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

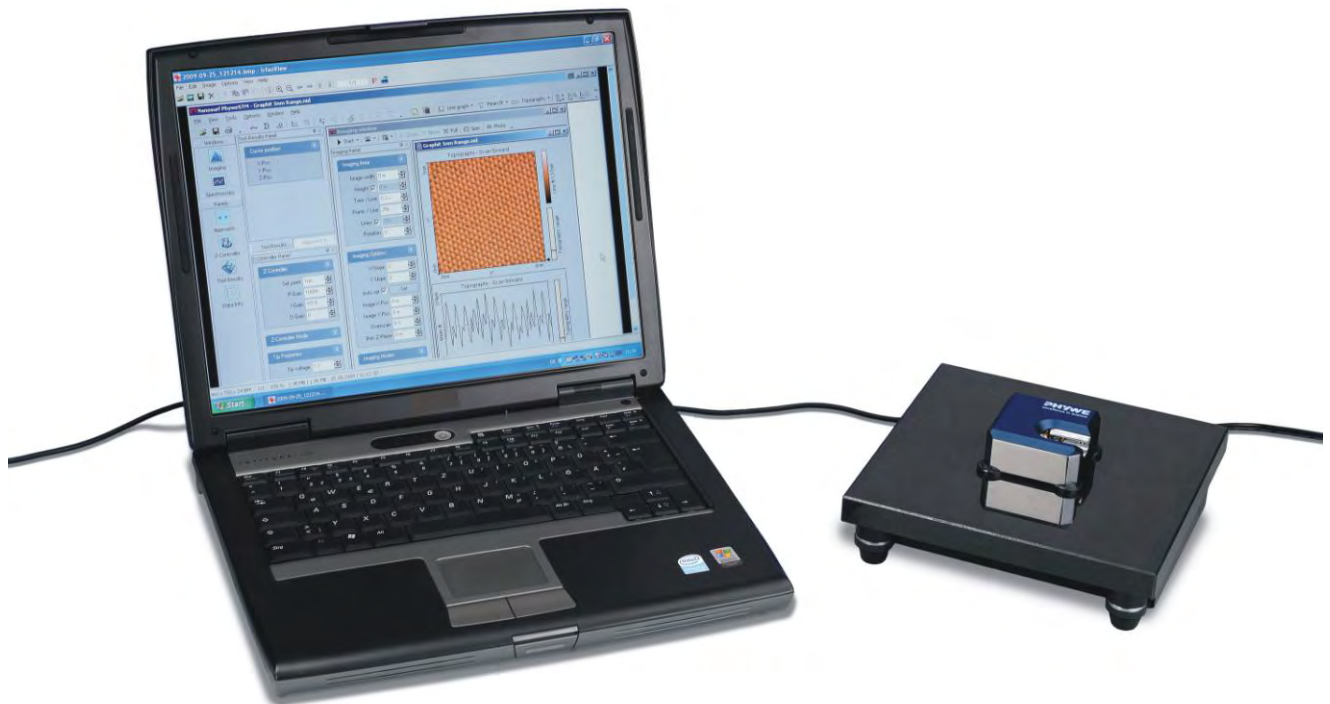**Additionally needed**

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 = 0.25mm, l = 30 cm	(10)
1	Sample Holder	(11)
1	Graphite sample (HOPG)	(12)
1	Gold sample	(13)
4	Spare sample support	(14)

User Manual

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

Fig. 2:   STM set.

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.
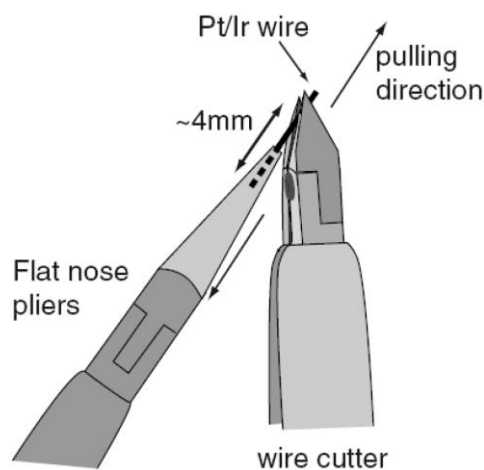- Holding the wire with the pliers, move the cutters at a length of approximately 4 mm, as obliquely

