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1 Preparation

1.1 Introduction STM

This experiment deals with the investigation of material surfaces in the Å range. In doing so, the scanning tunnel microscope as a measuring device that enables the aforementioned analyzes of the material surface is learned.
A scanning tunneling microscope, which is used in this practical experiment, scans the surface of a material with a fine tip. This tip is only a few Å above the material surface during the scanning process. The sample material and the needle are connected to a voltage source, which means that there is an electrical potential difference between the needle tip and the sample. This potential difference is equalized in that electrons tunnel from the occupied states of the sample material into the unoccupied states of the needle. This tunnel current depends on the distance between the sample surface and the needle tip. The needle moves along the surface and tries to keep the tunnel current as constant as possible by varying the distance between the surface of the sample material and the needle tip.

1.2 Theoretical Basics

When two atoms form a bond, the outer electron orbitals of the two atoms combine to form a common molecular orbital. This creates energy levels that differ from the energy levels of a single atom. In a composite of many identical atoms, two new energy levels are created for each atomic bond, which are known as energy bands. Between these bands there are forbidden areas, so-called "band gaps", in which there is no energy level.
At a temperature of 0 K the valence band is fully occupied and the energy levels are completely filled by the electrons up to a limit, the Fermi energy E_F. The distribution is described by the Fermi-Dirac distribution:

$$f_F(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} . \tag{1}$$

442 / 5000 Übersetzungsergebnisse If the material is at a higher temperature than 0 K, due to the thermal movements, not all places below the Fermi energy can be occupied and the electrons are forced to assume states that are greater than those of the Fermi energy and land in the conduction band, which is above the valence band. In this case, the distribution is described by the Maxwell-Boltzmann distribution:

$$f_B(E) = \exp\left(\frac{E-\mu}{k_B T}\right) . \tag{2}$$

Depending on the occupation of the bands, materials can be divided into conductors, semiconductors and insulators. In insulators, there is a band gap between the valence and conduction bands, while this is not present in conductors. The electrons in the conduction band can move freely. In semiconductors, the band gap between the valence and conduction bands is so small that electrons can be excited by further excitation, e.g. the supply of heat, can tunnel into the conduction band. This effect can be increased by adding foreign atoms with different electron configurations, known as doping.

1.3 The tunnel effect

The quantum mechanical tunnel effect enables the electrons in the scanning tunneling microscope to tunnel through the potential barrier between the surface of the sample material and the tip of the needle. If the energy of the electron is too low to overcome the potential barrier, the electron should not be able to leave the sample material in a non-quantum mechanical view. From a quantum mechanical point of view, however, the wave function of the electron does not disappear behind the barrier but falls exponentially behind it. With a limited thickness of this potential barrier, the wave function can still propagate behind it. The electron has the opportunity to penetrate the potential barrier. The potential barrier can be described in the form

of a potential wall. The solution of the Schrödinger equation for this problem shows that the tunnel current is distance-dependent with the decay constant

$$\kappa^2 = \frac{2 \cdot m}{\hbar^2} \overline{\phi} \tag{3}$$

$$I_T \approx \exp\left(-2 \cdot \kappa \cdot d\right) . \tag{4}$$

Here $\overline{\phi}$ is the potential barrier that the electron overcomes. The following applies:

$$\overline{\phi} = \phi - E = \frac{\phi_1 + \phi_2}{2} + \frac{e \cdot U_T}{2} - E . \tag{5}$$

For small values, the tunnel voltage is proportional to the tunnel current: $U_T \; approx I_T$. When the surface is scanned, not only the surface quality but also the electrical conductivity of the sample material is measured. It should not be forgotten that in reality disruptive factors still influence the tunnel effect. This includes foreign molecules such as B. Air or impurities in the sample material. The electrons hit these impurities on their way to the needle tip.

1.4 Sample materials

Not all materials are suitable for examination with a scanning tunneling microscope. Since the needle is moved in the Å area, only surfaces with unevenness in the Å area can be examined. Furthermore, the property of whether the material is electrically conductive or not has an impact on the investigability:

- **Insulators** cannot be investigated because of the band gap between the valence band and the conductor band
- **Conductors** can be investigated because the electrons can move freely
- **Semiconductors** have free valence electrons on their surface and can therefore be examined in an ultra-high vacuum with high tunnel voltages.

