STM Investigations of hillocks on HOPG generated by incident highly charged ions

Lukas Süss
Projektarbeit: "Interactions with Surfaces" 134.114
Betreuerin I. C. Gebeshuber
Institut f. Allgemeine Physik, TU Wien
e-Mail: lukas.suess@student.tuwien.ac.at

October 8, 2008

Abstract

Measurements on highly ordered pyrolytic graphite (HOPG) irradiated with highly charged ions (HCI) were taken with a scanning tunneling microscope. Hillocks from high charge states of Argon were investigated and compared to the values obtained earlier by measurements of Xenon with similar potential energy (summarized amongst others in [1]) in order to assure that the choice of element as charge carrier has no notable influence on the diameter of the generated hillocks. The result indicates that the hillock diameters stay about the same independent of the nuclear charge of the projectile.

1 Scanning Tunneling Microscopy

Scanning tunneling microscopy (STM) is an imaging method invented by Gerd Binnig und Heinrich Rohrer in 1981 on which they recieved the Nobel Prize in Physics in 1986. In contrast to conventional microscopy it is not based on focused light- or electron waves so its resolution is not restricted to the the wavelength of light or the minimal de Broglie wavelengths of electrons imposed by sample heating. [1]

An STM acquires images by scanning over a surface with a sharp tip[2] and uses the quantum mechanical tunneling current to maintain a defined distance between tip and surface. There is no "physical" contact and are no mechanical forces between them. To get the DC tunneling current the samples have to be electrically conductive what imposes by far the biggest restriction to STM. In contrast in the case of atomic force microscopy AFM (which is the mechanical pendant to STM) the tips are on flexible cantilevers and do have direct contact to the surface in most imaging modes. AFM is less gentle to the surface and has in most cases lower resolution but can also probe isolators, and provides information about other interaction forces[3].

In more detail the working principle of the STM is as follows. With a combination of a

[1] with near field scanning optical microscopy SNOM which is a combinaton of SPM and conventional microscopy optical properties below abbes limit can be examined

[2] widely used tip materials are W, IrPt, Au

[3] based on surface scanning there ermerged many other scanning probe microscopy SPM techniques such as: AFM with functionalized tips, magnetic force microscopy MFM, near-field scanning optical microscopy SNOM

coarse stepper motor and piezo stack actuators for fine motion control the tip gets approached to close proximity (a few Angström) to the surface so that a constant current whose variations later are used to regulate the distance between surface and tip is established. To prevent a crash of the tip with the surface and severe image distortions STM and in general all scanning probe microscopy SPM techniques have to be damped from external vibrations appropriately which can pose substantial effort. Now images can be recorded from the current and the piezo deflection signal while scanning over the surface. When feedback is maximized one gets more contrast in the piezo voltage and less in current signal. This is called the constant current mode CCM. It is important to keep in mind that the images must be interpreted more as heights of constant carge density[4] than only actual height defined by van der Waals interactions as in AFM images. When feedback is set small the most information gets into the current image and the image represents a plane cut through the carge density. This mode is called constant height mode (CHM) in this mode it is possible to scan faster but the surface must be extremely flat to omit collisions between surface and tip.

The tunneling current is dependend on the overlapping of the spacial exponenially declining wave functions of surface and tip and so itself is exponentially declining with distance. $I = f(U)exp\left(-\sqrt{8m_e/\hbar^2}\sqrt{\phi}d\right)$ [5]

It is about one magnitude by 1Å. This makes a high vertical resolution in the pm range archievable. Also a high lateral resolution is possible that is mainly defined by the geometry of the orbitals of the front atom at the tip. So if the tip is sharp enough the acquired images can be of atomic resolution. Additionally to the passive way of observing the tip provides the unique possibility to directly manipulate atomically precise the subject under investigation. Which is one of the reasons that make STM and other SPMs so interesting to various fields of research such as material sciences, molecular biology, tribology, electronics, nanomechanics and many more. A restriction to atomical resolution is that on steep edged surface features one usually gets a convolution of the tip and the surface in the recorded image due to current flowing over multiple contacts and one gets to see parts of the tip structure in the images.

STM can be performed in air but many surfaces of interest are unstable under environmental pressure so ultra-high-vacuum (UHV) systems are needed. To test atomical resolution especially stable easily claeavable layered materials such as MoS_2 and $HOPG$ are used. They are also useful as the simplest base materials that can be prepated for further structural investigations such as performed in this study.

