals, there is relatively small variation in the density of states due to the large electron delocalization, the density of energy levels in semiconductors varies noticeably. Thus, knowledge about DOS is of immense importance for electronic applications involving semiconducting materials, where the availability of empty valence and conduction states (states below and above the Fermi level) is crucial for the transition rates. In comparison to Figure 2 that visualizes tunneling between metals, Figure 4.4 illustrates the tunneling mechanism

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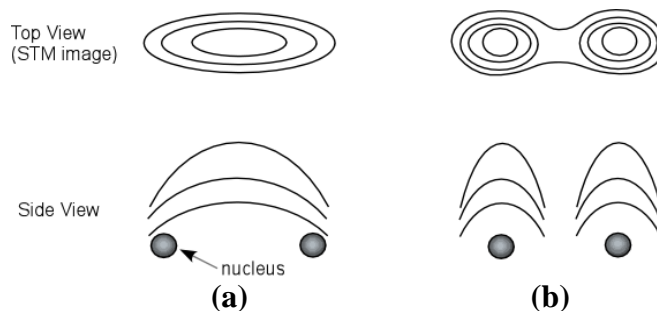
involving a semiconductor. The filled area (grey) is not uniform, representing the variation in electron density, and the lines in the unoccupied levels represent the variation in density of the energy levels that the tunneling electrons can occupy.



**Figure 4.4:** (a) Schematic of a metal-insulator-semiconductor tunneling junction and (b) corresponding normalized differential tunneling conductance.

### STM and Local Density of States

STM constant current maps provide information about the variations in the electron density, and do not necessarily correspond to the location of atoms (nuclei). Figure 4.5 illustrates that a location of high tunneling current in a STM image can be either a compounded affected of two atoms, leading to a current maximum in between the atoms, or be identical with the location of an atom. This is for instance found for the silicon (001)  $2 \times 1$  surface.<sup>3</sup> A  $\pi$  molecular orbital of the silicon-silicon dimers ( $\text{Si}=\text{Si}$ ) creates the highest electron density (probability) at the center of the dimers, while an anti-bonding  $\pi^*$  molecular orbital has a node (a location where the probability is zero) at the center of the dimers. Thus, when a negative bias is applied, the electrons in the  $\pi$ -molecular orbital (occupied state) tunnel and the resulting image, similar to the case shown in Figure 4.5(a), will be obtained. When a positive bias is applied, the electrons of the tip tunnel into the anti-bonding  $\pi^*$  molecular orbital (unoccupied state), revealing a gap between the dimers, as in Figure 4.5(b). When the variation in the local DOS (LDOS) of metals is small, the contour of STM images often can be safely interpreted as the topography of the atomic lattice.<sup>†</sup>



**Figure 4.5:** Sketch of possible STM images relative to the nucleus locations. Top view is the contouring lines of STM images and the corresponding side view on the bottom. STM image shows high tunneling location (a) at center of two nuclei and (b) at the top of each nucleus.

<sup>†</sup> See next section on LDOS on variety of systems.

### STM Measuring Modes

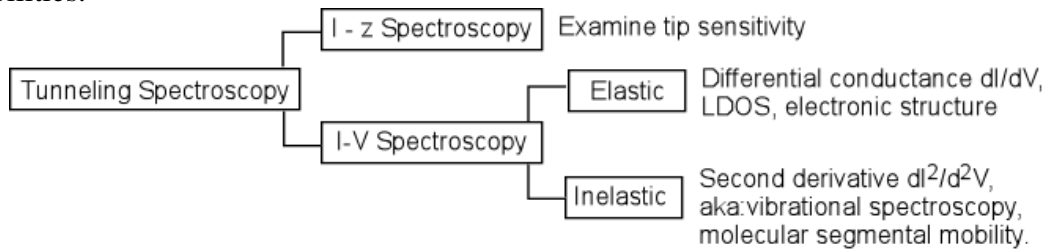
STM can be operated in three major operation modes: (1) imaging mode, (2) spectroscopy mode, and (3) manipulation mode. There are two imaging modes: Constant current imaging and constant height imaging. In constant current imaging, the vacuum or air insulating gap,  $z$ , between the tip and the sample is controlled by a current feedback control system. Scanning results in a constant current map of the surface. In contrast, the feedback is turned off, and the tip is scanned at a sample topography independent constant height, which results in a locally changing tunneling current map.