1.5 Graphite

Graphite is characterized by its hexagonal structure. Graphite consists of many planar layers, so-called "basal planes", which are only held together by Van der Waals interactions instead of atomic bonds. Such a plane consists of covalently linked hexagons with sp^2-hybridized carbon atoms and bond angles of 120°. Within a plane the binding energy is 4.3 eV and between the planes only 0.07 eV. Graphite is also electrically conductive. Graphis can be easily split along the layers and has no free valence electrons on its surface.
Contrary to all expectations, an image of graphite in air does not show a hexagonal structure but a triangular structure. This is because there are C atoms that have a C atom below them (α-space) and C atoms that only have a C atom below them in the next but one layer (β-Place). These different places have different density of states, which are mapped differently in the recording. You can see triangles instead of hexagons.

1.6 Gold

After gold has been heated and cooled again, it forms flat plateaus. These plateaus are well suited for an examination with a scanning tunneling microscope. By examining gold, the Z-movement of the piezo crystal for controlling the needle tip can be calibrated.

1.7 Question 1: Material conditions

The materials should be electrically conductive, otherwise no current can flow to the sample, as a result no tunnel current can be detected. If a sample does not conduct, it has to be coated beforehand, e.g. with gold. The material should also not have any great differences in height, since the movement space is limited in all directions by the piezo crystals.
When experimenting in air, care should also be taken to ensure that the material does not react with air.

1.8 Question 2: Informations from the recordings

The information contained in the measurement data in constant altitude mode is how large the tunnel current is with a fixed applied voltage in the poses approached in the x and y directions.
In the constant tunneling current mode, the information from the experiment shows at which point (x, y and z) the needle is located when the controllers on the piezo elements maintain a constant tunneling current.

From this, conclusions can be drawn about the surface. In constant height mode, the tunnel current is converted into a z-distance.
In the constant tunnel current mode, it is assumed that the surface of the sample is parallel to the surface traced with the tip.
Both methods lead to errors when disturbances occur, e.g. through contamination on the surface of the sample or through a double tip.

1.9 Question 3: Tunnel current, tunnel voltage and distance

If the tunnel current I is increased, the distance d between the tip and the sample decreases. The exponential relationship $I\ proptoe^{-2d\ kappa}$ applies here. Conversely, if the tunnel current is reduced, the distance increases.
A lower tunnel voltage also means that the distance d becomes smaller with a constant tunnel current, since the tunneling is made more difficult. Conversely, a higher tunnel voltage favors tunneling and the distance is chosen to be larger in order to compensate for this again.

1.10 Question 4: Electron flow

The number of electrons n per second is calculated as follows

$$n = \frac{I \times 1\,\mathrm{s}}{e} = \frac{1\,\mathrm{nC}}{e} \approx \frac{6.242 \times 10^9 e}{e} = 6.242 \times 10^9. \tag{6}$$

1.11 Question 5: Influences of air

The particles and air may make tunneling easier or harder. In this case you can see elevations or depressions in the surface that actually did not exist. The exact influence of air and particles is part of current research.
In addition, it is possible that an air cushion forms between the tip and the sample, which exerts a force on the sample or tip at very short distances, which changes the distance. In this case, different results are obtained in a vacuum than in air.
The influence of air and particles in the air that settle on the sample surface, however, is neglected here when experimenting; mathematically it is also relatively small.

1.12 Question 6: Gold vs. Graphite

As a metal, gold has free external electrons that are not clearly localized. This is because the highest occupied bands are above the Fermi level. That makes it hard to get atomic resolution.
Graphite is a layered material with anisotropic properties. It behaves like a metal along the layers; a free exchange of electrons is possible here. However, this is not possible between the shifts. It is therefore easy to achieve atomic resolution here while ensuring that the top graphite layer is supplied with electrons (otherwise no current can flow). Because of these properties, graphite is also called a semi-metal.