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.
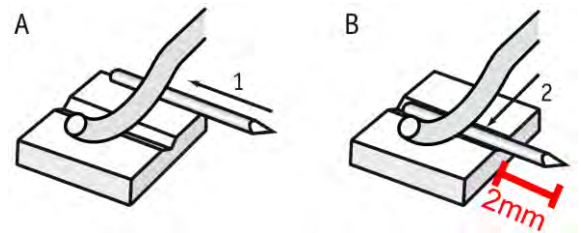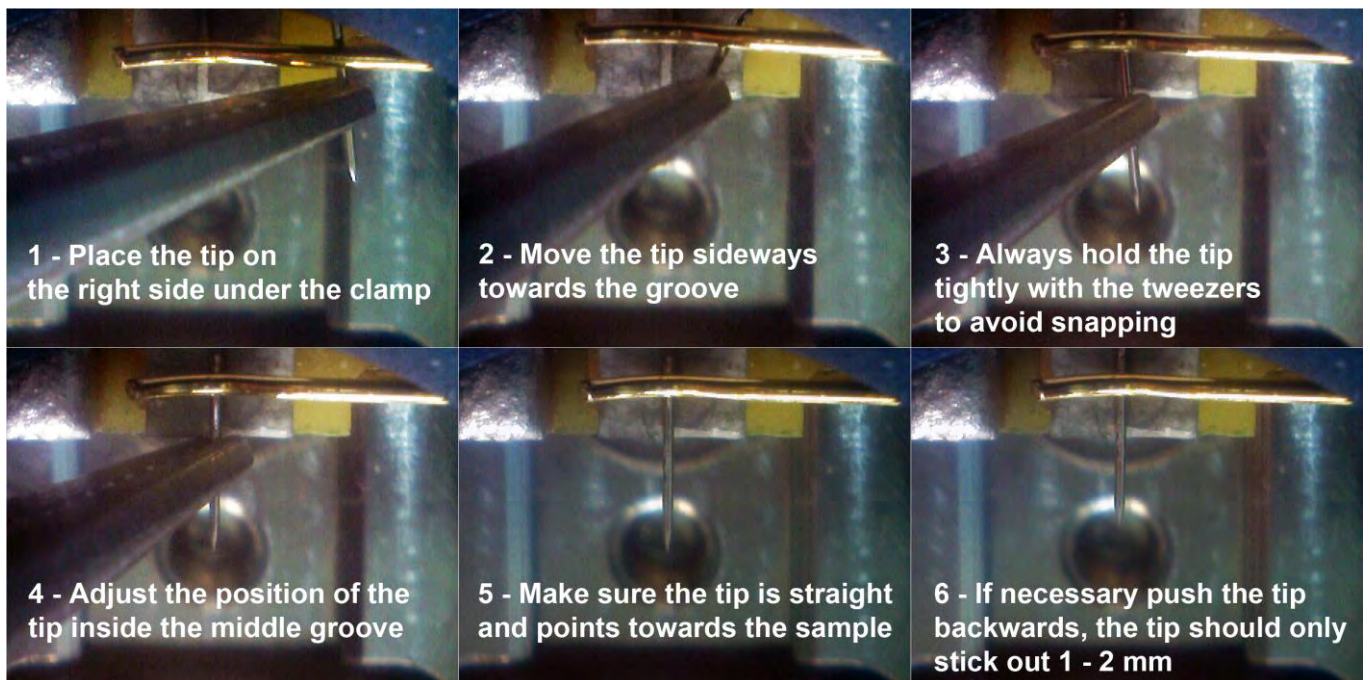

Fig. 4:   Sketch of the tip mounting.

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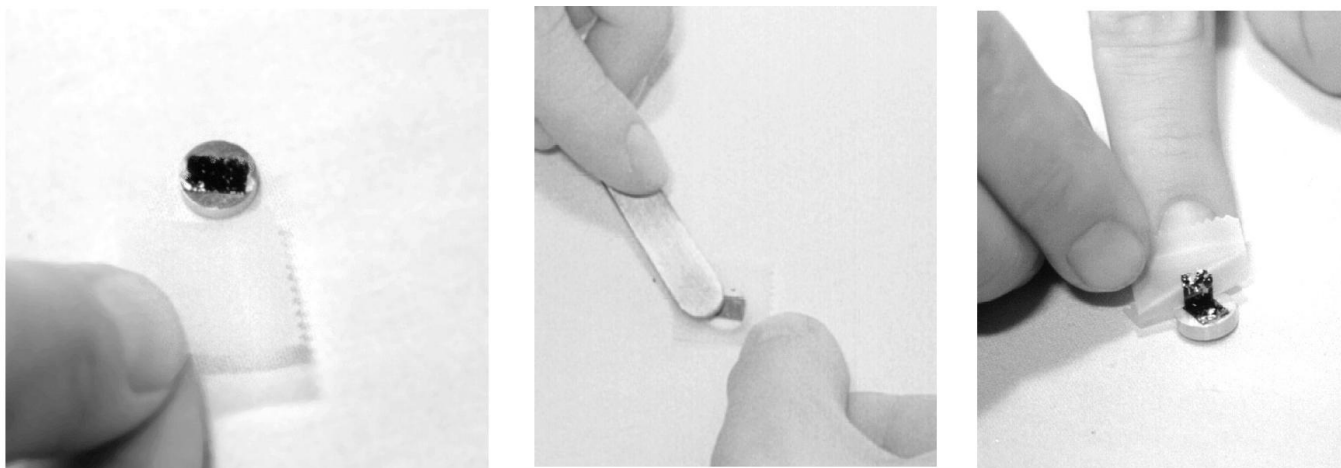
Fig. 6:   Step by step pictures of the HOPG sample surface preparation.

