Addition 2

Test Measurements on the Graphite (0001) Surface

Graphite

For STM test measurements a standard sample is graphite, which has been used in this work under ambient conditions. Graphite as a layered material consists of chemically inert layers which are held together by the weak van der Waals forces (*Fig.1*). Layers are built up by a honeycomb arrangement of the carbon atoms which are strongly covalently bonded to each other. Neighbouring layers are shifted relative to each other by an AB AB AB stacking sequence. This stacking sequence gives rise to two non-equivalent carbon atom sites within the 2D surface unit cell: One carbon atom (A-site) has a neighbouring carbon atom directly below in the next layer whereas the other carbon atom (B-site) is located above the center (hollow site) of the sixfold carbon ring in the second layer. During the STM imaging of the graphite surface only one site of the atoms (B-site) is imaged.

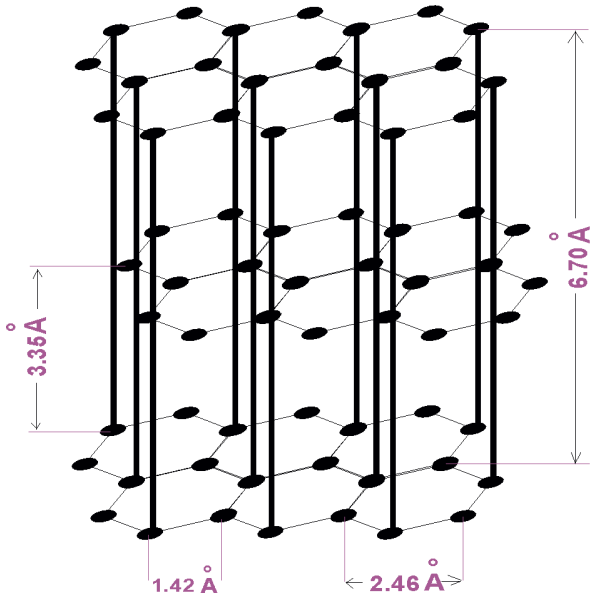

Fig.1

Graphite structure.

Graphite can easily be cleaved by peeling off a few carbon sheets with adhesive tape. Cleaving provides atomically flat terraces up to several thousand square $\mathring{A}$ and furthermore cleaving does not create dangling bonds and the freshly cleaved surface may stay clean for a long time.

Since naturally occuring graphite single crystals are relatively small and difficult to obtain, the most widely studied form of graphite by STM is Highly Orientated Pyrolytic Graphite (HOPG). It has a hexagonal structure and a relatively large grain size of about 3-10 μm .

Giant corrugations

In STM measurements graphite exhibits giant corrugations from $1\mathring{A}$ up to $8\mathring{A}$ [1]. Such corrugations are observed on a graphite surface on air in the constant current mode of operation. The corrugation is voltage dependent and independent of the polarity. By helium atom scattering (HAS) the corrugations observed on the graphite surface are about $0.2\mathring{A}$ [2]. The giant STM corrugations were attributed to the elastic deformation of the graphite surface induced by atomic forces between tip and sample surface, adding to the electronically based corrugation (*Fig.2*), see also discussion in the STM theory chapter.

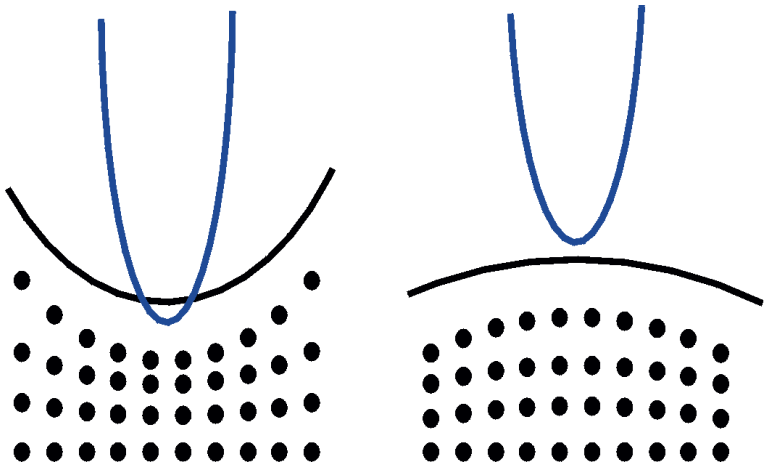

Fig.2

Giant corrugations on the graphite surface.

For the first time it was realized that the STM image contrast may not always be determined by the LDOS, but can in special cases be dominated by the tip – sample interaction, particulary at a small tip – sample separation. Hence the forces between tip and sample have to be taken into account whenever soft samples such as graphite and other layered materials are studied by the STM.

Despite the relatively simple structure and easy surface preparation, interpretation of the STM results for graphite is far from being straightforward.