1.13 Question 7: Problems with piezo crystals

There are three major problems the piezo elements can cause.
First, the behavior of piezo elements is partially non-linear. Effects are a distorted picture. When driving,

care is therefore taken to keep the field strength small so that the behavior remains linear. This is achieved with larger piezo elements, in which the deflection is distributed over a longer crystal, which is why the field strength is smaller.
Second, the piezo elements creep in response to a larger change in voltage. This means that when the voltage changes, they initially change their position quickly, but still move slowly to their end position. This causes distorted images and different results in the same shot. This can be avoided by changing the voltage on the piezocrystals only a little or by waiting for larger changes until the end position is assumed. This can be checked if two pictures are taken of the same area after moving.
Third, thermal drift is a problem. Everything can shift here if something is mechanically distorted due to heating and different expansion coefficients. When designing the RTM, care should be taken to use only materials with similar expansion coefficients.

1.14 Question 8: Test and manipulate tunnel contact

In order to check the stability of the tunnel contact, several current-voltage lines with the same setting must be carried out one after the other. If these do not show any major changes, the tunnel contact is stable.
The tunnel conditions can be manipulated by changing the tunnel voltage. For example, a high voltage can be used to clean the tip of foreign atoms.

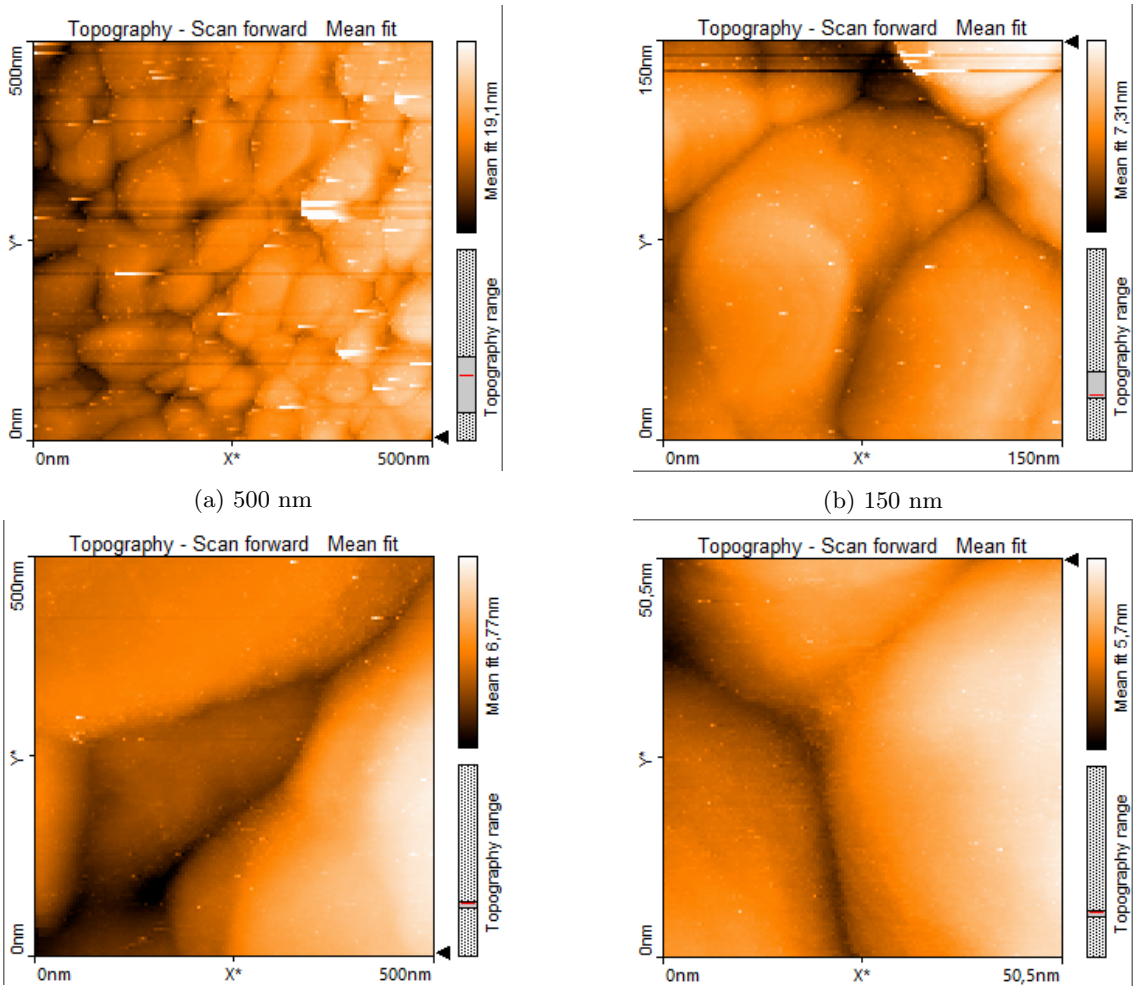
2 Prepairing the tip

The STM used is a all-in-one STM from NanoSurf. It consists of a head, where the probe is put in a probe holder. The probe can be moved fastly by a motor (move advance). The tip needs to be put in every time and is clamped down by a wire. The tip is moved by piezos.
The Software used for controlling the microscope is called 'Easyscan 2'. It is used to controll the rough z-positon of the probe holder and the piezos directing the tip as well as the voltage and current. The piezos for x and y are directly controlled, the piezo for z is controlled by a PID-controller, so that the set current is held unchainged.
