Practical Exercises in Physical Chemistry
Advanced Level

Institute of Physical and Theoretical Chemistry, Freie Universität Berlin

19: Scanning Tunneling Microscopy (STM)

1 Introduction

The invention of the scanning tunneling microscope (STM) by Binnig and Rohrer in 1982 revolutionized surface science. Both were awarded with the Nobel Prize in Physics for their technical breakthrough which facilitates the visualization of the atomic structure of surfaces in real space. The nobel lecture can be found in [1]. Since its invention the STM has undergone constant further development. Today, STM studies are no more bound to ultrahigh vacuum conditions as in the early years. Tunneling microscopes have been developed that can be operated at atmospheric pressure to study, e.g., morphological changes at catalyst surfaces under reaction conditions or the atomic structure of electrodes in electrochemical environments. Some of the most impressive insights into have taken place in the field of fundamental surface physics. For example, it has been shown that electron waves (to be precise: the square of the wave function representing the probability density) can directly be imaged: an example is shown in fig. 1, where the waves of conduction electrons from Cu trapped in a circular potential well of adsorbed Fe atoms at a Cu(111) surface can be seen [2].

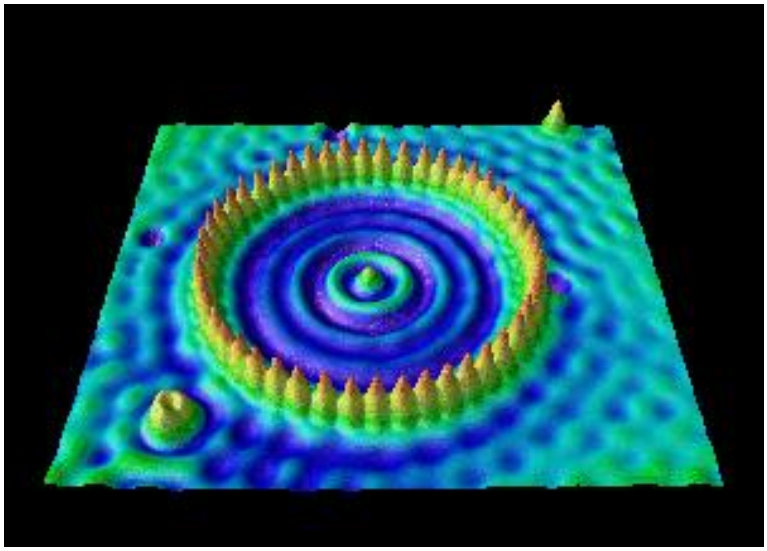

Figure 1: Standing electron waves observed in a circle of iron atoms

2 Theoretical Background

Before starting this experiment, you must be familiar with the following concepts:

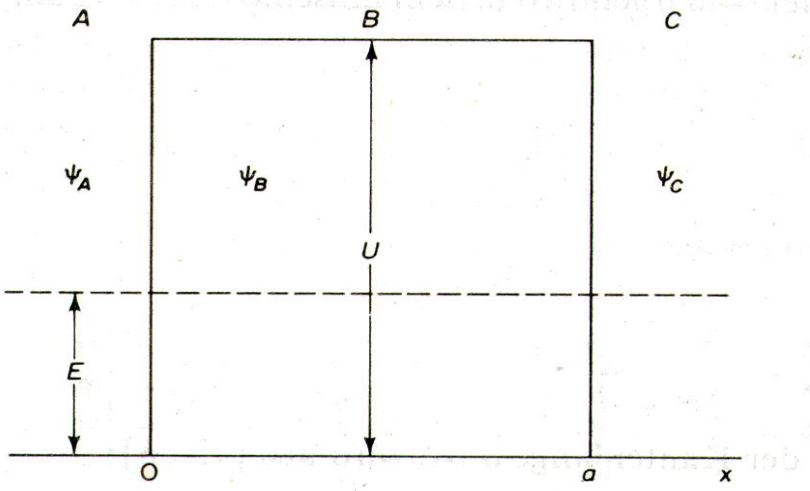

Figure 2: Further information concerning the tunneling of electrons

- The Schrödinger equation
- Tunneling phenomena
- The electronic structure of metals (density of states, Fermi level)
- Work function
- Physical properties and crystal structure of graphite
- Piezo-driven actuators

Note that the following section is intended as introductory reading only. To carry out the experiment you must read the literature listed at the end of this document.

