

Imaging graphite in air by scanning tunneling microscopy: Role of the tip

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We have been successful in obtaining atomically resolved images of highly oriented pyrolytic graphite (HOPG) in air at point contact. Direct contact between tip and sample or contact through a contamination layer provides a conduction mechanism in addition to the exponential tunneling mechanism responsible for scanning tunneling microscopy (STM) imaging. Current-voltage (I - V) spectra were obtained while scanning in the current imaging mode with the feedback circuit interrupted in order to study the graphite imaging mechanism. Multiple tunneling tips are probably responsible for images without the expected hexagonal or trigonal symmetry. Our observations indicate that the use of HOPG for testing and calibration of STM instrumentation may be misleading.

I. INTRODUCTION

Scanning tunneling microscopy (STM) is one of the newest and fastest growing techniques for characterizing surfaces.¹ The rapid growth of this technique has produced the need for instrument test and calibration standards. Imaging of highly oriented pyrolytic graphite (HOPG) has become the benchmark for STM instrument test and calibration because HOPG can be readily cleaved to give large, atomically flat areas that are relatively clean and inert. In addition, atomically resolved images of HOPG are easily obtained in air and liquids as well as in high vacuum. However, researchers have observed numerous anomalous characteristics of the graphite surface including the following: (1) low barrier heights (2) large distance dependencies, (3) giant atomic corrugations up to 2.4 nm, (4) enhanced spatial resolution over that obtained on other surfaces, (5) absence of surface defects, and (6) unusual and varying images.

In order to explain some of these anomalies, tip-surface contact through a contamination layer and/or surface-tip deformation has been proposed. By invoking a tip-contamination-sample contact mechanism, Coombs and Pethica assert that the nonconducting contamination layer causes elastic deformation of the surface.² With this model, anomalously low barrier heights and distance dependencies can be explained. Elastic deformation³ and contamination-mediated deformations⁴ have also been invoked to explain giant corrugations. Pethica⁵ has proposed an STM imaging mechanism in which sliding graphite planes under the tip result in a variation in tunneling current depending on lattice registry. Enhanced spatial resolution is a consequence of the electronic structure of graphite for which the Fermi surface collapses to a point at each corner of the surface Brillouin zone.⁶ As of yet, unusual image patterns (hexagonal rings, dots, rows) and the absence of surface defects have not been adequately addressed.

The role of the tip in imaging of HOPG has been discussed as a function of the methods required to produce a function-

ing tip. Hansma⁷ has reported a tip preparation method of crashing the tip repeatedly against the surface. Sometimes, however, merely waiting a sufficient period of time allows for atomic imaging. In either instance, the possibility of creating a tip with a graphite flake or graphite contamination exists. With these tip-surface interactions in mind, we began to investigate the interaction of a graphite tip with the HOPG surface. With a graphite tip, we can address the questions of sliding graphite planes and graphite tip contamination.

We recently reported⁸ that we could reproducibly obtain atomic resolution with either a pencil lead (graphite) tip or a tungsten (W) tip coated with graphite. In this paper, we report further studies of the role of the tip in imaging of HOPG.

Analyses of the tip composition and structure were performed in order to characterize the tips. In addition to imaging, current-voltage (I - V) spectra of the tunneling junction were also measured. Conductance curves were plotted in order to determine zero-bias resistances R_0 . Images were obtained as a function of R_0 . The results of the spectroscopic studies suggest a point-contact imaging mechanism. In this model, contact occurs between tip and sample such that either a contamination layer or actual tip-sample contact provides a current conduction mechanism which becomes convoluted with the exponentially dependent current from one or multiple tunneling points. The suggestion of multiple tunneling points is supported by the results of numerical simulations of graphite imaging with multiatom tips.

II. EXPERIMENT

The experiments were done on an HOPG⁹ sample in air using an STM which is described elsewhere.¹⁰ Images were obtained in the current imaging mode with typical tip scanning frequencies of 250 Hz in x and 5 Hz in y . The initial approach of the tip to the sample was done under feedback control; however, subsequent imaging was done with the

feedback circuit interrupted and the voltage applied to the z piezo held constant. Images were displayed on a variable persistence oscilloscope and recorded on videotape via camera. Selected images were digitized into 320×200 pixels with four gray levels.¹¹ The images were then smoothed into 256 gray levels with a 15×15 pixel sliding window average; image resolution was not a function of window size even for somewhat larger windows. Images presented here are photographs of smoothed data displayed on a graphics monitor.^{12,13}

The I - V spectra were obtained with constant voltages applied to the x , y , and z piezos. Bias voltage control and data acquisition were under microcomputer control.¹⁴ The output of a differential amplifier was monitored to measure the voltage of the sample relative to the tip, and the voltage drop across a resistor was monitored to measure the current. In a typical experiment 200 voltage sweeps, each with 150 data points, were averaged to make one I - V curve in ~ 20 s.

