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Citation: Applied Physics Letters **48**, 112 (1986); doi: 10.1063/1.96968
View online: http://dx.doi.org/10.1063/1.96968
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/48/2?ver=pdfcov
Published by the AIP Publishing

Tunneling microscopy of graphite in air

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(Received 20 September 1985; accepted for publication 4 November 1985)

Images of graphite have been recorded with a scanning tunneling microscope operating in air at ambient pressure. The results, which are in agreement with theory and previous experiments in vacuum, confirm that with a surface such as graphite the tunneling microscopy in air can be used to examine the geometry of the surface with a resolution that is less than 2 Å.

The scanning tunneling microscope (STM) as introduced by Binnig *et al.*[1] provides us with a superb tool for surface science. The scanning mechanism, the control of vibration, and the formation of the tip are all problems that have been solved. It is now known that the STM can be used to define the spatial positions of atoms on surfaces of metals and semiconductors. Much of the definitive work has been carried out with the STM mounted in UHV stations in order to conform to the requirements of surface science. A notable exception is the work of Coleman *et al.*[2] in liquid nitrogen.

In this letter we report that the STM operating in air can generate images with atomic resolution. Hansma *et al.*[3] have reported previously on their preliminary results with an STM operating in air. We have selected graphite as the sample crystal because it is inert and free from contamination. For bulk graphite the atomic structure is well known and electronic states are simple to calculate.[4,5] However, the structure of the surface layer is less well known and it is important to gather information on these surfaces.

Graphite has been studied by others. Baro *et al.*[6] have pointed out that this is an ideal substrate for the STM since large atomically flat net planes are available. The most definitive study was carried out by Binnig *et al.*[7] in a UHV station. They have reported on the hexagonal structure of the surface layer. Their results are in agreement with the theory of Selloni *et al.*[8] who used a model calculation to show that the height corrugation is voltage dependent.

Our experimental results are similar to those of Binnig *et al.*[7] and agree with the predictions of Selloni *et al.*[8] They demonstrate that our instrument can generate images with a resolution that is better than 2 Å. This suggests that the "effective tip" must consist of a single atom.

The experiments were a test run of our new STM that was designed to fit into a UHV system together with surface physics instruments. Our instrument was operated without special precautions in ambient pressure where the sample turn-around time is measured in minutes rather than hours. The condensation of water molecules on the tip does not appear to be a problem with the field strength used here.[9] The images are easily repeated with different samples and different tips. We believe that the results are significant since we can record definitive information on surface structure in this environment. We wonder what it is about the graphite surface that allows us to do this.

The instrument that we are using has several innovative features that make it useful for our purposes, but it is derived from the design that was shown to us by the IBM group in Zurich. The details of this STM will be described elsewhere; here we will only outline the essential features. The entire microscope is mounted on a 10-in. o.d. UHV flange which can be inserted into the vacuum chamber through an 8-in. i.d. port from the side. For vibration isolation, we use conventional double stage spring suspension with eddy-current damping. The stray magnetic field is reduced by encasing the entire microscope within a mu-metal sheet and mounting the magnets in the form of octopoles. The mu-metal cover can be opened for sample transfer. The sample holder is mounted on a sturdy translation stage and the two vibration isolation stages have a lock to provide rigid support during the sample transfer operation. The translation stage is driven by a UHV compatible stepper motor via a worm gear. It moves in steps of 1500 Å over a range of 5 mm. The scanner is formed with three orthogonal PZT bars each with a maximum range of 1 μm. It was calibrated and tested for orthogonality with laser interferometer. We used commercial tungsten tips with an approximate radius as determined by the SEM of 1000 Å.

The thermal drift, one of the most important factors in successful tunneling microscopy, becomes more critical when the instrument is operated in air. In order to provide thermal insulation, we used multilayers of lint-free paper and vinyl wrap on the mu-metal cover of the microscope. The temperature of the unit was maintained at 27 °C with a temperature controller driving a built-in heater. The temperature variations were less than a milli degree over the period of several minutes.