2 Sample Preparation and Measurement Setup

The HOPG samples[6] were irradiated in Caen at the ARIBE facility at the high intensity beam lines. Kinetic energies around 180keV were used. Immediately after irradiation they investigated them with AFM. The hillocks were only visible in the friction image and way larger than expected. The samples were then transported to the Institut für Allgemeine Physik on the Technical University of Vienna. After 30 days storage under enviroumental pressure conditions the measurements on STM whose results are preseted here were

[4] more exakt the surface of constant local density of states (LDOS)

[5] I ... tunneling current; U ... gap voltage; f ... material dependend polinomial function; ϕ ... work function with typical 4,5eV; d ... tip-surface distance

[6] MikroMasch HOPG ZYA/1mm

taken to get complementary information. For all the measurements Veeco Platinum/Iridium tips were used[7]. The pressure level was kept below $2*10^{-9}hPa$ and unless not stated otherwise all pictures are taken with 0.3nA setpoint current and +0.7V gap voltage.

3 Results

Data of impacts on HOPG from Ar^{9+}, Ar^{14+}, Ar^{16+} and Xe^{23+} were recorded. The measured irradiation dose was close to the expected $6 * 10^{11}cm^{-1}$ for Ar samples except for the Ar^{16+}. On Xe^{23+} there were $3*10^{11}$ expected and $1.4*10^{11}$ encountered. Interestingly in contrast to the lower yields at the two higher charge states in the AFM inverstigations the yield increased with increasing charge state.

Encountered hillock densities on Ar sampes:

Ar^{9+}: $7.5 * 10^{11}cm^{-2}$
Ar^{14+}: $6.8 * 10^{11}cm^{-2}$
Ar^{16+}: $2.9 * 10^{11}cm^{-2}$

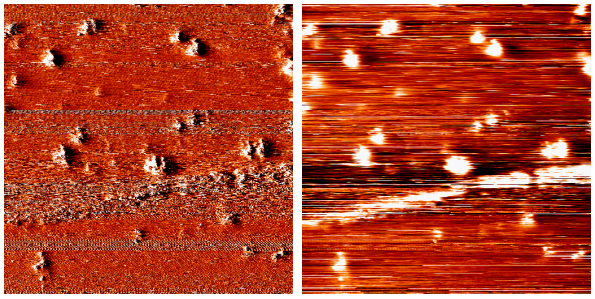

Figure 1: Xe^{23+} different sized hillocks; image size $100 \times 100nm^2$; current and height image

For Ar^{9+}, Ar^{14+} and Xe^{23+} (Fig.1) the images taken for statistical analysis were square with a sidelength of 100nm. For Ar^{16+} the sidelength was 200nm (Fig.2). Especially on the images of hillocks from higher charged ions a distribution of hillock sizes is apparent (Fig.1 and Fig.7 upper left). The diameters and heights are summarized in Tbl.1 and diameters are graphed in Fig.4.

4 Data Acquisition

For Ar^{9+} and Ar^{14+} diameters were acquired by counting the number of pixels parallel to central hillock crossing scanlines in the current image. Heights were acquired from height images after plane substraction and linewise levelling via averaging over a circle with radius of 2 pixels. The hight zero level was taken for every hight measurement independently from beside the accordant hillocks. For Ar^{16+} diameters were acquired with height profiles parallel to scanlines where amplitude is fallen to $\frac{1}{e}$ of the maximum value (Fig.2). Hights out of hight profiles normal to scanlines in (Fig.7) upper left. And for Xe^{23+} height diameter pairs (diameter as for Ar^{16+} at h_{max}/e) were extracted from profiles normal to scanline direction to prevent randomness from the choosen scanline. [8]

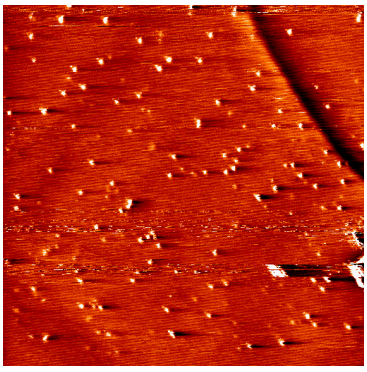

Figure 2: Ar^{16+} different sized hillocks; image size $200 \times 200nm^2$; current image

[7] Veeco STM Probes Cut Platinum/ Iridium 6mm S/N:031207 Model:DPT Part:DPT (03/07)

[8] The programs used were Scala Pro v5.0 and Gwyddion v2.7.

