3.02 Scanning Tunnelling Microscopy

(6 points)

1 Introduction

You will be aware, from your courses in quantum mechanics, that electrons have both wave- and particle-like properties. In this experiment, you will take advantage of the wave-like nature of electrons to investigate one of the many remarkable methods which have been developed to study the properties of surfaces at the molecular level.

Scanning probe microscopes are used in research as a means of interrogating the chemical and electronic structure of surfaces. The term *Scanning Probe Microscope* encompasses several types of instrument, which have similar architecture and features. In each case, a tiny sharply-pointed probe is positioned very close to a surface (typically closer than a nanometer), and moved in a raster fashion across it (just as an electron beam is swept across the screen of a television set). Measurements of the height of the tip above the surface or the current passing between it and the surface are taken at regular intervals during a scan (usually at a rate of several kHz) and the very fine positional capability of the probe enables one to investigate such factors as electron energy states, magnetic field strengths or interatomic forces at the surface, depending upon the type of instrument.

These instruments work at close to atomic resolution, so their use has opened up a wide range of new and fruitful areas of research, including studies of semiconductor structure, atomic level topography, probing of organic conductors, properties of Buckeyballs and nanotubes, and studies of the interaction between biomaterials and biological tissues. They are now used by various research groups in Oxford Chemistry, both in the Physical Chemistry Laboratory and other sub-departments.

In this experiment you will use a Scanning Tunnelling Microscope to take images of surfaces including a gold grating and graphite at atomic resolution.

2   Principles of the technique

Scanning tunneling microscopy (STM) is one of the newest and fastest growing techniques for characterizing surfaces [1] and can be used to investigate a wide range of surfaces such as gold, graphite or platinum. HOPG (highly oriented pyrolytic graphite) has been used as a standard sample for STM because of the stability of its surface obtained when cleaved, even in air. The adsorption of other species on graphite has opened up the possibility of studying insulating substances, for example alkanes, by STM [2, 3] and this has led to a plethora of studies on large organic molecules adsorbed on graphite [4, 5, 6].

Graphite forms intercalation compounds which have many interesting properties differing from those of the host material, eg superconductivity and low dimensional conductivity [7]. Recently it was found that HOPG treated with NaOH solutions had an X-ray diffraction pattern characteristic of a new stage-8 structure. The STM results obtained from a Burleigh ISTM confirmed the presence of a super structure of graphite intercalation compound; in this experiment you will repeat this work.

The electrons at the surface of a solid or liquid form an electron cloud, the density of which decreases exponentially with distance from the surface (Fig. 1). If a fine tip of conducting material is positioned very close to the surface, electrons may be drawn out from the surface, and tunnel to the tip through the potential barrier provided by the gap. (This tunnelling illustrates the quantum-mechanical behaviour of an electron, since the electrons have insufficient energy to cross the gap "classically" unless the tip is actually "in contact with" the surface).
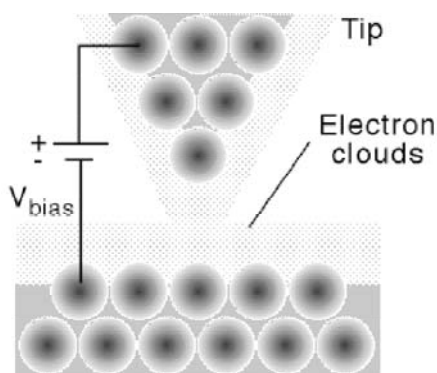

Fig. 1. The principle of the STM.

When an STM is operating, the tip is positioned a few Angstroms from the surface and a bias voltage applied to it (in other words, the tip is given a more positive potential than the surface). This difference in voltage between surface and tip encourages electrons to tunnel across the gap and into the tip. The probability of such tunnelling, like the electron density, decreases exponentially with tip-to-surface distance, so the current generated by the passage of electrons into the tip is a sensitive measure of the distance between the tip and the surface.