Big area HOPG images

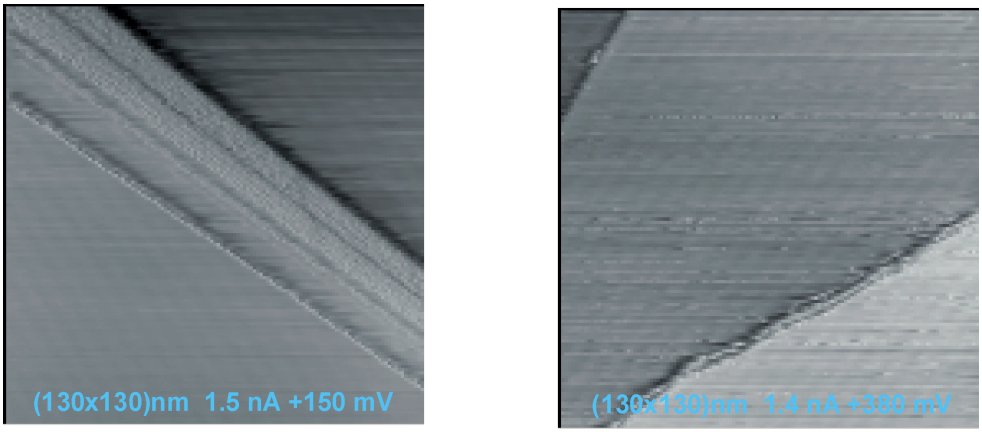

Fig.3
(130x130) nm big scale HOPG images.

In the images shown in *Fig.3* it is possible to see steps, bunches of steps, steps which are crossing each other and steps which are changing their directions.

In the images shown in *Fig.4* it is possible to see more complicated surface structures, e.g. bunches of stripes which are crossing each other at variable angles (90°, 100°, etc.). The fact that the crossing angles are different from 60° and multiple 60° can be explained by the fact that the surface is not in the energy minimum state and that is why the various angles are allowed.

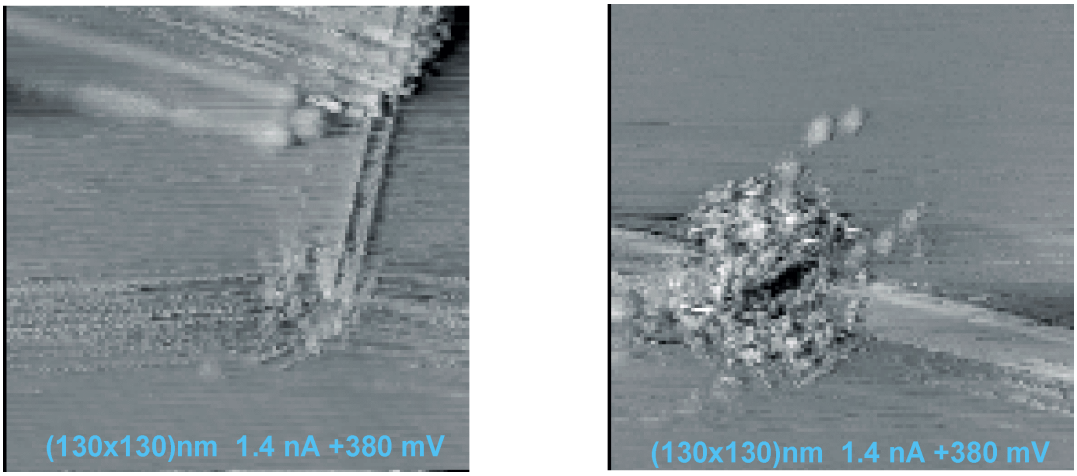

Fig.4
Big scale (130x130) nm HOPG images.

In the right image of *Fig.4* one can see the result of the tip crash (a hole and an island of the graphite material around it). This image is quite unusual because in the ordinary case the graphite surface does not modify after tip crashes. Usually the surface simply `escapes` elastically from being touched by the tip.

Forward and backward images

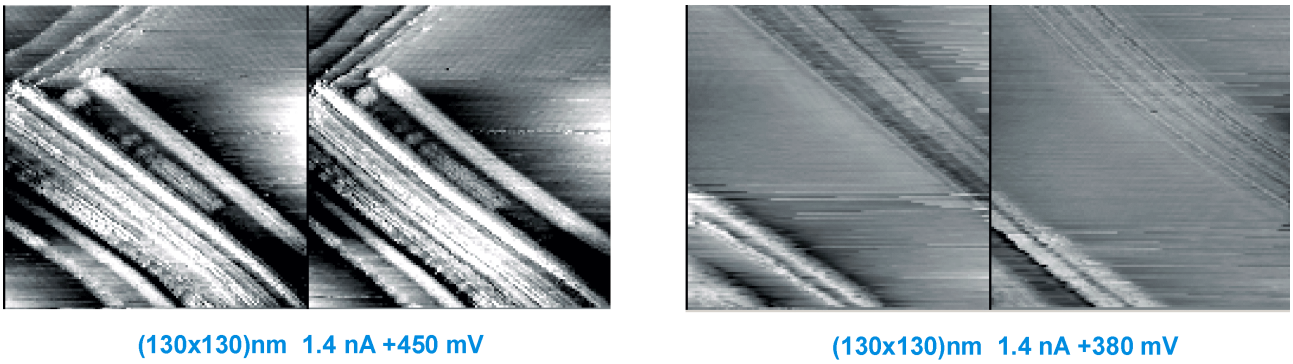

Fig.5
HOPG forward and backward images.

