

Related Topics

Tunneling effect, Hexagonal Structures, Scanning Tunneling Microscopy (STM), Imaging on the subnanometer scale, Piezo-electric devices, Local Density of States (LDOS), Constant-Height and Constant-Current-Mode

Principle

Approaching a very sharp metal tip to an electrically conductive sample by applying an electrical field leads to a current between tip and sample without any mechanical contact. This so-called tunneling current is used to investigate the electronic topography on the sub nanometer scale of a fresh prepared graphite (HOPG) surface. By scanning the tip line-by-line across the surface, graphite atoms and the hexagonal structure are imaged.

Caution!

- Set up your system on a very steady table
- Do your experiments in a calm, vibrational free environment

Equipment

- | | |
|---|----------|
| 1 Compact-Scanning Tunneling Microscope, complete set incl. tools, sample kit and consumables, in aluminum case | 09600.99 |
| 1 Graphite model, 2D | 09620.00 |
| 1 Crystal lattice kit: graphite | 39840.00 |

Additionally needed

- 1 PC, Windows® XP or higher
- Adhesive tape

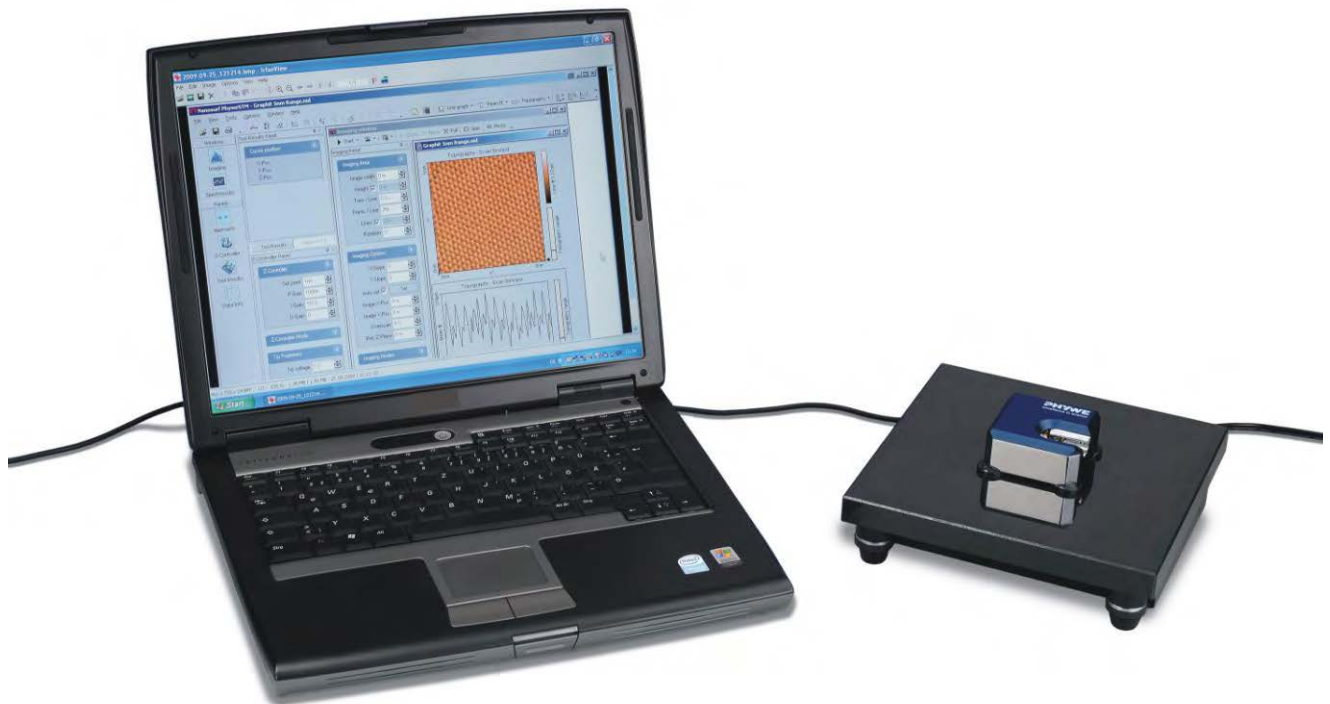


Fig. 1: Experimental setup.

PHYWE Compact-STM set

- | | |
|--|-----|
| 1 Control unit with mounted scan head | (1) |
| 1 Magnifying cover glass (10X Magnification) | (2) |
| 1 USB cable | (3) |
| 1 Power cord and adapter | (4) |
| 1 MeasureNano Software | (5) |

PHYWE STM Tool Box

- | | |
|--|------|
| 1 Wire cutter | (6) |
| 1 Flat nose pliers | (7) |
| 1 Pointed tweezers | (8) |
| 1 Rounded tweezers | (9) |
| 1 Pt/Ir-wire, $d = 0.25\text{mm}$, $l = 30\text{ cm}$ | (10) |
| 1 Sample Holder | (11) |
| 1 Graphite sample (HOPG) | (12) |
| 1 Gold sample | (13) |
| 4 Spare sample support | (14) |



Fig. 2: STM set.

User Manual

- | | |
|---|------|
| 1 Scanning Tunneling Microscopy (STM) – Operating Instruction and Experiments | (15) |
|---|------|

Tasks

1. Prepare a Pt-Ir tip and the graphite (HOPG) sample and approach the tip to the sample.
2. Investigate the topography of clean terraces and the step height between neighboring terraces in constant-current mode.
3. Image the arrangement of graphite atoms on a clean terrace by optimize tunneling and scanning parameters. Interpret the structure by analyzing angles and distances between atoms and atomic rows and by using the 2D and 3D graphite model.
4. Measure and compare images in the constant-height and constant-current mode.

Set-up and Procedure

To prepare a fresh tip for STM measurements follow the steps mentioned here or have a look in the Quick-Start-Guide or chapter 5 of the PHYWE STM user manual respectively. Make sure you have already set up your microscope on a very steady table in a quiet environment with a low level of building vibrations (e.g. basement). Your microscope should be set up on a separate table than your PC or laptop. Keep some free space on the table to prepare the sample and the measurement tips. Have a look in the STM user manual, make sure the software starts cleanly and that you have set appropriate parameters to do measurements on the graphite HOPG sample (Chapter: 5.3.3. in the user manual / e.g. Set point=1 nA, Tip voltage=50 mV).

Start the tip and sample preparation by taking the necessary tools out of the toolbox. You will need parts 6 to 12 from the list mentioned above and some adhesive tape (scotch tape, not included).

Tip preparation

- Use the pointed tweezers to carefully remove the old tip from the tip holder.
- Hold the end of the wire tightly with the pliers.
- Holding the wire with the pliers, move the cutters at a length of approximately 4 mm, as obliquely

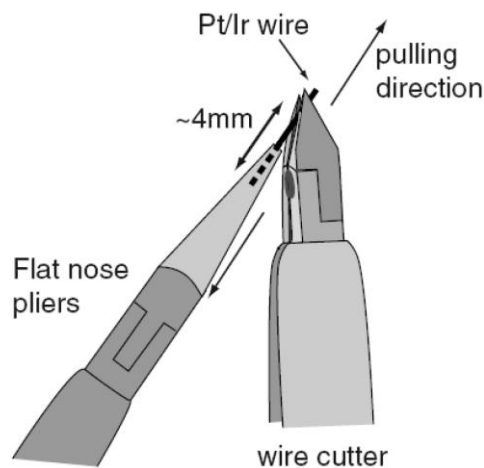


Fig. 3: Sketch of the tip preparation.

as possible (in a very sharp angle).

- Close the cutters until you can feel the wire, but do not cut the wire.
- In order to obtain the required sharpness, the tip needs to be torn off by pulling the wire cutter quickly away from you, rather than cutting cleanly through the wire.
- Use the pointed tweezers to hold the tip wire right behind the tip.
- Release the flat pliers.
- Transfer the tip to the microscope.

Tip mounting

- Put the tip wire underneath the clamp on the tip holder (A), parallel to the groove and push it all the way to the end.
- Move the tip wire sideways until it is in the groove and held securely under the clamp (B). It should stick out about 1–2 mm beyond the tip holder. See also Fig. 5 for step-by-step pictures.

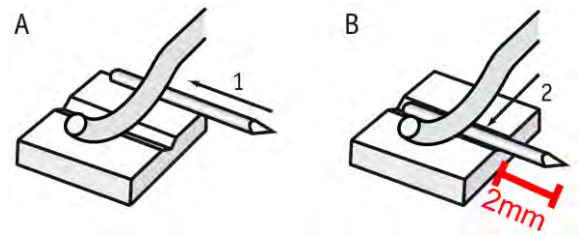


Fig. 4: Sketch of the tip mounting.

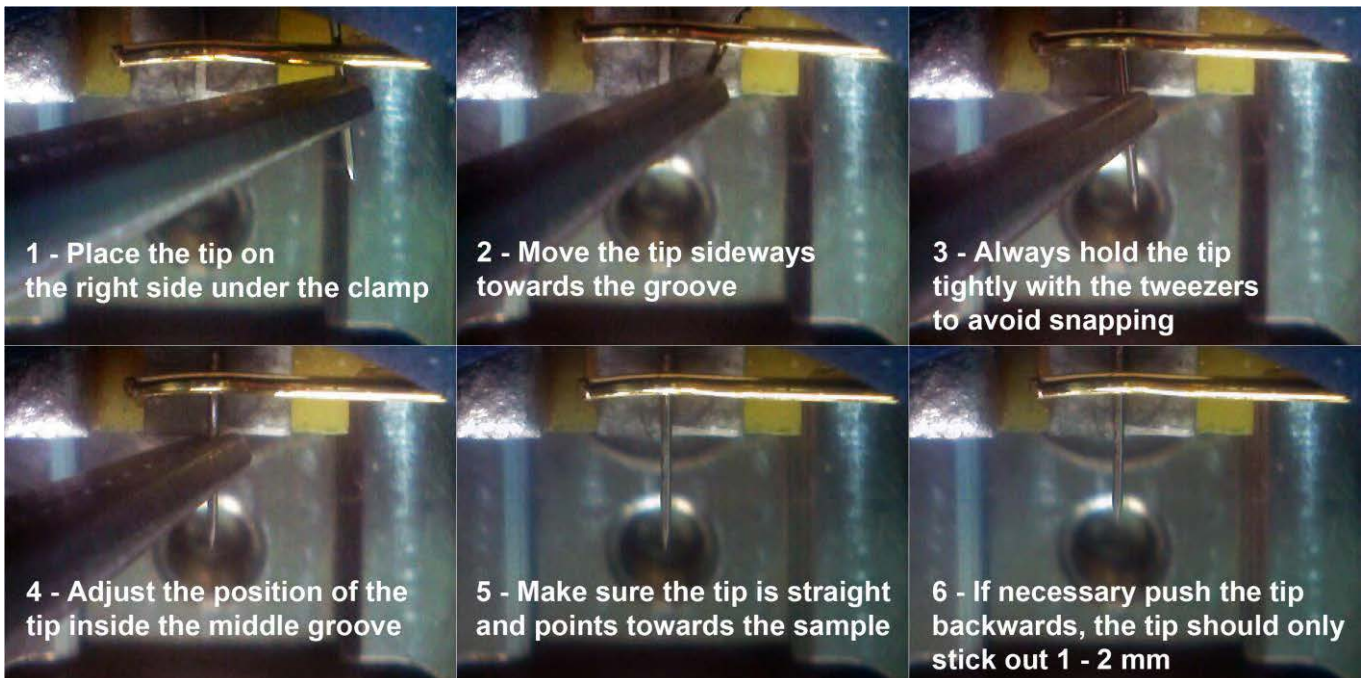


Fig. 5: Step by step pictures of the tip mounting.

Now that you have prepared a new a tip and mounted it in the tip holder's groove proceed with preparing the sample surface.

Sample preparation

In most cases it is enough to cleave the graphite sample once in a while. If you have problems to find a clean area or you don't get good images with several freshly prepared tips, clean the sample surface as described below. Highly oriented pyrolytic graphite (HOPG) consists of weakly bonded (van der Waals bonding) layers.

Due to this layered structure of graphite, it can easily be cleaved using a piece of adhesive tape:

- Put the sample on the table using a pair of tweezers.
- Stick a piece of adhesive tape to the graphite surface and apply very little pressure with your thumb or the end of the tweezers.
- Use the tweezers to go under the adhesive tape and press the sample down to the table.

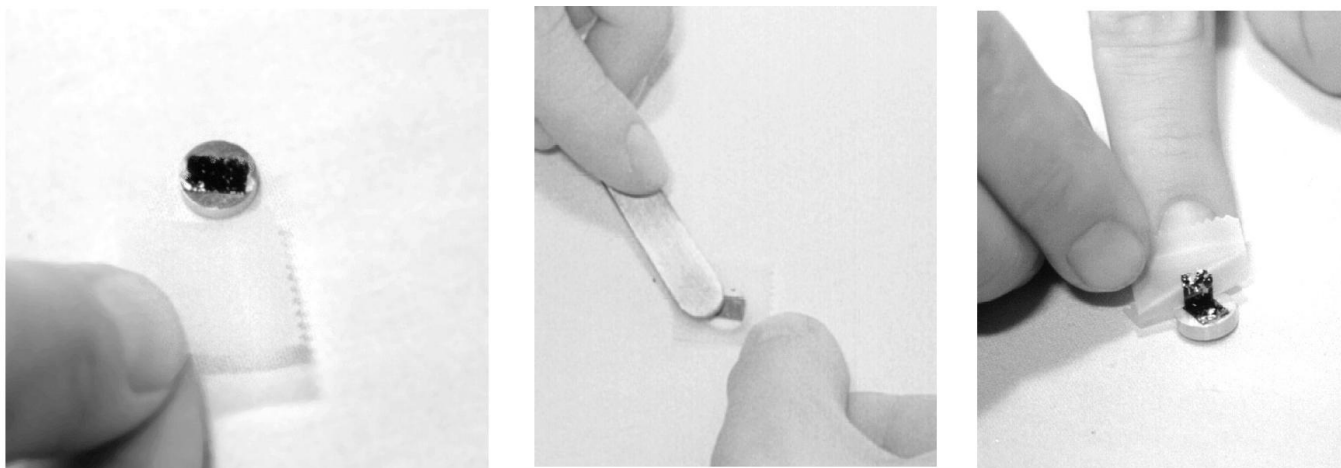


Fig. 6: Step by step pictures of the HOPG sample surface preparation.

- Pull off the adhesive tape gently. The topmost layer of the sample should stick to the tape. If you are not satisfied with the cleaving (e.g. the surface looks uneven or there are too many flakes remaining), start from the beginning. The middle of the sample surface should be very flat and mirror-like. Any loose flakes in the outer regions of the sample can be removed with the tweezers. The graphite sample is now ready to use and should not be touched anymore. Now that you have prepared the sample you need to mount it onto the sample holder.

Mounting the sample and the sample holder

- Unpack the Sample Holder touching only its black plastic handle.
- Use the tweezers to push the sample to the edge of the supporting magnet in the sample package.
- Grab the sample with the tweezers (as shown in Fig. 7) and place it on the magnet of the sample holder.
- Put the sample holder down on to the sample holder guide bars first Fig.8 (a) and release it gently on to the approach motor's support (Be careful: the magnet that holds the sample holder in its place can drag the sample off the sample holder, make sure you bring the sample behind it).

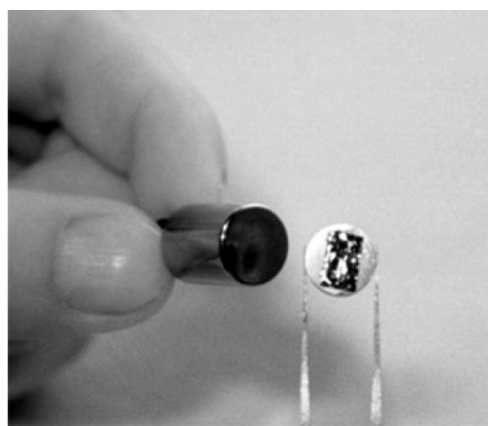


Fig. 7: Place the sample in the middle of the sample holder.

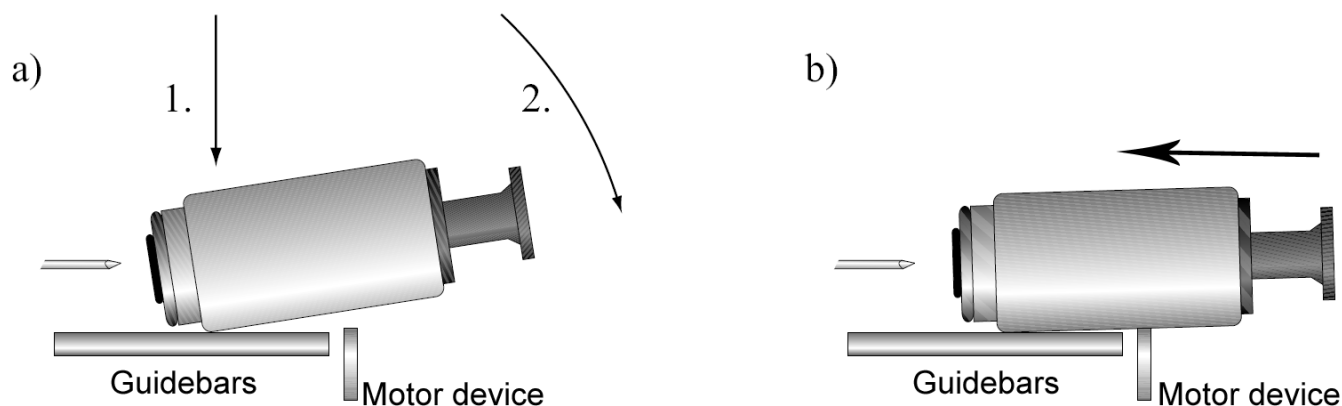


Fig. 8: Sketch of the manual approach of the sample to the tip.

- Push the sample holder carefully in the direction of the tip (b), but don't let it touch the tip (1 cm distance). See also the step-by-step pictures in Fig. 9.

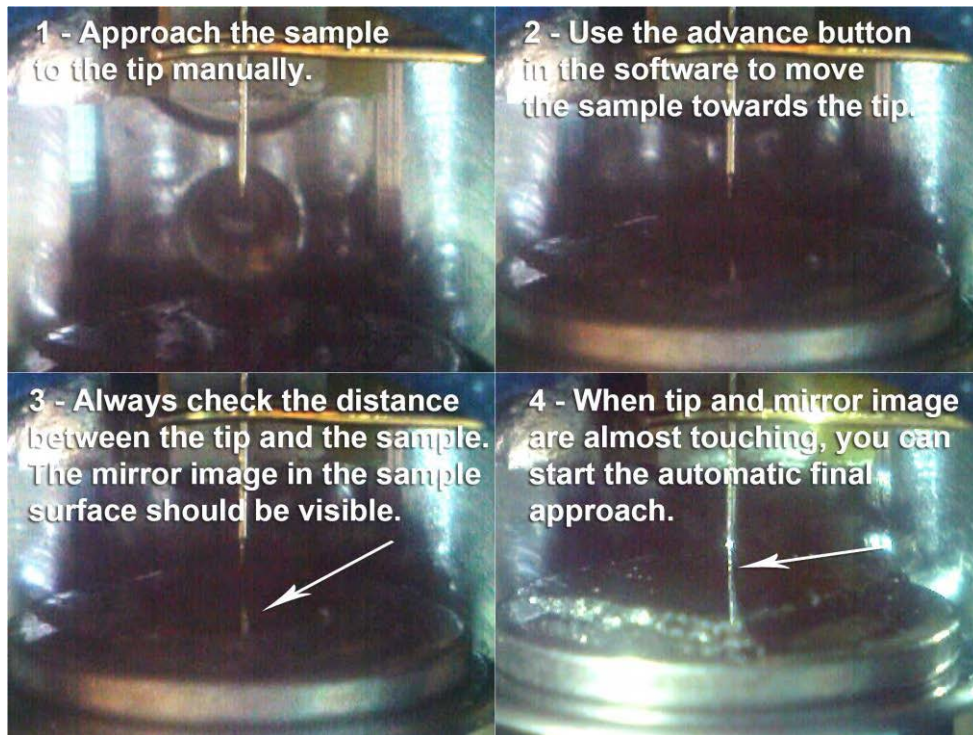


Fig. 9: Step by step pictures of the software supported approaching of the sample to the tip.

Now that you have approached the sample manually, use the approach panel in the measurement software to drive the sample towards the tip ("Advance" button). To determine the distance between the tip and the sample, adjust the lighting conditions in a way you can see the mirror image of the tip in the sample surface. During this procedure you should also check the probe status light in the software. The status light has to be orange. If the probe status switches to red you crashed the sample into the tip. You can try to use the "Withdraw" button to drive the sample a small step backwards and start with the final approach, but it is likely that you have to start again with the preparation of a new tip. When the tip and its mirror image are about to touch you can proceed with the automatic final approach (press the "Approach" button). The automatic approach can take several minutes, please be patient as the duration depends on the gap you left over from the manual approach.

After the successful approach the probe status light will switch to green. Then the software will do a slope correction and starts measuring right away.

Theory and Evaluation

Tunneling

Tunneling is a functioning concept that arises from quantum mechanics. Classically, an object hitting an impenetrable barrier will not pass through. In contrast, objects with a very small mass, such as the electron, have wavelike characteristics which permit such an event, referred to as tunneling. In other words, the probability to find an electron behind a barrier is unequal zero. Inside the barrier the wave function of the electron decays exponentially.

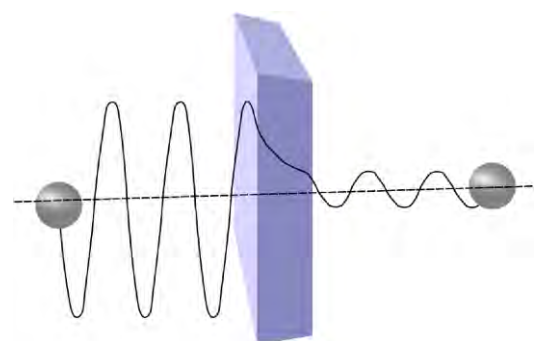


Fig. 10: Sketch of the tunneling of an electron through a barrier.



STM – Scanning Tunneling Microscopy

The size of an atom in relation to the tip is that of a golf ball to a mountain. In your PHYWE measurement system a platinum-iridium tip is moved in three dimensions using piezo crystal translators that are driven with sub-nanometer precision (Fig. 11). The sample to be examined approaches the tip within a distance of about 1 nanometer ($1 \text{ nm} = 1/1,000,000,000 \text{ m}$). Classical physics would prohibit the appearance of electrons in the small gap between the tip and the sample, but if a sharp tip and a conducting surface are put under a low voltage ($U \sim 0.1 \text{ V}$), a very small tunneling current ($I \sim 1 \text{ nA}$ with 1 nm tip sample distance) though may flow between tip and sample. The resulting tunneling current is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample, this information is displayed on the computer monitor as 2D color mapped image. The strength of the tunneling current depends exponentially on the distance between the tip and the sample (d_z), usually referred to as z-distance, the applied bias (U) and constant factors (c_1 and c_2)

$$I \propto c_1 \cdot U \cdot \exp(-c_2 \cdot d_z) \quad [1]$$

This extreme dependence on the distance makes it possible to measure the tip–sample movement very precisely. One of the three piezo crystals, the z-piezo, can now be used in a feedback loop that keeps the tunneling current constant by appropriately changing the z-distance. The elongation of a piezo crystal is proportional to a device specific constant which is a temperature dependent parameter and the applied voltage (Elongation = piezo constant · Voltage, e.g. $\Delta l = 500 \text{ pm/V} \cdot 10 \text{ V} = 5 \text{ nm}$). Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create uncertainty and errors in the expected values of your measurements.