The spectroscopy STM mode, involves either a bias voltage  $V_{bias}$  sweep, or distance  $z$  ramping. The resulting current  $I$  is monitored as a function of the changing parameters. According to Equation (1), the tunneling current exhibits a log-linear gap distance  $z$  relationship. A simplified form of Equation (1) can be used to estimate the barrier height,  $\phi$ , of the tunneling current, i.e.,

$$\text{Log}(I) = -A\sqrt{\phi} \cdot z + C \quad (2)$$

where  $A$  is  $1.025 \sqrt{eV}/\text{\AA}$ , and  $C$  is a constant. I- $z$  spectroscopy is useful for the characterization of the quality of the STM tip, its sharpness and cleanliness. In the groundbreaking article of Binnig and Rohrer, the sensitivity of a STM tip was attained by the I- $z$  curves and was observed to increase with successive cleaning procedures.

Tunneling spectroscopy as a function of the bias voltage, i.e., I-V curves, provides very important information about the surface electronic structure, such as the barrier heights and LDOS of the sample. While the experimental procedures is very similar for large variety of sample systems, i.e., the current is measured as a function of  $V_{bias}$ , the data analysis varies from system to system and is in more detail discussed below. As summarized in Figure 4.6, I-V spectroscopy offers with a first order analysis information about the electronics structure, and a second order analysis information vibrational mobilities.