To a first approximation, a measurement of the electron density across a surface provided by such an experiment describes the topography of the surface. In reality, the situation is a little more complicated, since the tip is really measuring what is known as the Local Density of States (LDOS) on the surface. This may provide information about atoms below the surface if, as in the case of graphite, there are significant interactions between electronic orbitals on atoms in the surface layer and that immediately below.

Positioning the tip within a nanometer of the surface and moving it across a possibly irregular surface while maintaining the separation to a precision of 10^{-10} m is a tricky feat, and is accomplished using piezoelectric devices. The current to be measured is extremely small, of the order of 10^{-9} A, so sophisticated circuitry is required. Nevertheless, operation of the equipment is relatively straightforward. The greatest operational difficulty is usually preparing a tip which is cut down to the radius of a single atom at its end.

3   Experimental

The fundamentals of scanning tunneling microscopy are first explored by obtaining images of a holographic gold grating. The images obtained will be presented at three different magnifications along with cross section and histogram data. It will help in subsequent parts of the experiment if the histogram data is understood, as this facilitates finding a flat portion of the surface for imaging.

A HOPG surface is then cleaved and images collected at a range of resolutions. Stable tunneling current and fine tuning of the instrument and tip will allow the collection of atomic resolution images after image filtering. The carbon-carbon bond length in graphite can then be calculated.

Finally, an intercalation compound is prepared using 0.1 M NaOH. The resulting surface is imaged and a new 'super structure' can be observed after image filtering.

3.1 Preliminaries

3.1.1   Turn on the computer, monitor and the electronic control unit for the ISTM.

3.1.2   If Windows is not running (a *C>* prompt might be all that is displayed) type **win** and press the return key.

3.1.3   Once Windows is running, start the ISTM control program by double clicking on the Burleigh icon (large "b" above a smaller "STM"). If you cannot see the Burleigh icon, check for an icon labelled **ISTM**. Double click on this to reveal the Burleigh icon. The program is security-protected, and will only run if the "dongle" is fitted to the appropriate port on the back of the computer. If the program fails to start check that the dongle is in place, or ask a demonstrator for help.

3.2 Prepare the tip

You do not need to do this! (The tip is prepared by cutting a length of Platinum-Iridium alloy wire down to a point one or two atoms across. This operation is not trivial, so it will be done by the technician or Laboratory Officer. The tip already loaded in the microscope may be suitable, but if you need a new tip do not try to cut one yourself.)

3.3 Load the sample

The first sample to examine is the gold-coated holographic grating. This is a single period hologram with a sinusoidal spacing of 2400 lines mm^{-1}. A hologram of the type seen on credit cards is composed of many such sinusoidal patterns of varying periods and orientation, which recreate the image when one views the light scattered from the surface.

Select the gold grating from the sample set. To determine the direction of the grating lines look at the surface of the sample along one of its edges. Light is diffracted by the grating along a direction perpendicular to the grating lines.

3.3.1 You must first remove any sample present in the instrument. To do this you need to move the tip and sample well away from each other. First press the **Coarse Retract** button on the electronics unit to raise the tip from the surface of the sample. While pressing this button, listen to the sound of the stepper motor in the microscope head as it moves the tip; if the tip reaches the upper limit of its travel and comes up against an end stop (after a few seconds) there will be a slight change in the sound. Immediately release the button if this occurs.

3.3.2 Lower the sample stage by rotating the knurled wheel on the front of the microscope in the direction marked DOWN. When the stage has been lowered enough that you can easily withdraw the sample, carefully slide the sample holder out horizontally and place it on the bench. The holder may need to be tilted up slightly as you slide it out, but it is vital that the sample does not touch the end of the tip - even the slightest contact will destroy the tip. In case of difficulty, seek help!

3.3.3 Lift the stub to which the sample is bonded off the sample holder, holding the stub around its waist. Do not touch the surface of the sample.

3.3.4 Place a protective rubber boot over the sample once you have lifted it off the holder, being careful once more to avoid touching its surface with either your fingers or the boot.