Tungsten tips were prepared using either an ac or dc electrochemical etching procedure.¹⁵ The graphite-coated tips were made by dipping tungsten tips into a colloidal graphite suspension.¹⁶ The graphite tips were standard mechanical pencil lead.¹⁷ X-ray diffraction measurements were done on powdered pencil lead and on a colloidal graphite-coated glass slide. X-ray photoemission spectroscopy (XPS) spectra were obtained with a Surface Science Laboratories SSX 100-03 spectrometer using a monochromatized Al $K\alpha$ x-ray source (1486.6 eV). Energy dispersive analysis of x rays (EDAX) and transmission electron microscopy (TEM) were done on a 300-keV JEOL 430 transmission electron microscope using copper grids.

III. RESULTS AND DISCUSSION

A. Characterization and analysis of graphite tips

We recently reported⁸ that by dipping a nonimage producing tungsten (W) tip in colloidal graphite, we could achieve atomic resolution on HOPG. Further, using a common pencil lead, images were easily obtained. In order to characterize the tips and understand the mechanism responsible for this resolution, further analyses of the graphite tips were performed.

The surface composition of the pencil lead determined by x-ray photoelectron spectroscopy is given in Table I. The tip is composed mainly of carbon and smaller amounts of oxygen and silicon. The carbon exists in at least two distinct chemical states; one carbon species has a photoelectron binding energy of 284.6 eV due to carbon bonded to carbon (C-C), or graphiticlike carbon, and the other carbon species has a photoelectron binding energy of 285.7 eV due to carbon singly bonded to a hydroxyl group (C-OH). The C-C:C-OH ratio is $\sim 12:1$. The oxygen species is only weakly observed as a broad asymmetric peak with a photoelectron binding energy centered around 532.0 eV. The lower binding energy oxygen species is probably due to oxygen bonded to silicon. The higher binding energy oxygen species is due to the hydroxyl oxygen that is bonded to carbon. The silicon species is present in an oxidized form probably associated with the clay used to harden pencil leads. This tip has a

TABLE I. Composition of graphite tips determined by x-ray photoelectron spectroscopy.

Tip material	Elemental composition (at. %)			
	Carbon	Oxygen	Other	C/O ratio
Pencil lead	89	6	5	(Si) $\sim 15:1$
Colloidal graphite	84	13	3 (N)	$\sim 6:1$

relatively low oxygen content, where the C:O ratio is $\sim 15:1$, and should be extremely resistant to further oxidation. The presence of silicon was confirmed by EDAX.

The surface composition of the colloidal graphite is also given in Table I. The colloidal graphite is composed mainly of carbon and smaller amounts of oxygen and nitrogen. This graphite has a C:O ratio of $\sim 6:1$, corresponding to a higher oxygen content than found in the pencil lead. This higher oxygen content is due primarily to a higher concentration of the oxidized carbon species with a photoelectron binding energy of 286.1 eV. The C-C:C-OH ratio is $\sim 5:1$ compared to 12:1 for the pencil lead. The higher oxygen content is also due to a measurable amount of adsorbed water. The observed nitrogen is presumably due to atmospheric contamination or to a nitrogen containing species used in the formulation of the colloidal graphite.

X-ray diffraction confirms the graphitic composition in both the pencil lead and colloidal graphite. TEM images of the pencil lead show jagged edges of protruding graphite planes. The graphite-coated W tip, on the other hand, has a continuous coating of randomly oriented graphite at least 5 nm thick. Edge fringes of aligned graphite are evident on both the tip and the colloidal graphite alone.

The colloidal graphite appears to easily coat the tip to produce a relatively thick film with good adhesion. The random alignment of the graphite would allow for realignment of the sheets upon contact with the HOPG surface (possible sliding planes) and provide a mechanism for deformation of either the sample or the tip coating. As the tip is pushed into the sample, more colloidal graphite would come into contact with the HOPG. The jagged edge of the pencil lead would also have successively more contact and possibly produce multiple tunneling points as the tip is moved toward the sample.