-    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).
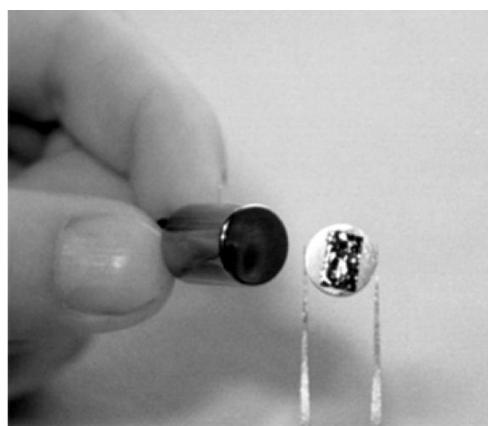

Fig. 7:   Place the sample in the middle of the sample holder.
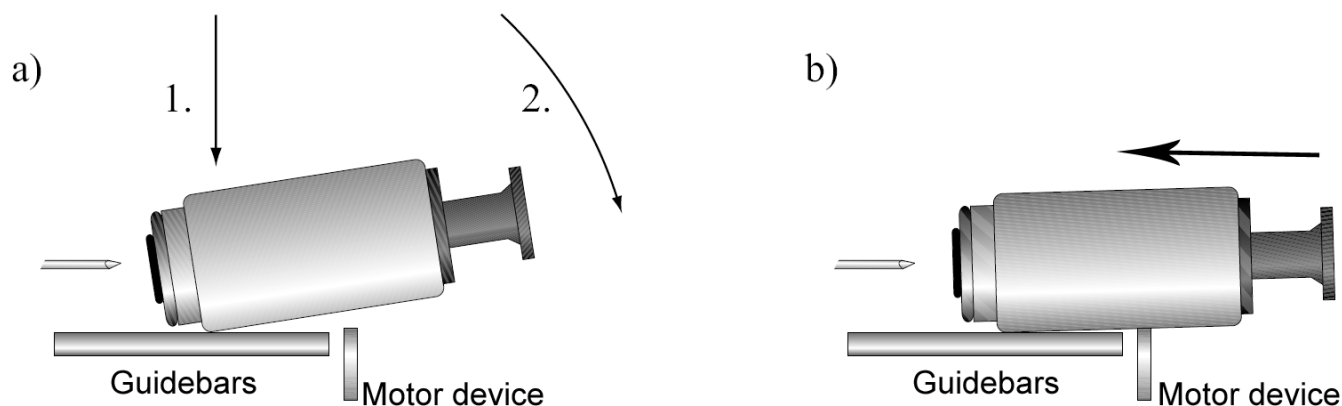

Fig. 8:   Sketch of the manual approach of the sample to the tip.

- 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.
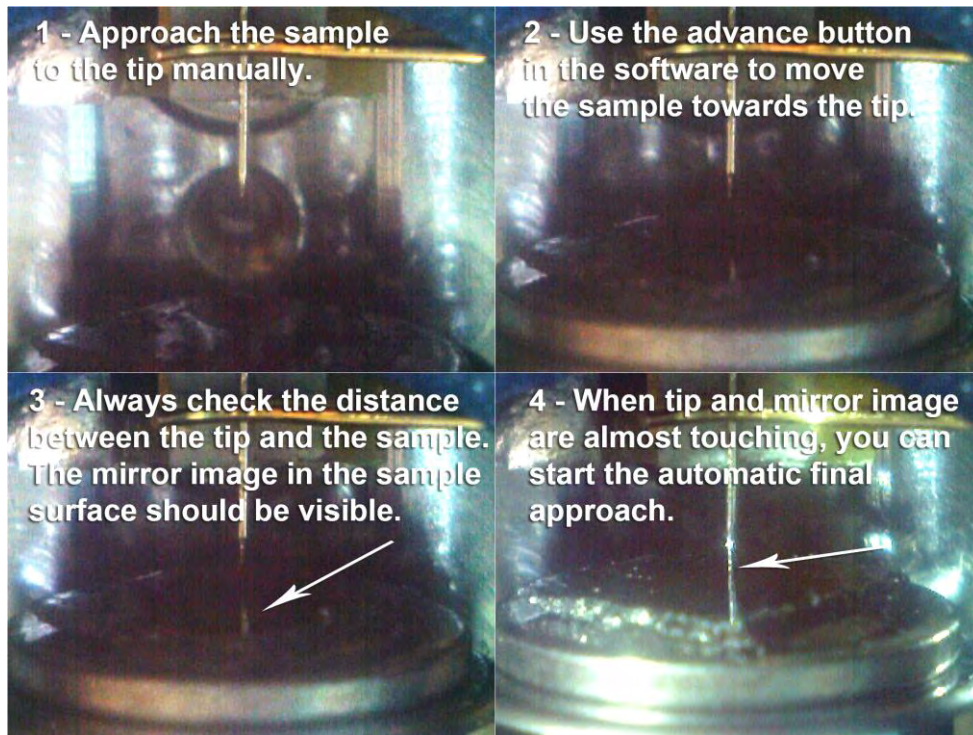

Fig. 9: Step by step pictures of the software supported approaching of the sample to the tip.