Finding atomic terraces on the sample surface

To activate the full measurement-range of your device click the  Full button in the imaging window. For good results you can use image sizes of about $0.2 \mu\text{m}$. When you are lucky you find a terrace in your first measurement. If that is not the case you can either use the  Move tool in the imaging window to start the measurement at a different spot on the surface or you retract the sample from the tip and turn carefully the sample holder with the black plastic handle. Afterwards you approach the sample again.

In Fig.12 you can find examples of terrace like structures at different spots on the sample surface. Make sure you adjust the parameters of the feedback loop to achieve good image quality. You may switch to the standard or advanced level of the software user interface (“Options” → “Config User Interface”) to obtain the possibility to adjust the P-

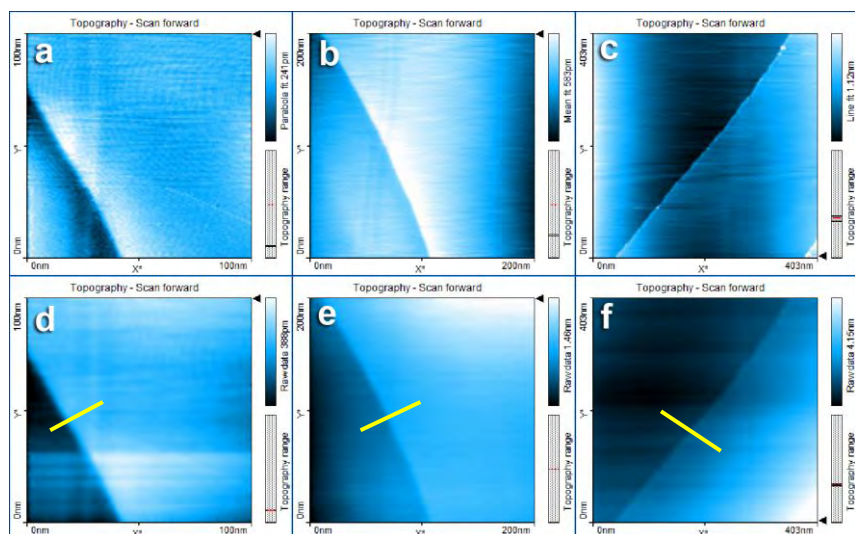


Fig. 12: Original images of different atomic terraces (a, b, c) and their processed images (d, e, f). Yellow bars indicating the place of the cross sectioning (see below). (Time/Line: 0.2 s, Set point: 1.2 nA, P-gain: 1000, I-gain: 1200).

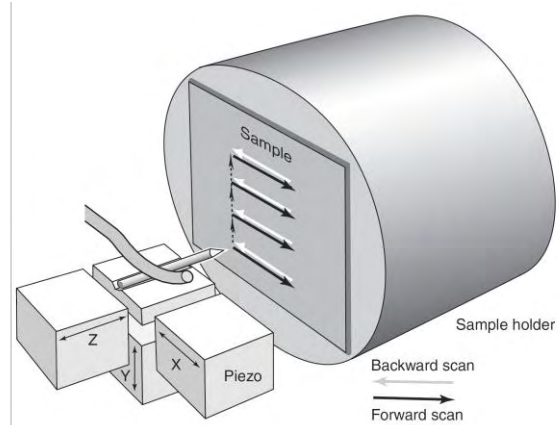



Fig. 11: Sketch of the piezo electric device driving the tip movement.

and the I-gain individually. Too high values in the P- and I-gain will be noticeable in the line graph as very high peaks and a very rough line structure. Adjust the gain values to smooth the line graph and your image respectively. When you are satisfied grab a good image by clicking the  **Photo** button. Now you can apply some filters to reduce noise, adjust scan line levels and remove a background distortion.


The recommended procedure would be:

- Apply glitch filter.
- Apply noise filter.
- Do a background subtraction and/or correct scan line levels.

If you are not sure that the corrected image is the better one, go a step backwards and start over again. Your corrected image should be almost free of strong gradients, one plane of the sample surface should have the same color in every point.

Estimating the step height of terraces

Then you can start to analyze your data. At first use the "Create Cross section" tool. Place a line on the image you want to analyze. If you want to estimate the step height of terraces you should make sure the line is perpendicular to the edge of the terrace. Click "Cut out line". This will create a new graph image with the z-information corresponding to the cross sectioning line you have drawn (Fig. 13). Avoid creating cross sections from spots with scan or correcting artifacts (strange gradients or other jumps in the coloring of the surface).

Now you can use the  „Measure Distance“ tool. It allows you to draw two straight lines between which the distance is measured. The advantage of using the line measurement instead of a point measurement is, that it is possible to reduce the influence of the surface roughness or noisy data by placing the lines between the lowest and the highest values of each terrace.

When you do measurements keep in mind that you always have errors influencing your results. Errors arise from the scanning itself (temperature dependence of the piezo electric device) but even more due to a bad z-leveling or background correction. Your results should not exceed a relative error of about 5% to literature values (the lower the better). When you have completed some measurements it is recommended to calculate the mean value of your data for each proposed step size.

Add up every value (v_j) and divide the sum by the number of values you added up.

$$\bar{m} = \frac{1}{N} \sum_{j=1}^N v_j \quad [2]$$

The standard deviation is another calculation which tells you the accuracy of your measurement.

$$s = \frac{1}{N-1} \sum_{j=1}^N \left(v_j - \bar{m} \right)^2 \quad [3]$$

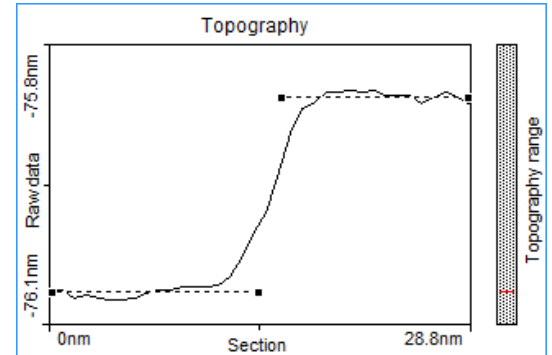


Fig. 13: Cross section of image d (see above). Distance: $\Delta z=332.2$ pm.

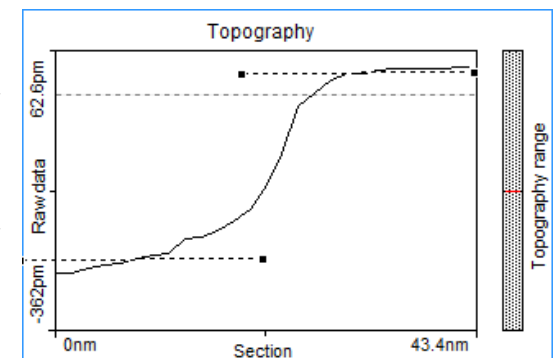


Fig. 14: Cross section of image e (see above). Distance: $\Delta z=333.9$ pm.

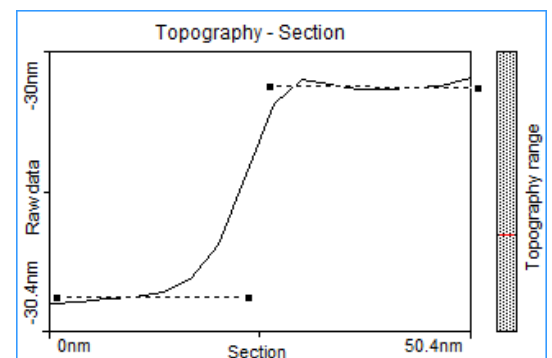


Fig. 15: Cross section of image f (see above). Distance: $\Delta z=686.1$ pm.

This allows you to overview quickly your results in this form: $\bar{m} \pm s$.

Table 1: Results

Measurement No. (Fig. 12)	Step height Δz / pm	Literature [*]	No. atomic layers	% Error	Δz single step own data
d	332.2	single graphene layer step $\Delta z = 334.8$ pm	0.99 \rightarrow 1	-0.8	333.05 [\pm 1.20] pm
e	333.9		0.99 \rightarrow 1	-2.6	
f	686.1		2.05 \rightarrow 2	2.5	-

Atomic resolution on graphite

To decrease the imaging area:

- Click the color map chart to activate it. A blue square is now drawn around the color map chart.
- Click "Zoom" in the upper tool bar, move the mouse cursor to a flat region (similar color) in the color map and click on it. The software will now draw a square that indicates the new scan range. The size of the new scan range is displayed in the "Tool Results" panel.
- Change the size of the new scan range to about 30–50 nm (Fig. 16) by clicking and dragging a corner of the square with the mouse cursor.
- Double-click the color map when the new scan area is set as you want it (or press "Zoom" in the "Tools Result" panel). The imaging settings are now set in such a manner that the new measurement will correspond to the area that was indicated by the square you have set. Let the topography reproduce stably again.

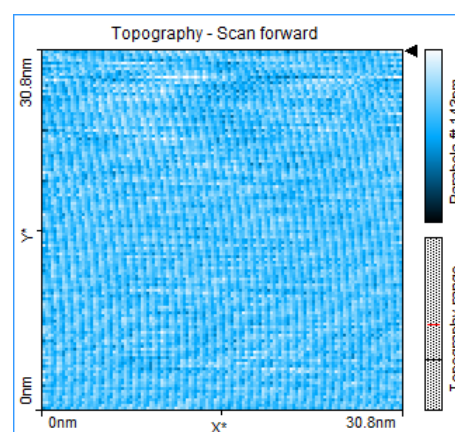


Fig. 16: Image size: 30 nm, Time/Line: 0.13 s, Set point: 1.2 nA, P-gain: 1200, I-gain: 1500.

To achieve atomic resolution, the image size should be decreased even further, considering that one nanometer is the diameter of between four and eight atoms. Atomic arrangements can normally be recognized at an image size of about 10 - 3 nm (Fig. 17). Therefore: Set the image size in the imaging panel to 3 nm or use the "Zoom" option on your last image (Fig. 18). Some parts of the scan head react to the slightest temperature changes. Since these thermal fluctuations influence the measurement on the nanometer scale, the sample has to be scanned as fast as possible: Set the "Time/Line" in the imaging panel to 0.03s (with 128 "Points/Line") for atomic resolution. With a good tip and properly set parameters, you should be able to observe atomic arrangements like those shown in the pictures. The imaged data corresponds to a topographic representation of the LDOS (near the Fermi edge) of surface atoms in the HOPG sample.

Before we start to interpret the images let's have a look at the atomic arrangement of HOPG and the question what are the bright protrusions in the images we observe.

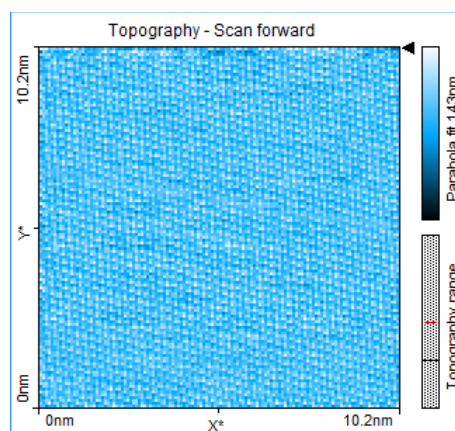


Fig. 17: Image size: 10 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1200, I-gain: 1500.

* : D. Sands, Introduction to Crystallography (Benjamin Cummings, Reading, Massachusetts., 1969)

Hexagonal Structures

The lattice structure of graphite is the so called hexagonal-closest-packing (h.c.p) with a “ABA” pattern. Have a look at your 3D model of the graphite lattice to get used to arrangements of neighboring atoms and graphene sheets (one layer). Assemble your 3D model according to the instructions (Fig. 19). A graphene sheet consists of carbon atoms (black balls in your 3D model) in their sp^2 - hybridized state with an angle of 120° for each bonding in the x-y-plane (Fig. 20). These are covalent bonds (indicated with white connection pieces) from atom to atom within one layer (C_6 -rings). From one layer to the other we observe electrostatic interactions – Van der Waals forces. In the 3D model this loose connection from p-orbital repulsion is indicated by the violet connection pieces. The distance between two adjacent graphene sheets in the graphite lattice is 0.3348 nm (334.8 pm) (see Fig. 21).

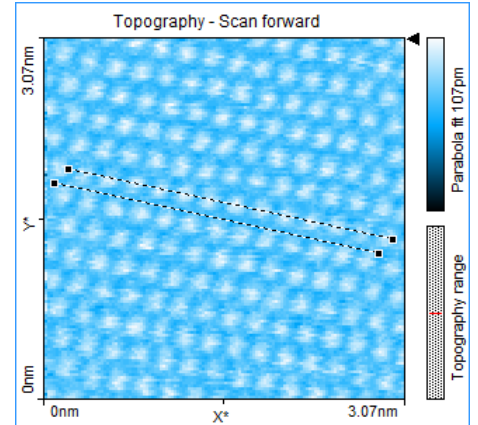


Fig. 18: Image size: 3 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1300, I-gain: 850. Distance between lines: $d=138 \text{ pm}$

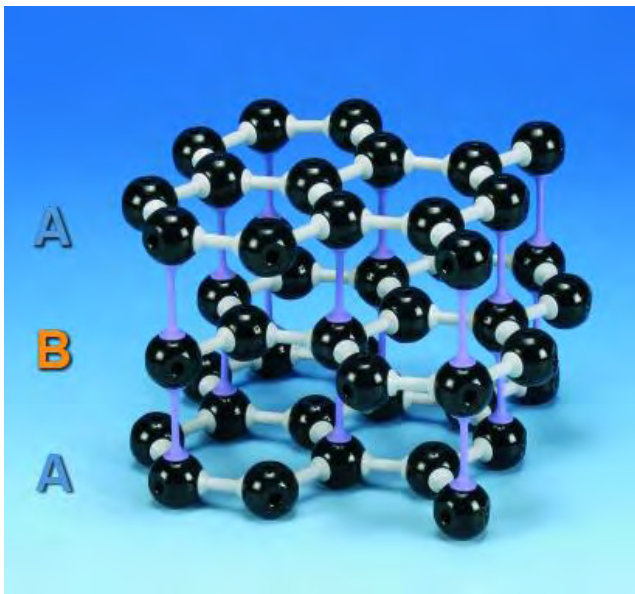


Fig. 19: PHYWE 3D model of the graphite lattice (Crystal lattice kit: graphite, 39840.00).

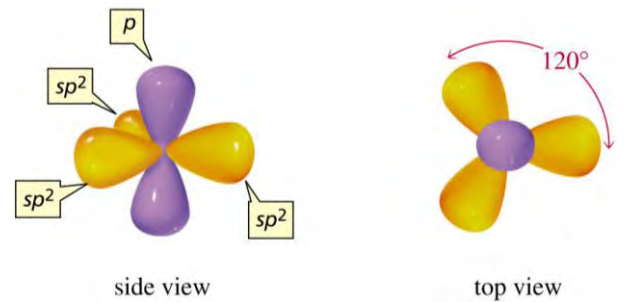


Fig. 20: Sketch of sp^2 - hybridized carbon atoms.

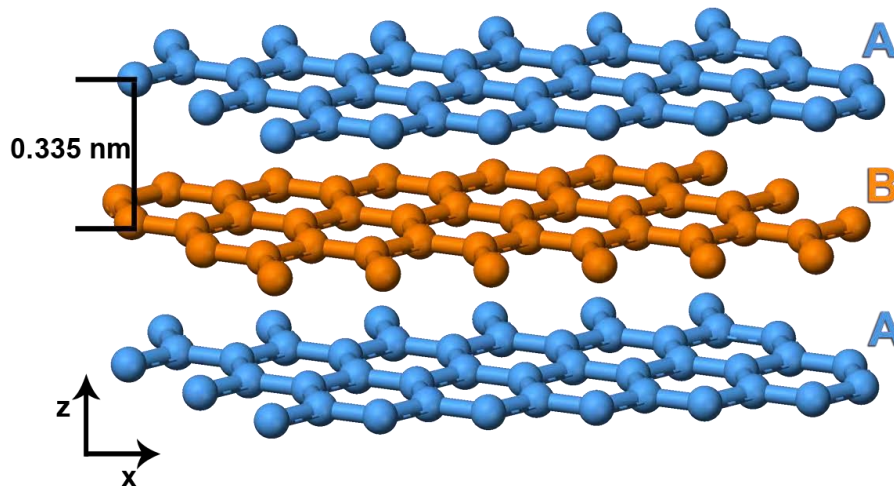


Fig. 21: 3D sketch of the graphite lattice structure (side view).

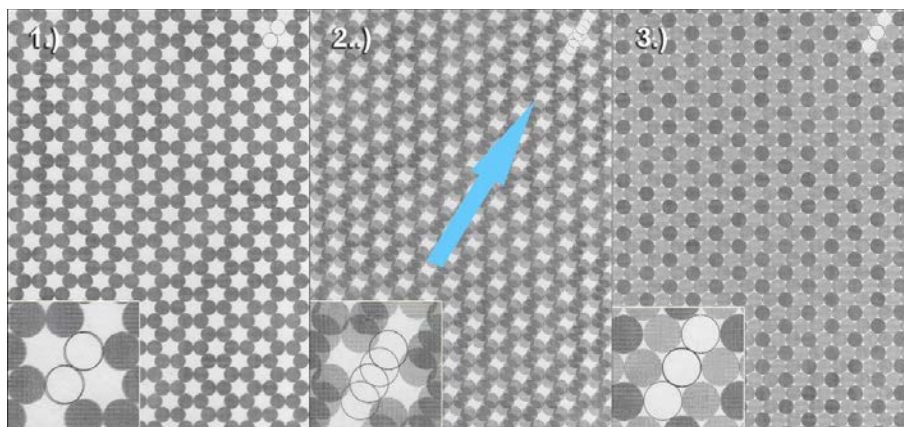


Fig. 22: PHYWE 2D model (09620.00) of the graphite surface atoms and an underlying graphene sheet (top view).

The second aid you can use to get along on the atomic scale is the 2D model of graphite (Fig. 22). Start by bringing the foil matching on top of the paper, the marker should show two circles. Then translate the foil diagonal. Afterwards the markers should show three circles indicating that you translated correctly. The atoms from the surface layer with a neighbor in the layer below appear darker as those without a direct neighbor, they appear brighter. This view corresponds to the imaging data of your HOPG sample you collect with your STM. The distance between two rows of atoms of the same type is 245 pm. From one atom to its next neighbor, this distance is 140 pm (Fig. 23).

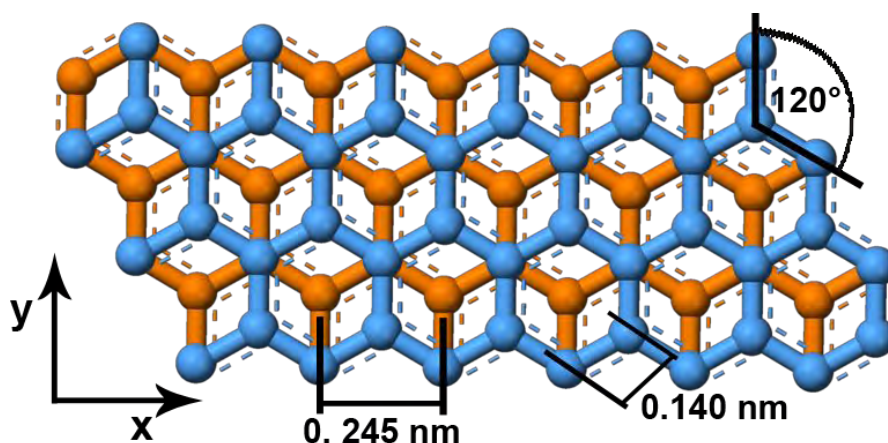


Fig. 23: 2D sketch of the graphite lattice structure (top view).

Measurements on atomic arrangements

Keep in mind that you can't see every atom of a C_6 -ring (as a bright spot), but every second. Use your 2D model of the graphite surface to compare it with the images you took (also see Fig. 24). Every second atom has a neighbor in the layer beneath it. Each atom from the upper layer loses electron density to the direct neighbor in the layer below it, making them to appear darker in STM images. Atoms without a direct neighbor in the layer beneath have the full electron density and appear as bright spots. As mentioned above it is useful to do measurements with lines ("Measure Distance") instead of a measurement from point to point ("Measure Length"). Now determine the spacing between atoms. You can either draw lines for the measurement between neighboring atoms (Fig. 23) or

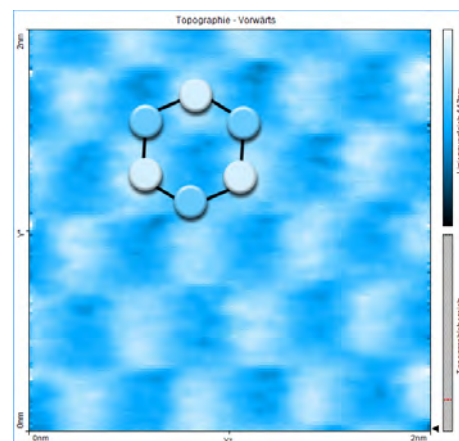


Fig. 24: Hexagonal pattern reveals electronic and topographic structure of surface atoms

between atoms of the next following row (Fig. 25). It is also possible to gain the desired information from a cross sectioning. Draw a line through a row of atoms and do the distance measurement in the graph image. Here you can decide again if you want to measure from one atom to the other (hill to valley, distance approx. $d = 140 \text{ pm}$) or from atom row to atom row (hill to hill see Fig. 26 or valley to valley, distance approx. $d = 245 \text{ pm}$).

To increase the accuracy of your measurement and reduce systematic errors, measure the distance of 5 to 10 rows and divide it by the number of rows and you also end up with the distance from row to row. For example a single measurement in Fig. 26 gives a distance from row to row of $d=248.5 \text{ pm}$, doing the same measurement over 5 rows ($d=1231.5 \text{ pm}$) reduces this value to $d=246.3 \text{ pm}$. For comparison of the constant current and the constant height mode measure the distance from the hilltop to the valley (in Fig. 26 the distance is $\Delta z=15.3 \text{ pm}$).

Do the measurements as exact as possible, minimal differences in the line drawing (only a few pixel) can make a big difference in your resulting values. To further support your results do a quick estimation of mean values (see above) from at least three to five measurements (more will increase the accuracy even further). The bonding angle between atoms you are able to determine by using the "Measure Angle" tool (Fig. 27).

Imaging with the constant height mode

All images so far have been acquired in the constant current mode where the current between the tip and the sample is kept constant. The distance between them is proportional to the flowing tunneling current so the distance is also kept constant. The measurement signal here is the elongation of the z-piezo which drives the tip movement and follows the surface topography. Let us now switch to the constant height mode. It is an advanced measurement mode where you fix the tip height above the sample surface to a specific value. The measurement signal is the tip current flowing between the tip and the sample.

Be careful: When you change scanning parameters too drastically it is likely that you crash the tip into the sample.