The advantages of these tips are numerous. Atomic resolution is readily obtained with a graphite tip. A nonimage producing tungsten tip can be easily treated to produce a functional tip. Due to the graphitic composition, the tips are relatively oxide-free and resistant to further oxidation. In the case of imaging HOPG, these tips may also present a higher contact area which would allow for more rigidity and better image quality. The disadvantages of these tips may be those of limited applicability and the possibility of having multiple tunneling points which distort the image.

B. Effect of tip geometry and orientation on the image of HOPG

As mentioned above, several models use sample-tip contact to explain the anomalous tunneling behavior of graphite. In Pethica's model proposing the sliding of graphite planes under the tip, fluctuations in the current between the tip and sample occur as the planes pass into and out of registry.⁵ In order to simulate this contrast mechanism, we have developed a numerical simulation for scanning a single- or multiatom tip over a large plane of graphite while summing the electron charge density at each tip atom. The graphite surface is represented by a hexagonal array of 77 atoms that has the appropriate C-C bond length for graphite, i.e., 0.142 nm. Each atom is surrounded by a spherically symmetric electron cloud derived from the hydrogen 1s wave function in order to simulate an exponentially decaying charge density.

The tip has been modeled with several different structures consisting of single or multiple atoms. The multiatom tip shown in Fig. 1(a) represents a small trigonally symmetric plane of graphite. The center atom of the tip is 0.142 nm away from the three outer atoms. As the tip is scanned over the graphite surface, the tip atoms go into and out of registry with the surface atoms. A single-atom tip or a trigonally symmetric three-atom tip [the tip shown in Fig. 1(a) but without the center atom] produces an image of the surface consisting of hexagonal rings where each of the six atoms in the ring has the same electron density. The trigonally symmetric four-atom tip shown in Fig. 1(a) produces, however, a trigonally symmetric image where only three of the carbon

atoms in the hexagonal ring have the same electron density. This image is commonly observed by STM for graphite and is believed to represent the correct surface structure of graphite.¹⁸ The experimental gray scale images shown in Fig. 1(a) show a ring structure (bright or raised area) around a hexagonal arrangement of holes (dark areas).

Rotating the trigonally symmetric tip between 0° and 60° with respect to the surface plane produces other trigonally symmetric features such as triangular or "clover" patterns arranged in a hexagonal array. The formation of a row pattern (horizontal, vertical, or diagonal) never appears when trigonally symmetric tips are used in the model.

An asymmetric tip structure, shown in Fig. 1(b), produces an image of reduced symmetry, and if the plane of the tip atoms is rotated parallel to the plane of the surface atoms, the image collapses into a row pattern. The image in Fig. 1(b) was formed by deleting two atoms from the symmetric four-atom tip and rotating the tip by 40°. The resulting image produces a staircase of diagonal rows. Diagonal rows are also observed in STM images of graphite as illustrated by the experimental images in Fig. 1(b).

Row pattern images can also be generated by placing two or more "tunneling" tips at arbitrary points in the plane above the surface. In fact, row pattern images are observed when two randomly oriented trigonally symmetric tips are placed in a plane above the graphite surface.

These observations support the premise that the different image patterns observed for graphite by STM can be explained by the presence of multiple tunneling points. Some of the images obtained using the graphite tips described in this paper show clear evidence for multitip tunneling.

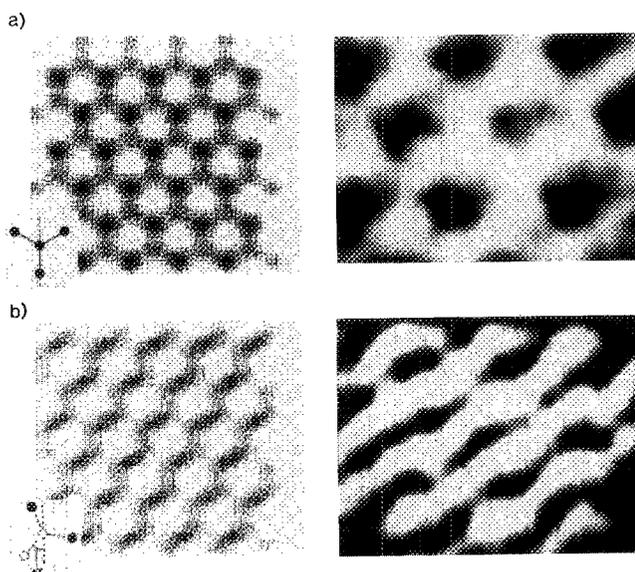


FIG. 1. Comparison of images created by numerical simulation (left-hand panel) with experimental images (right-hand panel) for HOPG. The images derived from numerical simulation were calculated using the trigonally symmetric, four-atom tip or the asymmetric two-atom tip shown by the insets. The experimental images are gray scale plots obtained with (a) a tungsten tip and (b) a graphite tip in the current-imaging mode. The numerical and experimental images are not the same scale.