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 lightning 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 hast 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.
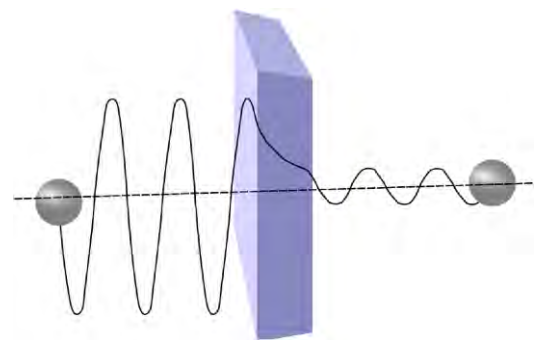

Fig. 10: Sketch of the tunneling of an electron through a barrier.

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 ex-amined 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~0.1 V), a very small tunneling current (I~1 nA with 1 nm tip sample distance) though may flow between tip and sam-ple. The resulting tunneling current is a function of tip po-sition, 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 exponen-tially 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)

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

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

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. Δl = 500 pm/V . 10 V = 5 nm). Always keep in mind to do measurements preferably at the same room temperature. Temperature dependencies create un-certainty 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 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 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 ("Op-tions" → "Config User Interface") to obtain the possibility to adjust the P-
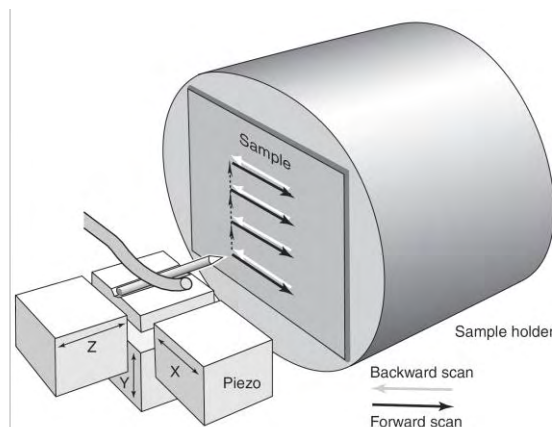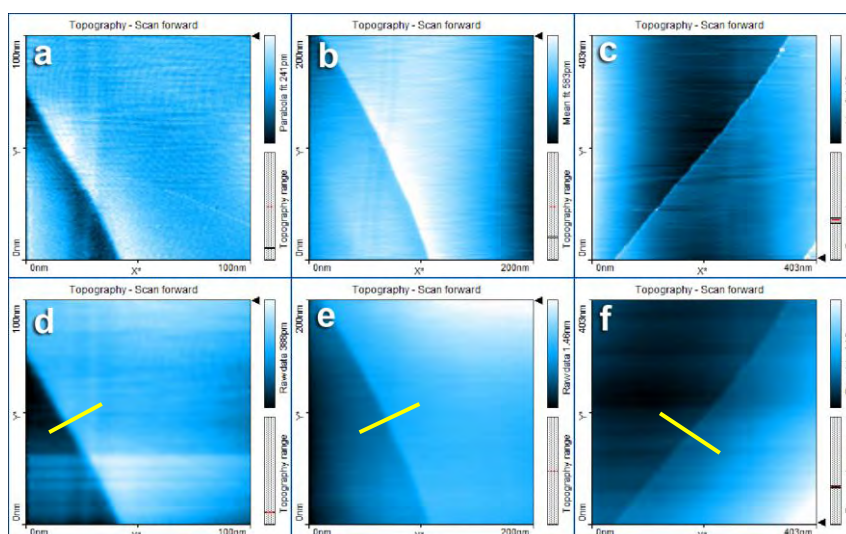
Fig. 12: Original images of different atomic terraces (a, b, c) and their processed images (d, e, f). Yellow bars indicating the place of the cross sectioning (see below).(Time/Line: 0.2 s, Set point: 1.2 nA, P-gain: 1000, I-gain: 1200).

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 substraction 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.

Fig. 13: Cross section of image d (see above). Distance: Δz=332.2 pm.

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 highes values of each terrace.

Fig. 14: Cross section of image e (see above). Distance: Δz=333.9 pm.

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.

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

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

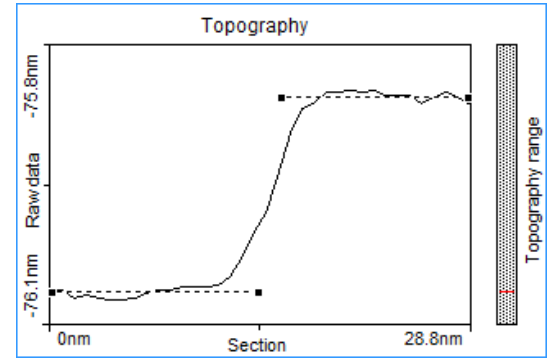$$s = \frac{1}{N-1} \sum_{j=1}^{N} \left(v_j - \overline{m} \right)^2 \ \ [3]$$