Table 1: Hillock Diameters

Ion	Diameters and Heights			Heights			Count
	Mean (nm)	St.dev. (nm)	Error of Mean (nm)	Mean (nm)	Sz.dev. (nm)	Error of Mean (nm)	
Ar^{9+}:	1.67	0.45	0.05	1.27	0.76	0.10	75; 60
Ar^{14+}:	1.79	0.60	0.07	0.37	0.11	0.02	66; 45
Ar^{16+}:	2.17	0.46	0.04	0.78	0.37	0.07	115; 32
Xe^{23+}:	2.45	1.19	0.30	1.34	0.38	0.11	14; 14

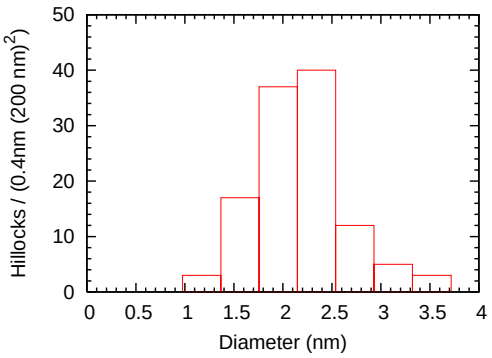

Figure 3: Ar^{16+} hillock diameter distribution

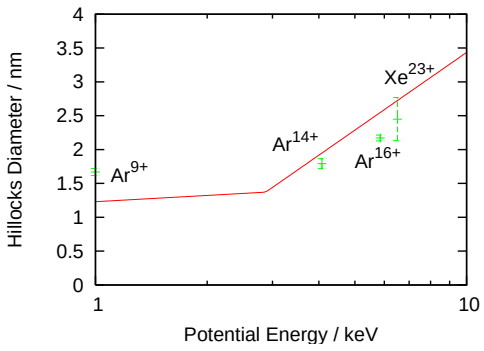

Figure 4: Ar^{16+} mean hillock diameter over potential energy

5 Conclusions

Out of individual measurements of hillocks on HOPG which got collected in [1] there is a linear dependence between hillock diameter and logarithmized potential energy visible. At a potential energy of approximately 2.9keV there is an aprupt rise of slope apparent (Fig.4).

The linear approximations[9] are taken out of [1] and the potential energies corresponding to the charge states out of [5]. It is believed that there is a critical potential energy that causes this kink and the change from Ar to Xe should have no influence on the shape of the curve. So that the parts overlapping in energy of different elements should be equal. This is exactly what was observed (Fig.4). The locally slightly negative deviation of Ar^{14+}, Ar^{16+} and Xe^{23+} diameters to the linear approximation out of [1] is in correspondence with the measurements of Xe^{23+} made by [2] done by different kinetic energies. Strangely the hight values seem very different from those summarized by Terada [4].

On the sample irradiated with Ar^{14+} in an area with a low hillock density of $0.4 * 10^6 cm^{-1}$ one time an astounding crater like structure were encountered (Fig.5). The geometric data:

- overall diameter 1.6nm
- rim-to-rim diameter 0.8nm hillock
- rim height varies from 0.3nm to 0.5nm
- crater bottom at a height of 0.2nm

Sadly something courious like this wasn't found again.

[9] d(E)=a*log(E)+b
where (a,b)=(0.31,1.23) for E<2.9keV
and (a,b)=(3.81,-0.38) for E>2.9keV