The sample was highly oriented pyrolytic graphite as described by Moore.[5] This layered material is easily cleaved. Alternatively, Scotch tape can be used to remove the top layers. We used these techniques to expose fresh layers and found that the quality of the image was unchanged after several days of exposure to air.

In Figs. 1 and 2 we display two images obtained from the raw data (a) and from the digital filtered data (b). All images span 20 Å in both x and y. The scanning speed along a line, the x axis, was 4 Hz in Fig. 1 and 10 Hz in Fig. 2. The tip with 10 mV was positive with respect to the graphite and the average value of the tunneling current was 5 nA. The variations in tunneling current during the scan provided the signal that we used for the image. In order to remove the noise from the raw data, we have used the Weiner optimum filter[10] with the assumption that we have $1/f$ noise along the x axis and white noise along the y axis. This power spectrum of the noise was deduced from the momentum space spectrum of the data and the noise could be removed more efficiently

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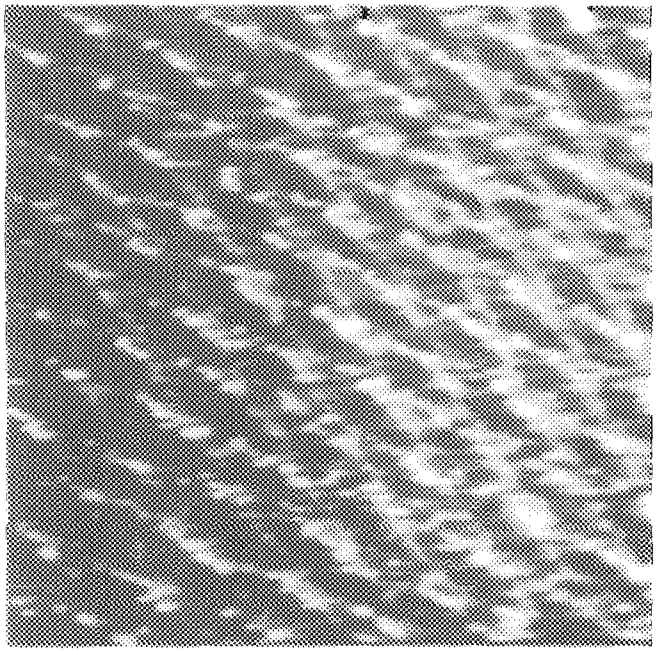
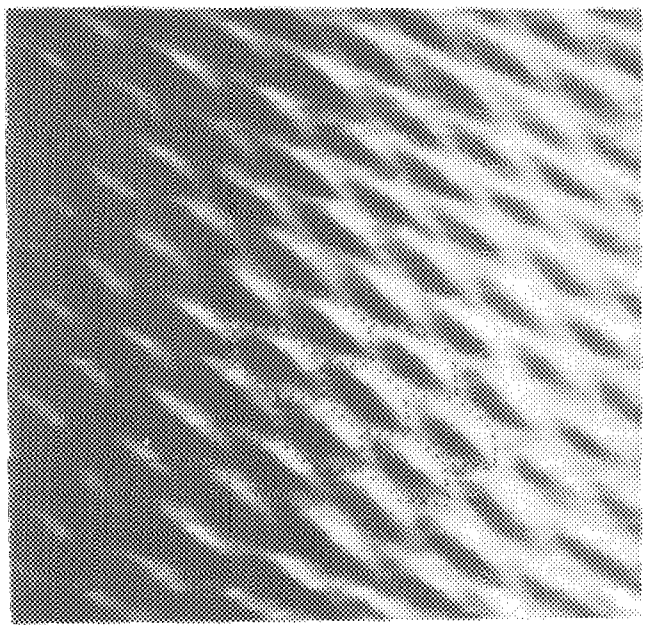
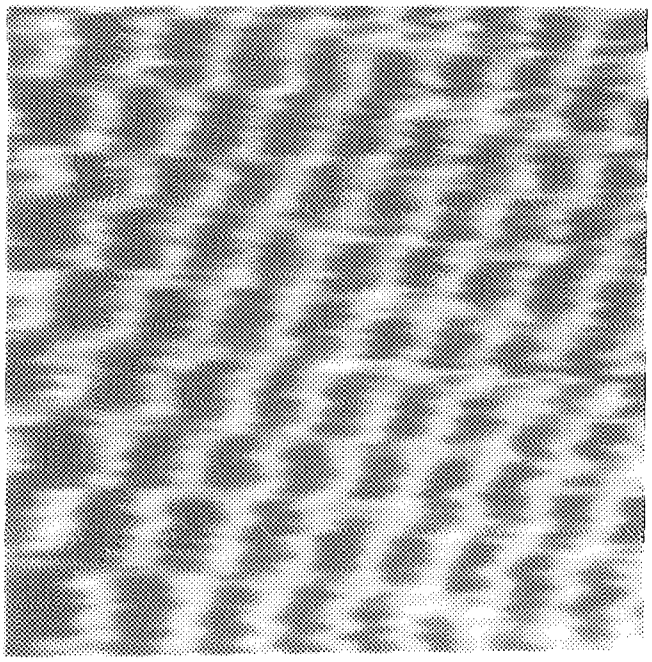