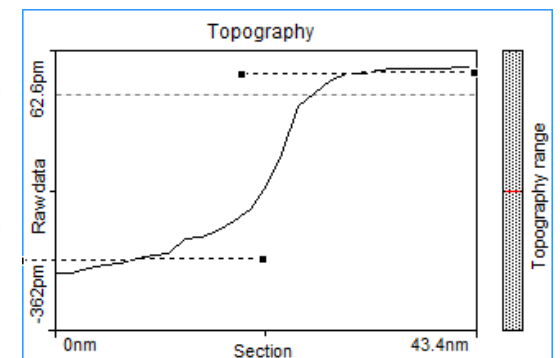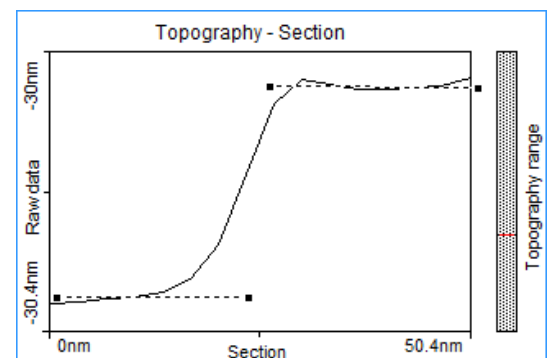Fig. 15: Cross section of image f (see above). Distance: Δz=686.1 pm.

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

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 → 1	-0.8	333.05 [± 1.20] pm
e	333.9		0.99 → 1	-2.6	
f	686.1		2.05 → 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.
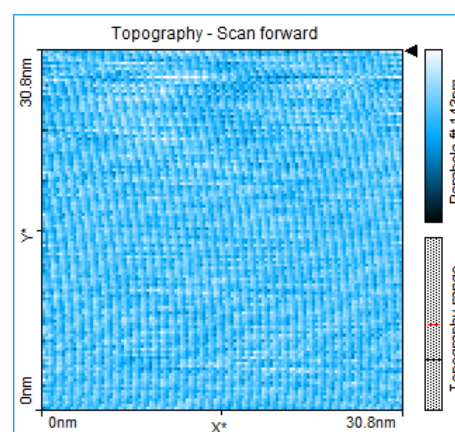

Fig. 16: Image size: 30 nm, Time/Line: 0.13 s, Set point: 1.2 nA, P-gain: 1200, I-gain: 1500.

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.
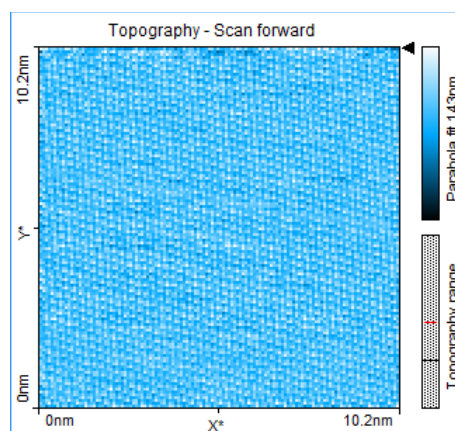

Fig. 17: Image size: 10 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1200, I-gain: 1500.

* : 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).
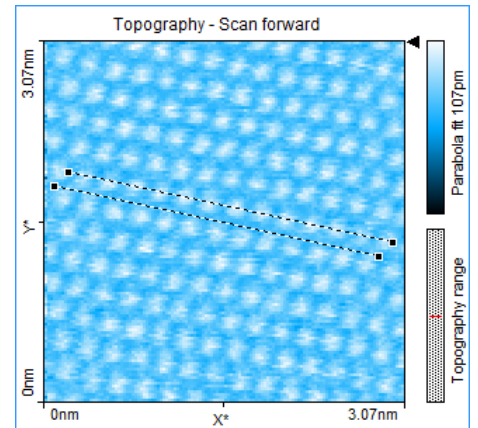

Fig. 18: Image size: 3 nm, Time/Line: 0.03 s, Set point: 1.2 nA, P-gain: 1300, I-gain: 850. Distance between lines: d=138 pm
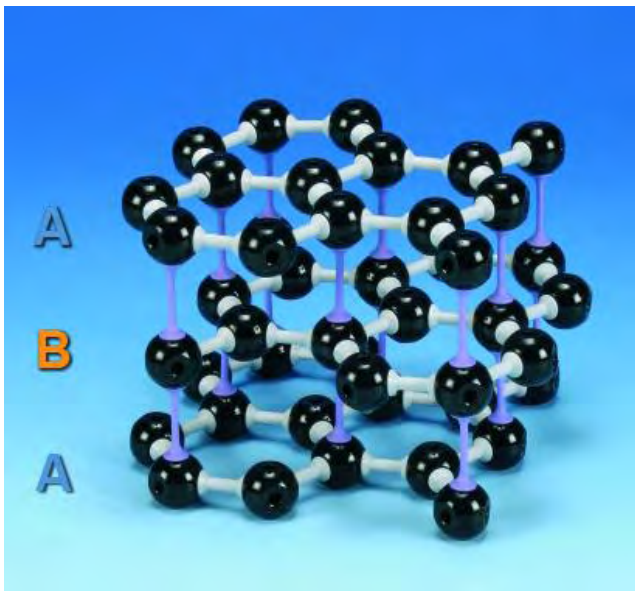