At first enable the advanced user interface of the software ("Options" → "Config User Interface"). Now you will find several options and parameters to adjust. To do a measurement in the constant height mode check the "Const.-Height mode" in the "Imaging Modes" panel in the imaging window (Fig. 28). Now you can adjust the "Rel. Tip-Pos.", this is the distance by which the tip is moved away or towards the sample from the position that corresponds to the set point. A negative setting will move the tip away from the sample.

The scanner now scans along a straight line that should be parallel to the sample surface. The slope of the line is defined by the x- and y-slope parameters in the imaging options section of the imaging panel. The height of the line is determined at the start of each scan line: First the z-controller is turned on. Once the tip position is stable, the z-controller is turned off and the tip is moved away from the sample by the distance set by the parameter "Rel. Tip-Pos."

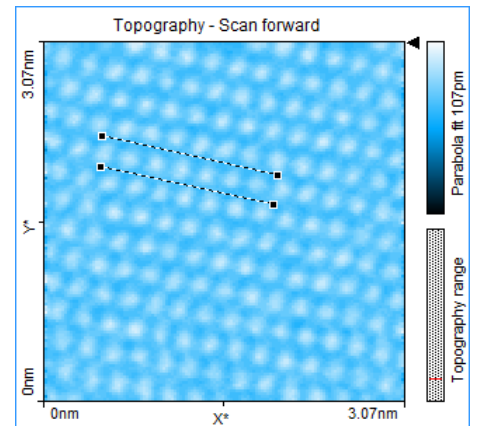


Fig. 25: Distance measurement. Distance between lines: $d=252.7 \text{ pm}$

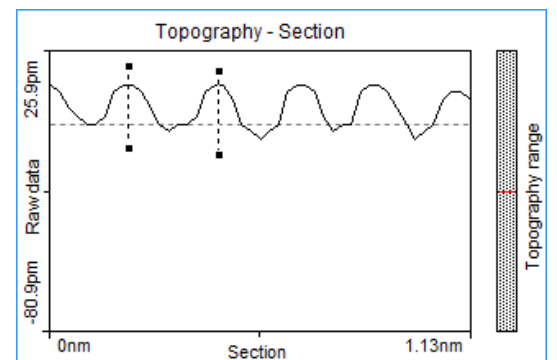


Fig. 26: Cross section through a row of atoms (see Fig. 17). Distance between lines: $d=248.5 \text{ pm}$ (hill to hill). $\Delta z=15.3 \text{ pm}$ (hill-top to valley).

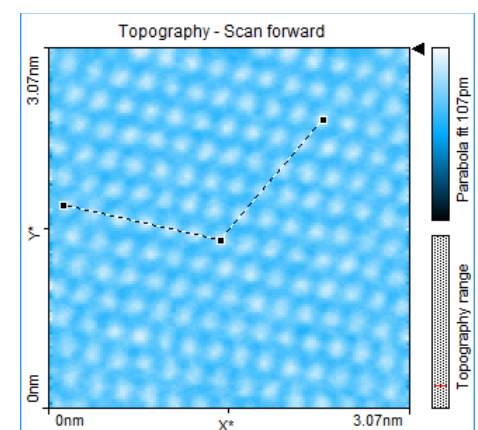


Fig. 27: Angle measurement. Angle between lines: $\alpha=118.8$

Start imaging with relatively large image size 40 – 60 nm and get used to this mode (Fig. 29). Switch to the appropriate measurement signal (Tip Current) in the “Select Signal” drop down menu located in the main tool bar. Most of the times you need some attempts to get a good value for the relative tip position. Start with safe values of about -25 nm, if you end up with a blank (black) imaging window you can decrease the value in small increments (to -15, -5, -1, -0.5, -0.25, -0.125, -0.075 nm etc.). Watch the imaging window carefully and wait until you get a reproducing tip current signal. Adjustments to the scanning can only be done by changing the tip current (set point), the tip voltage and the relative tip position above the sample surface. The images you take seem to be affected by noise much more than images taken in the constant current mode, because the feedback loop is turned off and slightest topographic differences will give a change in the tip current signal. Some other features of your sample like special electronic states of surface atoms might only be visible in this mode.

Step heights of terraces can't be measured directly within this mode because you have the tip current as the z-signal. What you can do, you can correlate values of the tip current to a step height of a terrace you measured before in the constant current mode by a cross sectioning. For this you can use the “Measure Length” tool to look at the Δz values displayed in the „Tool Results“ panel (see Fig. 30). Measuring distances follows the same procedure as mentioned above. Choose your measurement points wisely, avoid tilted planes and scanning artifacts.

Remember the exponential dependence of the tunneling current and the gap distance: $I \propto c_1 \cdot U \cdot \exp(-c_2 \cdot d_z)$. Measuring the difference in the current in Fig. 30 gives $\Delta I = 578.6$ pA and corresponds to the step height of one atomic terrace with $\Delta z = 334.8$ pm. The cross sectioning through an atomic row (Fig. 32) reveals that the difference in the current from the hilltop to valley is $\Delta I = 81.68$ pA and corresponds to the $\Delta z = 15.3$ pm we found earlier (Fig. 26).

Height differences (tip sample distance) of 0.1 nm will increase the measured current by about one order of magnitude.

In Fig. 31 an example for a measurement from one row to the next one (atom to atom) gives a distance of $d = 150.1$ pm. Here we find an error of about 6% and is out of the bounds to be in good agreement with expected values from the theory (140 pm). Repeat your measurements to have the possibility to reduce errors and to get better values by averaging your data (see above). Using the second method to measure the distance over several rows (here 5, $d = 720.5$ pm) reduces the value to 144.1 pm, with an error of 2%.

If you are not satisfied with the image quality, try to adjust the tip current and the relative height above the sample. Decreasing the tip current will bring the tip in a larger distance to the sample reducing the possibility that the tip hits obstacles on the sample surface (increasing the relative height will have a similar effect without reducing the tip sample interaction).

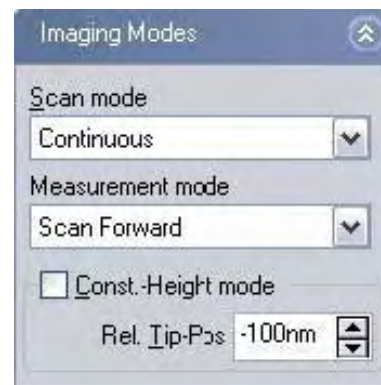


Fig. 28: Imaging modes panel in the imaging window (advanced user interface).

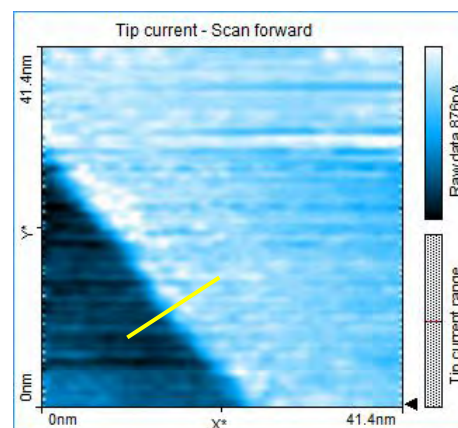


Fig. 29: Constant height image. Image size: 40 nm, Time/Line: 0.2 s, Set point: 1.2 nA, Rel. Tip-Pos.: -0.05nm.

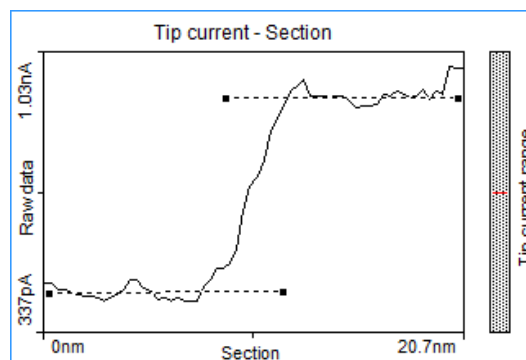


Fig. 30: The step size corresponds to a difference in the tunneling current of 578.6 pA (or 334.8 pm, one atomic layer).

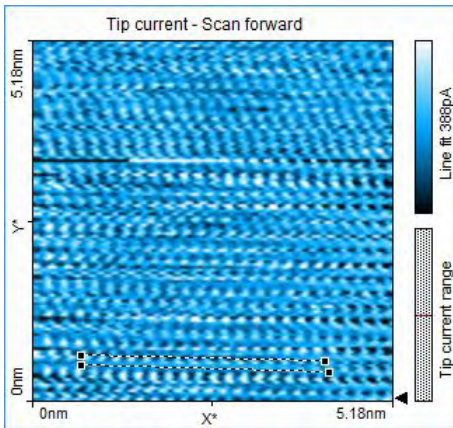


Fig. 31: Constant height image. Image size: 5 nm, Time/Line: 0.03 s, Set point: 1.2 nA, Rel. Tip-Pos.: -0.14nm. Distance between lines: $d=150.1$ pm

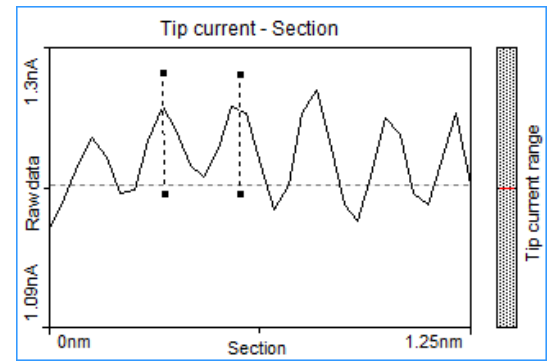


Fig. 32: Cross sectioning: Distance between lines: $d=235.1$ pm (hill to hill, hill to valley gives: $d=117.4$ pm. The z-distance from hilltop to valley corresponds to the measured current: $\Delta I=81.68$ pA.

When you have finished your measurements you also have the possibility to present your data in 3D (Fig. 33) (see chapter 4.4.3 and 4.5 of the user manual). Select “3D View” in the “Select Chart Type” drop down menu. Then adjust the appearance until you are satisfied with the look:

Always click and hold the left mouse button on the 3D view chart while changing the 3D view. The surface is reduced in feature complexity as long as the left mouse button is pressed. Press the following additional keys/buttons to determine what chart property is changed:

- Surface rotation mouse left/right
- Surface tilt mouse up/down.
- Size displayed surface “Ctrl”- key + mouse up/down
- Surface position “Shift”-key + mouse up/down/left/right Z-scale magnification left mouse button + right mouse button + mouse up/down
- Light source direction (360°) “Shift”+“Ctrl”-key + mouse left/right
- Light source height (0°–90°) “Shift”+“Ctrl”-key + mouse up/down

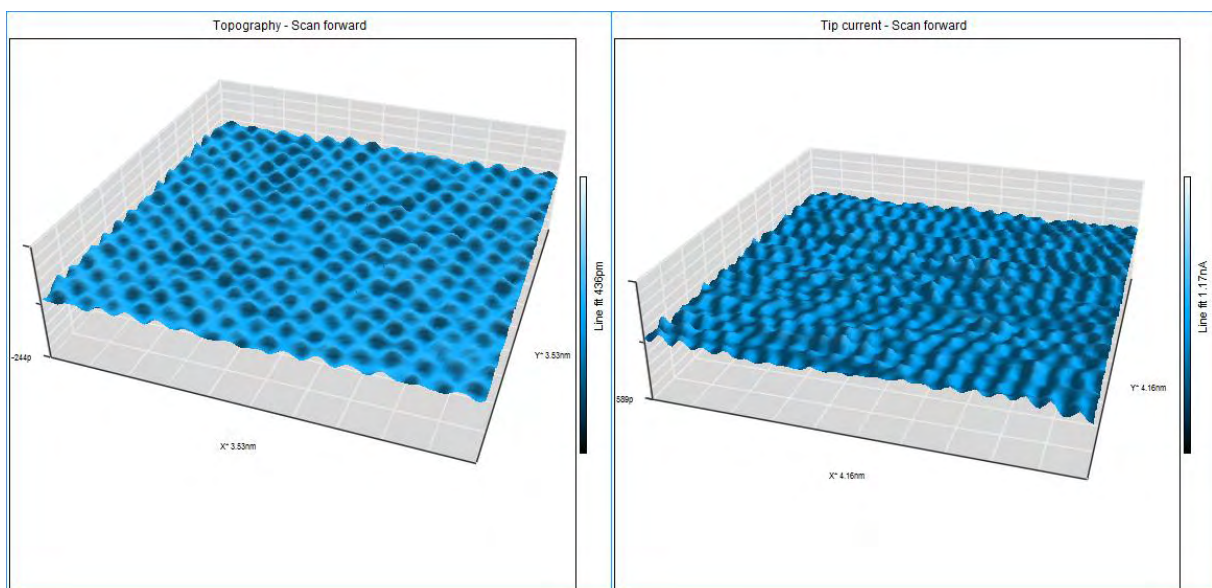


Fig. 33: 3D representation of constant current data (left) and constant height data (right).

Using the 2D Graphite Model to understand high resolution STM images of Graphite (HOPG)

Extract of the Experiment P2532000 "Atomic resolution of the graphite surface by STM"

Following the detailed instruction given in the experiments description of P2532000, you should be able

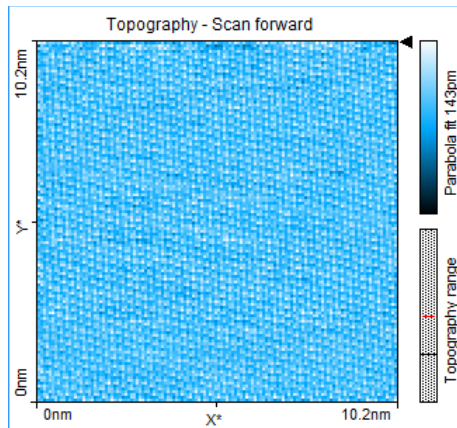


Fig. 1: Image size: 10 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1200, I-gain: 1500.

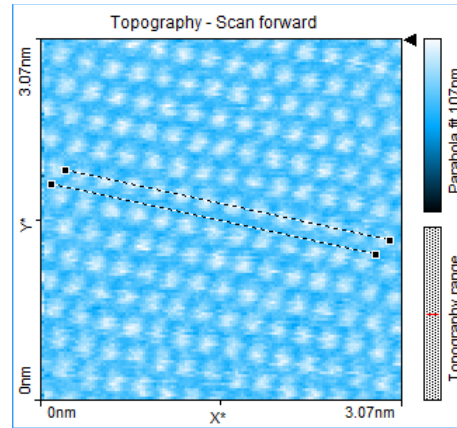


Fig. 2a: Image size: 3 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1300, I-gain: 850. Distance between lines: $d=138$ pm

to observe atomic arrangements like those shown in the pictures.

The imaged data corresponds to a topographic representation of the LDOS (near the Fermi edge) of surface atoms in the HOPG sample.

Before we start to interpret the images let's have a look at the atomic arrangement of HOPG and the question what are the bright protrusions in the images we observe.

Hexagonal Structures

The lattice structure of graphite is the so called hexagonal-closest-packing (h.c.p) with a "ABA" pattern.

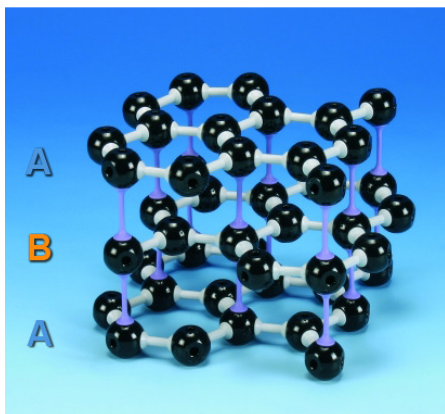


Fig. 3: PHYWE 3D model of the graphite lattice (Crystal lattice kit: graphite, 39840.00).

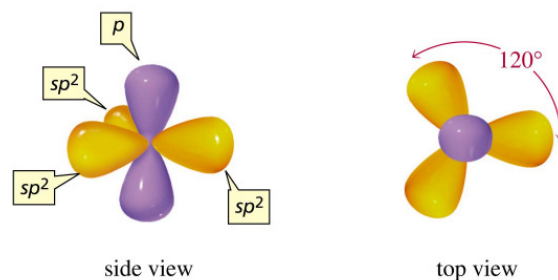


Fig. 4: Sketch of sp^2 -hybridized carbon atoms.

The 3D model of the graphite lattice shows the arrangements of neighboring atoms and graphene sheets (one layer, Fig. 3).

A graphene sheet consists of carbon atoms (black balls in the 3D model) in their sp^2 -hybridized state with an angle of 120° for each bonding in the x-y-plane (Fig. 4). These are covalent bonds (indicated with white connection pieces) from atom to atom within one

Related Topics

Tunneling effect, Defects, Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), Local Density of States (LDOS), Work function, Surface activation, Catalysis

Principle

Scanning tunneling microscopy is used to image the (electronic) topography of a freshly prepared graphite (HOPG) and gold surface. By spectroscopic measurements (I-z) the local effective work function can be determined in dependence of the material and the nanomorphology of the sample. The results are discussed with respect to surface activation and catalysis.

Caution!

Set up your system on a very steady table.

Do your experiments in a calm, vibrational free environment

Equipment

- 1 Compact-Scanning Tunneling Microscope, complete set incl. tools, sample kit and consumables, in aluminum case 09600-99

Additionally needed

- 1 PC, Windows® XP or higher
Adhesive tape
PHYWE *measure*

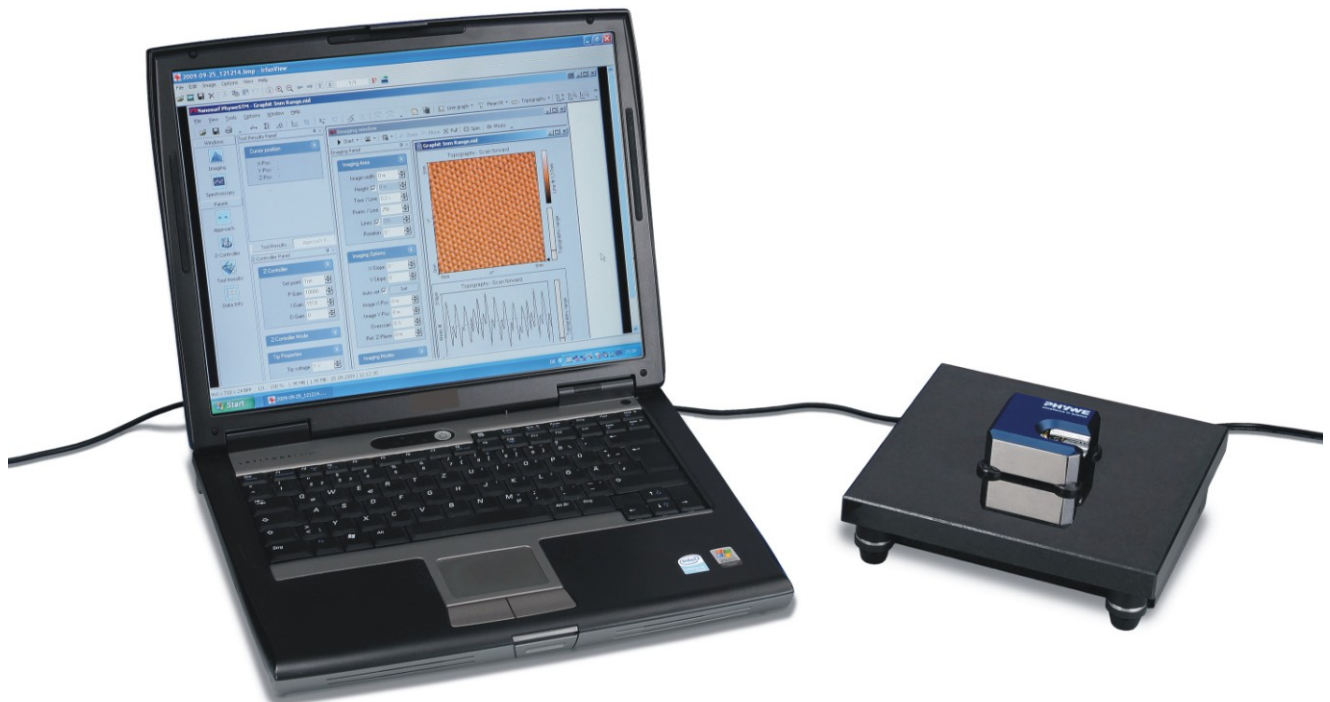


Fig. 1: Experimental setup.

PHYWE Compact-STM set

- | | |
|---|------|
| 1 Control unit with mounted scan head | (1) |
| 1 Magnifying cover glass (10X Magnification) | (2) |
| 1 USB cable | (3) |
| 1 Power cord and adapter | (4) |
| 1 MeasureNano Software | (5) |
| 1 PHYWE STM Tool Box: | |
| 1 Wire cutter | (6) |
| 1 Flat nose pliers | (7) |
| 1 Pointed tweezers | (8) |
| 1 Rounded tweezers | (9) |
| 1 Pt/Ir-wire, $d = 0.25 \text{ mm}$, $l = 30 \text{ cm}$ | (10) |
| 1 Sample Holder | (11) |
| 1 Graphite sample (HOPG) | (12) |
| 1 Gold sample | (13) |
| 4 Spare sample support | (14) |
| 1 Scanning Tunneling Microscopy (STM) –
Operating Instructions and Experiments | (15) |



Fig. 2: Content of 09600-99.

Tasks

1. Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.
2. Investigate the topography of the gold and HOPG sample on clean terraces and defects in constant-current mode.
3. Switch to spectroscopy mode. Measure and compare images recorded on terraces and defects in Z-Axis mode (I-z spectroscopy).
4. Determine the local work function for the different areas and interpret the results.

Set-up and Procedure**Task 1: Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.**

For preparation of tunneling tips and the approaching procedure please refer to experiment *P2532000 "Atomic Resolution of the graphite surface by STM"*, the quick start guide (QSG), or, the operating manual (OM), Chapter 5. You'll find an electronic version of the QSG and OM under the help menu of the measure nano software.

In most cases it is enough to cleave the graphite sample once in a few weeks. If you have problems to find a clean area or you don't get good images with several freshly prepared tips, clean the sample surface using scotch tape as described in the QSG or OM.

The gold sample normally need not to be cleaned. However, if you experience bad scans throughout or accidentally touched the sample you can lay a lint-free cloth on top of the sample surface and drip some alcohol on it. Remove the wet cloth by carefully wiping and wait until the alcohol has dried completely. To avoid any scratches or other irreversible surface modifications it is important that the surface does not experience pressure at any time!

Theory and Evaluation

Tunneling

Tunneling is a functioning concept that arises from quantum mechanics. Classically, an object hitting an impenetrable barrier will not pass through. In contrast, objects with a very small mass such as the electron, have wavelike characteristics which permit such an event, referred to as tunneling. In other words, the probability to find an electron behind a barrier is unequal zero. Inside the barrier the wave function of the electron decays exponentially (Fig. 3).

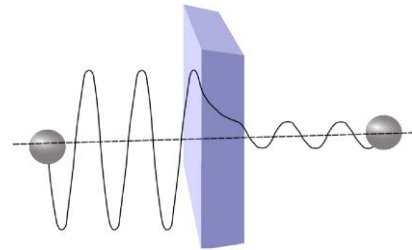


Fig. 3: Sketch of the tunneling of an electron through a barrier.