Always, when working with the microscope, we used gloves. The first thing we did was insert a tip into the microscope. We used a PtIr-wire to cut the tip out of. The wire was cleaned with alcohol, then the tip was cut using pliers while pulling on the wire to create a very pointy end. Then the tip was clamped down in the microscope. For first testing, we inserted a gold probe. Using the software, we set the microscope to approach the probe and start scanning. From the first few pictures we knew our tip was good. We then proceeded with the other tasks.

3 Gold

3.1 Looking at the surface

After inserting the tip and the gold probe we started taking pictures with the STM. The pictures we took with the gold probe are in figure 1.



(a) 500 nm

(b) 150 nm

(c) 75 nm

(d) 50 nm

Figure 1: Pictures of gold taken by STM

All pictures are of the same probe with different magnification. More pictures of different gold probes were taken, but they don't yield any more information.
Very clearly can the gold flakes be seen. In figure 1a, the biggest picture, a lot of flakes can be seen. Then the other pictures show increasing magnification of the gold flakes. The flakes look like three-dimensional blobs. It is also possible to see plateaus, an example for the crystal structure of gold. In those unedited images we could not see any plateaus, but as seen in the calibration part, there actually are visible plateaus, if the pictures are enhanced by Gwyddion.

3.2 Voltage dependence of tunnel current

Now the tunnel currend has to be measured depending on the tunnel voltage. The software 'Easyscan 2' has a mode where the tunnel distance is kept contstant (probe not moving) and the tunnel current is measured as a function of the tunnel voltage. The measured data can be seen in figure 2.

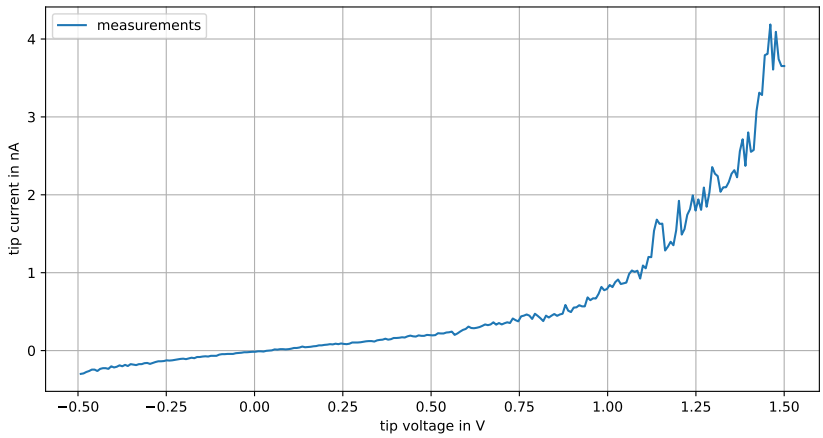


Figure 2: raw data of tunnel current depending on tunnel voltage

For lower voltages the relation to the current seems linear. Also, there is very little noise for lower voltages.
In contrast, for higher voltages, the dependence seems to become exponential. Furthermore, there is a lot of noise for the higher voltages, the curve is very volatile. This may be caused by interaction between the tip and the absorber layer. As the experiment was not done in a vaccum but instead in open air, the air molecules or other molecules in the air can influence the conductivity by a lot.