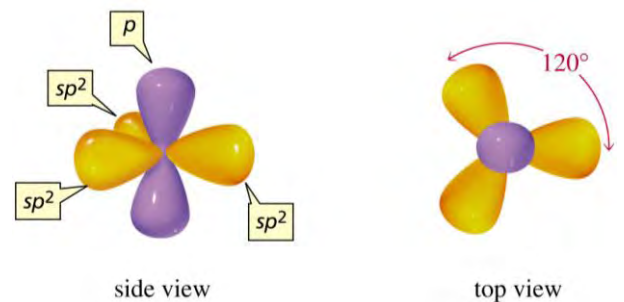Fig. 19: PHYWE 3D model of the graphite lattice (Crystal lattice kit: graphite, 39840.00).

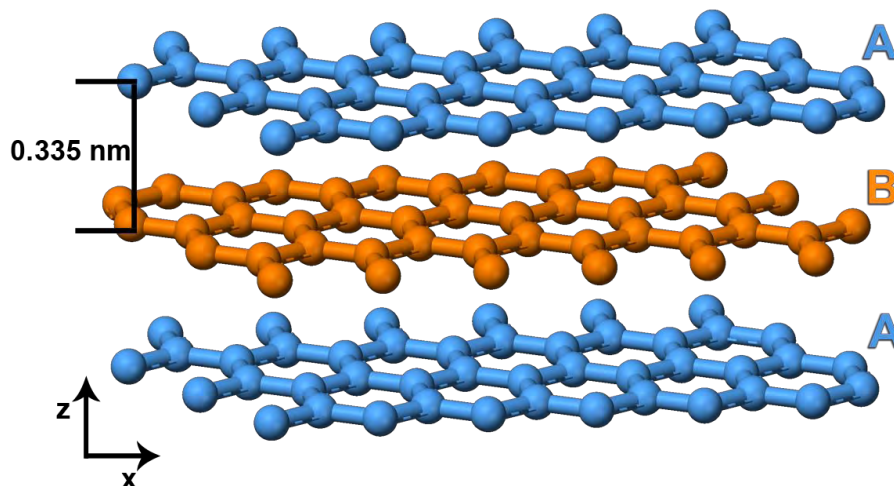Fig. 20: Sketch of sp^2- hybridized carbon atoms.

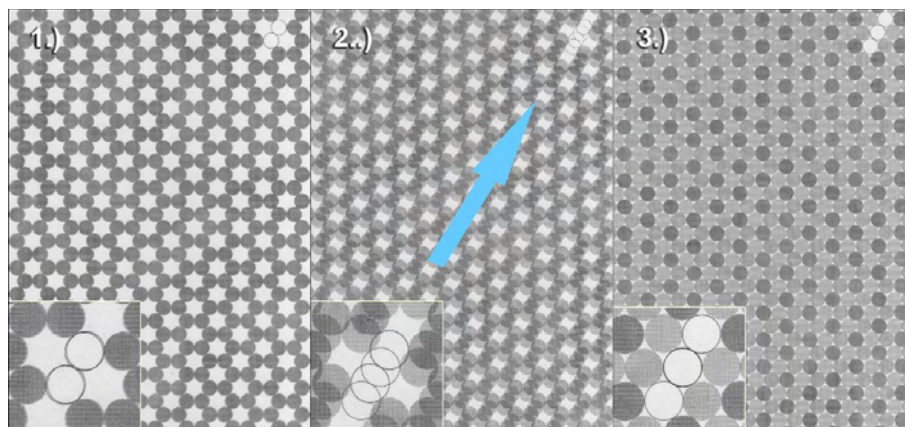Fig. 21: 3D sketch of the graphite lattice structure (side view).

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).
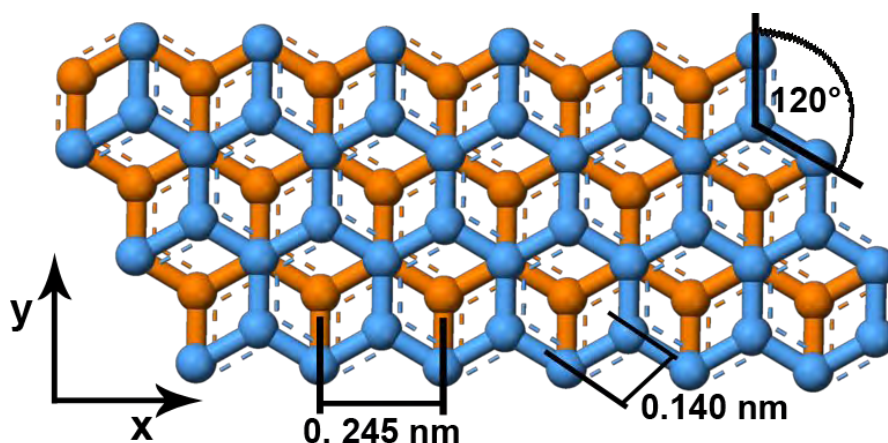

Fig. 23:   2D sketch of the graphite lattice structure (top view).