STM – Scanning Tunneling Microscopy

The size of an atom in relation to the tip is that of a golf ball to a mountain. In your PHYWE measurement system a platinum-iridium tip is moved in three dimensions using piezo crystal translators that are driven with sub-nanometer precision (Fig. 4). The sample to be examined approaches the tip within a distance of about 1 nanometer ($1 \text{ nm} = 1/1,000,000,000 \text{ m}$). Classical physics would prohibit the appearance of electrons in the small gap between the tip and the sample, but if a sharp tip and a conducting surface are put under a low voltage ($U \sim 0.1 \text{ V}$), a very small tunneling current ($I \sim 1 \text{ nA}$ with 1 nm tip sample distance) though may flow between tip and sample.

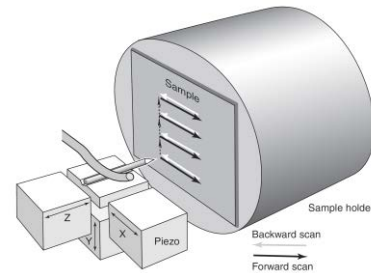


Fig. 4: Sketch of the piezo electric device driving the tip movement.

The resulting tunneling current is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample, this information is displayed on the computer monitor as 2D color mapped image. The strength of the tunneling current I depends exponentially on the distance between the tip and the sample (d_z), usually referred to as z -distance and the applied bias (U). From Schrödinger's equation one can find that

$$I = f(U) \exp(-A\sqrt{\phi}d_z) \quad [1]$$

where

$$A = 2\sqrt{\frac{2m_e}{\hbar^2}} = 10.25 \text{ nm}^{-1} \text{ eV}^{-0.5}.$$

Here ϕ is the effective work function. This is an actual workfunction mainly influenced by surface adsorbates and the high electrical field density at the tip.

The extreme dependence on the distance makes it possible to measure the tip–sample movement very precisely. By keeping the tip voltage constant and measuring the tunnel current I in dependency of d_z the effective work function can be determined either by fitting an exponential function to the measured tunnel current [1] or by applying the logarithm to [1] which leads to

$$\ln(I) = -A\sqrt{\phi}d_z + \ln(f(U)). \quad [2]$$



This is a linear function of d_z so ϕ can be determined from the slope of the expected straight line by a linear fit.


By the combination of the high resolution of the tunnel microscope and the spectroscopy function it is possible to determine work functions at the nanoscale.

Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create uncertainty and errors in the expected values of your measurements.

Task 2: Investigate the topography of the gold and HOPG sample on clean terraces and defects in constant-current mode.*Finding atomic terraces on the sample surface*

It is recommended to start over by checking and optimizing the quality of the tip with the graphite sample before using the gold sample.

To activate the full measurement-range of your device click the  Full button in the imaging window. For good results you can use image sizes of about 0.2 μm . When you are lucky you find a terrace in your first measurement. If that is not the case you can either use the  Move tool in the imaging window to start the measurement at a different spot on the surface or you retract the sample from the tip and carefully turn the sample holder with the black plastic handle. Afterwards you approach the sample again.

In Fig. 5 you can find examples of terrace like structures at different spots on the HOPG and gold sample surface. Make sure you adjust the parameters of the feedback loop to achieve good image quality. You may switch to the standard or advanced level of the software user interface (“Options” \rightarrow “Config User Interface”) to obtain the possibility to adjust the P- and the I-gain individually. Too high values in the P- and I-gain will be noticeable in the line graph as very high peaks and a very rough line structure. Adjust the gain values to smooth the line graph and your image respectively. When you are satisfied grab a good image by clicking the  Photo button. Now you can apply some filters to reduce noise, adjust scan line levels and remove a background distortion. The recommended procedure would be:

- Apply glitch filter.
- Apply noise filter.
- Do a background correction and/or correct scan line levels.

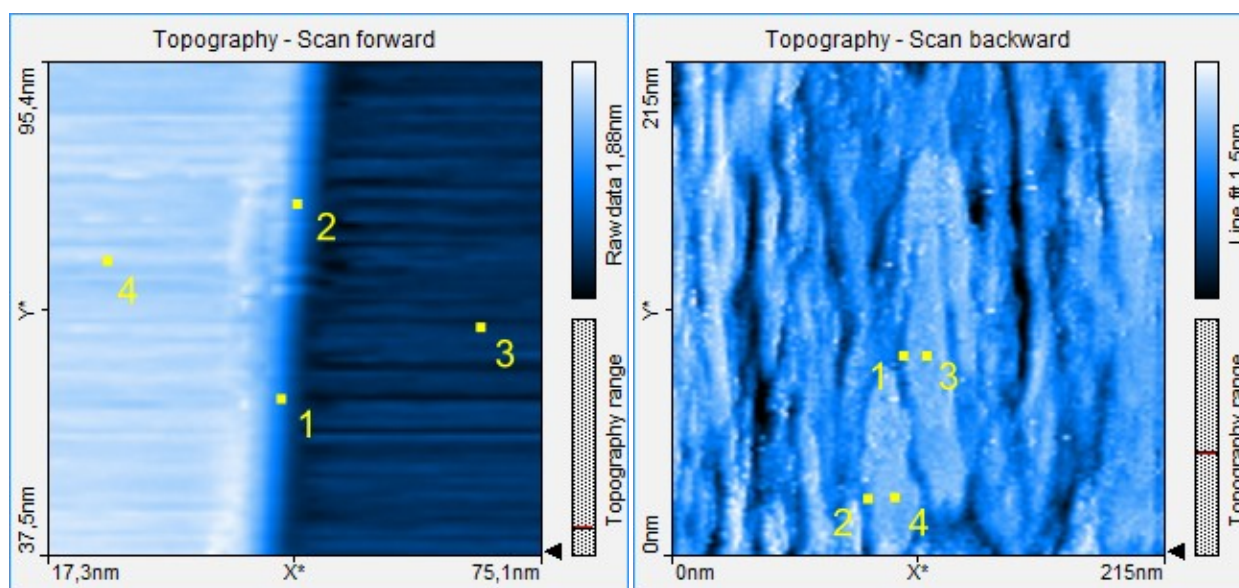

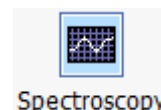


Fig. 5: Examples of terraces on HOPG (left) and gold (right) recorded at tunnel current 0.5 nA, tip voltage 0.1 V.

Task 3: Switch to spectroscopy mode. Measure and compare images recorded on terraces and defects in Z-Axis mode (I-z spectroscopy).*I-z spectroscopy*

After grabbing a good image switch to the Spectroscopy mode by clicking the “Spectroscopy” button in the navigator, or by clicking  Spec in the Imaging bar. In a spectroscopic measurement, the tunneling current is measured as a function of either the z-distance or



Spectroscopy

the tip voltage. To determine the work function select “Z-Axis” as modulated output. Pin down values of your measurement parameters accurately. If you experience problems in measuring the desired behavior, try to adjust your parameter values. For example you can start experimenting with the following set of parameters for HOPG:

- Set point 0.5 nA
- P-Gain 500
- I-Gain 500
- Tip voltage 0.1 V
- Start value 0 nm
- End Value -5 nm
- Modulation time 0.2 s
- Data points 128
- Averages 16

By using this set of parameters, the device will divide the distance from 0nm to -5nm from the current tip position into 128 points and measure the tunnel current at each of them. The time used for one series of measurements is 0.2 s. This process will be repeated 16 times. The resulting curve is the average of the 16 measurements.

Notice:

- For gold you will need higher gain values than for HOPG to be able to see the step structure as shown in Fig. 5.
- Positive Start and End values will bring the tip closer to the surface: 1 nm will change the tunnel current about 1 magnitude!
- High tunnel currents may influence the structure of the tip and/or the surface. Therefore try choosing a lower set point or lower start and end values if you receive high currents (>20nA) and the curve is not exponential.
- As long as you are in the spectroscopy mode the piezo controllers are inactive. Because of thermal drift you might receive different results when measuring the same point multiple times, especially when using high resolutions. Also modifications of the local tip geometry can occur during the measuring procedure indicated by noisy and “jumpy” spectra. Therefore **check the topography after every spectroscopic measurements to evaluate the results!**

Before you start measuring switch to a dual-line graph first (right-click → “chart type”). Then prepare a measurement by clicking on “Point” and putting the cursor on the surface of your scanned image where you want to take the spectroscopy data. Press the “Start” button. After a few seconds the end of the measurement is indicated when the “Stop” button changes back to “Start” and when your data curve doesn’t change anymore. The “Probe Status” should be green during the whole measurement. If the “Probe Status” changes to orange switch to the “Imaging Window” approach the sample again and take a new surface scan, afterwards switch back to the “Spectroscopy” window.

After the measurement is finished you should be able to see two curves in the dual-line graph like in Fig. 6. One for the forward measurement and one for the backward measurement. You should see an exponential dependence of current to distance for both of them. If not repeat the same measurement pressing “Start” again. If you still don’t get the desired curves switch back to the imaging mode and repeat the process.

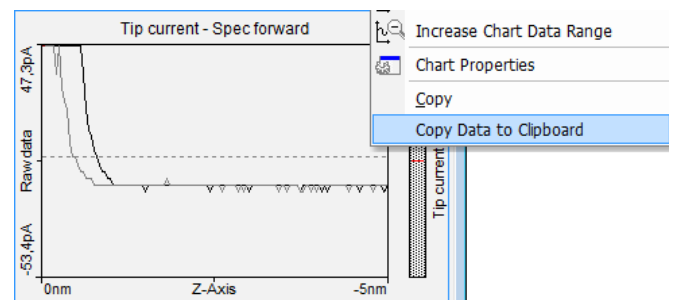


Fig. 6: Sketch of the dual-line graph

To analyze the current-distance curves right-click the dual-line graph and click “Copy data to clipboard” (Fig.

6). Now open the analyzing software PHYWE *measure* and paste the data by pressing ctrl+v or using

“Measurement” → “Import Data”. A dialog will pop up. Select “Sort data. Ask again if any x-values occur twice”. You should receive a graph as shown in Fig. 7. Now go back to PHYWE *measure nano* and switch the spectroscopy signal of the dual-line graph by right-click → “Signal”. Export this curve to PHYWE *measure* in the same way. Now compare the curves for forward and backward measurement.

You will see the both curves to be different because of surface adsorbates which impact the tunnel current. When retracting the tip from the surface these adsorbates will provide a direct connection decreasing the actual work function. Therefore we will only analyze the backward spec data which are less affected by this effect and leave the forward spec data aside.

Task 4: Determine the local work function for the different areas and interpret the results.

To determine the effective work function we need to fit an exponential function. Therefore go to “Analysis” → “Function fitting” in PHYWE *measure* and select “exponential function” in the uppermost drop-down dialog. After clicking “calculate” you will obtain the fit parameters. By clicking “Add new curve” the fit curve will be drawn into the diagram, so you can visually evaluate the quality of the fit (Fig. 7).

From [1] we know for our fit parameter $b = A\sqrt{\phi}$ and therefore

$$\phi = \frac{b^2}{A^2}$$

To obtain correct values for the work function ϕ , it is important to take the units of b into account.

Now that you are familiar with the procedure, apply the spectroscopy mode on some points on clean terraces and defects like step edges or holes on HOPG and Gold and compare the measured work functions. The measured data will vary for each tip. In order to compare results you should use the same tip for the different measurements.

For example the measurement on a clean terrace on the HOPG sample (Fig. 5, point #3) gives the curve in Fig. 7. From the fit we know that

$$b = 8.78 \text{ nm}^{-1}$$

so

$$\phi = \frac{b^2}{A^2} = \frac{8.78^2}{10.25^2} \text{ eV} = 0.73 \text{ eV}.$$

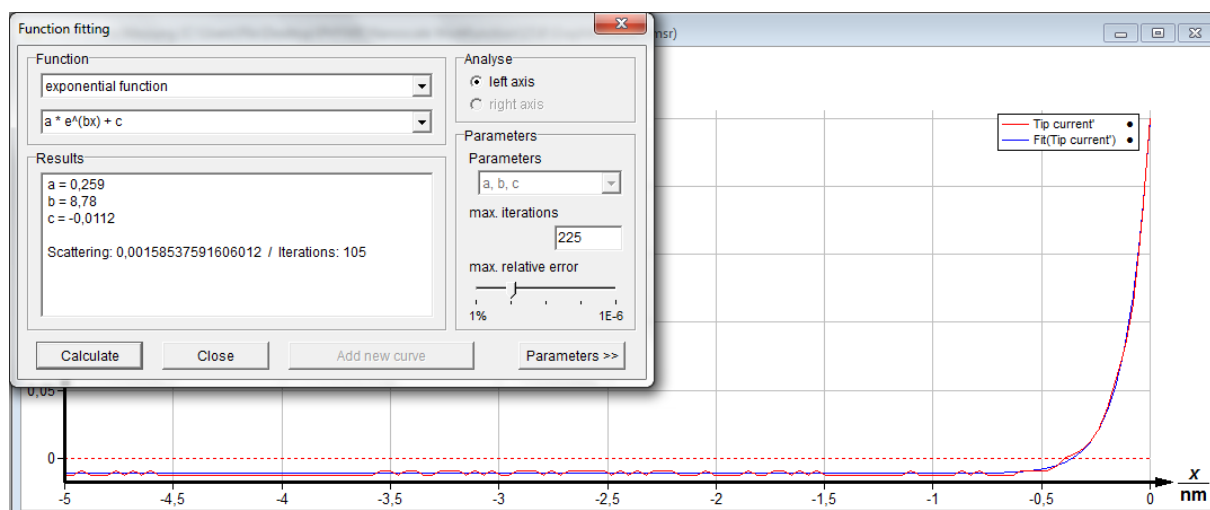


Fig. 7: Function fitting window in PHYWE *measure*

For the other points in Fig. 12 one can calculate the work function in the same way. The results are

Point #	HOPG	Gold
1	0.27 eV	0.11 eV
2	0.26 eV	0.12 eV
3	0.73 eV	0.21 eV
4	0.64 eV	0.18 eV

You can see that the measured effective work functions for gold are lower than for graphite, although the actual work function should be higher for gold. This comes from the different outside influences mentioned above and different tips which have been used for the different samples.

One can see that for similar regions on one sample the work functions will not scatter a lot. Yet more important is the observation that the work function is generally smaller at defects than on clean terraces!

This can be explained by Smoluchowski's model. In this model the valence electrons in a metallic (metallike) solid are almost free and flow along the atomic cores. Defects in the solid's surface result in the expose of atomic cores while the electrons flow smooth across the defect (Fig. 8). This results in an abundance of electrons in certain areas (=negative charged regions with higher potential energies of electrons) for example the lower edge of step edges which then can be extracted easier.

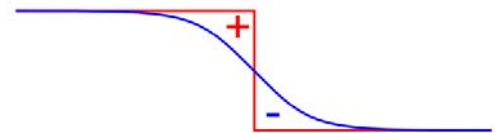


Fig. 8: Sketch of the charge distribution at a surface defect

Interpretation

The result of a smaller work function is a higher reactivity of a solid surface and therefore defects in the surface make solids more chemically active.

One application of this effect is to increase the effectiveness in catalysts by using materials with rough surfaces, where rough means the surface has a high density of defects.

It was shown that STM is a powerful tool to determine work functions of nano structures. This ability can be used for many purposes e.g. measuring the work function of optically stimulated surfaces or nanostructures.

layer (C_6 -rings). From one layer to the other only electrostatic interactions take effect (Van der Waals forces). In the 3D model this loose connection from p-orbital repulsion is indicated by the violet connection pieces. The distance between two adjacent graphene sheets in the graphite lattice is 0.3348 nm (334.8 pm) (see Fig. 21).

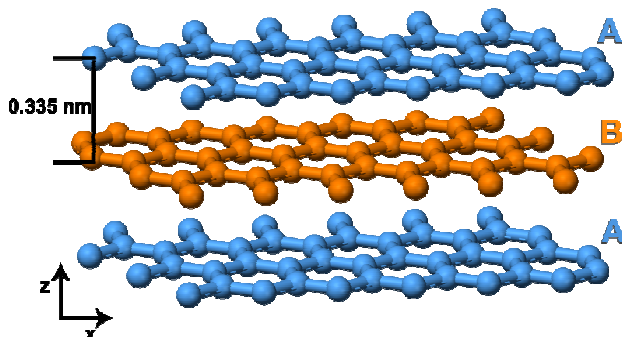


Fig. 5: 3D sketch of the graphite lattice structure (side view).

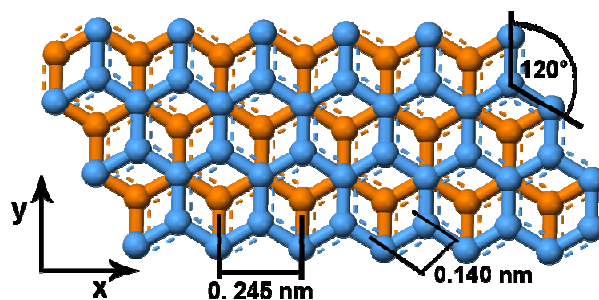


Fig. 6: 2D sketch of the graphite lattice structure (top view).

The second aid you can use to get along on the atomic scale is the **2D model of graphite** (09620-00, Fig. 7).

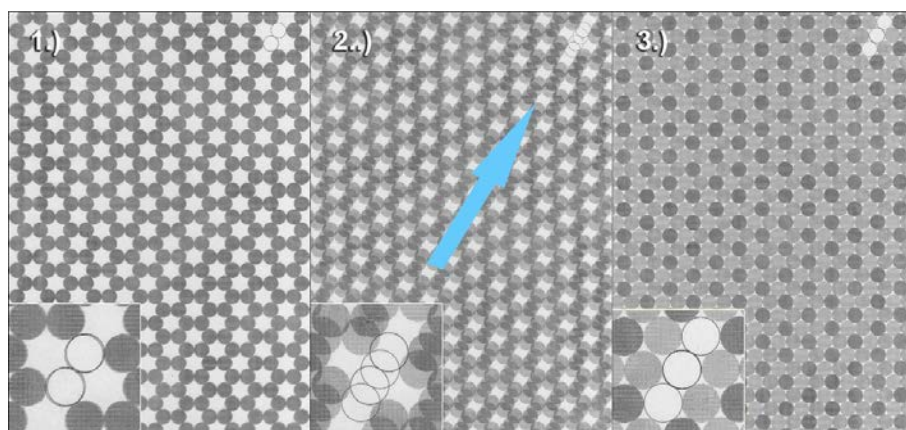


Fig. 7: 2D model of the graphite surface atoms and an underlying graphene sheet (top view) (09620-00).

Start by bringing the foil matching on top of the paper, the marker should show two circles. Then translate the foil diagonally. Afterwards the markers should show three circles indicating that you translated correctly. The atoms from the surface layer with a neighbor in the layer below appear darker as those without a direct neighbor, they appear brighter. This view corresponds to the imaging data of your HOPG sample you collect with your STM. Every second surface atom is imaged.

The distance between two rows of atoms of the same type is 245 pm. From one atom to its next neighbor, this distance is 140 pm (Fig. 6).

Measurements on atomic arrangements

Keep in mind that you can't see every atom of a C_6 -ring (as a bright spot), but every second. Use the 2D model of the graphite surface to compare it with the images you took (also see Fig. 7). Every second atom has a neighbor in the layer beneath it. Each atom from the upper layer loses electron density to the direct neighbor in the layer below it, making them to appear darker in STM images. Atoms without a direct neighbor in the layer beneath have the full electron density and appear as bright spots.

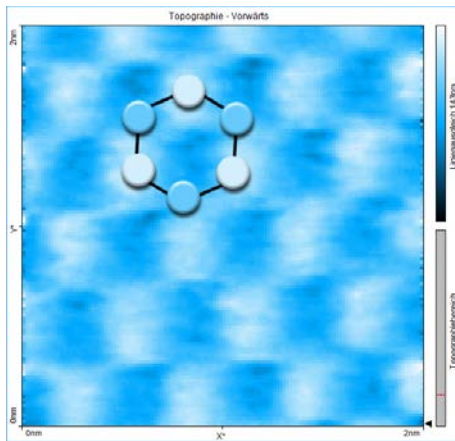


Fig. 2b: Hexagonal pattern reveals electronic and topographic structure of surface atoms

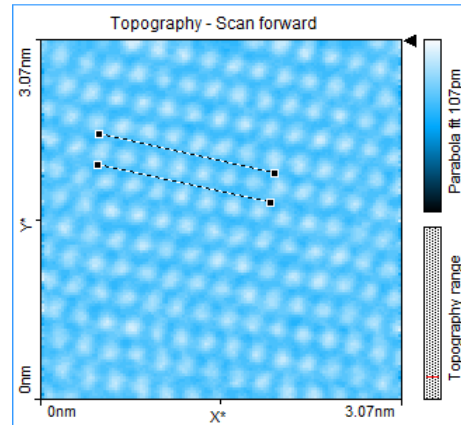


Fig. 8: Distance measurement. Distance between lines: $d=252.7$ pm

Due to the accuracy of measurement values it is useful to do measurements with lines (“Measure Distance”) instead of a measurement from point to point (“Measure Length”). Now determine the spacing between atoms: You can either draw lines for the measurement between neighboring atoms (Fig. 2 and 6) or between atoms of the next following row (Fig. 6 and 8). It is also possible to gain the desired information from a cross sectioning. Draw a line through a row of atoms and do the distance measurement in the graph image. Here you can decide again if you want to measure from one atom to the other (hill to valley, distance approx. $d = 140$ pm) or from atom row to atom row (hill to hill see Fig. 9 or valley to valley, distance approx. $d = 245$ pm).

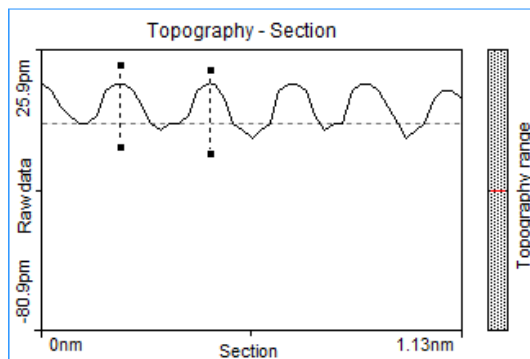


Fig. 9: Cross section through a row of atoms (see Fig. 17). Distance between lines: $d=248.5$ pm (hill to hill). $\Delta z=15.3$ pm (hill-top to valley).

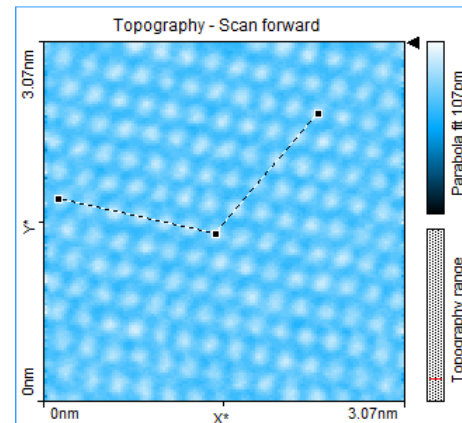


Fig. 10: Angle measurement. Angle between lines: $\alpha=118.8$

To further increase the accuracy of your measurement and reduce systematic errors, measure the distance of 5 to 10 rows and divide it by the number of rows and you also end up with the distance from row to row. For example a single measurement in Fig. 9 gives a distance from row to row of $d=248.5$ pm, doing the same measurement over 5 rows ($d=1231.5$ pm) reduces this value to $d=246.3$ pm.