3.3.5 Put the stub which holds the grating in place so that the grating lines are parallel to the sample carriage handle, and return it to the microscope stage, being careful to avoid any contact with the end of the tip.

3.4 Position the sample and tip

3.4.1.   Turn the sample position dial until the sample range indicator is close to the middle of the range or the sample-tip spacing is less than 0.75mm. Be careful not to let the tip touch the sample, since if it touches the sample, the sample will be damaged (at the molecular level) but the tip will be destroyed and you will need to wait for a new tip to be prepared.

3.5 Set the parameters

The steps required to start scanning are not very dependent upon the type of sample, although the conditions required to get a good image are. The following general instructions will apply both the the gold grating and to later samples, except where noted.

You need to set parameters both on the electronics unit and within the software.

3.5.1 Start by setting up the software: To scan a sample, you need to load an image file which has previously been stored on the computer. This will set default parameters for you. Choose **Load....** from the **File** menu, and select the file **test.img** which should be in the images sub-directory (double-click on the name of the directory to open it. If this file is missing, open a different one; in the next step you can adjust any parameters which are incorrect). This will load an old image which can be safely overwritten. You may look at the other images, but please do not overwrite them.

3.5.2 In the **Collect** menu choose **Configuration** and check that the parameters are set as follows:

Data points in X-direction: 256
Data points in Y-direction: 256
Max scanner range in X: 70000
Max scanner range in Y: 70000
Max scanner range in Z 15000
Scan range in X direction: 30000
Scan range in Y-direction: 30000
Bias voltage 1.00
Tunnelling current: 8.00
Scan delay 0.2 mS/sample
Scan magnification: 2
Continuous scan mode
In this scan you will monitor height variations so choose Topographic data type
Tilt removal: both options off

3.5.3   On the electronics unit, set the **Bias Voltage** to about 1 volt (press the **Bias Voltage** button to display the voltage, then turn the appropriate knob; the bias voltage can be set to a value between +10V and -10V). Set the **Reference Current** to 8nA, the **Gain** and

the **Filter** to their maximum values, the **Time Constant** to minimum, the **Magnification** to X1, and the **X** and **Y** offset sliders close to their central positions. Set the servo loop response for constant current mode of operation. Press the tunneling current button to monitor tunneling current (it should read about zero)

3.6   Move the tip into position

3.6.1 Press the **tunnelling current** button so that the digital display shows the tunnelling current (which should be close to zero).

Press the **Coarse retract** button momentarily to reset the motor controls. Press the **Auto Approach** tunneling button and wait ; you should just be able to hear the sound of the stepper motor moving the tip towards the sample surface. Monitor the tunneling current; it should remain at zero before suddenly rising to about 8 nA (equal to the reference current) as the tip reaches the surface.

[Note: While this is happening, watch the indicator to the upper left of the front face of the microscope. If you have positioned the sample correctly, the red line should not be able to get near the bottom. If it does, the sample was initially positioned too far away from the tip. When this is the case, there is a danger that the tip will wedge itself in the down position at the bottom of its travel and you will need to call for help to release it. In addition, the best results are obtained when the tip is in roughly the central position. If the red line moves significantly below the half-way mark, stop the movement by pressing and holding down the **Coarse Retract** button until the tip has returned to the top of its travel, raise the sample a bit using the knurled wheel and then use the **Auto Approach** button once again.]

Once a tunneling current is established, if the PZT voltage oscillates, reduce the gain and filter or increase the Time Constant to stop the oscillation.

3.7   Scanning

3.7.1 Once tunneling is achieved and the tunneling current is stable, start a unidirectional scan (Collect/Scan Unidirectional). Scan repeatedly until you are satisfied with the appearance of the scan. You may make small adjustments to try to improve the quality of the image. Once the tip has made about half a dozen passes across the surface (i.e. the figure on the screen has been redrawn about six times) you can start making changes. It is best to make a small change to one parameter, then wait for about half a scan to be gathered before judging what effect the change has made.