3.3 Calibrating z

Using gold, we finally want to calibrate the z-piezo of the microscope. Therefore, we should use flame-annealed gold. However, we could not tell the probes apart from the non-flame-anneald ones.
Flame-annealed probes are shortly heated in a flame. Because of that, the atoms can rearrange and develop plateaus. It is also possible for non-flame-annealed gold to have plateaus. Those plateaus are only a singe atomic layer tall, their height is known to be the layer height of gold, close to 2.4 Å. This will be used to calibrate the piezo.
Looking through our pictures we found a picture containing plateaus seperated by an atomic step. Actually, the picture used for the calibration is the already shown figure 1b.
Using the software 'Gwyddion' we enhanced and analyzed the picture. It can be seen in figure 3.

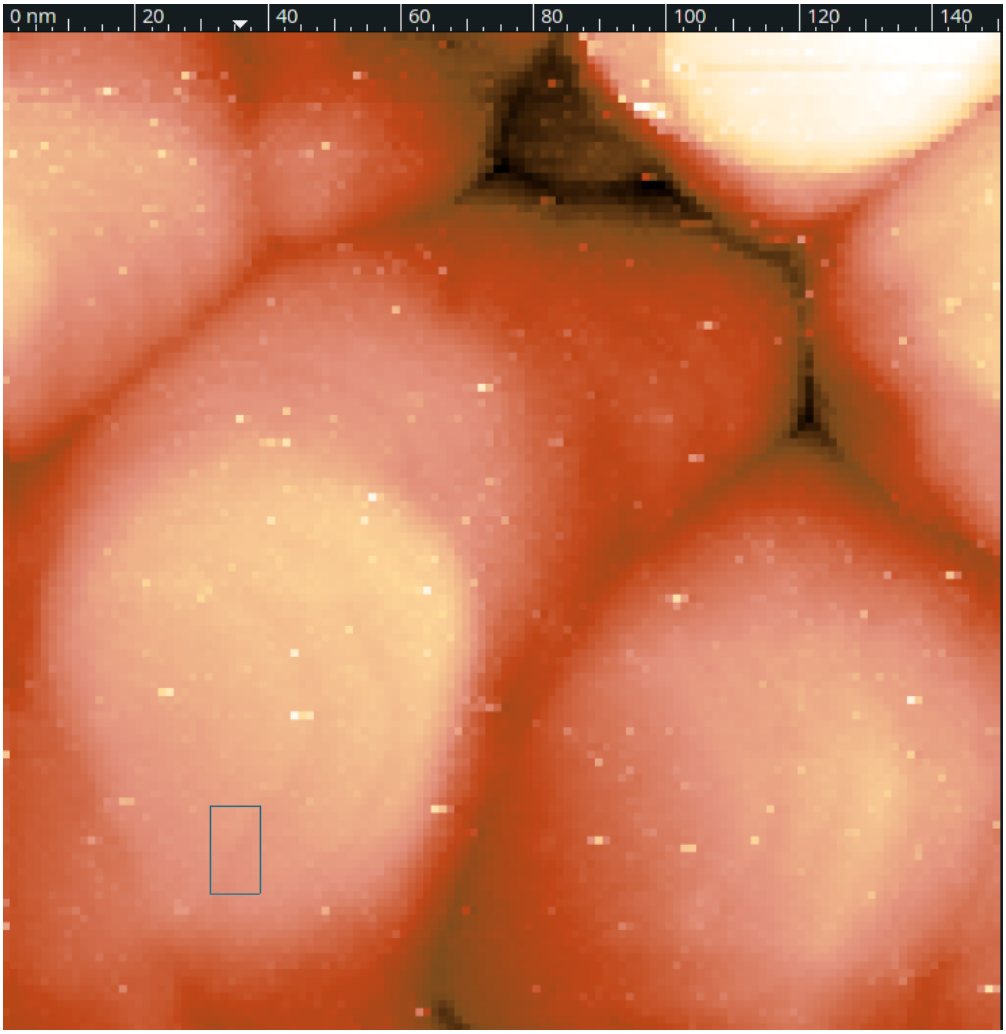


Figure 3: Picture of gold with atomic step between plateaus, enhanced with Gwyddion

Continuing using 'Gwyddion', we were able to extract height distribution data from the marked step. The data is shown is figure 4.