Do the measurements as exact as possible, minimal differences in the line drawing (only a few pixel) can make a big difference in your resulting values. To further support your results do a quick estimation of mean values (see above) from at least three to five measurements (more will increase the accuracy even further).

The bonding angle between atoms you are able to determine by using the “Measure Angle” tool (Fig. 10).

After finishing the measurements you also have the possibility to present the data in 3D (Fig. 11) (see chapter 4.4.3 and 4.5 of the user manual). Select "3D View" in the "Select Chart Type" drop down menu. Then adjust the appearance until you are satisfied with the look:

Always click and hold the left mouse button on the 3D view chart while changing the 3D view. The surface is reduced in feature complexity as long as the left mouse button is pressed. Press the following additional keys/buttons to determine what chart property is changed:

- Surface rotation mouse left/right
- Surface tilt mouse up/down.
- Size displayed surface "Ctrl"- key + mouse up/down
- Surface position "Shift"-key + mouse up/down/left/right Z-scale magnification left mouse button + right mouse button + mouse up/down
- Light source direction (360°) "Shift"+"Ctrl"-key + mouse left/right
- Light source height (0°–90°) "Shift"+"Ctrl"-key + mouse up/down

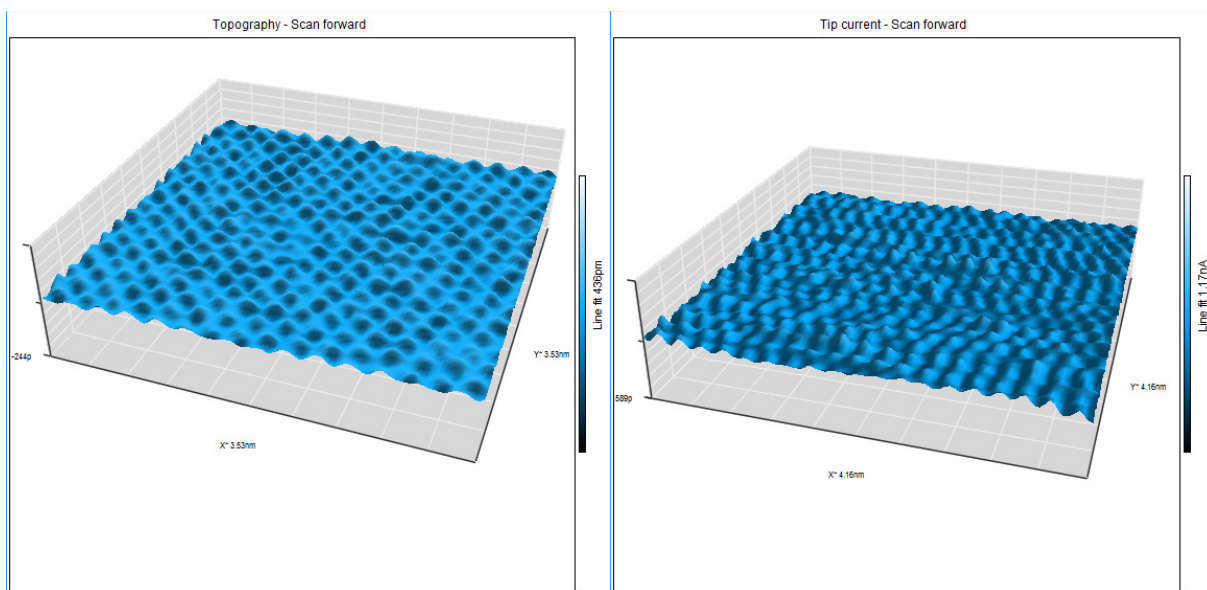


Fig. 11: 3D representation of constant current data (left) and constant height data (right).

Related Topics

Scanning Tunneling Microscopy and Spectroscopy, Tunneling Effect, Local Density of States, Peierl's Theorem, Peierl's Transition, Charge Density Waves, Commensurability, Incommensurability, Transition Metal Chalcogenide, Band Structure

Principle

In addition to the tunneling effect measured by tunneling spectroscopy another quantum mechanical effect the charge density waves are investigated for different samples. Charge density waves are modulated electron waves due to static and periodic lattice distortion and therefore mappable with scanning tunneling microscopy. The lattice distortion is caused by a lowering of the total energy of the system due to a Peierl's transition (Nesting of Fermi surfaces).

Caution!

- Set up your system on a very steady table
- Do your experiments in a calm, vibrational free environment

Equipment

- | | |
|---|----------|
| 1 Compact-Scanning Tunneling Microscope, complete set incl. tools, sample kit and consumables, in aluminum case | 09600-99 |
| 1 TaS ₂ on sample support, natural | 09612-00 |
| 1 TaSe ₂ on sample support | 09611-00 |
| 1 WSe ₂ on sample support | 09610-00 |

Additionally needed

- 1 PC, Windows® XP or higher
- Adhesive tape
- PHYWE *measure*



Fig. 1: Experimental setup.

PHYWE Compact-STM set

- | | |
|---|------|
| 1 Control unit with mounted scan head | (1) |
| 1 Magnifying cover glass (10X Magnification) | (2) |
| 1 USB cable | (3) |
| 1 Power cord and adapter | (4) |
| 1 MeasureNano Software | (5) |
| 1 PHYWE STM Tool Box: | |
| 1 Wire cutter | (6) |
| 1 Flat nose pliers | (7) |
| 1 Pointed tweezers | (8) |
| 1 Rounded tweezers | (9) |
| 1 Pt/Ir-wire, $d = 0.25 \text{ mm}$, $l = 30 \text{ cm}$ | (10) |
| 1 Sample Holder | (11) |
| 1 Graphite sample (HOPG) | (12) |
| 1 Gold sample | (13) |
| 4 Spare sample support | (14) |
| 1 Scanning Tunneling Microscopy (STM) –
Operating Instructions and Experiments | (15) |



Fig. 2: Content of 09600-99.

Tasks

1. Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.
2. Investigate the tunneling effect at HOPG and Gold by Scanning Tunneling Spectroscopy (Current-Distance-Spectroscopy).
3. Imaging and characterization of charge density waves at different substrates. Interpret the results regarding to the bandstructure.
4. Investigate in charge density waves at different voltages and interpret the imaged states (filled and empty).

Set-up and Procedure**Task 1: Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.**

For preparation of tunneling tips and the approaching procedure please refer to experiment *P2532000 "Atomic Resolution of the graphite surface by STM"*, the quick start guide (QSG), or, the operating manual (OM), Chapter 5. You'll find an electronic version of the QSG and OM under the help menu of the measure nano software.

In most cases it is enough to cleave the graphite sample once in a few weeks. If you have problems to find a clean area or you don't get good images with several freshly prepared tips, clean the sample surface using scotch tape as described in the QSG or OM.

The gold sample normally need not to be cleaned. However, if you experience bad scans throughout or accidentally touched the sample you can lay a lint-free cloth on top of the sample surface and drip some alcohol on it. Remove the wet cloth by carefully wiping and wait until the alcohol has dried completely. To avoid any scratches or other irreversible surface modifications it is important that the surface does not experience pressure at any time!

Normally the other samples have not to be prepared by a special procedure. If you still have problems to image the surfaces carefully cleave the samples with the scotch tape method.

Theory and Evaluation

Tunneling

Tunneling is a functioning concept that arises from quantum mechanics. Classically, an object hitting an impenetrable barrier will not pass through. In contrast, objects with a very small mass such as the electron, have wavelike characteristics which permit such an event, referred to as tunneling. In other words, the probability to find an electron behind a barrier is unequal zero. Inside the barrier the wave function of the electron decays exponentially (Fig. 3).

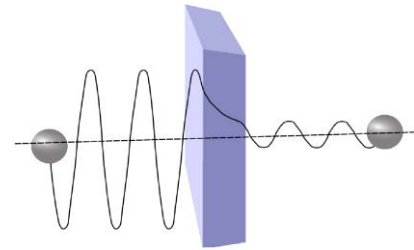


Fig. 3: Sketch of the tunneling of an electron through a barrier.

STM – Scanning Tunneling Microscopy

The size of an atom in relation to the tip is that of a golf ball to a mountain. In your PHYWE measurement system a platinum-iridium tip is moved in three dimensions using piezo crystal translators that are driven with sub-nanometer precision (Fig. 4). The sample to be examined approaches the tip within a distance of about 1 nanometer (1 nm = 1/1,000,000,000 m). Classical physics would prohibit the appearance of electrons in the small gap between the tip and the sample, but if a sharp tip and a conducting surface are put under a low voltage ($U \sim 0.1$ V), a very small tunneling current ($I \sim 1$ nA with 1 nm tip sample distance) though may flow between tip and sample. The resulting tunneling current is a function of tip position, the applied voltage, and the local density of states (LDOS) of the sample, this information is displayed on the computer monitor as 2D color mapped image.

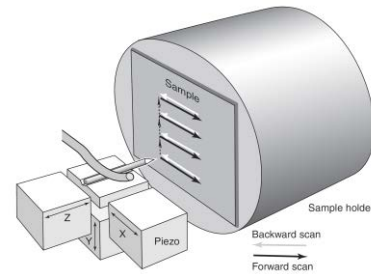


Fig. 4: Sketch of the piezo electric device driving the tip movement.

Task 2: Investigate the tunneling effect at HOPG and Gold by Scanning Tunneling Spectroscopy (Current-Distance-Spectroscopy).

The strength of the tunneling current I depends exponentially on the distance between the tip and the sample (d_z), usually referred to as z-distance and the applied bias (U). From Schrödinger's equation one can find that


$$I = f(U) \exp(-A\sqrt{\phi}d_z) \quad [1]$$

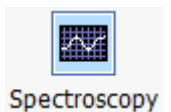
where

$$A = 2\sqrt{\frac{2m_e}{\hbar^2}} = 10.25 \text{ nm}^{-1} \text{ eV}^{-0.5}.$$

Here ϕ is the effective work function. This is an actual workfunction mainly influenced by surface adsorbates and the high electrical field density at the tip.

The extreme dependence on the distance makes it possible to measure the tip-sample movement very precisely. By keeping the tip voltage constant and measuring the tunnel current I in dependency of d_z the effective work function can be determined by fitting an exponential function to the measured tunnel current [1]. Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create uncertainty and errors in the expected values of your measurements.

To evaluate [1] the following procedure can be used: After grabbing a good image switch to the Spectroscopy mode by clicking the "Spectroscopy" button in the navigator, or by clicking  Spec in the Imaging bar. In a spectroscopic measurement, the tunneling current is measured as a function of either the z-distance or the tip voltage. To determine the work function select "Z-Axis" as modulated output. Pin down values of your measurement parameters accurately. If you



experience problems in measuring the desired behavior, try to adjust your parameter values. For example you can start experimenting with the following set of parameters for HOPG:

- Set point 0.5 nA
- P-Gain 500
- I-Gain 500
- Tip voltage 0.1 V
- Start value 0 nm
- End Value -5 nm
- Modulation time 0.2 s
- Data points 128
- Averages 16

By using this set of parameters, the device will divide the distance from 0nm to -5nm from the current tip position into 128 points and measure the tunnel current at each of them. The time used for one series of measurements is 0.2 s. This process will be repeated 16 times. The resulting curve is the average of the 16 measurements.

Notice:

- When measuring on gold you will need higher gain values than for HOPG
- Positive Start and End values will bring the tip closer to the surface: 1 nm will change the tunnel current about 1 order of magnitude!
- High tunnel currents may influence the structure of the tip and/or the surface. Therefore try choosing a lower set point or lower start and end values if you receive high currents (>20nA) and the curve is not exponential.
- As long as you are in the spectroscopy mode the piezo controllers are inactive. Because of thermal drift you might receive different results when measuring the same point multiple times, especially when using high resolutions. Also modifications of the local tip geometry can occur during the measuring procedure indicated by noisy and “jumpy” spectra. Therefore check the topography after every spectroscopic measurements to evaluate the results.

To evaluate the exponential correlation between tunneling current and d_z click “Point” in spectroscopy mode and select a point in the topography. Now press the “Start” button. After a few seconds the end of the measurement is indicated when the “Stop” button changes back to “Start” and when your data curve doesn’t change anymore. The “Probe Status” should be green during the whole measurement. If the “Probe Status” changes to orange switch to the “Imaging Window” approach the sample again and take a new surface scan, afterwards switch back to the “Spectroscopy” window.

After the measurement is finished you should already be able to identify a exponential curve in the line graph. Now you can rightclick the graph and select “Copy data to clipboard” (Fig. 5) and paste the data in PHYWE *measure* analysis software by pressing ctrl+v. Here you can fit an exponential function by clicking “Analysis” → “Function fitting” and selecting “exponential function” in the uppermost drop-down dialog (Fig. 6). Now click “calculate” to receive fitting parameters and “Add new curve” to draw the calculated curve into the diagram.

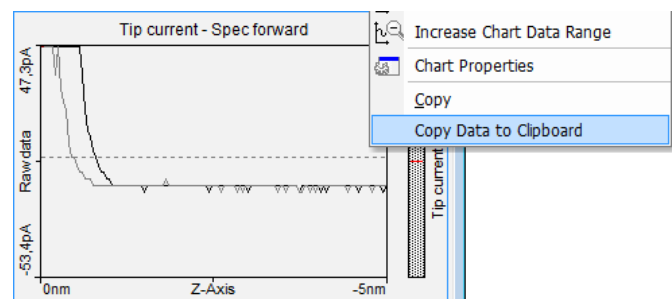


Fig. 5: Sketch of the dual-line graph

You should be able to see the exponential function fits the measured data pretty good. One can assume the exponential correlation is correct.

Furthermore you can determine the effective workfunction for we know for our fit parameter $b = A\sqrt{\phi}$ and therefore

$$\phi = \frac{b^2}{A^2} \cdot 1$$

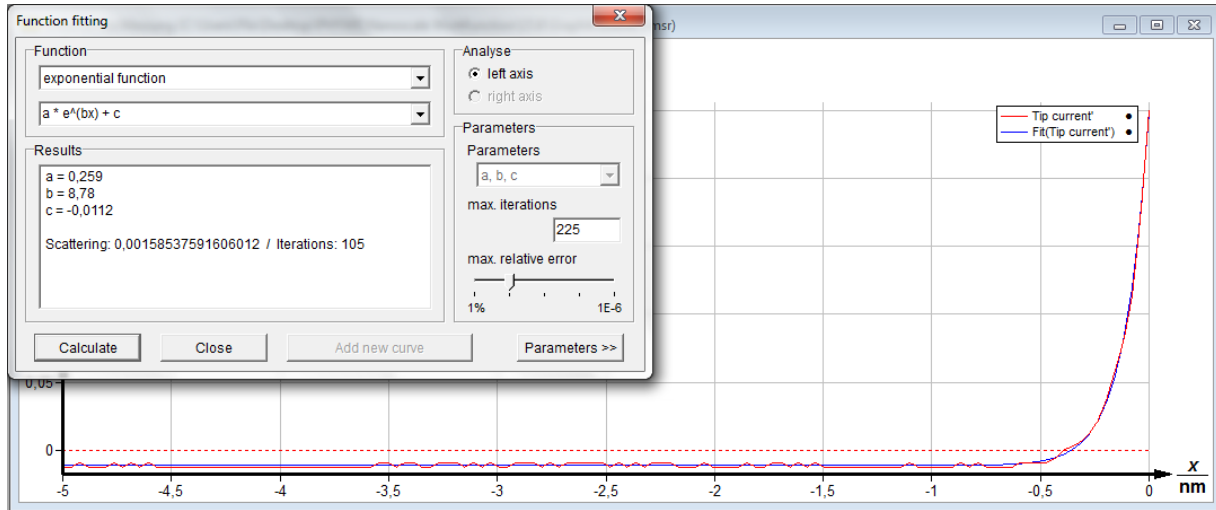


Fig. 6: Function fitting window in PHYWE measure

Task 3: Imaging and characterization of charge density waves at different substrates. Interpret the results regarding to the bandstructure.

Charge Density Waves (CDW)

Low Dimensional metals (quasi-1D or 2D) can undergo a phase transition involving electron phonon coupling. Hereby the atoms of the lattice change their equilibrium position. This is only possible if the cost of elastic energy needed for this deformation is compensated by the gain of the electron energy. The phase transition results in a new electronic band structure and periodicity of the lattice. CDW are interesting for a couple of reasons including the propose that such a state could lead to superconductivity and a special AC/DC response.

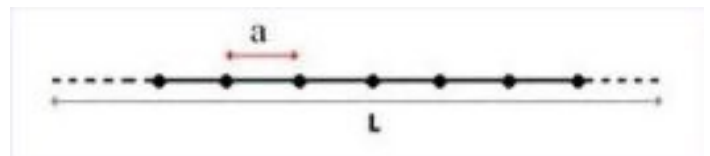


Fig. 7: Lattice with Period a

Fig. 7 shows a 1D-lattice with lattice parameter a. A possible second state is shown in Fig. 8. Here the atoms are successively displaced left or right by $b \ll a$. The new Lattice Parameter is $2a$. Other displacements with different lattice parameter are possible, too. Eventual, the lattice will configure in the energetically most favorable setting. That is also the reason why only certain materials are observed to form CDW.

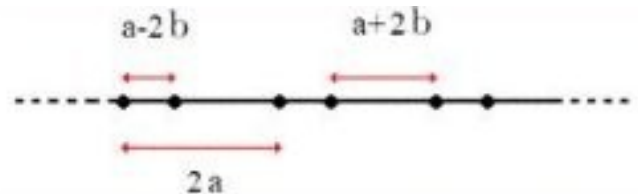


Fig. 8: Lattice after displacement of atoms

Rudolf Peierls was the first one to explain this effect: In one dimension the periodicity of the crystal creates energy band gaps in the $E(k)$ diagram at multiples of the value $k = \pi/a$. In the model the ions each contribute one electron, then the band will be filled up to the Fermi-energy E_F i.e. up to values of $k_F = \pm\pi/2a$ in the ground state as shown in Fig. 9 (a).

¹ For details see „Nanoscale workfunction measurements by scanning tunnel spectroscopy“ by PHYWE

If the lattice period changes to $2a$ by lattice distortions as in Fig. 9 (b), this has the effect of introducing new band gaps at $k = \pi/2a$. This causes the electrons to be at lower energy than in the original lattice. Hence, this lattice distortion becomes energetically favorable when the energy savings because of the new band gaps is larger than the elastic energy cost of the lattice deformation. This effect will only be noticeable when the electrons are arranged in states close to the ground state meaning the lattice needs to be under a characteristic temperature, the Peierls temperature.

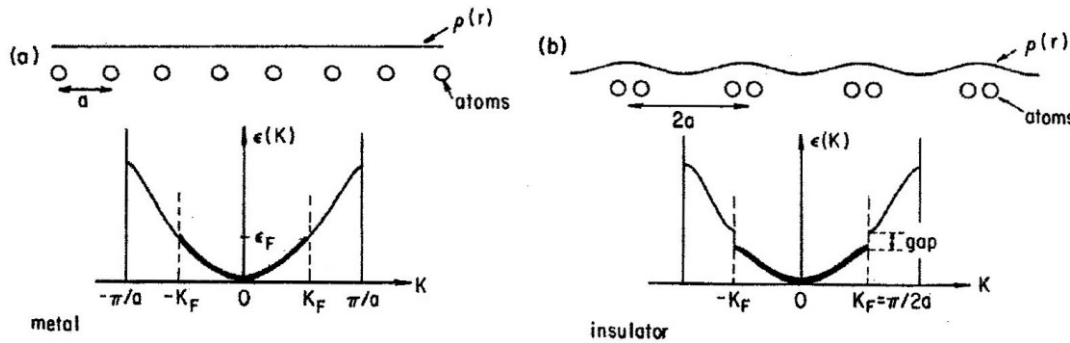


Fig. 9: Band structure of a 1D-lattice with Period a

As we can see also from Fig. 9 the CDW state leads to a transition from a conductor to a semiconductor (insulator) because of the new bandgap.

Although CDW typically are an one dimensional effect they can occur in higher dimensions. However the theoretical background is much more complex.

CDW on TaS₂

TaS₂ is a transition metal chalcogenide in the 1T phase. This means each layer of Ta is packed between layers of S as shown in Fig. 10. The weak van-der Waals bonding between the single layers are the reason for CDW in the two dimensional layers.

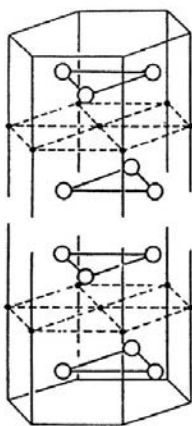


Fig. 10: Layer packing of samples

O: S
·: Ta

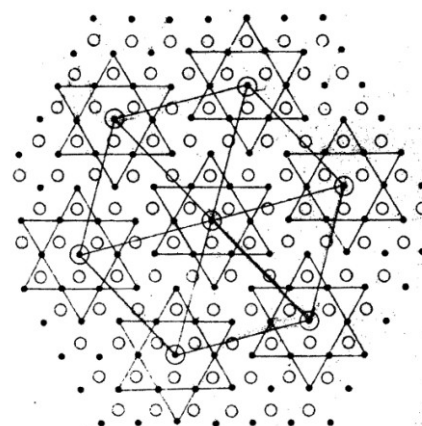


Fig. 11: Nearly commensurate phase CDW on TaS₂

O: S
·: Ta


The CDW can form a commensurate or incommensurate superlattice. Commensurate means the ratio between CDW period and atomic lattice period is rational whereas it is incommensurate when it's irra-

tional. Furthermore semicomensurable phases are possible in which there are areas with commensurable period as well as incommensurable.

Below 183K TaS₂ forms a commensurable phase. Between 183K and 353K TaS₂ forms a commensurable phase and an incommensurable $\sqrt{13} \times \sqrt{13}$ superlattice. This nearly commensurable phase is what we will observe and is shown in Fig. 11. Above 353K TaS₂ forms an incommensurable phase.

The new setting of the electrons can be directly investigated by STM. In the scans the CDW superimposes the atomic structure. To see both structures it is needed to bring the tip very close to the sample surface.