You may find it helpful to first change the **Reference Current** and **Voltage**, then the **Gain**, **Time Constant** and **Filter** to try to get the best possible image. Adjustment of these controls can be made while a scan is in progress. You can also make small changes using the X- and Y-sliders on the electronics units while a scan is in progress to move the area of scan. However, make such changes cautiously, or you run the risk of

dragging the end of the tip across an obstruction on the surface, which will immediately damage the tip beyond repair.

3.7.2 To save a scan, press **C** on the keyboard. The current scan will be completed, scanning will halt and the scan will be displayed. It can be saved (use **Save As...** in the **File** menu, choosing a new name for the image each time) and can be manipulated using the various options in the **Display, Filter** and **Analysis** menus.

3.7.3 To print an image, choose **Print Image** from the **File** menu. You may wish to use the options in the **Display** menu to change the colour of the display to enhance the appearance of the image.

Change the scanner range by turning the magnification dial. Set the software size correctly in the menu by setting the zoom factor (collect/configure). Collect an image at each setting and print it out.

The large scan range of the gold grating should reveal a sinusoidal surface with a period of 4000A and height variations of 400 - 500 Angstrom. As you zoom in, the details of the gold crystallization process on the surface should become apparent.

Perform a cross sectional analysis on the largest scan range image to look at the height variation across the grating and a histogram analysis to look at the distribution of heights on small sections of the sample. Print out examples of these analyses and discuss the significance of the data.

It is possible to calibrate the range of the PZT motion using the grating. How could this be achieved?

3.7.4 When you have finished with the sample, stop the scan by pressing **H** on the keyboard. Before touching the scanning unit, move the tip well away from the surface by pressing the **Coarse Retract** button. Watch the tip position indicator on the tip unit, and release the **Coarse Retract** button when the indicator is near the top. It is essential this is done when you have finished with a sample even if you are not immediately planning to study a further sample, since as soon as you turn off power to the unit, the tip is likely to crash into the surface if it has not been lifted away from it.

3.8 Atomic Resolution Images of Graphite

The image taken by STM reflects the density of the cloud of electrons around the atoms of the surface. It is the electron density of the highest energy electrons that is responsible for the tunneling. Because an atom on the top plane of the surface can interact with atoms below it, the energy of the electrons in the surface atoms will sometimes be affected by atoms in the body of the solid. This effect is shown in graphite: the highest energy electrons in the top plane will only be on the β atoms (see figure below). To the STM it is as if the α atoms have disappeared. Therefore, in an

ideal STM image one should see a triangular lattice of β atoms rather than the honeycomb lattice of all the surface atoms.

Select the HOPG (graphite) from the sample set and cleave the sample using sellotape as shown below. Just touch the sellotape lightly on the surface, otherwise when you remove it you will strip many layers from the graphite sample which is extremely expensive.
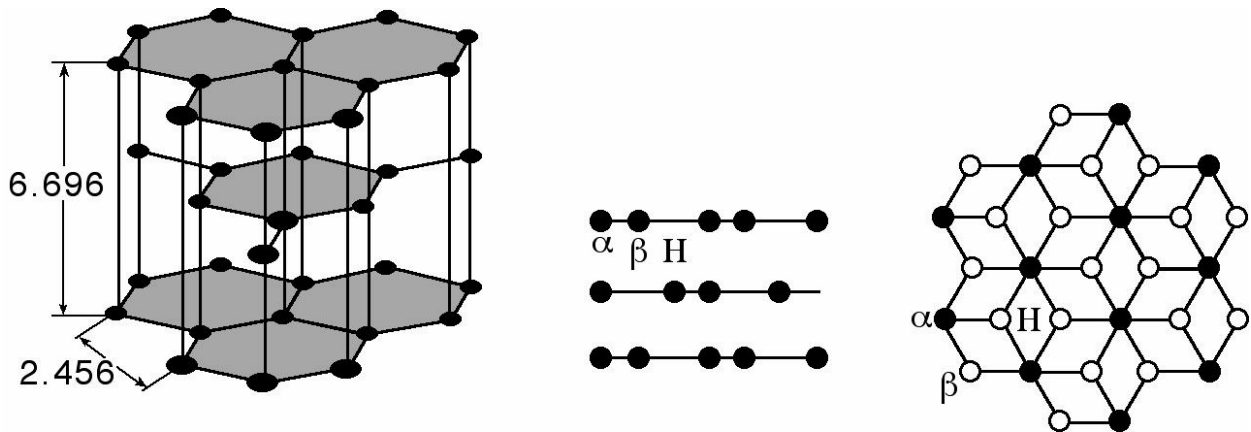