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
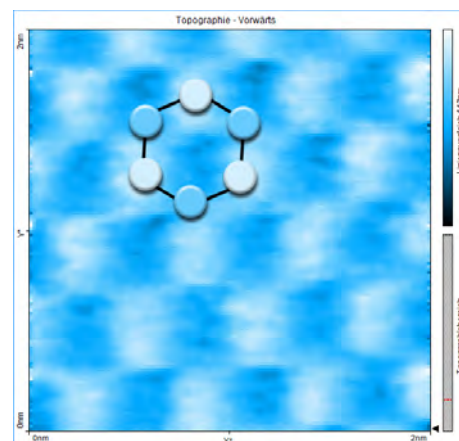

Fig. 24:   Hexagonal pattern reveals electronic and topographic structure of surface atoms

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. $d = 140$ pm) or from atom row to atom row (hill to hill see Fig. 26 or valley to valley, distance approx. $d = 245$ 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 $d=248.5$ pm, doing the same measurement over 5 rows ($d=1231.5$ pm) reduces this value to $d=246.3$ 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. $\Delta z=15.3$ pm).

Fig. 25: Distance measurement. Distance between lines: $d=252.7$ 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.

Fig. 26: 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 (hilltop to valley).

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.".
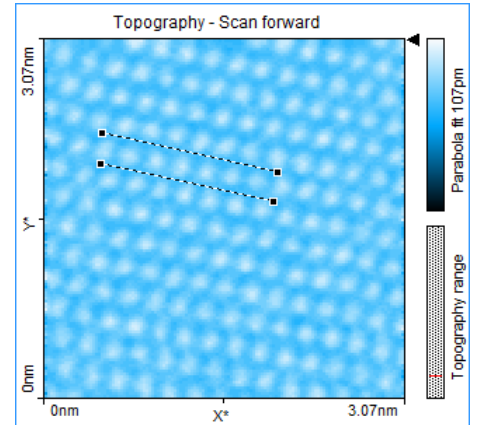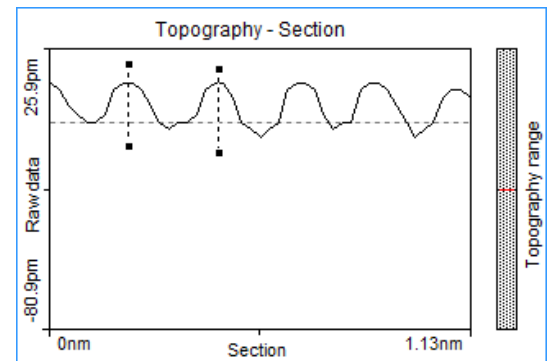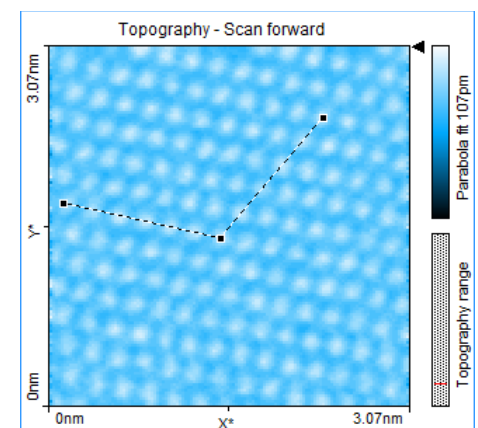

Fig. 27: Angle measurement. Angle between lines: $\alpha=118.8$

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.

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

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 ΔI=578.6 pA and corresponds to the step height of one atomic terrace with Δz=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 ΔI=81.68 pA and corresponds to the Δz=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%.

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

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).
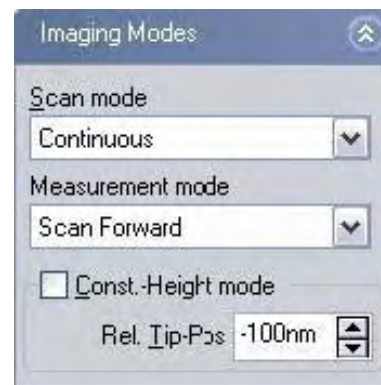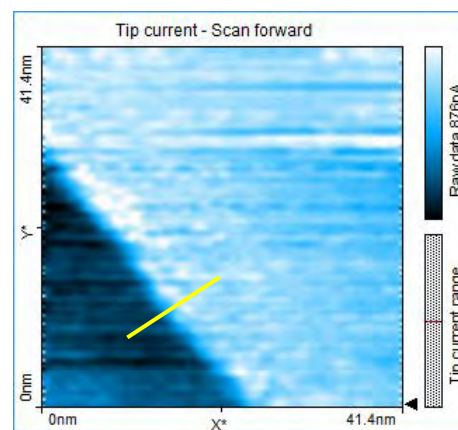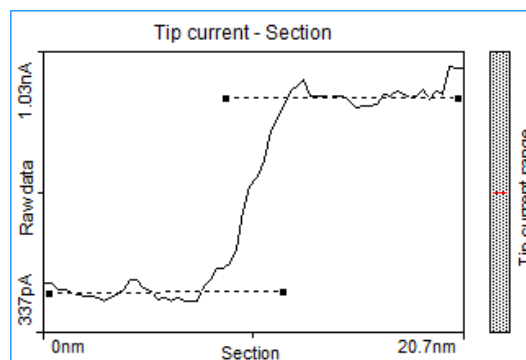