The principle of the STM is based on the *tunneling* of electrons through a potential barrier. Quantum mechanics predicts that there is a certain probability for particles to pass through a potential barrier even if their kinetic energy E_{kin} is lower than the barrier height V_0. It is said that some particles *tunnel* through the barrier. Not only electrons have the ability to undergo tunnelling: another well-known example is the emission of α-radiation from radioactive nuclei.

Qualitatively, the tunneling of electrons from the surface to the scanning probe tip is based on the application of the one-dimensional stationary *Schrödinger equation* for an electron with a total energy E_{tot} which shall be assumed to be lower than the height a potential barrier V_0 (see fig. 2). It can be shown [3] that the wave functions in the regions labelled A, B and C satisfy the expressions

$$\psi_A(x) = A \cdot e^{ik_1 x} + B \cdot e^{-ik_1 x} \quad (1)$$

$$\psi_B(x) = C \cdot e^{k_2 x} + D \cdot e^{-k_2 x} \quad (2)$$

$$\psi_C(x) = E \cdot e^{ik_1 x} + F \cdot e^{-ik_1 x} \quad (3)$$

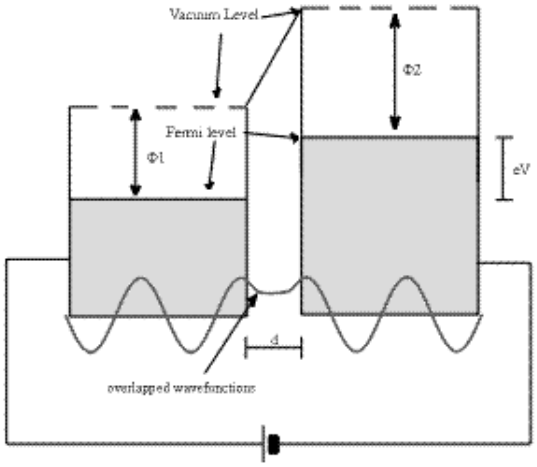

Figure 3: Tunneling of Electrons

with $k = \frac{1}{\hbar}\sqrt{2mE}$ and $l = \frac{1}{\hbar}\sqrt{2m(V_0 - E)}$. The constants A to F are determined by the boundary conditions that the wavefunction and its first derivative must be **continuous** at $x = 0$ and $x = d$. ψ_A(x) and ψ_C(x) represent the oscillatory solutions of the free electron($e^{ikx} = cos(kx) + isin(kx)$) while the solution in the classically forbidden region (ψ_B(x)) consists of an (exponentially) increasing and decreasing component. The **transmission coefficient T** giving the probability that the potential barrier is penetrated is then given by

$$T = \frac{|F|^2}{|A|^2} \simeq e^{-\frac{2d}{\hbar}\sqrt{2m(V_0 - E)}} \tag{4}$$

Assuming that the applied voltage between the STM tip and the sample is small, i.e.,

- $eU_T \ll V_0 = \phi$ and
- D(E) (the density of states)
  being constant in the range from E_f to E_f-eU_T

,

the tunneling current I_T can be approximated by

$$I_T \sim U_T \cdot e^{-\frac{2d}{\hbar}\sqrt{2m\phi}} \tag{5}$$

with d being the distance between tip and sample and ϕ being the "effective work function" $\phi = \frac{1}{2}(\phi_1 + \phi_2)$.

Fig. 3 shows a schematic energy diagram for the tunneling of electrons between two metals.

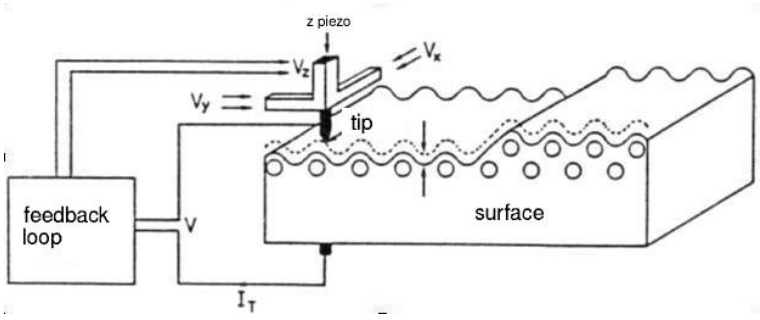

Figure 4: General setup of an STM

3 Experimental

3.1 Scope of the experiment

In this experiment, you will

- prepare a clean highly oriented pyrolytic graphite (HOPG) surface
- take images of this surface (from panoramic scans down to atomic scale scans)
- measure the tunneling current I as a function of the distance z from the HOPG surface (I/z scans)

3.2 Experimental Setup

The most crucial part of the STM is its metal tip, which is usually made from tungsten or platinum/iridium alloy wires. The sample is mounted opposite this tip on a sample holder that can be driven in x-,y- and z-direction by means of piezo-motors. A feedback loop monitors the tunneling current continuously, allowing controlled movement of the surface relative to the tip with an accuracy of a few Å(see fig. 4).