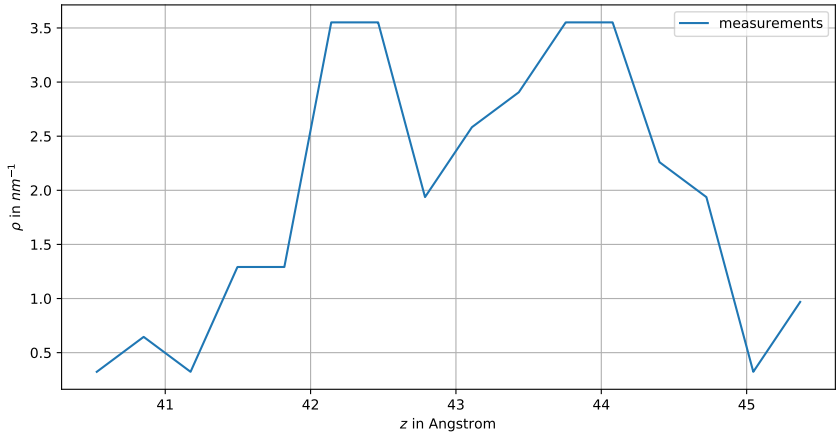


Figure 4: Height distribution extracted with Gwyddion

It can clearly be seen, that there are two peaks for the heights of the two plateaus. Manually, we seperated the data. The outer points from the height distibution were not used for further analysis, as they were most likely noise or belong to another layer, but without enough data they can't be evalueted properly. The center points are split for the upper and lower stair. The selected data points can be seen in picture 5.

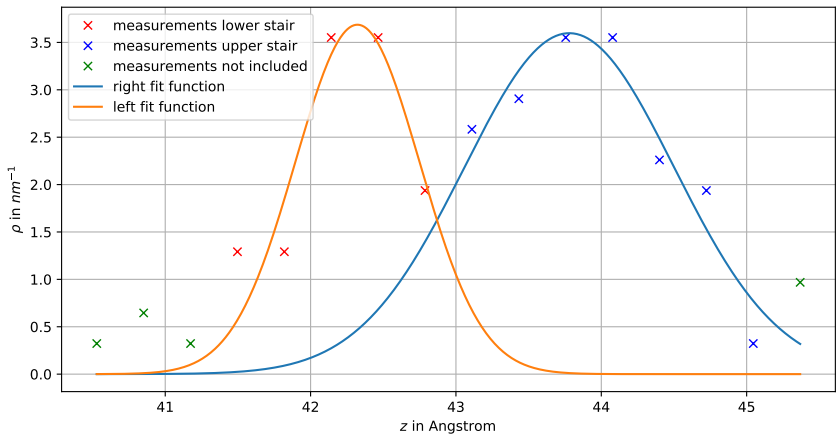


Figure 5: Seperated height data with fit functions

To get a good medium value for each set of points, a fit of least squares was done. The function used for fitting is a not normalized gauss function

$$f(z) = Ae^{-\frac{(x-\mu)^2}{2\sigma^2}}. \tag{7}$$

The fit functions are also visible in figure 5. The fit parameters are in table 1.

Table 1: parameters from the regression

parameter	left regression	right regression
A in nm^{-1}	3.7(6)	3.6(3)
μ in Å	42.32(8)	43.78(7)
σ in Å	0.43(9)	0.72(9)

For further calculations, A and σ are not used, only μ and its error are used. Using the final values, we get a plateau height of 1.46(10) Å as difference between the two μ. That translates to a calibration value of 1.65(12). All z values of the microscope have to be multiplied by this calibration value in order to get the actual values.