**Figure 4.6:** Modes of tunneling spectroscopy.

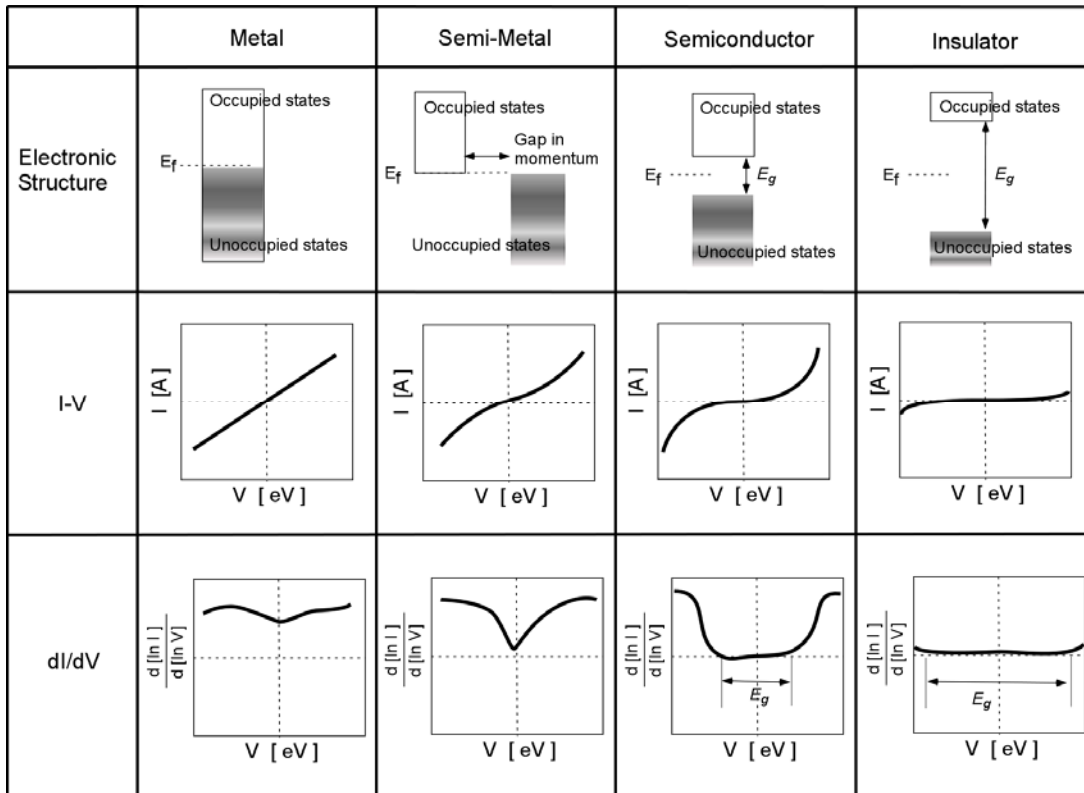
### Tunneling Spectroscopy

In the STM imaging mode, the tunneling current  $I$  is continuously recorded at each location  $(x,y)$  at a constant bias voltage  $V_{bias}$ , generating a two-dimensional map of tunneling conductance  $I/V_{bias}$ . In contrast, tunneling spectroscopy (I-V curve) focuses on the tunneling conductance, or commonly, a normalized differential tunneling conductance  $(dI/dV)/(I/V) = d[\ln(I)] / d[\ln(V)]$ . Tunneling spectroscopy studies are usually performed without scanning at a particularly chosen location, based on an initial STM current or height map. However, it is also possible to scan while the bias is ramped (scanning tunneling spectroscopy (STS)). Consider the aforementioned example, silicon 001 (2x1), it is evident that the spectroscopy at a location right above a nucleus would exhibit a I-V curve that is different from that of a center of two nuclei. In fact I-V

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spectroscopy on silicon 111 (7x7) surface is location specific.<sup>4</sup> Interestingly the average I-V curves at various locations closely resembles to data obtained by ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPS). It suggests that UPS and IPS are the area average of the differential conductance, while STM tunneling spectroscopy is capable of resolving local information, e.g. local DOS rather than average DOS.

The general profile of the density of state around the Fermi level, i.e.,  $(dI/dV)/(I/V)$ , can be used to classify the material based on its conductivity, as illustrated in Figure 4.7. As shown, metals do not possess a gap between the occupied states (valence band) and the unoccupied states (conduction band) and the variation in DOS is relatively small. Thus, the I-V curves are linear for the most part, resulting in a very small  $dI/dV$  gradient. Semi-metals also do not have a gap between the occupied and unoccupied states. There is, however, a gap in the momentum space (the waves are out of phase) that depresses the conductance around the Fermi level, and consequently bends the density of states at low voltages. For semiconductors and insulators, the conductance around the Fermi level is zero. The threshold voltage, i.e., band gap,  $E_g = |V_{+bias}| + |V_{-bias}|$ , is relatively small for semiconductor ( $< 3\text{eV}$ , used as definition for semiconductors). As shown in Figure 4.7, semiconductors show a highly bend DOS, which is flat as for insulators at low voltages, where the energy gap  $E_g$  cannot be bridged. It is well known that doping semiconductors with impurities or defect sites affect reduce  $E_g$ , and thus, can modify the density of states at the Fermi level to such a degree that it resembles nearly a semi-metal.



**Figure 4.7:** The electronic structures and corresponding IV curves and  $dI/dV$  curves of tunneling spectroscopy.

So far, we have discussed elastic tunneling spectroscopy, in which the energy of the tunneling electrons is conserved. In inelastic tunneling spectroscopy, the counter electrode is not the material under investigation; rather it is the gap that is examined. In general, the material of interest is placed on top of the counter electrode or fills the insulating gap completely as a thin film. When the tunneling current travels through the material, a part of tunneling electron energy is dissipated by activating various modes of the molecular motion, e.g. C-H stretching of hydrocarbon chains. Thus the modes of the molecular motion can be deduced based on the extensive data base of infrared spectroscopy (IR). Experimentally, the I-V curve is obtained in the same manner as the elastic tunneling spectroscopy. To identify the modes of the molecular motion, the second derivative,  $d^2I/d^2V$ , is calculated, which contain multiple number of sharp peaks. The modes of molecular motion are then identified by the locations of the peak  $V_{peak}$ .

### Layered Structure of HOPG

Highly ordered pyrolytic graphite (HOPG) consists of layers of carbon sheets, forming a semi-metallic system. While the carbons within a sheet are covalently bonded to form a hexagonal lattice structure, the layers are held together by Van der Waals forces. The in-plane lattice constant (repeating unit length) and the z-axis lattice constant are 2.46Å and 6.7 Å respectively and the in-plane atom-to-atom distance is 1.42 Å. The sheets are arranged such that the every other carbon on a layer has a carbon in the neighboring sheets, Figure 4.8. The carbons in the first layer that have a carbon in the second layer right below are called an A-site carbons, and the carbons without a carbon directly below are called B-site carbons.