Most STMs can be operated in *scanning modes* (see fig. 5):

- Constant Current Mode
  The tip is moved across the surface while a constant tunneling current is maintained by the feedback loop. The voltage U_z applied to the piezo-driven z-actuator to keep constant current depends on the electronic properties of the sample surface at the position of the tip. As the electronic structure of the surface is correlated with its atomic structure, an image of the sample surface s obtained by plotting maps of U_z as a function of the x- and y-coordinates.
- Constant Distance Mode
  In this mode, U_z is kept at a constant value, i.e., the tip is moved at a constant z-position. The distance between tip and sample surface thus varies as the tip is moved over the

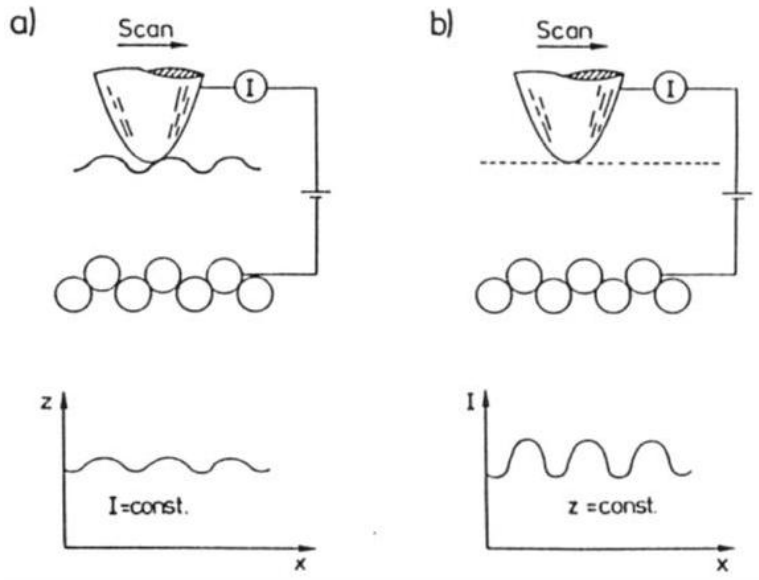

Figure 5: The different scanning modes applied in STM

sample. The tunneling current is a function of the distance between tip and sample so that it can be used to show the structures. Note that this method can only be applied for samples flat at an atomic scale, as otherwise there is a high risk of crashing the tip into corrugations at the sample surface. A major advantage of this mode is its higher scan rate, which can help to reduce the effect of thermal drift on the measurement.

3.3 Instructions for the Experiment

3.3.1 Preparation of the Sample

This step should usually not be necessary. **Contact your supervisor to clarify this point.**

To prepare a clean surface you have to remove the top layers of the graphite. Attach some sticky tape to the surface and carefully remove it. You should see a thin layer of graphite on the tape.

3.3.2 Insertion of the Sample

Use the gloves provided when handling the sample holder. If you accidentally touch it without gloves, clean it with some ethanol as it is very sensitive to contamination.
Put the sample on the magnetic sample holder. Insert the sample holder in the STM (see fig. 6). **Be careful, don't touch the tip**!.

Place the sampleholder very careful on the piezo motor (first put it onto the little rails, then slide it onto the motor itself). The sample must not crash on the motor device because otherwise it will be damaged. Note especially that there is a magnet below the piezo motor!

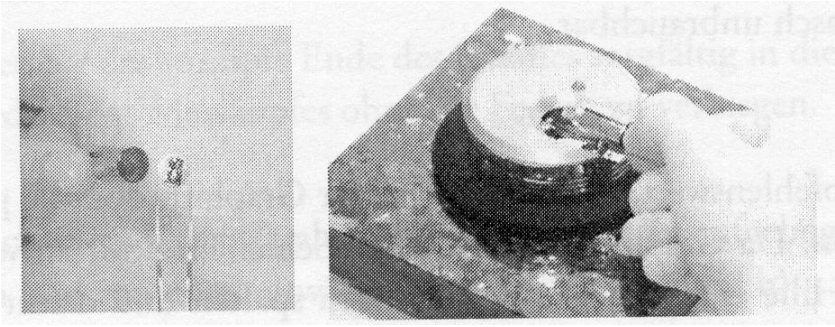

Figure 6: Mounting the sample on the magnetic sample holder (left) and insertion of the sample holder in the STM (right)