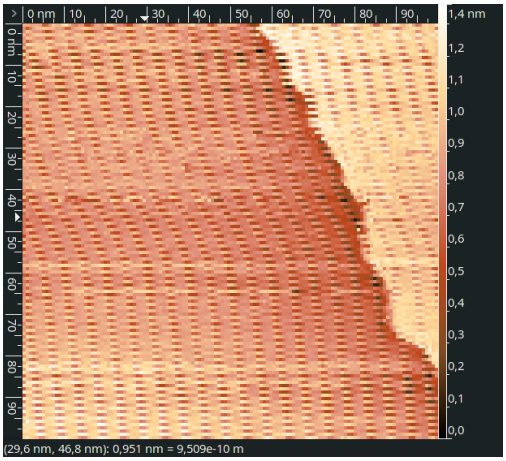
4 NanoGrid

This experiment was not done.

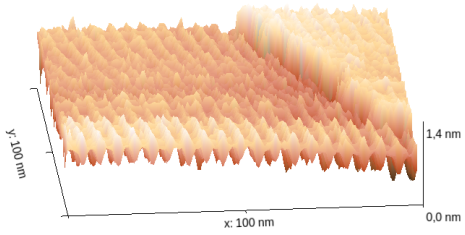
5 Graphite

5.1 Surface of graphite

To demonstrate the atomic resolution of the STM some pictures of graphite were taken. Graphite consists of many layers on top of each other that can be easily separated. Therefore the surface of the probe is cleaned by sticking a stripe of tape on it and removing it again. As a result of that the upper layers of the graphite should be removed because they're sticking on the tape. After inserting the probe the picture in figure 6a and figure 6b was made. It shown that the surface is, compared to gold, pretty flat. Furthermore it shows that there is a step in the upper right area which might appear from a layer that lay above the layer that has been scanned in the rest of the image and has not been removed completely while cleaning the surface with a piece of tape. This step has been measured with a height difference of 0.5 nm. Compared to the distance ot the single layers in HOPG, which is, as read in the documents given fir preparation for this experiment, 0.335 nm high, this step seems to have the height of multiple layers of graphite.In the images the atoms take a drift to the left side in the middle arrea. This might be a thermal drift which appeared during the scanning process.

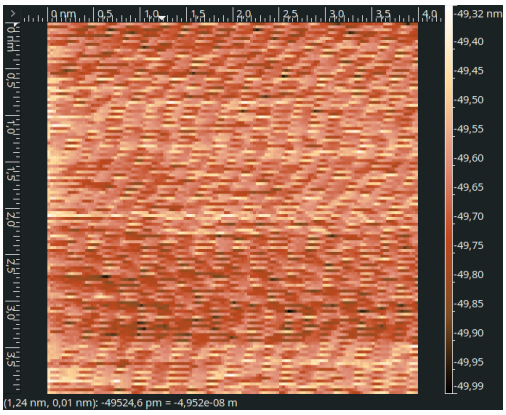


(a) Scan of a graphite area

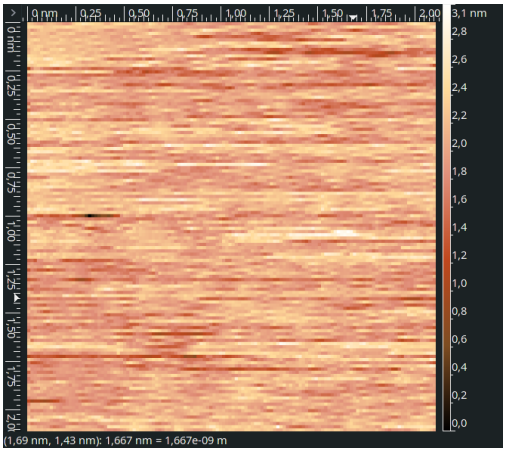


(b) 3D view of figure 6a

To achieve a better image quality, the tunnel voltage, tunnel current and the values for the PID controller have been reduced. For usual this shoud lead to a better image quality for scanning a smaller area. In our case the images got even worse with every try. After spending a lot of time trying to achieve a better image we were running out of time. Therefore the whole analysis of graphite has to be done with the image in figure 6a. Nevertheless we took some of these unusable images to demonstrate the effects of a too high scan speed (low scan time) in figure 7a, showing only noise because the tip started to oscillate, and a too high value for the P gain of the PID controller in figure 7b