Mount the freshly-cleaved sample. Turn the sample position dial until the sample range indicator is close to the middle of the range and the sample to tip separation is less than 0.75 mm. Be careful not to let the sample and tip touch! Place an optically flat portion of the sample under the tip. You may have to adjust the tip position using the coarse approach or retract on the control electronics. Use the control electronics to make sure there is enough range for the tip to reach the sample.
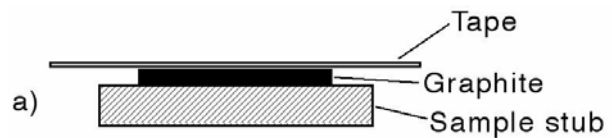
Set the Scan Delay (Collect/Configure) to 0.0 mS/Sample

In this scan you are measuring current variations at constant height, so set the data type to current (Collect/Configure)
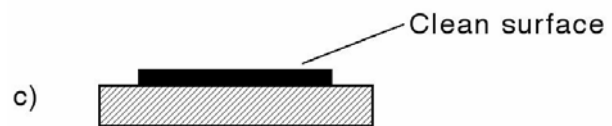
Set the Bias Voltage to about 20 mV and the Reference Current to 5 nA

For approach always set up the servo loop response for maximum rate of response. This corresponds to setting the Gain close to maximum, the Filter close maximum, and the time constant to minimum.

Set the magnification to X 250. Set the X and Y offset slides at their middle range.

Press the tunneling current button to monitor tunneling current (it should read about zero). Press the **coarse retract** button momentarily to reset the motor controls Press the **Auto Approach** (Tunneling) button for approach and wait.

Monitor the tunneling current until it reaches about 5nA (equal to the reference current).

Once tunneling is achieved, set the Servo Loop Response for constant height mode of operation. Turn the dials slowly to disrupt the tunneling current as little as possible. Set the gain close to minimum. Leave the filter at its maximum. Set the time constant to maximum.

When the tunneling current has settled down, (this may take up to five minutes as the tip needs some conditioning to remove contaminants) start a unidirectional scan (Collect/Scan Unidirectional). Scan over a few areas of the surface by using the X and Y sliders and use the histogram to find a relatively flat region. When using the X and Y sliders be careful not to move the sliders frequently or for large distances since this will distort the image.

Be patient and take scans when the tunneling current is stable or the images will be meaningless. Collect images and save one at this range. Do not be discouraged if the image is not very good. Performing a filter will in most cases improve the resolution of the image significantly.

Change the software and dial settings to acquire images with effective sizes of 1000 A x 1000 A, 500 A x 500 A and 40 A x 40A.

3.9 Image Processing With True-Image

For each image fitering is essential if you want to bring out higher detail and in the case of 40 A x 40A , atomic resolution.

Make sure you have saved your images in their original form. Perform a Wiener Filtration by selecting it from the filter menu. Begin with the maximum filter strength, you can repeat the procedure to 'tweak' filtering later. The Wiener filter performs an optimal Wiener smoothing filter on the raw data of the image. The strength of the filtering algorithm can be any integer between 1 and 200. The Wiener filter removes the I/frequency noise along the Y direction predominantly. This is particularly important in STM applications because the majority of uncorrelated noise lies along the Y direction of the scan.

Next perform a Fourier Transformation by selecting the FFT option from the filter menu. Choose the log method. This transforms the raw data of the image into a representation of the spatial frequencies present in the image data. The resultant is what is known as the power image of the data. The lowest frequencies present in the data are at the center of the FFT image; the frequencies represented are higher as the

image is traversed in both the X and Y directions from the center. Once an FFT has been executed, two other filtering operations become operational. These are the Low Pass and Band Stop filter commands.