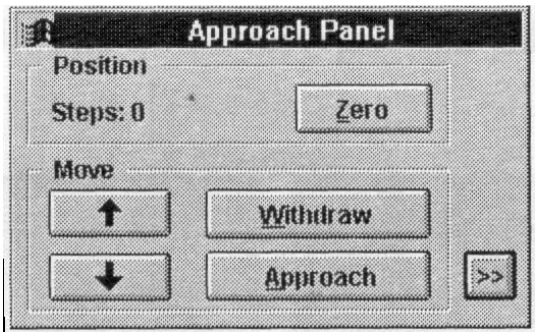

Figure 7: The approach panel provided by the EASYSCAN software

Avoid any mechanical force! Do not touch either sample or tip.

3.3.3 Approaching the Tip

This part of the experiment is done in three steps:

manual approach Carefully move the sample towards the tip while using the lenses provided to monitor its movement. Adjust the position of the sample so that a good quality part of the surface is in front of the tip. The distance between tip and sample should be approximately 1 mm.

coarse approach using the piezo motor Put the lid onto the STM. Use the lens inside the tip and the arrow button in the approach panel to move the sample towards the tip (see fig 7).

Use the mirror image of the tip on the sample surface to adjust the position of the sample. **Take time. Do not move the sample too close! If the tip crashes into the sample, a new tip has to be prepared.** The LED on the STM provides information on the status of the approach:

- orange means that the sample is too far away from the tip to detect a tunneling current

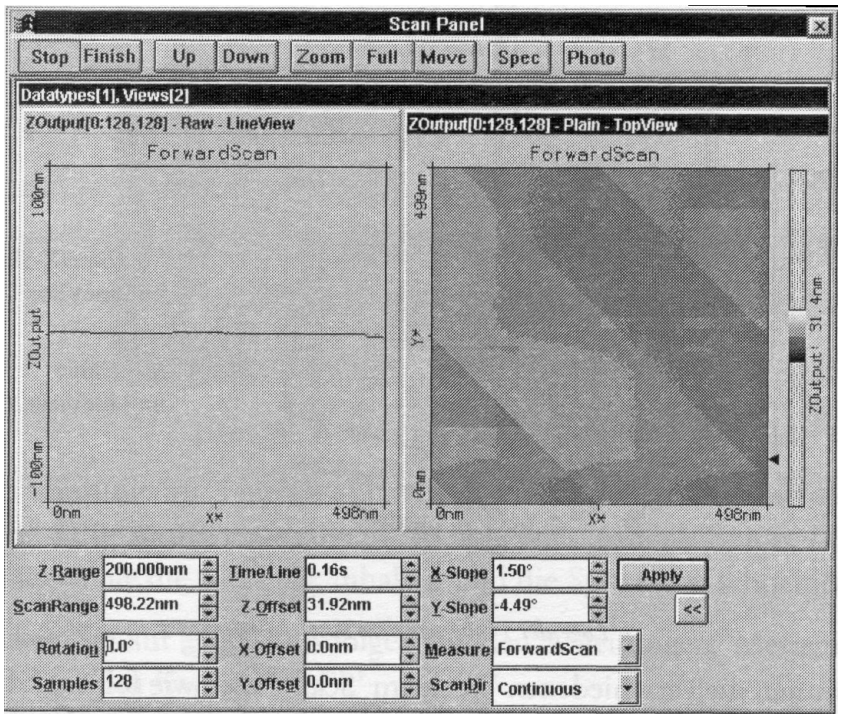

Figure 8: The scan panel of the EASYSCAN software

- green means that the sample is well-positioned, a tunneling current is detected. This colour only appears after step 3, fine approach using the piezo motor
- red means that you have crashed the sample into the tip (you need to call the experimental supervisor).

fine approach using the piezo motor Push the **Approach** button in the approach panel. The sample now approaches the tip continuously in small steps until a tunneling current is detected by the feedback loop. This step will take some time. It depends on how well the pre-adjustment using the coarse approach was performed. Do not be impatient! If the approach is successful, a dialogbox **Approach done** appears and the LED turns green.

3.3.4 Imaging the Surface

Fig. 8 shows a screenshot of EASYSCAN'S scan panel.