(a) Noise because the scanning went to quick



(b) Noise comming from a too high P gain

5.2 The atomic structure

The image in figure 6a shows, apart from the thermal drift, a nearly rectangular structure from the graphite atoms. This is uncommon because graphite exists out of hexagonal rings of carbon atoms. Therefore a hexagonal structure might be expected. Because graphites exsists of multiple layers of atome there are carbon atoms which have another carbon atom in the next layer below (α) and some who have another carbon atom in the next but one layer below (β). The position of these atmos influences the electron density which is measured with the STM. Therefore only every second carbon atom is visible with an STM which results in a triangular structure in images taken with an STM.

Because we were not able to get an image with a better resolution of the area our tries to calibrate the y-direction of the STM did not deliver any useful results. We tried to use the periodicits in y-direction to calibrate the y-axis of the STM. Therefore we measured the distance betwen 20 of those black points in the image. We have expected a distance of 4.9 nm but we got a value of circa 10 nm which is way too mutch. Therefore we were not able to calibrate the y-axis with the images we made from the oscilloscope. The calibration of the axis can be useful to detect possible deviations caused by vibrations, inaccuracies in the tip or thermal drifts.

6 Distance dependence of tunnel current

From the graphite probe we have measured the current depending on the distance between the tip and the probe. This process has been done two times. The expected behaviour is that the curent drops exponentially with a higher distance. The measured values can be seen in figure 8. Furthermore the measured values have beeen fitted with a curve. In the figure the current axis has a linear scale. Therefore the fit function is a linear function applied on the logarithm of the measured current. From the fitting parameters the barrier distance Φ can be calculated.

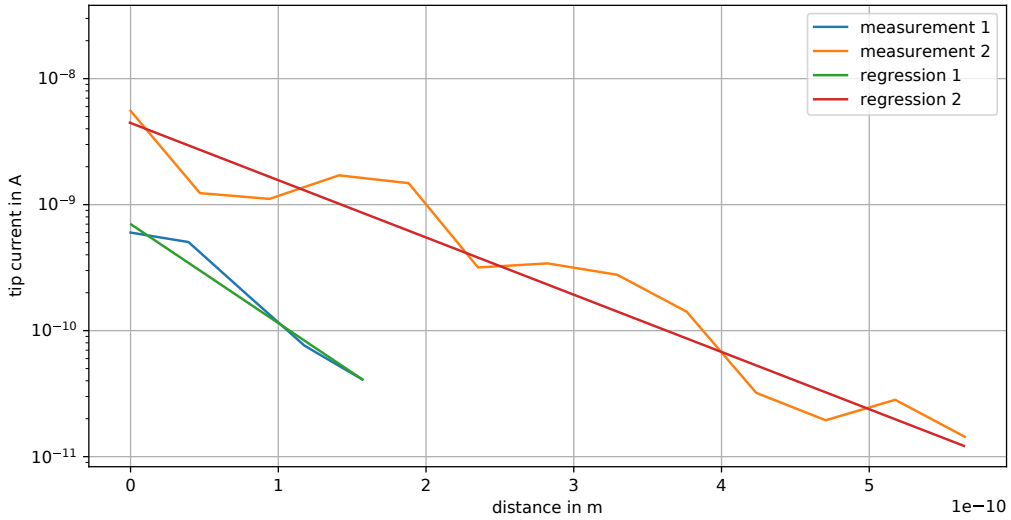


Figure 8: current depending from the distance between the tip and the probe

From the regression we get an average value for the pitch of the linear curve of

$$m = -2.15(2) \times 10^{-9}\,\mathrm{m}^{-1}\,. \tag{8}$$

From that value we can calculate the barrier voltage via the formula

$$\Phi = \frac{m^2 \cdot \hbar^2}{8 \cdot m_e} - \frac{e \cdot U_T}{2} \tag{9}$$

where we use the value for the tunnel voltage we set in the program: $U_T = 886\,\mathrm{mV}$. Therefore we get the results for the barrier voltage:

$$\Phi = 0.064(6)\,\mathrm{eV}\,. \tag{10}$$

Compared to the given value in the preparation of 4 eV to 5 eV this seems to be realy tiny.