The recommended procedure to achieve good scans is:

1. Prepare a tip and do a surface scan on HOPG to check if the tip is good by resolving single atoms (set point=1nA; tip voltage=50mV)
2. Change to a sample which forms CDW
3. Set image size to approximately 100nm, tip voltage to 20mV, set point to 4nA and approach the sample
4. You should see terrace like structures (comp. fig. 12), if not try using the “cleaning pulse” button or withdraw the sample and reapproach a different spot on the sample
5. Zooming into a clean terrace, you should be able to see the CDW at a resolution of about (30nm)² (fig. 13)
6. Continue zooming into an area with high periodicity until you receive the desired resolution
7. To obtain atomic resolution it is needed to increase the set point up to about 30nA (withdraw and reapproach the sample). When increasing the set point remember decreasing the I- and P-gain respectively.
8. When obtaining the desired image adjust the gain values to smooth the image. You can also try to increase the points / line for even better scan quality. When you are satisfied grab a good image by clicking the  Photo button.
9. Now you can apply some filters to reduce noise, adjust scan line levels and remove a background distortion. The recommended procedure would be:
 - Apply glitch filter.
 - Apply noise filter.
 - Do a background subtraction and/or correct scan line levels

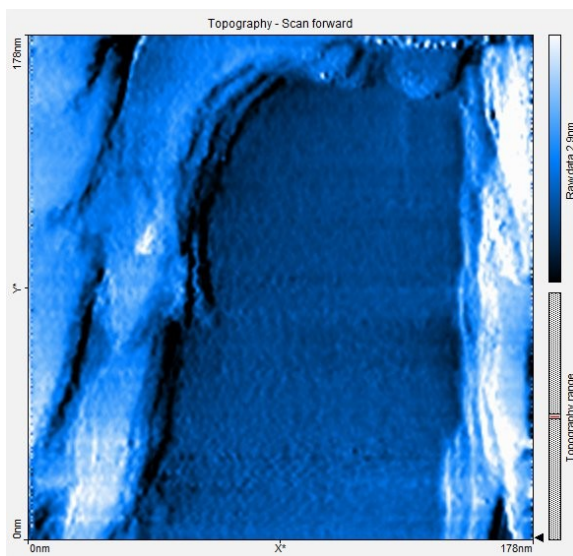


Fig. 12: Surface of TaS₂

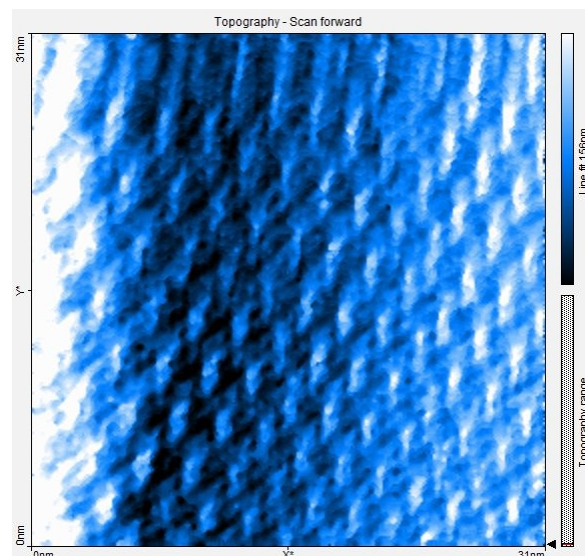



Fig. 13: CDW at (31nm)²

In theory the lattice parameter of TaS₂ is $a = 3.346 \text{ \AA}$. From the scan shown in fig. 13 one can determine the measured lattice parameter and period of CDW e.g. by using the

Measure Length tool .

As shown in fig. 15 we receive a mean horizontal period of $a_h = 3.433 \text{ \AA}$ and a vertical period of $a_v = 4.633 \text{ \AA}$. The mean period of the CDW maxima is 1.216 nm horizontally and 2,078 nm vertically leading to lattice periods $a_h' = 1.216 \text{ nm} / \sqrt{13} = 3,377 \text{ \AA}$ and $a_v' = 2.078 \text{ nm} / \sqrt{13} = 5.772 \text{ \AA}$.

Furthermore we can measure the angles of the structure using the *Measure Angle* tool  as in fig. 16. We receive an angle of 109.5° between the maxima of the CDW. From fig. 11 we know the angle between the hexagonal arranged CDW maxima is 120°.

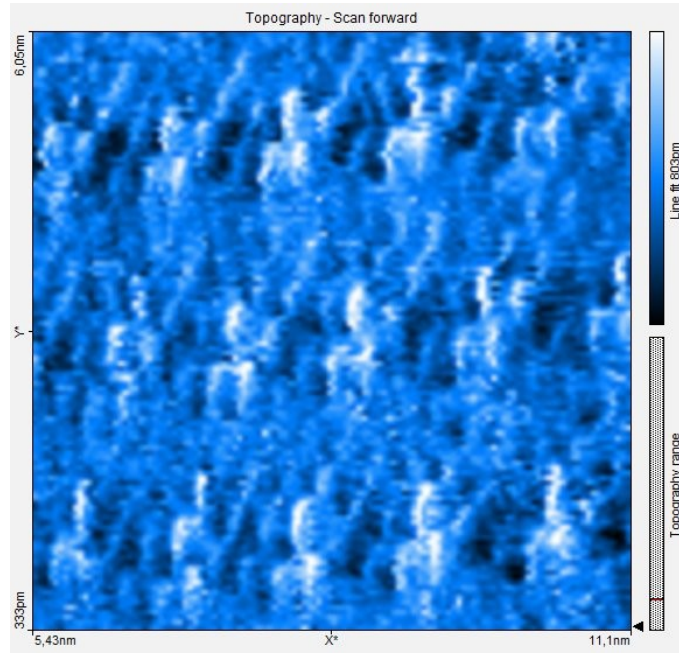


Fig. 14: CDW on TaS₂

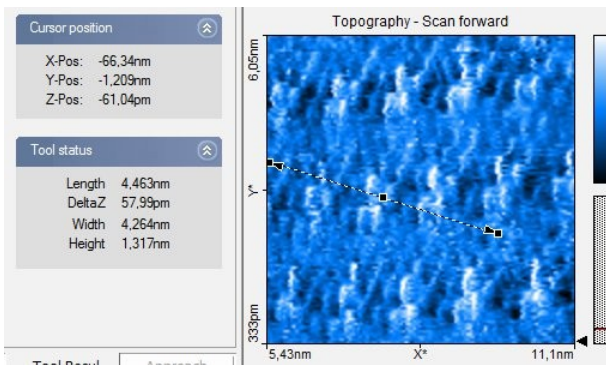


Fig. 15: Length measurement spanning 13a

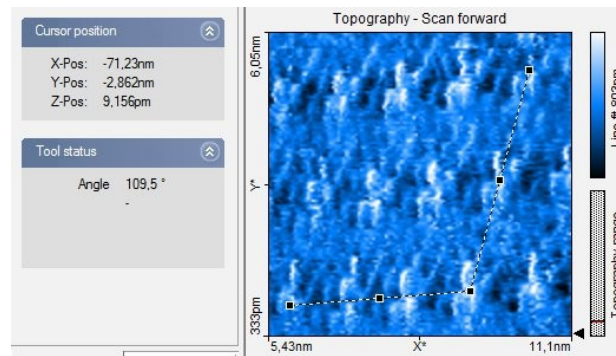


Fig. 16: Angle measurements of CDW maxima

Both, lattice period and angle measurement indicate that our scan is deformed. From the lattice period we know that the scan is ok in horizontal orientation but not in vertical. This could be reasoned by a not perfectly shaped tip, the thermal drift of the sample, which plays an important role at atomic resolution, creep or piezo in-linearity. The reason for the last point is that piezo crystals only move slowly into an equilibrium position after their elongation has been changed.

Task 4: . Investigate in charge density waves at different voltages and interpret the imaged states (filled and empty).

In the theory the band structure of the two dimensional sample is split up into three different bands instead of two as in the one dimensional case. This has the effect that the DOS is not very symmetrical around E_F . Only for higher energies the DOS becomes nearly symmetrical and is mainly leading to a contrast inversion when the bias voltage is inverted as shown in fig. 17. Here the positive tip voltage images the filled states whereas the negative tip voltage images the empty states.

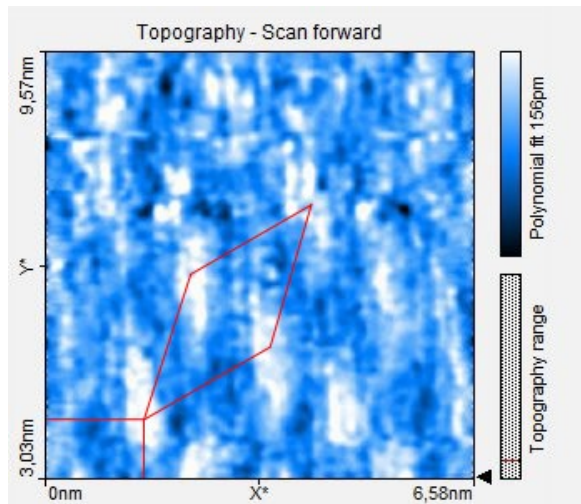


Fig. 17(a): CDW at +30mV tip voltage

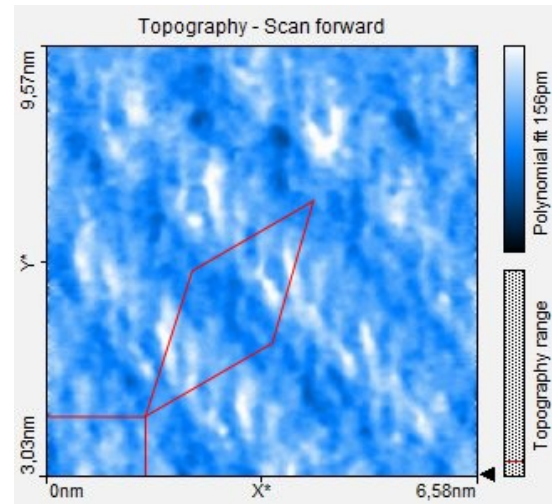


Fig. 17(b): CDW at -30mV tip voltage at same location

For lower bias voltages the CDW can appear similar to 17(a) or (b), or even just as an array of dark spots.

Conclusion

All our measurements reflect the theory very good. Mainly image deformations lead to deviations in the tomic lattice and CDW periods.

All measurements done on TaS₂ can also be done analogously on other CDW forming materials such as WSe₂, another transition metal chalcogenide.

Related Topics

Tunneling effect, Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), Local Density of States (LDOS), Band structure, Band Gap, k-Space, Brioullin Zone, Metal, Semi-Metal, Semiconductor

Principle

The tunneling current between a very sharp metal tip and an electrically conductive sample is used to investigate the current-voltage characteristics at a nanoscopic scale. The bandstructure of gold, graphite (HOPG) and MoS₂ are investigated.

Caution!

- Set up your system on a very steady table
- Do your experiments in a calm, vibrational free environment

Equipment

- | | | |
|---|---|----------|
| 1 | Compact-Scanning Tunneling Microscope, complete set incl. tools, sample kit and consumables, in aluminum case | 09600-99 |
| 1 | MoS ₂ sample | 09609-00 |

Additionally needed

- | | |
|---|--|
| 1 | PC, Windows® XP or higher
Adhesive tape
PHYWE <i>measure</i> |
|---|--|

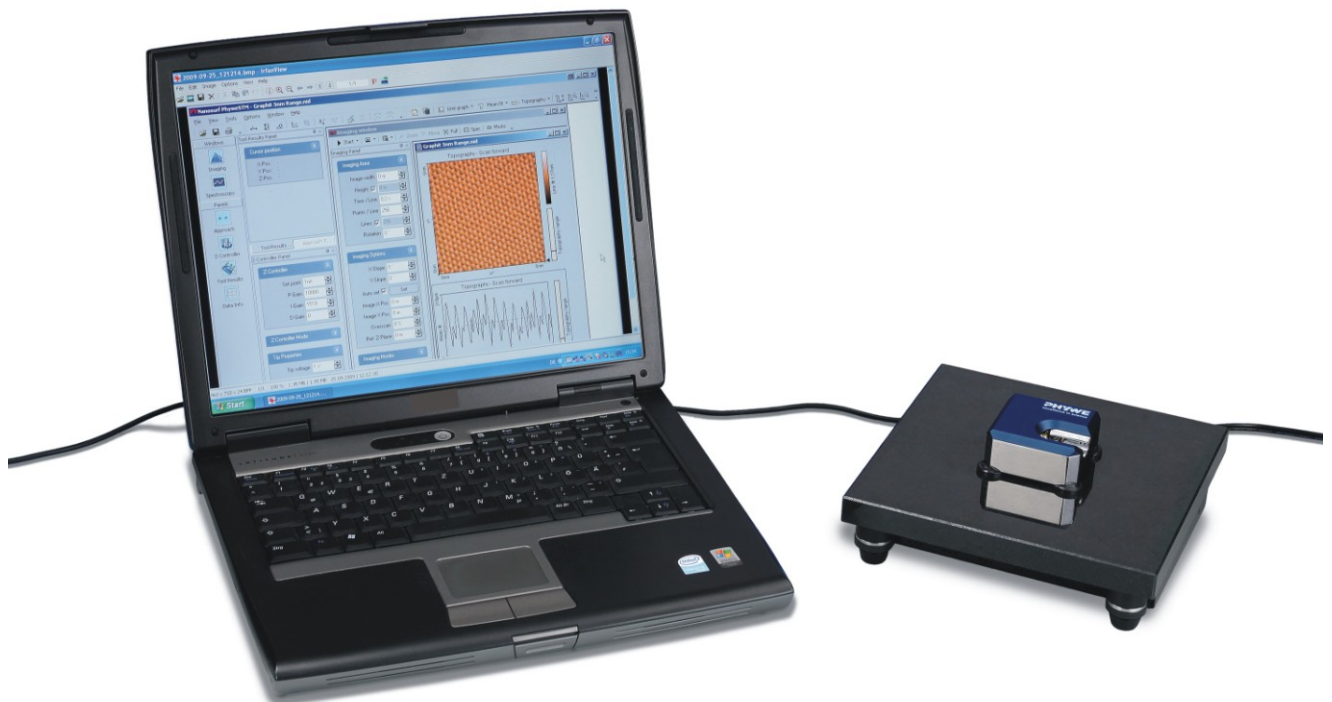


Fig. 1: Experimental setup.

PHYWE Compact-STM set

- | | |
|---|------|
| 1 Control unit with mounted scan head | (1) |
| 1 Magnifying cover glass (10X Magnification) | (2) |
| 1 USB cable | (3) |
| 1 Power cord and adapter | (4) |
| 1 MeasureNano Software | (5) |
| 1 PHYWE STM Tool Box: | |
| 1 Wire cutter | (6) |
| 1 Flat nose pliers | (7) |
| 1 Pointed tweezers | (8) |
| 1 Rounded tweezers | (9) |
| 1 Pt/Ir-wire, $d = 0.25 \text{ mm}$, $l = 30 \text{ cm}$ | (10) |
| 1 Sample Holder | (11) |
| 1 Graphite sample (HOPG) | (12) |
| 1 Gold sample | (13) |
| 4 Spare sample support | (14) |
| 1 Scanning Tunneling Microscopy (STM) –
Operating Instructions and Experiments | (15) |



Fig. 2: Content of 09600-99.

Tasks

1. Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.
2. Investigate the topography of the gold, HOPG and MoS_2 sample in constant-current mode.
3. Switch to spectroscopy mode. Measure and compare images recorded on the different materials in Tip-voltage mode (I-U spectroscopy).
4. Interpret the results regarding to the bandstructure.

Set-up and Procedure**Task 1: Prepare a Pt-Ir tip and the sample surfaces. Approaching the tip towards the sample.**

For preparation of tunneling tips and the approaching procedure please refer to experiment *P2532000 "Atomic Resolution of the graphite surface by STM"*, the quick start guide (QSG), or, the operating manual (OM), Chapter 5. You'll find an electronic version of the QSG and OM under the help menu of the measure nano software.

In most cases it is enough to cleave the graphite sample once in a few weeks. If you have problems to find a clean area or you don't get good images with several freshly prepared tips, clean the sample surface using scotch tape as described in the QSG or OM.

The gold sample normally need not to be cleaned. However, if you experience bad scans throughout or accidentally touched the sample you can lay a lint-free cloth on top of the sample surface and drip some alcohol on it. Remove the wet cloth by carefully wiping and wait until the alcohol has dried completely. To avoid any scratches or other irreversible surface modifications it is important that the surface does not experience pressure at any time!

Normally the MoS_2 sample have not to be prepared by a special procedure. If you still have problems to image the surfaces carefully cleave the samples with the scotch tape method.

Theory and Evaluation

Tunneling

Tunneling is a functioning concept that arises from quantum mechanics. Classically, an object hitting an impenetrable barrier will not pass through. In contrast, objects with a very small mass such as the electron, have wavelike characteristics which permit such an event, referred to as tunneling. In other words, the probability to find an electron behind a barrier is unequal zero. Inside the barrier the wave function of the electron decays exponentially (Fig. 3).

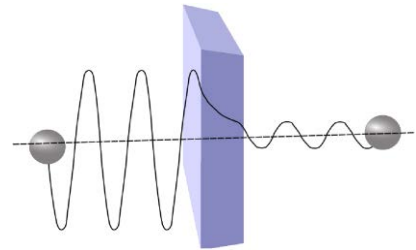


Fig. 3: Sketch of the tunneling of an electron through a barrier.

STM – Scanning Tunneling Microscopy

The size of an atom in relation to the tip is that of a golf ball to a mountain. In your PHYWE measurement system a platinum-iridium tip is moved in three dimensions using piezo crystal translators that are driven with sub-nanometer precision (Fig. 4). The sample to be examined approaches the tip within a distance of about 1 nanometer (1 nm = 1/1,000,000,000 m). Classical physics would prohibit the appearance of electrons in the small gap between the tip and the sample, but if a sharp tip and a conducting surface are put under a low voltage ($U \sim 0.1$ V), a very small tunneling current ($I \sim 1$ nA with 1 nm tip sample distance) though may flow between tip and sample.

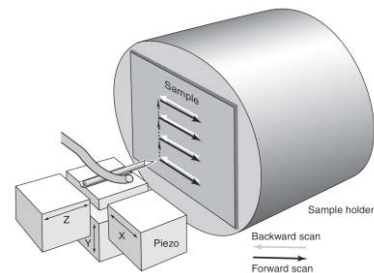


Fig. 4: Sketch of the piezo electric device driving the tip movement.

The resulting tunneling current is a function of tip position, the applied voltage, and the local density of states (LDOS) of the sample, this information is displayed on the computer monitor as 2D color mapped image.

The strength of the tunneling current depends exponentially on the distance between the tip and the sample (d_z), usually referred to as z-distance, the applied bias (U) and constant factors (c_1 and c_2)

$$I = c_1 U \exp(c_2 d_z) \quad [1]$$

In $I(U)$ -spectroscopy the distance between tip and sample is constant. Only the applied voltage is changed. Regarding [1] one would expect a linear curve from the spectroscopic measurement. However, the results differ from the expectation because of the band structure of the investigated materials.

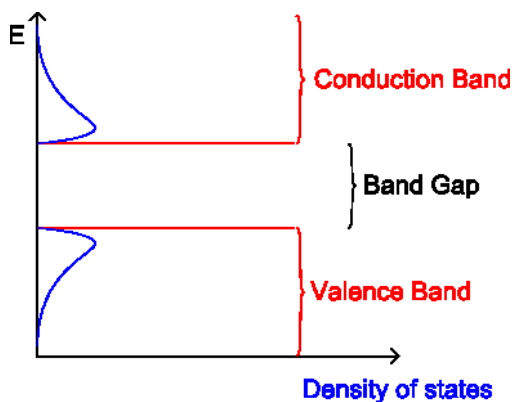


Fig. 5: Sketch of the band structure of an insulator/semi conductor

The electrons of a single atom can occupy discrete energy levels forming atomic orbitals. Several atoms together into a molecule will form molecular orbitals. The number of molecular orbitals is proportional to the number of atoms in the molecule.

When large numbers of atoms ($>10^{20}$) are brought together to form a solid there are large numbers of energy levels occupied by electrons and the difference between them becomes very small, forming energy bands. However depending on the atoms forming the solid there are energy intervals which cannot be occupied by electrons no matter how many atoms are aggregated. Such intervals are called band gaps (Fig. 5). Band gaps only occur at semi conductors (small band gap < 3 eV) and insulator (large band gap). Solids which have no band gap, meaning Conduction band and Valence band overlap, are called conductors.

Regarded in detail, the electronic band structure of a solid is very complex. It depends on the properties of the underlying crystal lattice and is described by graphs as shown in Fig. 6.

Here the energy is plotted as a function of the wave vector k , which describes the motion of the electrons in the lattice. The wavevector k takes on values within the Brillouin Zone, which is a model to describe unit cells, corresponding to the crystal lattice. Particular directions/points in the Brillouin Zone are assigned conventional names like Γ , Δ , Λ , Σ , etc. The areas, electrons are allowed to be are highlighted grey.

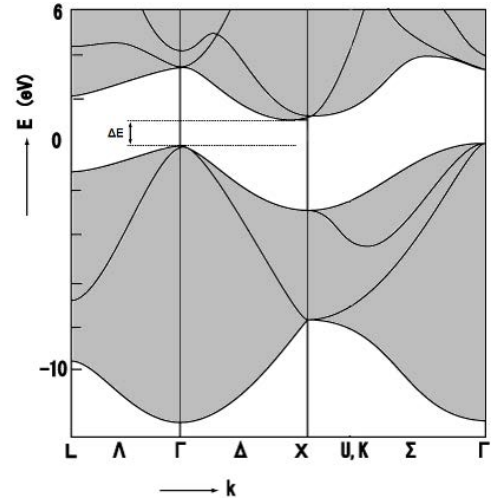


Fig. 6: Reduced band structure of Si with marked bandgap ΔE

Regarding the possible configurations in Fig. 7 one can see the difference between the different types of conductors. The materials used in our measurements are a conductor/metal (gold), a semi conductor (MoS_2) and a semi metal (HOPG).

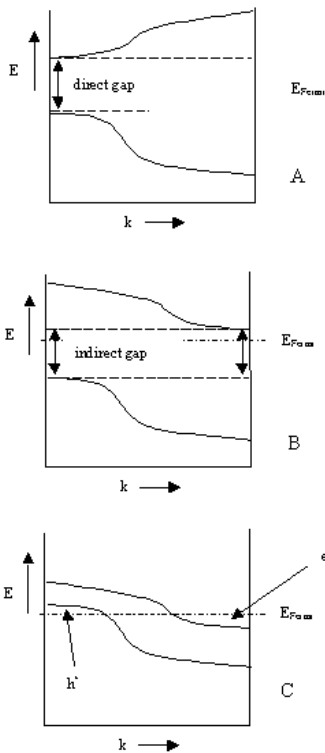


Fig. 7:
 A: Direct band gap semi conductor
 B: Indirect bandgap semi conductor
 C: Semi metal

The electron distribution among the allowed energies is determined by the local density of states (LDOS). The LDOS is a space-resolved description of the number of states at each energy level which are available to be occupied in a electronic system. The LDOS is proportional to the slope of the characteristic curve received from $I(U)$ -Spectroscopy when regarding the tip's density of states to be with no structure. We will use this to image the band structure of (semi-)conductors. The measured curves are an overlay of the bands in the corresponding band schematic. The expected results are shown in Fig. 8.



	Metal	Semi-Metal	Semiconductor
Electronic Structure			
I-V			
dI/dV			

Fig. 8: Properties of different kinds of conductors

Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create uncertainty and errors in the expected values of your measurements.

Task 2 and 3: Investigate the topography of the gold, HOPG and MoS₂ sample in constant-current mode. Switch to spectroscopy mode. Measure and compare images recorded on the different materials in Tip-voltage mode (I-U spectroscopy).

Investigation of band structure

The procedure imaging the I(U)-spectroscopy curve is the same for all three samples. After you approached the sample click the  Full button in the imaging window to activate the full measurement range. Now Zoom in to atomic resolution to check the tip. Adjust the parameters so that you can see a detailed picture of the surface. You can save the picture by clicking the  Photo button. If you do, you can apply some filters to reduce noise, adjust scan line levels and remove a background distortion.