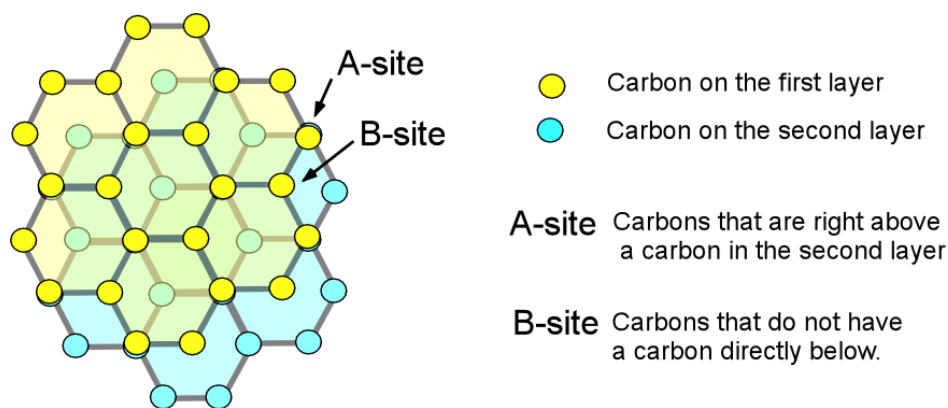
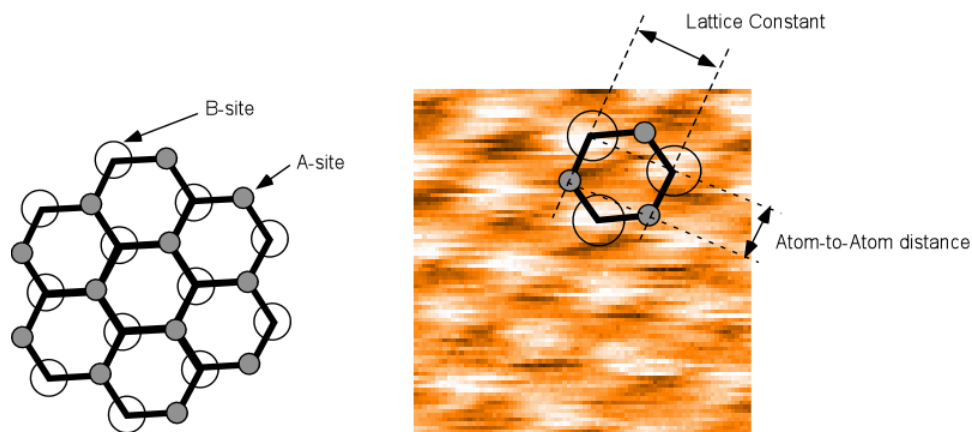


Figure 4.8: Layered structure of HOPG.

In STM images, the two types of carbons (A-site and B-site) appear differently. As shown in Figure 4.9, the B-site carbons exhibit a higher LDOS (i.e., topography) than the carbons at the A-site, exhibiting the *three-fold-hexagon* pattern.



**Figure 4.9:** Interpretation of HOPG's *three-fold-hexagon* pattern of STM images

While most of STM study of HOPG shows this *three-fold-hexagon* pattern, there are reports on various other patterns of HOPG, such as true hexagon and linear row structure. A possible explanation is given by multiple tip artifacts. Simulations of multiple tip contacts showed superimposed signal collection.

## References

- <sup>1</sup> G. Binnig, H. Rohrer, C. Berber, and E. Weibel, *Appl. Phys. Lett.* **40** (2), 178 (1981).
- <sup>2</sup> E. Meyer, H. J. Hug, and R. Bennewitz, *Scanning Probe Microscopy*. (Springer, Berlin, 2004).
- <sup>3</sup> R. J. Hamers and Y. J. Wang, *Chemical Reviews* **96** (4), 1261 (1996).
- <sup>4</sup> R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. Lett.* **56** (18), 1972 (1986).

## Recommended Reading

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Pearson/Benjamin Cummings, San Francisco, 2006.

*Scanning Probe Microscopy and Spectroscopy, Methods and Applications*, by Roland Wiesendanger, Cambridge University Press, Cambridge, 2<sup>nd</sup> ed. 1994.

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