(a)

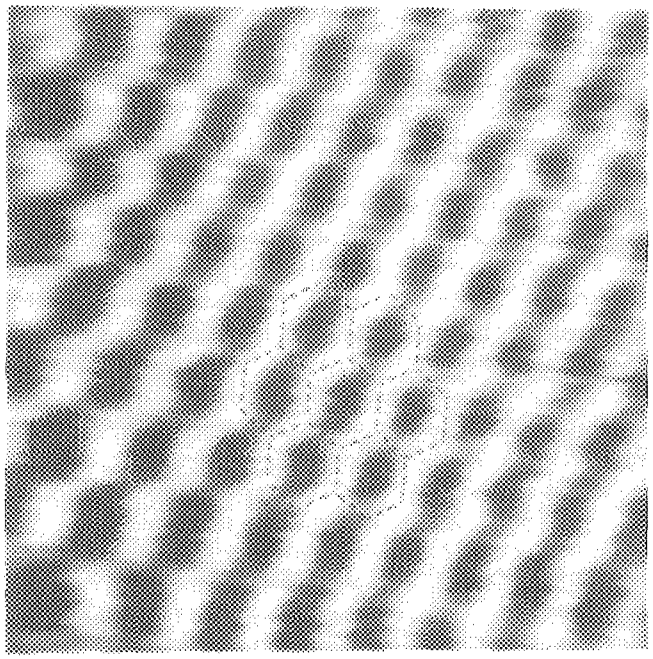


(b)

FIG. 1. STM image of the basal plane of graphite obtained with (a) the raw data and (b) the digital filtered data. The scanning rate is 4 Hz and the scal is 20 Å × 20 Å. The hexagonal grid (shown in Fig. 3) is superimposed so as to visualize the unit cell.



(a)



(b)

FIG. 2. Another image of graphite via STM at 10 Hz scanning rate. The image in (b) is digital filtered and the original image appears in (a). Each image is 20 Å × 20 Å.

with this assumption.

We found that the quality of these images was not degraded with time and it could be recorded repeatedly with various scanning range and speed. The hexagonal pattern of the atomic structure is evident in all figures even though the image in Fig. 1 is elongated diagonally as a result of the residual thermal drift.