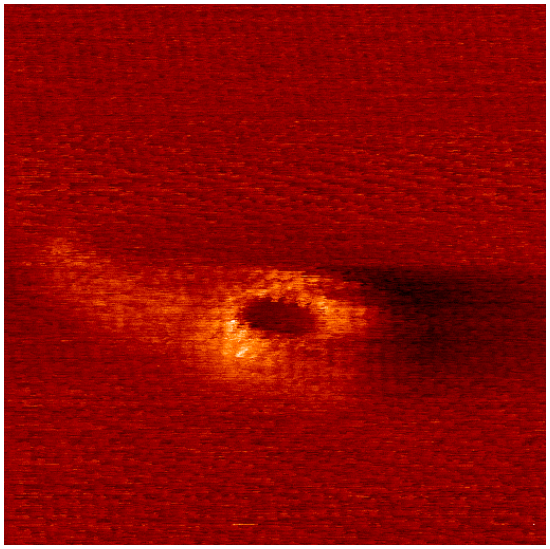

Figure 5: Ar^{14+} structure which looks like a crater

6 Further observations

On Ar^{16+} and Xe^{23+} a very interesting property could be observed. Along with the "normal hillocks" there appeared "closed hillocks". Here the undisturbed HOPG surface seems to extend over the whole hillock and shield it from the environment so they are only visible in the overall change of current or constant-current-height and not in structural changes of the hexagonal graphite lattice. The upper left side of Fig.7 shows Ar^{16+}-hillocks from which all the smaller ones that look smooth are like the ones pictured on the upper right. The lower two are Fourie filtered closeups[10] where the smaller one has a diameter of 1.4nm when measured at 1/e of the maimum hight value and 1.1nm when measured at half of the maximum hight (FWHM) and a height of 1.0nm whereas the bigger one has a larger diameter of 4.75nm (1/e) and 3.75nm (FWHM) and an height of 0.35nm. In Fig.2 the 115 hillocks divide into 51 closed and 64 normal hillocks 44% and 56% respectively. Because of bad hight resolution the closed hillocks are not percievable in the corresponding hight image, but in the hight image corresponding to Fig.7 upper left they are. Here the hillock type splitup is visible in a broadened hight distribution with slight indications of two maxima as seen in Fig.6.

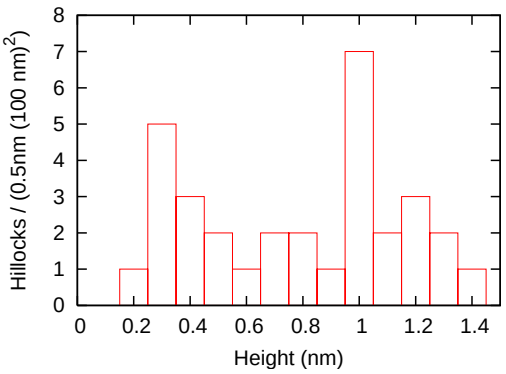

Figure 6: Ar^{16+} hillock height distribution

In [3] hillock-structures generated by Ar^{9+} with a kinetic energy of 150eV were observed which also could be divided into two categories. There were smooth atomically resolvable ones which were iterpreted as interstitial defects maybe caused by enclosed neutralized Ar atoms under the first few HOPG layers. Some of the observed ones of this type had a $\sqrt{3} \times \sqrt{3}\ R30^\circ$ reconstruction at the surface. The second type were higher ones that are seen as protrusions due to their their electronic structure. They were interpreted as vacancy deffects. The current results of measurements on Ar^{16+} show essentially the same splitup but with the difference that no surface reconstructions on the smooth hillocks occured at all and the protrusion like hillocks are higher and prone to cause STM-image distortions. Due to the one thousand times higher kinetic energy inclusion of Ar atoms right under the surface

[10] For better visualisation of atomic details constant height mode images are pictured.
The feature on the lower edge of the small hillock is not an atomic displacement but is due to an image distortion.

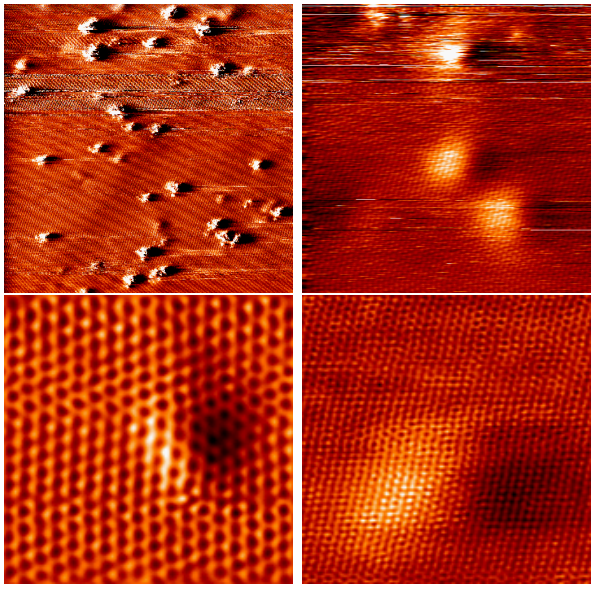

Figure 7: Ar^{16+}: hillocks without structural changes (upper left to lower right: 100nm current; 10nm height; 4nm current fft; 8nm current fft)