The recommended procedure would be:

- Apply glitch filter.
- Apply noise filter.
- Do a background correction and/or correct scan line levels.

The samples surfaces are shown in Fig. 9, 11 and 13. Furthermore the corresponding reduced band structures are shown in Fig. 10, 12 and 14.

Change back to full measurement range and switch to the spectroscopy mode. Choose “Tip voltage” as modulated output to record an I(U)-curve in a plane region. Pin down values of your measurement parameters accurately. If you experience problems in measuring the desired behavior, try to adjust your parameter values. For example you can start experimenting with the following set of parameters:

- Set point 1.0 nA
- P-Gain 1000
- I-Gain 2000
- Tip voltage 0.05 V
- Start value -0.5 V
- End Value 0.5 V
- Modulation time 0.2 s
- Data points 128
- Averages 16

By using this set of parameters, the device will divide the interval from -0.5 V to 0.5 V into 128 points and measure the tunnel current at each of them. The time used for one series of measurements is 0.2 s. This process will be repeated 16 times. The resulting curve is the average of the 16 measurements.

Notice:

- The device may cut off the graphs due to high tunnel currents. In this case adjust your Parameters to decrease the current (e.g. lower set point)
- High tunnel currents may also influence the structure of the tip and/or the surface. Therefore try choosing a lower set point or lower start and end values if the curve looks not as expected
- As long as you are in the spectroscopy mode the piezo controllers are inactive. Because of thermal drift you might receive different results when measuring the same point multiple times, especially when using high resolutions. Also modifications of the local tip geometry can occur during the measuring procedure indicated by noisy and “jumpy” spectra. Therefore check the topography after every spectroscopic measurements to evaluate the results.

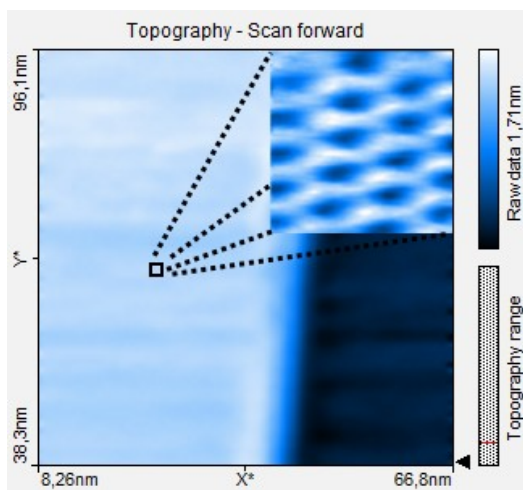


Fig. 9: Topography of HOPG

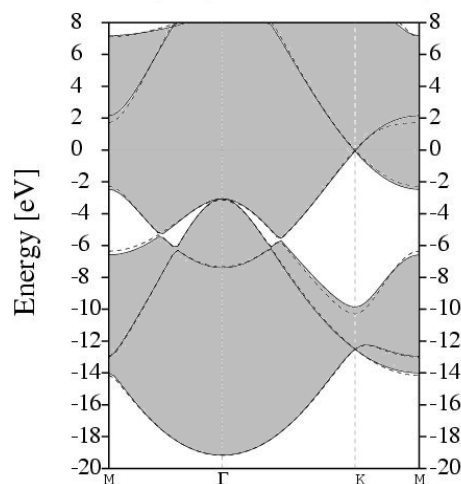


Fig. 10: Reduced band structure of HOPG

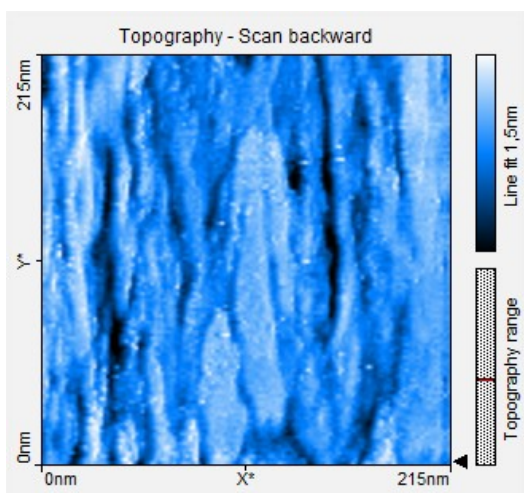


Fig. 11: Topography of gold

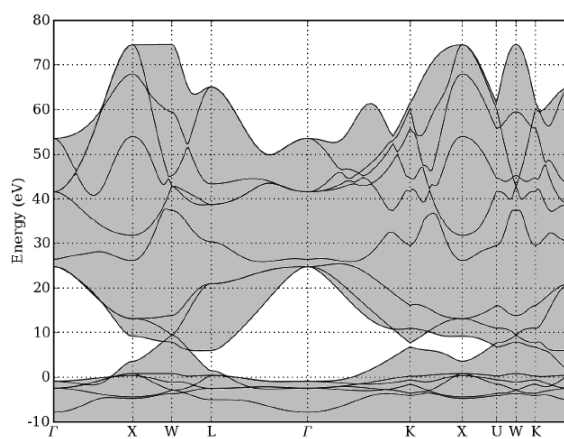


Fig. 12: Reduced band structure of gold

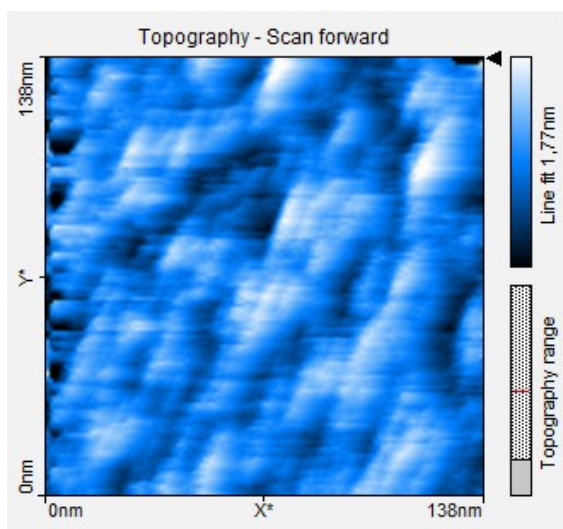


Fig. 13: Topography of MoS₂

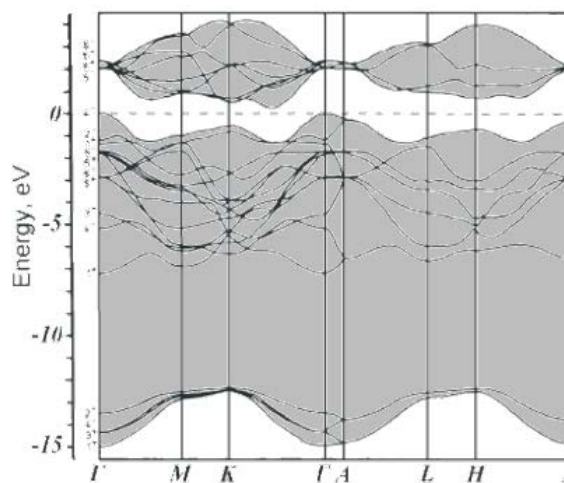


Fig. 14: Reduced band structure of MoS₂

Prepare a measurement by clicking on “Point” and putting the cursor on the surface of your scanned image where you want to take the spectroscopy data. Press the “Start” button. After a few seconds the end of the measurement is indicated when the “Stop” button changes back to “Start” and when your data curve doesn’t change anymore. The “Probe Status” should be green during the whole measurement. If the “Probe Status” changes to orange switch to the “Imaging Window” approach the sample again and take a new surface scan, afterwards switch back to the “Spectroscopy” window.

After the measurement is finished you can see the $I(U)$ -curve in the line graph. If your curve does not look as desired repeat the measurement by pressing “start” again. If you still don’t get the desired curves switch back to the imaging mode and repeat the process. To analyze the current-voltage curves right-click the line graph and click “Copy data to clipboard”. Now open the analyzing software PHYWE *measure* and paste the data by pressing $\text{ctrl}+\text{v}$ or using “Measurement” → “Import Data”. You should receive a graph as shown in Fig. 15.

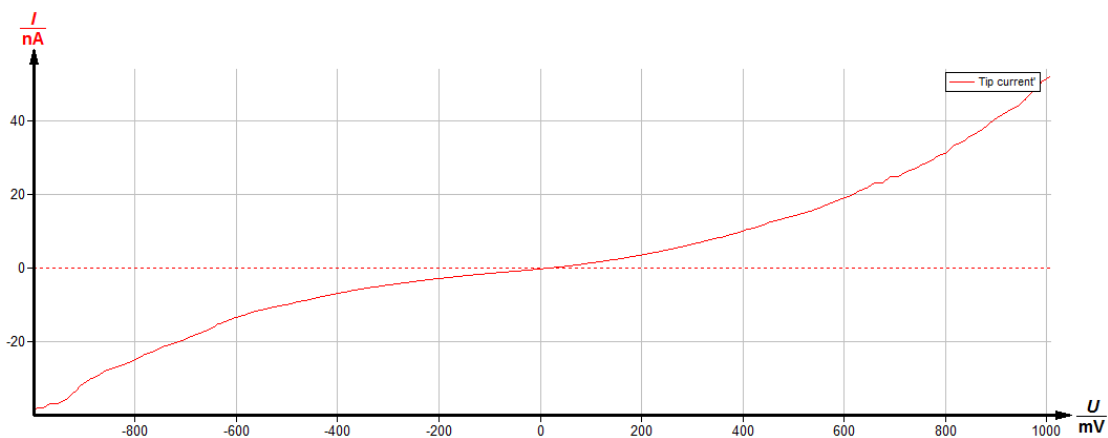


Fig. 15: $I(U)$ -spectroscopy curve of HOPG

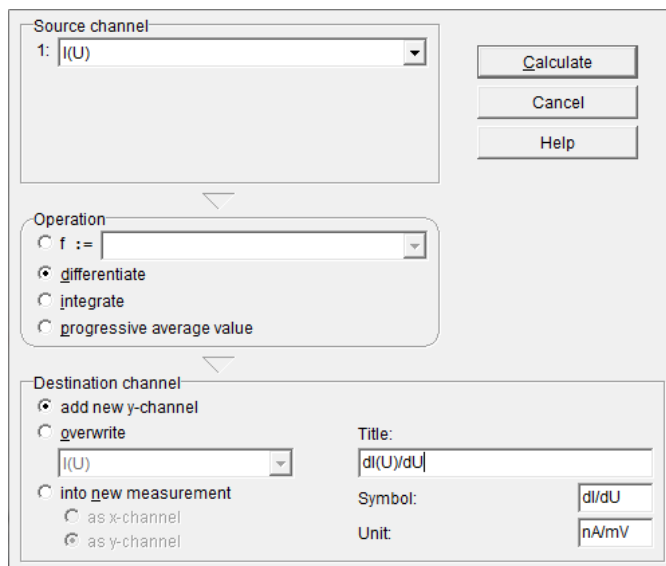


Fig. 16: Channel modification window

The derivate of the $I(U)$ curve is called specific resistivity and is proportional to the LDOS. To analyze the derivate it is recommended to smooth the curve first. Therefore go to “Analysis” → “Smooth”. Choose the strongest smoothing and overwrite the existent curve. Repeat the smoothing until you receive an appropriate curve as shown in the graphs. Now go to “Analysis” → “Channel Modification” and choose “differentiate” (Fig. 16). Now you can see the corresponding curve proportional to the LDOS.

Apply the spectroscopy mode on the other samples in the same way and compare the results. The resulting curves are shown in Fig. 17-20. Note: The x-axis are zoomed in a bit (use mousewheel on x-axis) because the smoothing process distorts the data at the edges.

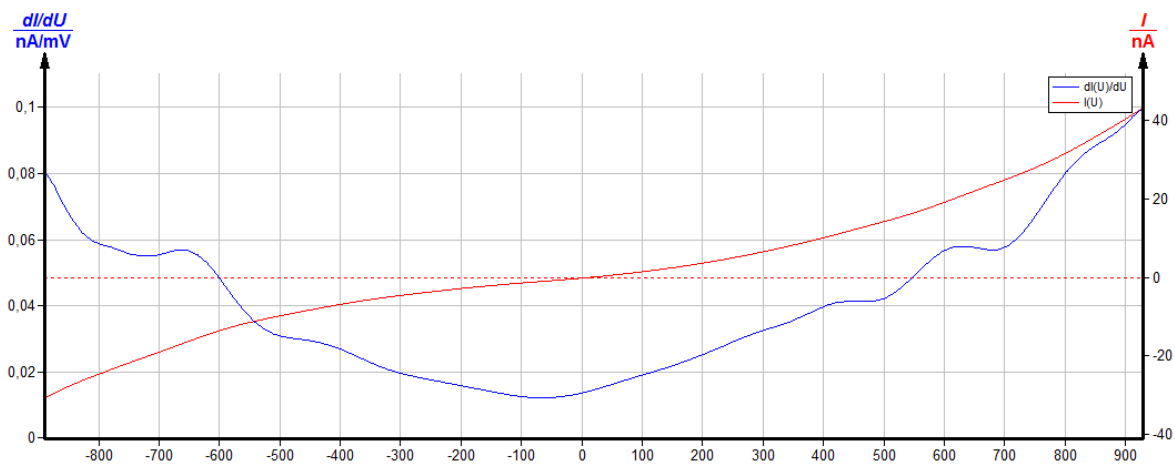


Fig. 17: Specific resistivity of HOPG

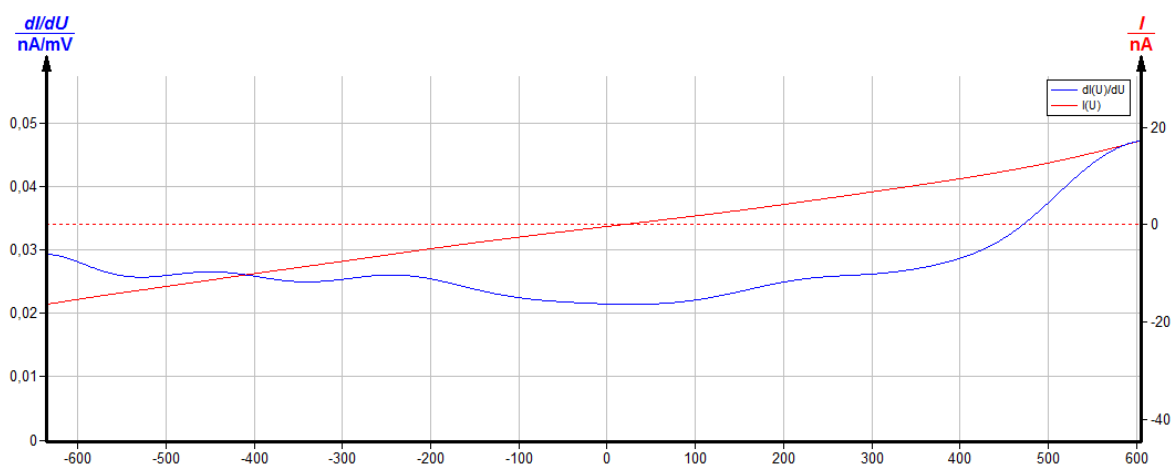


Fig. 18: Specific resistivity of gold

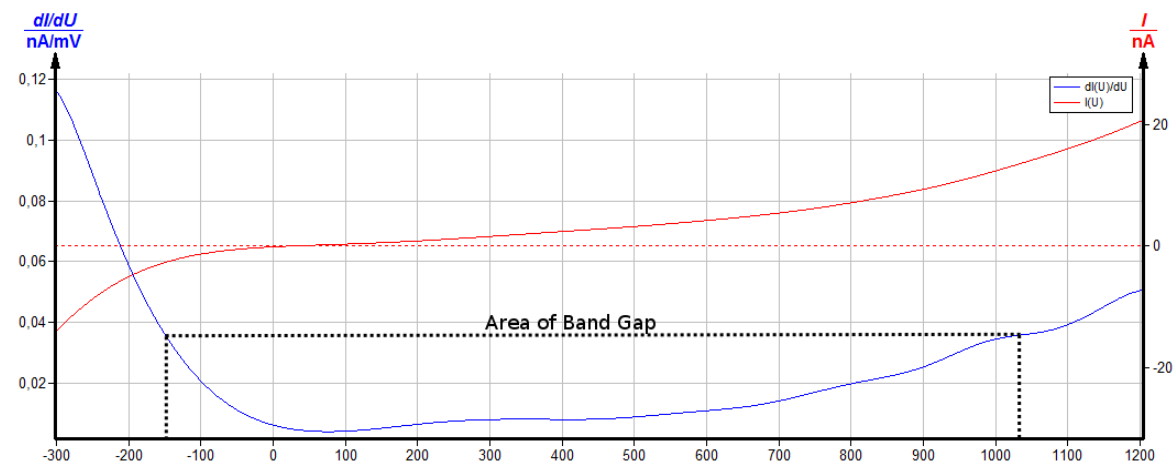


Fig. 19: Specific resistivity of MoS2 with marked band gap

Task 4: Interpret the results regarding to the bandstructure.

The first thing we see is that the LDOS of gold is described by a linear curve, while HOPG and MoS₂ are not.

This is the result of gold being a conductor. This means it has no band gap due to the valence and conduction band overlap, meaning electrons can move freely along the metal. The I(U)-spectroscopy-curve therefore images Ohm's law $U=RI$.

Regarding the band structure of HOPG and MoS₂ one sees there are regions where the LDOS is near zero. These regions are where the band gaps are. Theoretically we would expect the LDOS to be exactly zero, but impurities and the non ideal measurement environment (air, high temperature) influences the recorded data here.

Furthermore one sees the characteristics of the two curves (e.g. extrema) differ. Especially remarkable is that the curve of Graphite is approximately symmetric to 0V, whereas the curve of MoS₂ is not symmetric at all. This comes from the underlying band structure.

MoS₂ has two band gaps at 1.29V and 1.95V. We cannot image the 1.95V gap, because our voltage range is too limited, but the 1.29V gap can be seen in Fig. 19.

We have determined typical properties of (semi-)conductors from which we can determine the kind of a material by just seeing its I(U)-spectroscopy-curve.

This experiment demonstrates the potential of the scanning tunneling microscope to investigate not only the electrical characteristics in general but also at the nanoscopic scale. Especially for artificial nanostructures STS can be used to investigate the electrical characteristics.

Related Topics

Tunneling effect, Scanning Tunneling Microscopy (STM), Nano morphology, Roughness, Coining, Rolling, Tempering, Growing, Polishing, Etching

Principle

One crucial requirement for a successful functionalization of surfaces at the nanometer scale is their morphology at this scale. The tunneling current between a metallic tip and different metal surfaces is used to investigate the morphology on a nanoscopic scale of the samples by scanning across the surface and image the electronic topography. The samples have undergone different processes like coining, tempering, etching, polishing, etc and therefore their nano morphology widely varies while on a macroscopic scale the sample surfaces appear similar.

Caution!

Set up your system on a very steady table. Do your experiments in a calm, vibrational free environment

Equipment

1	Compact-Scanning Tunneling Microscope, complete set incl. tools, sample kit and consumables, in aluminum case	09600-99
1	Set samples nanomorphology	09613-00

Additionally needed

PC, Windows® XP or higher

Adhesive tape

Acetone, Alcohol and cleaning cloths

For further investigation optionally needed

Polishing of samples (Cu)

1	Microscopic slides, 50 pcs	64691-00
1	Diamond suspension, 1µm, 250g	70042-25

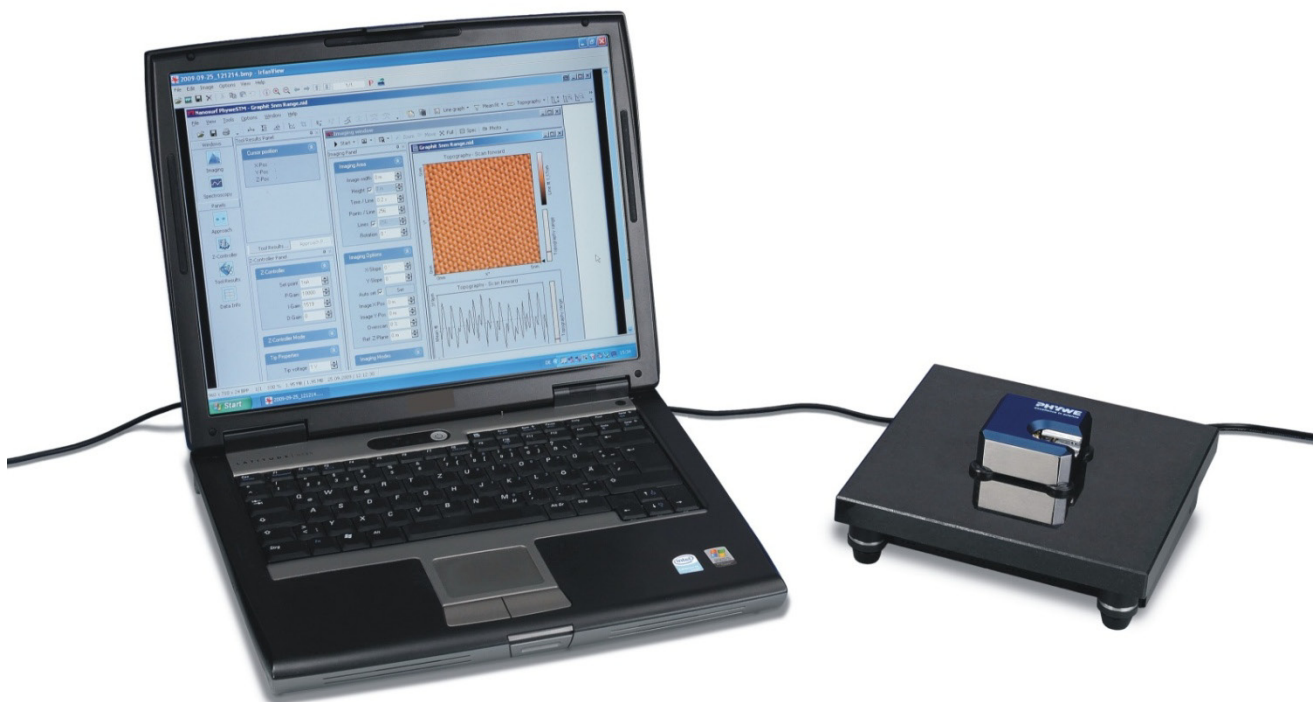


Fig. 1: Set-up of experiment P2537000

1	Diamond suspension, 0.25µm, 250g	70043-25
1	Lubricant RED, 1l	70061-70
1	Cleaning and polishing tissues, pkg. of 50	46417-00
1	Gloves, disposable, pkg. of 100	39175-03
1	Wash bottle, plastic, 1000ml	33932-00
1	Magnifier, 10x, dia. 25mm	87004-10

Etching of samples (Cu)

1	Hydrochloric acid, 30%, 500ml	48451-50
1	Iron-III chloride, 250g	30069-25
1	Safety goggles	46333-01
1	Pasteur pipettes, 3ml, PE, 500pcs.	36616-00
1	Beaker, low, 250ml	46054-00
1	Cleaning and polishing tissues, pkg. of 50	46417-00
1	Protective gloves	46347-00
1	Wash bottle, plastic, 1000ml	33932-00
1	Magnifier, 10x, dia. 25mm	87004-10
1	Water, distilled, 5l	31246-81

PHYWE Compact-STM set 09600-99 (ref. to Fig. 2)

- | | | |
|---|--|------|
| 1 | Control unit with mounted scan head | (1) |
| 1 | Magnifying cover glass (10X Magnification) | (2) |
| 1 | USB cable | (3) |
| 1 | Power cord and adapter | (4) |
| 1 | measureNano Software | (5) |
| 1 | PHYWE STM Tool Box, consisting of | |
| 1 | Wire cutter | (6) |
| 1 | Flat nose pliers | (7) |
| 1 | Pointed tweezers | (8) |
| 1 | Rounded tweezers | (9) |
| 1 | Pt/Ir-wire, $d = 0.25\text{mm}$, $l = 30\text{ cm}^*$ | (10) |
| 1 | Sample Holder | (11) |
| 1 | Graphite sample (HOPG)* | (12) |
| 1 | Gold sample* | (13) |
| 4 | Spare sample support* | (14) |
| 1 | Scanning Tunneling Microscopy (STM) –Operating Instruction and Experiments | (15) |

Tasks

- Preparation of Pt/Ir tunneling tips and different sample surfaces. Approaching the tip towards the sample.
- Investigate the topography of different rolled, coined, tempered, grown, etched or polished samples in constant-current mode.
- Compare the scanned images and apply the Roughness analysis tools.
- Interpret the results.