The dark regions represent the depressed hollows in the middle of the unit hexagon. The depth of this hollow is about 0.8 Å. In Fig. 1 the bright regions just next to this hollow may look strange, but this is a result of the response time of the feedback circuit. It is somewhat slow compared to the scanning speed and the probing tip cannot accurately follow the contour when the sample surface changes abruptly. This enhances the tunneling current and produces some distortion in the image. We can decrease the response time of the feedback circuit by increasing the gain or changing the RC filter, but there is a limit imposed by the instabilities of the loop. The image in Fig. 2 with the higher scan rates was taken with the time constant in the feedback circuit increased to the point where the tip could not follow sharp

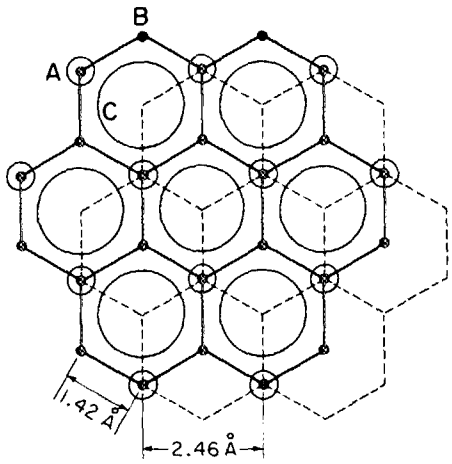


FIG. 3. Surface structure of graphite. There is a hollow in the middle of the unit hexagon (site C). The atom at site A has a neighboring atom in the lower layer (dashed hexagon). It is slightly higher than atom at site B which does not have a neighbor in the lower layer.

changes in the surface contour. This system is only suitable for flat surfaces such as graphite where the tip height can remain constant over the area of the image.

These contours are consistent with the calculations of Selloni *et al.*[8] They discuss the differences in height for three different sites marked A, B, and C in Fig. 3. At site A the atoms in the top layer coincide with those in the underneath layer, whereas the atom at site B does not have a corresponding atom in the underneath layer. At site C there is an atom in the underneath layer, but nothing in the top layer. Their calculations indicate that for electrons near the Fermi energy (zero bias on the tip) the maximum corrugation, with a height difference near 1 Å, should occur between the peak at site A and the hollow at site C. This corresponds with what we measure. They also find that the atom at site A is about 0.15 Å above the atoms at site B. This difference is difficult to distinguish in our results where the estimated vertical resolution is 0.1 Å. At the higher voltages they predict a change in this pattern with a reversal in the positions of the peak and the depressions. We could not verify this since the surface corrugations in our images decreased when we increased the tip voltage. Neither could we find the surface states that are predicted[11] for energies above 2.5 or 3 V. This is not unexpected since the resolution in the STM decreases at the higher voltages because of the increase in gap spacing.

The high resolution came as a surprise since the tip with a macroscopic radius of 1000 Å was used "as is"[12] without resorting to any of the procedures of "forming" that have been used with instruments operating in vacuum. The calculations relating to the resolution of the STM[13–16] suggest that our effective tip is a single atom. If this were not the case it is more probable, considering that the nearest neighbor distance in tungsten is 2.74 Å, that we would be imaging the tip rather that the graphite. This tip, where the single atom seems to be sitting at the edge of a terrace on the tungsten probe, may not be stable since we do see some variations in the texture of the image.

Finally, we want to point out that the remarkable effectiveness of the Weiner filter suggests that the noise must come from a physical process occurring in the tunneling region itself rather than random events in the electromechanical system. We have in mind the suggestion put forward by Gomer[17] that a study of the fluctuations in the tunneling current would yield important information on the surface diffusion of adsorbed molecules. A related problem that has been studied is the fluctuation in field emission current. Kleint,[18] who has measured the spectral density of flutuation in field emission current, reports that the noise spectra has a $1/f$ character in the presence of surface diffusion and "reveals mainly shot noise" when emitters are cleaned. It may turn out that with the Weiner filter we are removing the effects of surface diffusion and simulating the high vacuum environment.

We want to acknowledge the support from R. Nemanich and A. W. Moore in providing us with the Graphite, from A. Bryant and D. Smith for their discussions in tunneling, and from Ch. Gerber who looked at our data and said "Yes, those are the atoms!" G. Binnig offered us words of wisdom and encouragement. S. Doniach was helpful in our discussions on digital filtering. This program is supported by the Defense Advanced Research Projects Agency, and in part by a grant from the Office of Naval Research and from the IBM Corporation.

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