Perform a Low Pass Filter on the FFT image. This filter allows you to stretch a rectangle symmetrically about the center of an FFT image. The bounds of this rectangle represent the cutoff points for the spatial frequency filtering in both the X and Y directions. The lowest frequencies are at the center of an FFT image; this filtering will retain all spatial frequencies within the bounding rectangle and will attenuate all spatial frequencies outside it.

Perform a Band Stop Filter, this allows you to place a box at the center of the image which will filter out the low frequency noise in the same way.

Now select Inverse FFT to transform the image back to a representation of discrete data values which will then show the results of all your hard work. If these procedures do not work, ask the technician to change tips. You should also cleave the surface again if repeated attempts do not bring out atomic detail.

Print out the images before and after filtration and calculate the separation of atoms in the lattice. Perform a cross sectional analysis and note the variations in surface topology which should be of the order of 1-2 A.

3.10 Graphite Intercalation Compound

(Your understanding of this will be very much improved if you read reference 7)

3.10.1 Sample Preparation

Prepare the sample by dropping 0.1 M NaOH onto a freshly cleaved HOPG surface. Leave the solution on the surface for about one minute. Gently blow off the remaining solution and dry using argon from the gas cylinder.

3.10.2 Obtaining Images

Repeat the procedure used above to obtain constant height (data type = current) images of the pure HOPG surface. In this case, however, investigate the surface at a bias voltage of -20 mV and a reference current of 2.0 nA.

3.10.3 Analysis

Filter your images as previously for graphite and print out examples before and after filtering. Perform a cross sectional analysis and compare this with the previous analysis for graphite alone.
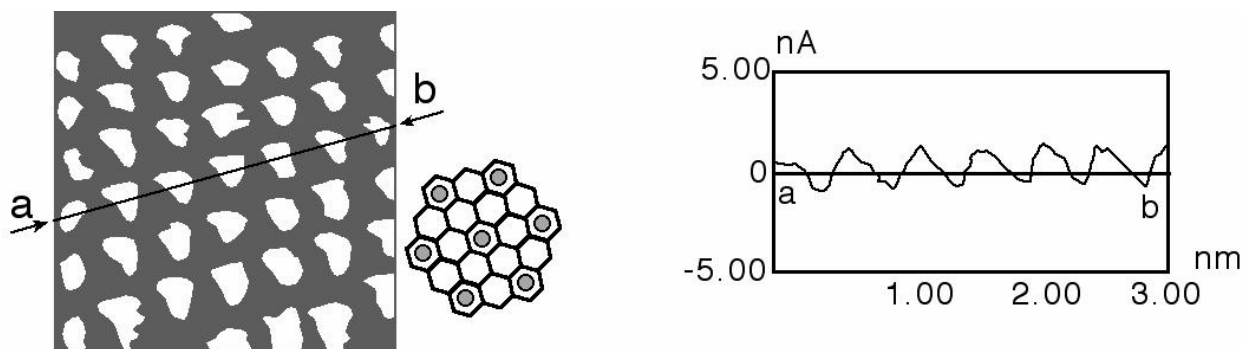
Note the distance between the protrusions and again compare these with HOPG alone.

Write an explanation of these results.

3.1   Writing Up

The results of the experiments should be presented for signing off fixed in your practical books with written explanations of the points indicated through the text. Images should be labeled, a bundle of printed images with no explanation or understanding is NOT acceptable.

4   Close down

IMPORTANT: Ensure that the tip is moved away from the sample, using the **Coarse Retract** button, before turning off the power.

Let the technician know that you have finished the experiment so that she can replace the graphite sample with the gold grating.

Exit from the Burleigh program. Turn off the computer monitor, but leave the computer itself running. Ensure the electronics control unit from the STM is off. Turn off the inkjet plotter at the mains.

5   References

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