Fig. 30: The step size corresponds to a difference in the tunneling current of 578.6 pA (or 334.8 pm, one atomic layer).
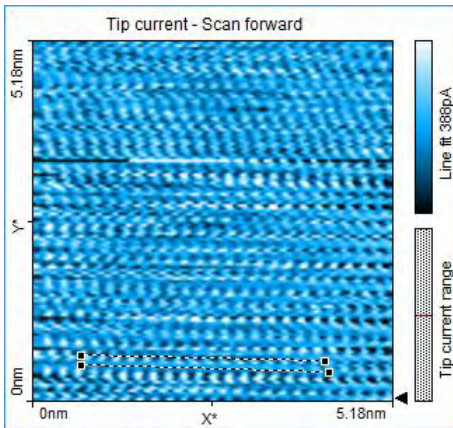
Fig. 31: Constant height image. Image size: 5 nm, Time/Line: 0.03 s, Set point: 1.2 nA, Rel. Tip-Pos.: -0.14nm. Distance between lines: d=150.1 pm
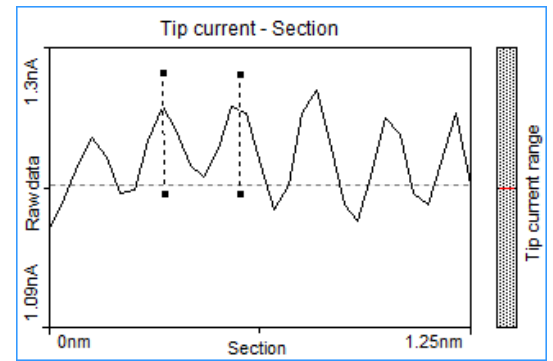

Fig. 32: Cross sectioning: Distance between lines: d=235.1 pm (hill to hill, hill to valley gives: d=117.4 pm. The z-distance from hilltop to valley corresponds to the measured current: ΔI=81.68 pA.

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
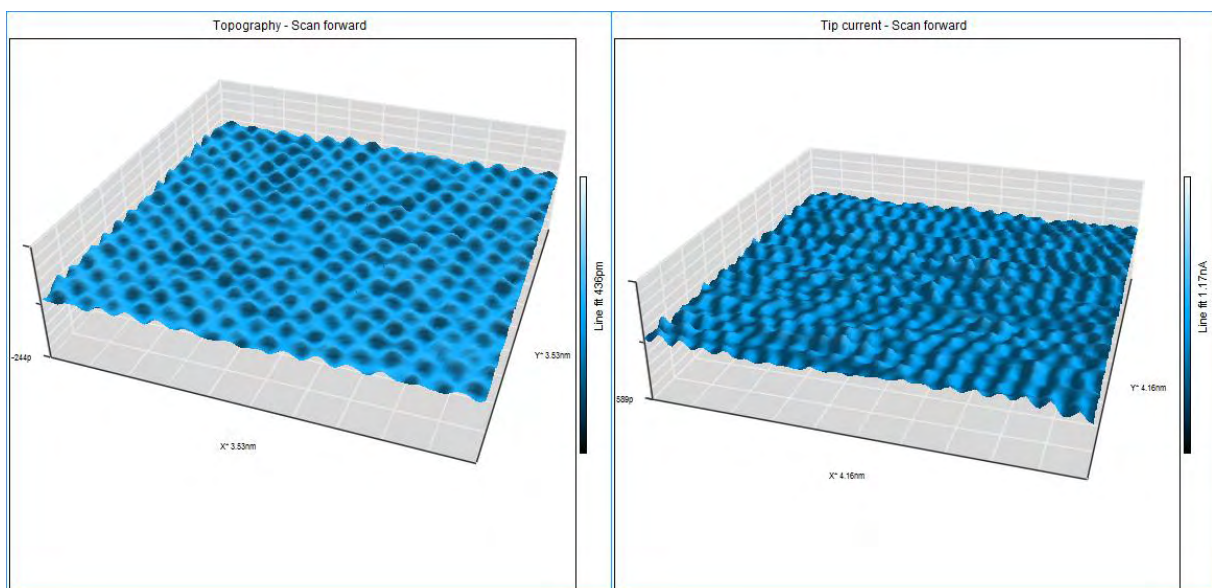

Fig. 33: 3D representation of constant current data (left) and constant height data (right).