Make sure that the **Line Math** is "raw". Apply the **Full** and the **Start** buttons in the scan panel. You should see the measured line scans in the left part of the display. Adjust the **Rotation** to 0 deg. If the measurement line looks noisy call the assistant (see fig. 9).

If the line scans appear to be of reproducibly good quality, you can adjust the slope of the line with the **x-slope** parameter. If the line is flat, adjust the **Rotation** to 90 deg and follow the above steps (see fig. 10.

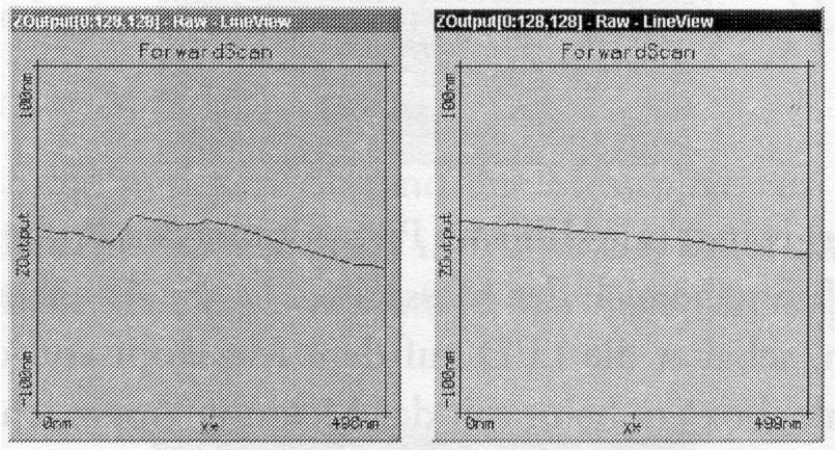

Figure 9: Good and noisy measurement lines

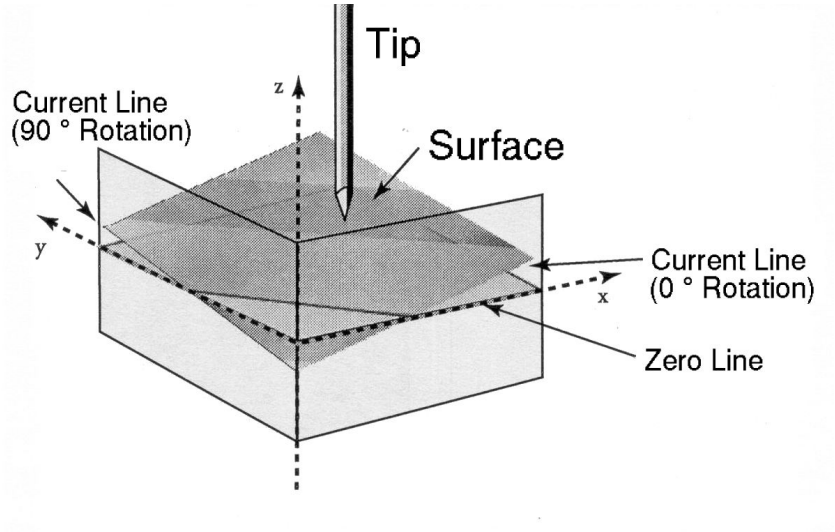

Figure 10: Adjusting the correct x and y slopes

Then turn back to a rotation of 0 deg. Adjust the view scale and the **z-range** so that you get a good image of the surface. Test the influence of the different parameters (time/line, points/line, etc.). When adjusting the z-range, make sure that the line scans do not rise into the upper third of the available range. If they do you must apply a larger value for the z. Once you get a good image, take a snapshot by means of the **Photo** button.
Once you have a good image of the surface, use the **Zoom** function to decrease the area you are looking at. Aim to choose an area that appears completely flat in the line scans. Take images at approximately 100 nm x 100 nm, 50 nm x 50 nm, 25 nm x 25 nm, 5 nm x 5 nm and 2.5 nm x 2.5 nm scan size. While zooming in, carefully decrease the **z-range**. Take snapshots of good images. When decreasing the scan range, look at the slope of the individual line scans. Sometimes, they have to be re-adjusted (remember the 90 deg rotation).

3.3.5 Some Hints for Obtaining Good Images at Atomic Scale

It is quite easy to get surface scans with large scan ranges. However, achieving atomic scale is more demanding. Here are some hints that should help you:

- It is essential to apply short scanning times to minimize thermal drift effects (set time/line to a minimum value).
- The **Rotation** parameter needs to be optimized. Take some images at different values and use the one with the best resolution.
- Bright light and movement near the STM setup interfere with the measurement. Avoid abrupt movements and walking around in the room.
- If a measurement looks good, wait a few minutes to obtain stable images.