Fig. 2: Content of 09600-99.

Set-up and Procedure**Task 1: Preparation of Pt/Ir tunneling tips and different sample surfaces. Approaching the tip towards the sample.**

For preparation of tunneling tips and the approaching procedure please refer to experiment *P2532000 "Atomic Resolution of the graphite surface by STM"*, the quick start guide (QSG), or, the operating manual (OM), Chapter 5. You'll find an electronic version of the QSG and OM under the help menu of the measure nano software.

In most cases it is enough to cleave the graphite sample once in a few weeks. If you have problems to find a clean area or you don't get good images with several freshly prepared tips, clean the sample surface using scotch tape as described in the QSG or OM.

Sample Cleaning (others than HOPG)

The other samples normally need not to be cleaned. However, if you experience bad scans throughout or accidentally touched the sample you can lay a lint-free cloth on top of the sample surface and drip some alcohol on it. Remove the wet cloth by carefully wiping and wait until the alcohol has dried completely. To avoid any scratches or other irreversible surface modifications it is important that the surface does not experience pressure at any time!

Assembling your own samples

Additionally to the supplied samples you can assemble samples of different materials on your own. Basically every conducting and not too rough surface is suited. To be able to scan the material you need to cut off a small piece of about the size of a free sample support supplied

with the STM and clean the sample using the above given procedure. Now glue the material on the sample holder using the silver paint. It's important the surface of the material, which will be scanned and the sample holder are as parallel as possible and you do not touch the sample surface with your fingers or scratch it with the tweezers. Afterwards wait at least 15 minutes to let the silver paint harden. Now you can scan your own sample as usual.

The set nanomorphology contains 8 different metal samples and the necessary tools and accessories to prepare and store the samples. Please follow the procedure mentioned above to prepare your own samples with the exception of the cent coin. It can be used without mounting on a sample support. Additionally the HOPG and Gold Sample both part of the Compact-STM set can also be analysed.

Sample etching

Beside the nano morphology of grown, rolled, coined, and tempered samples also the effect of etching on a nanoscopic scale can be investigated. For this please use the equipment given in the list and refer to the procedure given in the Experimental Guide *P5510200 "Metallographic Sample Preparation: Chemical Etching"*, available at www.phywe.com.

Sample polishing

Another standard procedure to process samples is the polishing of the surface. As an example the nanoscopic effect of polishing on copper foil before mounting on the sample support can be investigated. For this please use the equipment given in the list and refer to the procedure given in the Experimental Guide *P5510100 "Metallographic Sample Preparation: Grinding and Polishing of Metals"*, available at www.phywe.com. Instead a grinding and polishing machine use two microscopic slides. Put the sample together with the polishing material on one of the slides. Use the second slide for polishing the surface of the sample by a circular movement of the slide.

Task 2: Investigate the topography of different rolled, coined, tempered, grown, etched or polished samples in constant-current mode.


The difficulty in scanning extremely rough surfaces as we will do in this experiment is that the piezo crystals have a limited speed and range of operation. Therefore extreme

height differences in a small area can lead to scanning artifacts or even crashing the tip into the surface.

One way to prevent this from happening and achieving good images is to decrease the scanning speed meaning to increase the time per line of scanning. Furthermore it's recommended to start scanning just a small area of few 10nm² slowly increasing the image size as desired.

When receiving artifacts one can try to furthermore decrease the image size or scanning again with a higher tip-surface distance i.e. increasing the tip voltage or decreasing the set point followed by with-drawing and re-approaching the sample.

To receive good scans of large areas of a rough sample the sequence of procedure should be as followed:

1. Prepare a tip and do a surface scan on HOPG to check if the tip is good by resolving single atoms. For more details please refer to the experimental guide of P2532000 "Atomic resolution of the graphite (HOPG) surface by STM", available at www.phywe.com.
2. Change to the rough sample and start scanning with a low image size (e.g. 10nm x 10nm)
3. If you receive artificial structures in the scanned images try increasing the time / line or if this won't help increase the tip voltage and/or lower the set point, withdraw the sample and re-approach it
4. If still receiving artifacts repeat 3. until you receive good scans. If not receiving good scans even with tip voltage > 5V and set point < 0.5nA withdraw the sample and try scanning the surface at a different location
5. Increase the scanning area.
6. If receiving good scans repeat 5. Otherwise start over at 3.
7. When reaching the desired image size adjust the gain values to smooth the image. You can also try to increase the points / line for a better scan quality. When you are satisfied grab a good image by clicking the  Photo button.
8. Now you can apply some filters to reduce noise, adjust scan line levels and remove a background distortion. The recommended procedure would be:
 - Apply glitch filter.
 - Apply noise filter.
 - Do a background subtraction and/or correct scan line

levels.

Your corrected image should be almost free of strong gradients, one plane of the sample surface should have the same color in every point.

Theory and evaluation

Tunneling Effect

Tunneling is a functioning concept that arises from quantum mechanics. Classically, an object hitting an impenetrable barrier will not pass through. In contrast, objects with a very small mass, such as the electron, have wave-like characteristics which permit such an event, referred to as tunneling. In other words, the probability to find an electron behind a barrier is unequal zero. Inside the barrier the wave function of the electron decays exponentially.

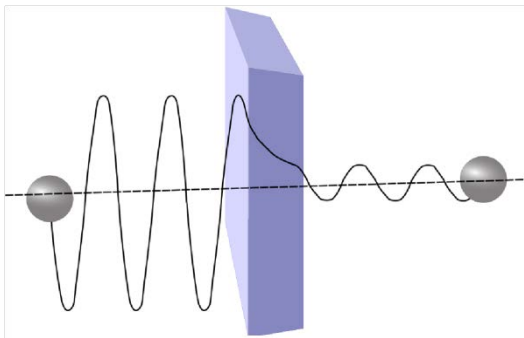


Fig. 3: Sketch of the tunneling of an electron through a barrier, illustrated by a ball and a wave function.

STM - Scanning Tunneling Microscopy

The size of an atom in relation to the tip is that of a golf ball to a mountain. In your PHYWE measurement system a platinum-iridium tip is moved in three dimensions using piezo crystal translators that are driven with sub-nanometer precision (Fig. 4). The sample to be examined approaches the tip within a distance of about 1 nanometer ($1 \text{ nm} = 1/1,000,000,000 \text{ m}$). Classical physics would prohibit the appearance of electrons in the small gap between the tip and the sample, but if a sharp tip and a conducting surface are put under a low voltage ($U \sim 0.1 \text{ V}$), a very small tunneling current ($I \sim 1 \text{ nA}$ with 1 nm tip sample distance) though may flow between tip and sample. The resulting tunneling current is a function of tip position, applied voltage, and the local density of states

(LDOS) of the sample, this information is displayed on the computer monitor as 2D color mapped image. The strength of the tunneling current I depends exponentially on the distance between the tip and the sample (d_z), usually referred to as z -distance, the applied bias (U) and constant factors (c_1 and c_2)

$$I \propto c_1 \cdot U \cdot \exp(-c_2 \cdot d_z) \quad (1)$$

This extreme dependence on the distance makes it possible to measure the tip-sample movement very precisely. One of the three piezo crystals, the z -piezo, can now be used in a feedback loop that keeps the tunneling current constant by appropriately changing the z -distance. The elongation of a piezo crystal is proportional to a device specific constant which is a temperature dependent parameter and the applied voltage (Elongation = piezo constant \cdot Voltage, e.g. $\Delta l = 500 \text{ pm/V} \cdot 10 \text{ V} = 5 \text{ nm}$).

Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create uncertainty and errors in the expected values of your measurements.

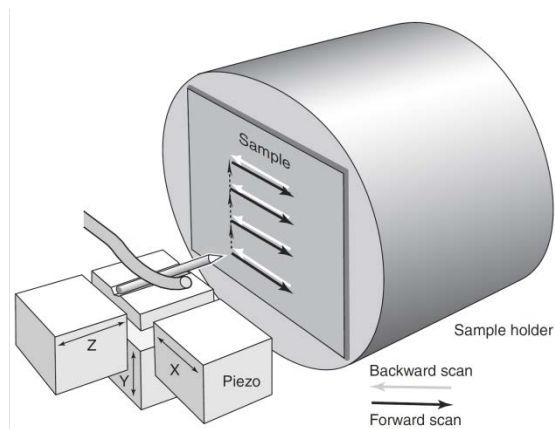


Fig. 4: Sketch of the piezo electric device driving the tip movement.

Task 3: Compare the scanned images and apply the Roughness analysis tools.

After scanning a sample use the integrated function *Calculate Area Roughness* to R_a mine the nanoscopic roughness of the sample. This will result in an output as shown in Fig. 12. You can look up the meaning of the single values in the *Operating Instructions and Experiments – Scanning Tunnel Microscopy (4.3.6) manual*.

Name	Value
Area	121,9fm ²
Sa	1067,5pm
Sq	1376,5pm
Sy	12,467nm
Sp	7,8143nm
Sv	-4,6525nm
Sm	3,7361fm

Fig. 12: Area Roughness measurement

single values in the *Operating Instructions and Experiments – Scanning Tunnel Microscopy (4.3.6) manual*.

We are mostly interested in S_y which is the maximum height difference of any two points on the surface because it reflects the roughness of the sample.

Comparison of Surfaces

Due to the different procedures of manufacturing we expect the surfaces to have characteristic structures. In the following you can see pictures taken from grown, rolled and coined surfaces. Some of the images are displayed as shaded map (in PHYWE *measure nano*: “right-click->Chart Type->Shaded map”).

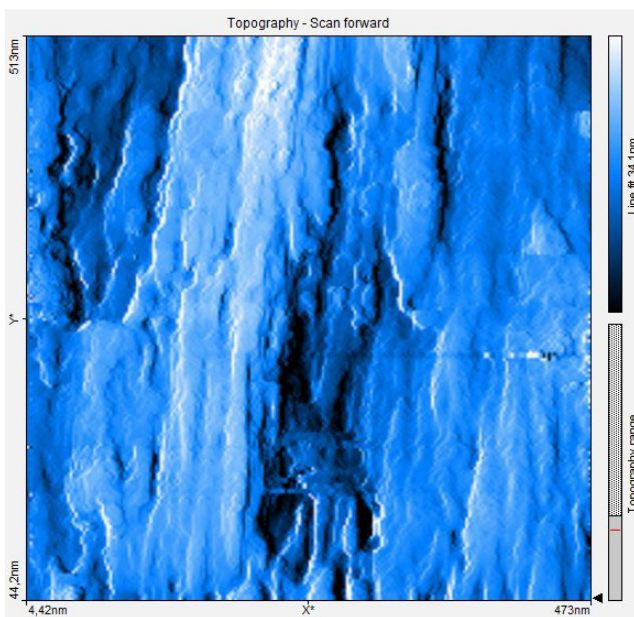


Fig. 5: Ta shiny

sheet on the nano scale. One sees the shiny side consists of longish structures whereas the dark side more likely has island-like structures.

Figure 7 shows the surface of a Copper sheet, which has also been rolled but its two surfaces do not differ. One immediately sees the similarities in Fig. 5 and Fig. 7.

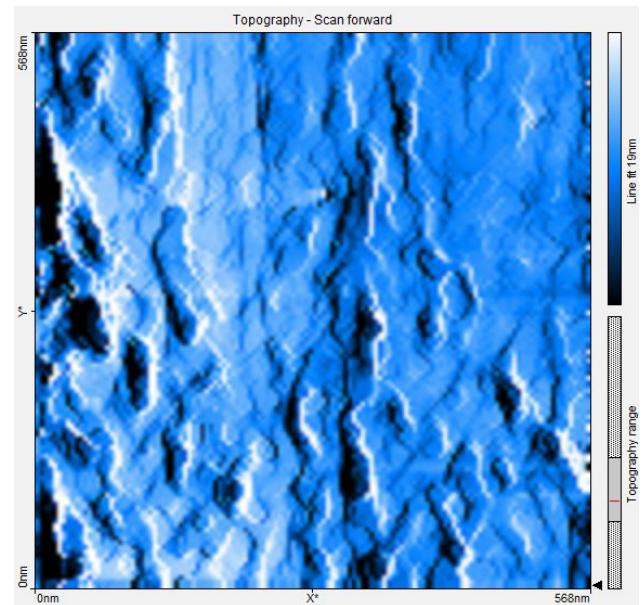


Fig. 6: Ta dark

Fig. 8 shows a coined copper surface of a European 1 cent coin. The structures are round and irregular.

Figure 9 shows HOPG which is grown and consist of single layers which are strongly bonded within themselves but only bonded among each other by the weak van-der-Waals force.

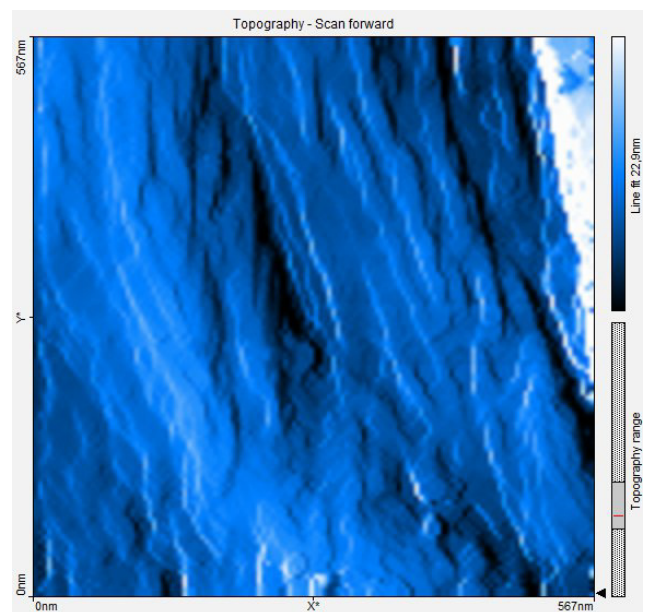


Fig. 7: Cu

Tantalum sheets are rolled and have a shiny and a dark side. Images 5 and 6 show the two surfaces of such a

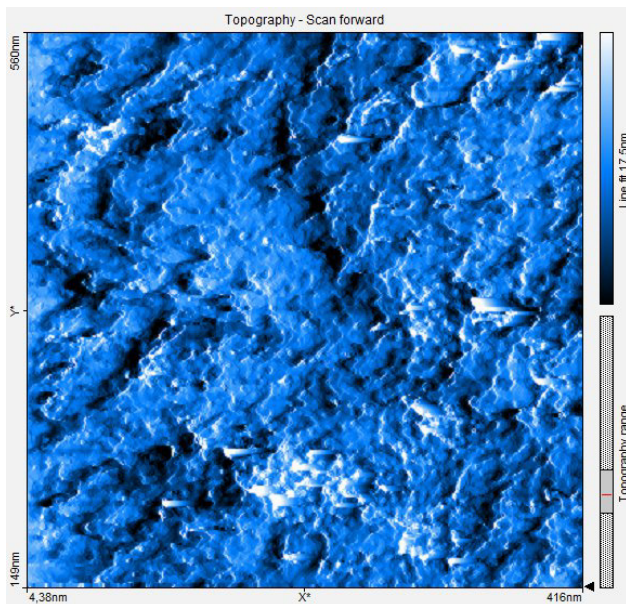


Fig. 8: 1 Euro Cent Coin (Iron based alloy with copper coating)

Furthermore the Gold in Fig. 10 is also grown. This image shows many mono atomic steps and some of higher order.

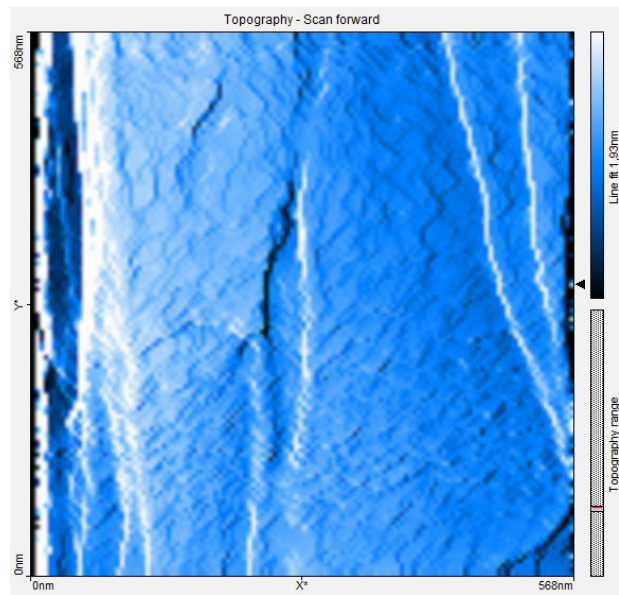


Fig. 10: Gold

Table 1 shows the outputs of S_y when applying the area roughness tool on the scans shown above. One sees the surfaces can be categorized by their roughness as done in table 2.

Rough	Plain
Cu	HOPG
Ta shiny	Gold
Ta dark	TaS2
Coin	
Sn	

Tab. 2: Materials categorized by roughness

Regarding the manufacturing procedures of the surfaces in table 2 the rolled and coined materials are rough and the grown materials are plain.

Conclusion

The longish nanoscopic structure of rolled materials can be explained by the stretching process the materials experience when they are flattened.

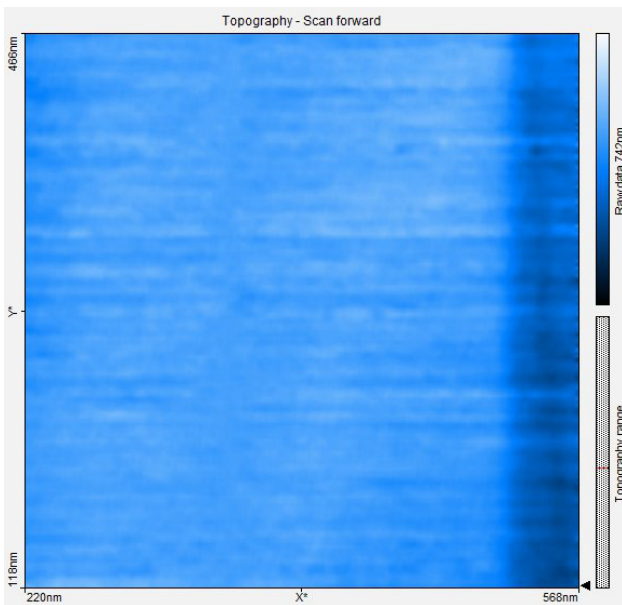


Fig. 9: HOPG

Tantalum disulfide (TaS_2 , Fig. 11) which is also grown consists of layers like HOPG but is much more brittle. This means the single layers are not as strong bonded within themselves as those of HOPG (Fig. 12).

The chaotic structures of the coin surface are reasoned in the fast coining process during which the surface is exposed to high forces and immediately cools down afterwards.

Material	Cu	Ta shiny	Ta dark	HOPG	Gold	Coin	Sn	TaS2
S_y [nm]	33.3	38.2	56.1	0.4	4.4	31.3	133.0	14.0

Tab. 1: Area Roughness

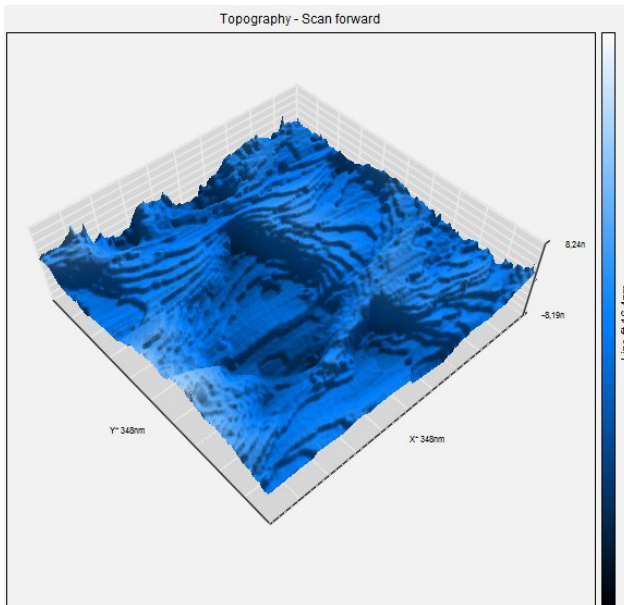


Fig. 11: TaS2

Furthermore we have seen that macroscopically shiny materials are not necessary plain on the nanoscopic scale and vice versa.

The plain surfaces of the grown materials are rooted in the growing process in which the single atoms lay down onto the surface slowly after each other. Because the smallest possible surface is energetically favorable the material will form plain structures.

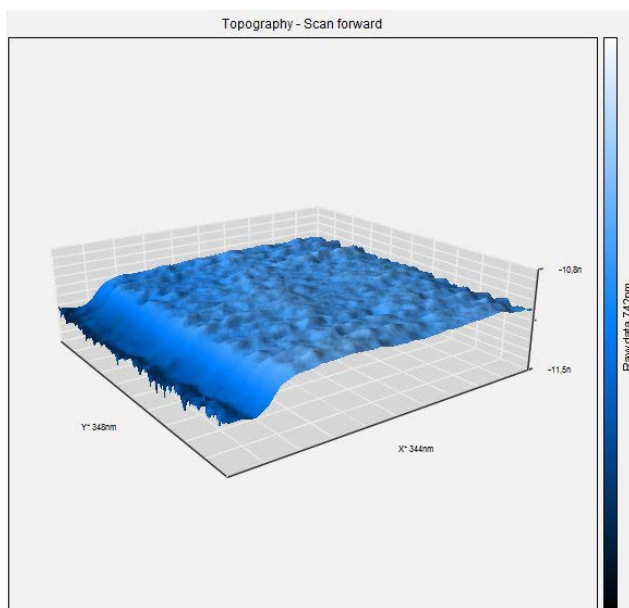


Fig. 12: HOPG

An important result of our measurements is that the surface roughness of coined materials does not differ from rolled but when looking at the topography one can identify the coined material by the round, chaotic structures whereas rolled materials have longish structures. Also the nanoscopic roughness of grown materials uses to be lower than that of rolled and coined materials.