responsible for visible smooth surface deformations can be ruled out in the current experiment and also seem more unlikely in the Ar^{9+} 150eV case. For comparison implantation density of Phosphor ions with $E_{kin} = 200$keV in Silicon is maximal at 30nm depth [6] and the mass ratio here $m_{Ar}/m_C = 3.3$ is higher than $m_P/m_{Si} = 1.1$ so that in the present case an even higher mean penetration depth is to be expected. More likely are enclosures of sp3 carbon or other structural changes shielded by the topmost HOPG layer. What is notable is that although the potential as well as the kinetic energy were very different in the former and current case nearly the same effect of split up into smooth and protrusion like hillocks could be observed and still in each experiment the two resulting hillocktypes were so different while all the parameters were constant. So we conclude that the ion energies and surface must be irrelevant for the hillocktype of outcome and the process must be a pure probabilistic one that occurs during cooldown of the hillock[11]. Though in both cases it is a probabilistic effect a difference is that in the current experiment the protrusion like hillocks seems to be no vacancy deffects but image deffects which occur whenever the hillock flank steepness reaches a critical value which causes multipointcontact with the tip. A second difference is that in the low potential energy case surface reconstructions of the smooth hillocks occured and in the case of Ar^{16+} surface reconstructions of smooth hillocks are supressed. Maybe this is due to the fact that the two measurements are on each side of the kink of the curve (Fig.4). But the number of atomically resolved smooth hillocks are too fiew to make the general claim that there really are non reconstructed or "prefect" ones.

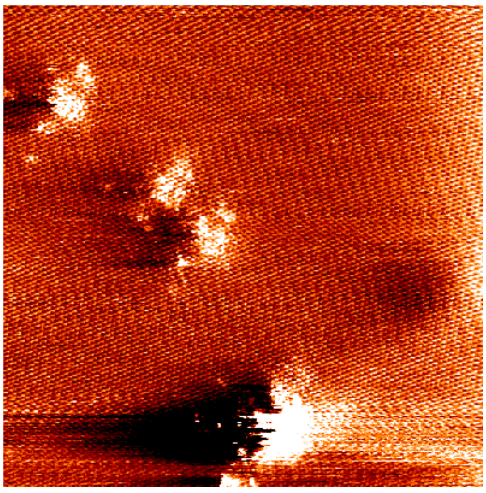

Figure 8: Ar^{16+} $25 \times 25nm$ current image; intermediate state hillock

Three extremes across the spectrum of different hillocktypes are present in Fig.8. On the right there is a part of a totally smooth one, three intermediate state hillocks are on the up-

[11]This also explaines that the splitup in the two hillocktypes is not visible in the histogram of diameters.

per left and a normal hillock is at the bottom. The intermediate state hillocks (of nearly the same hight) do all have similar anisotropical features which is a typical sign of tip structure in the image. In the case of the the normal hillock at the lower edge even more of the tip structure must be gone into the image so that isotropy is regained again and atomic resolution is lost for sure. The results with other tips of the same type are similar. So it seems hard or even impossible to archive atomic resolution on normal hillocks of chargestate like 16+ with conventional tips. The fact that all atomically resolved hillocks on Ar^{16+} are perfect or that there are no atomically resolved deffects corroborates that the split in hillocktypes at least on Ar^{16+} is only a matter of imaging, it could be possible that all hillocks are perfect but we can't see it because of too blunt tips. If they really are they may be suitable for tip structure characterisation.

7 Acknowledgements

Thanks to Ille Gebeshuber who gave me friendly support and did the proofreadig of this study, also thanks to Friedrich Aumayr and Walter Meissl who performed the irradiation and gave me basic Informations about the subject. Further I want to thank Cezary Piezcetowski who spent a bunch of time to give me a detailed instruction to the UHV-AFM/STM System. And also to Robert Ritter, Georg Kowarik, Arthur Golczewski and Paul Berlinger for support and help during troubleshooting.

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