In *Fig.5* forward and backward STM images are shown. This means that the tip in the first case is moving on the line from left to right (left hand images) and in the second case moving on the same line from right to left (right hand images). In the ideal case these images should be identical. The fact that they slightly differ from each other can be explained by the hysteresis of the piezoelectric material.

Because the piezoelectric material is a polycrystalline material the walls between the domains can move and during moving they can be pinned on defects. This results in a slight change of the image (we can, for example, see the distortion on the borders of the image, the steps which should go straight start to have noticeable curvature).

HOPG: atomic resolution

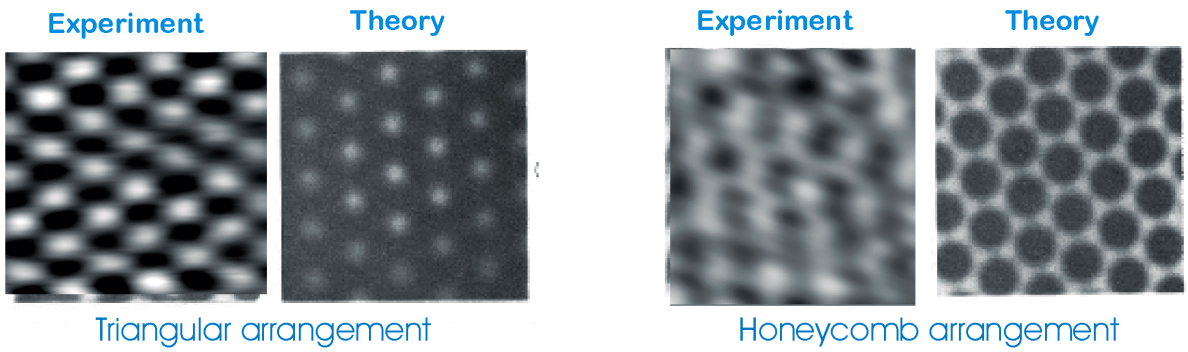

Fig.6
Atomic resolution HOPG images showing triangular and honeycomb atom arrangements. Experimentally (left images in each pair; our measurements) and theoretically obtained atomic resolution images (right images in each pair) of the HOPG surface [3].

In *Fig.6* two atomic resolution images of the graphite surface are shown. The first image shows a slightly distorted single tip image of the triangular lattice. The second image is a double tip image of a honeycomb array. The different appearances of the surface shall be explained in the next paragraph.

From linescans taken in different directions across the HOPG surface, a corrugation amplitude of about 1Å and a noise level of 0.1Å was determined. Such a value of the noise level is

high compared to STM measurements at low temperatures but for measurements in air and at room temperatures it is within expected limits (a corrugation amplitude and a noise level during UHV measurements at room temperature, see the Room Temperature STM instrumental chapter).

Multiple – tip interpretation of the anomalous STM images of HOPG

The tip dependent appearances of the HOPG surface will be explained following Mizes et al [3]. Tersoff and Hamann modeled a tip potential by a spherical potential well. The tunneling current is seen to be proportional to the LDOS for the sample at the Fermi energy, evaluated at the center of the tip (see also the STM theory chapter).

$$\mathrm{I}_0 \propto \sum_{\nu} \left|\Psi_{\nu}(r_0)\right|^2 = \rho(r_0, E_F) \tag{1}$$

Since a tip is composed of atoms, a nonideal tip can be approximated as a tip with a linear combination of two or more s-states, corresponding to the closest tip atoms to the sample.

$$\mathrm{I} \propto \sum_{\nu} \left| \sum_{\mu} \Psi_{\nu}(r_1) e^{i\Phi_{\mu 1}} + \Psi_{\nu}(r_2) e^{i\Phi_{\mu 2}} \right|^2 \tag{2}$$

Since the sum is over the tip wave functions with a wide variety of relative phases, the interference term will tend to sum to zero.

$$\mathrm{I} \propto \sum_{\nu} \left|\Psi_{\nu}(r_1)\right|^2 + \left|\Psi_{\nu}(r_2)\right|^2 = \rho(r_1, E_F) + \rho(r_2, E_F) \tag{3}$$

The STM image will be then a superposition of two images, the second shifted by a relative separation of two tip atoms.

- So the first images are the single – tip images of a triangular lattice.
- A honeycomb array will be imaged if one of the components suffers a reletive phase shift of π.

References

[1] H.-J. Güntherodt, R. Wiesendanger, *Scanning Tunneling Microscopy*, Springer-Verlag (1994)

[2] J.M. Soler, A.M. Baro, N. Garcia, H. Rohrer, PRL **57**, 444 (1986)

[3] H.A. Mizes, Sang-il Park, W.A. Harrison, PRB **36**, 4491 (1987)