3.3.6 Using the Spectroscopy Panel

Fig. 11 shows you the functions available here.

Once you achieved atomic resolution, apply the **Spec** button. The actual image is transferred to the spectroscopy panel. Use the **Point** button to position the tip above a carbon atom. Check the **rel** checkbox and select **Z-Axis** from the **Output** menu. Carefully increase the range of the scan by adjusting the **from** and **to** values. As you do not know the exact distance to the surface, you have to approach an x value where the current limitation prevents a further increase of the tunneling current. Save three I/z-Curves for further interpretation.

3.3.7 End of the Measurement

Once you have completed all of the above steps, use the **withdraw** button (apply it about three times) and the arrow button beside it to move the sample away from the surface. Put the sample in the sample box **(gloves)** and the sample holder in its case. Finally, close the lid.

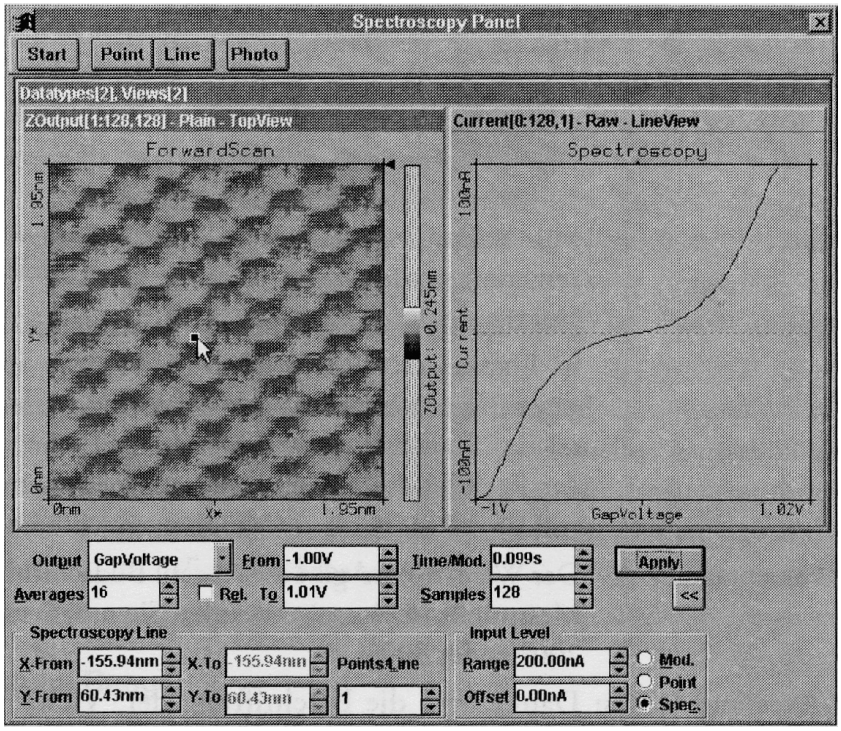

Figure 11: The spectroscopy panel of the EASYSCAN software

4 Data Evaluation

After the experiment you should have saved different images of the graphite surface and at least three I/z curves. For evaluating purposes, the STM software has been installed in the microcomputer room. The software provides you with tools to determine distances, angles, etc. Describe and print every image you have taken during the experiment. If you describe macroscopic features (steps, islands), calculate their size and height and discuss the results. On the atomic scale, locate the positions of the carbon atoms and measure all important distances and angles in the unit cell. Discuss your results.

For evaluating the I/z curves you have to export them as “Plotfile ASCII”. These files can be further processed with any program which is capable of linear regression (XMGR, EXCEL, GNUPLOT, ORIGIN). Calculate logarithmic plots of ln(I) vs. z and determine the slopes of these curves. Compare these slopes with values calculated by means of eqn. 5. Use work functions of 5.65 eV and 5.0 eV for platinum and graphite, respectively.

For printing your results, it is suggested that you use the laserprinters at the ZEDAT which are accessible from the MC room.

5 Some Words concerning the Report

Briefly describe how the STM works (physical principles and setup). Describe the advantages, disadvantages and applications of this instrument. Describe the experimental setup used for your own experiments and what you have done. Describe your images and the I/z-curves. The

Discussion of the results should be at least 25 % of the total length of your report.

References

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