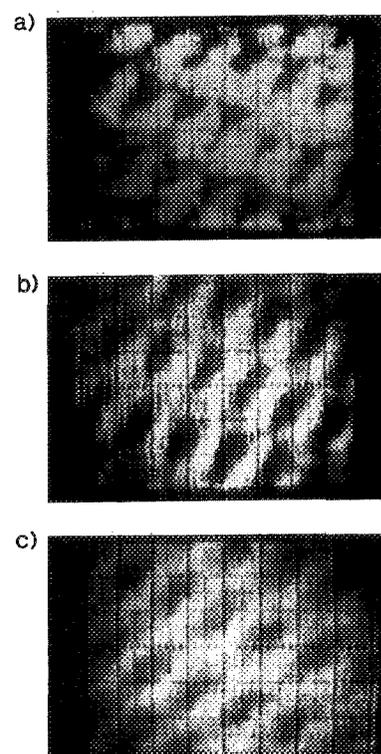


FIG. 2. STM images obtained in the current-imaging mode at -500 -mV sample bias using a graphite-coated tungsten tip on HOPG for the following conditions: Δz from $R_0 = \infty$, contrast current, tip-to-sample bias, and average tunneling current for (a) 8.5 nm, 5 nA, 250 mV, 25 nA; (b) 20.2 nm, 3 nA, 20 mV, 48 nA; and (c) 23.5 nm, 2 nA, 20 mV, 48 nA.

C. Point-contact imaging and spectroscopy

Spectroscopy measurements were performed to study the graphite imaging mechanism in air which is based on contact between tip and sample either directly or through a contamination layer. A series of images was obtained using a graphite-coated tungsten tip on a HOPG surface for four R_0 values as shown in Fig. 2. The position of the tip is given as Δz relative to the point at which a tunneling current is first detected (defined as $R_0 = \infty$). $I-V$ spectra were obtained while scanning in the current-imaging mode with the feedback circuit interrupted in order to correlate image quality with the $I-V$ characteristics at different R_0 values.

Anomalous tip-sample separation dependence on tunnel current is observed over a Δz range > 20 nm. This observation suggests that the z -piezo movement is not equivalent to the tip-sample separation and that a mechanism involving elastic deformation of the HOPG surface or the tip is probable. The data in Fig. 2 were correlated with $I-V$ spectra which are nonlinear at lower Δz (8.5 nm) and become nearly linear at higher Δz (20.2 and 23.5 nm), indicating that part of the tip is in Ohmic contact with the sample.

Image quality is highly dependent on R_0 values. Although the peak-to-valley variation in current (image contrast) decreases from 5 ($\Delta z = 8.5$ nm) to 2 nA ($\Delta z = 23.5$ nm), the image quality improves considerably. Images obtained at lower R_0 values are consistently stable and are atomically

resolved. It is surprising that images can be obtained in this regime because at least part of the tip is in Ohmic contact with the surface. Similar results have been obtained using tungsten and graphite tips. A conduction mechanism other than tunneling is necessary to explain the decreased contrast.

In order to study the $I-V$ relationships for the HOPG surface with tungsten, graphite-coated tungsten, and graphite tips, $I-V$ spectra were taken over a range of R_0 values at a single point above the surface. Figure 3 shows three $I-V$ curves for HOPG using a graphite-coated tungsten tip at R_0 equal to 20.7, 6.2, and 0.9 M Ω . The nearly linear spectrum at $R_0 = 0.9$ M Ω indicates Ohmic contact between part of the tip and the sample.

The $I-V$ spectra are asymmetric about zero bias, exhibiting a slight rectifying behavior; that is, the current is greater at a particular negative voltage than at the same positive voltage. The asymmetry with the tungsten tip alone is considerably less. (These asymmetries are also evident in the conductance spectra.)

The inset in Fig. 3 shows the conductance spectra obtained by numerical differentiation of the $I-V$ data. Two anomalous features appear: (1) the curves are nonparabolic and (2) a slight offset from zero bias at minimum conductance exists. The conductance at $R_0 = 20.7$ M Ω shows an abrupt minimum and essentially linear behavior at higher

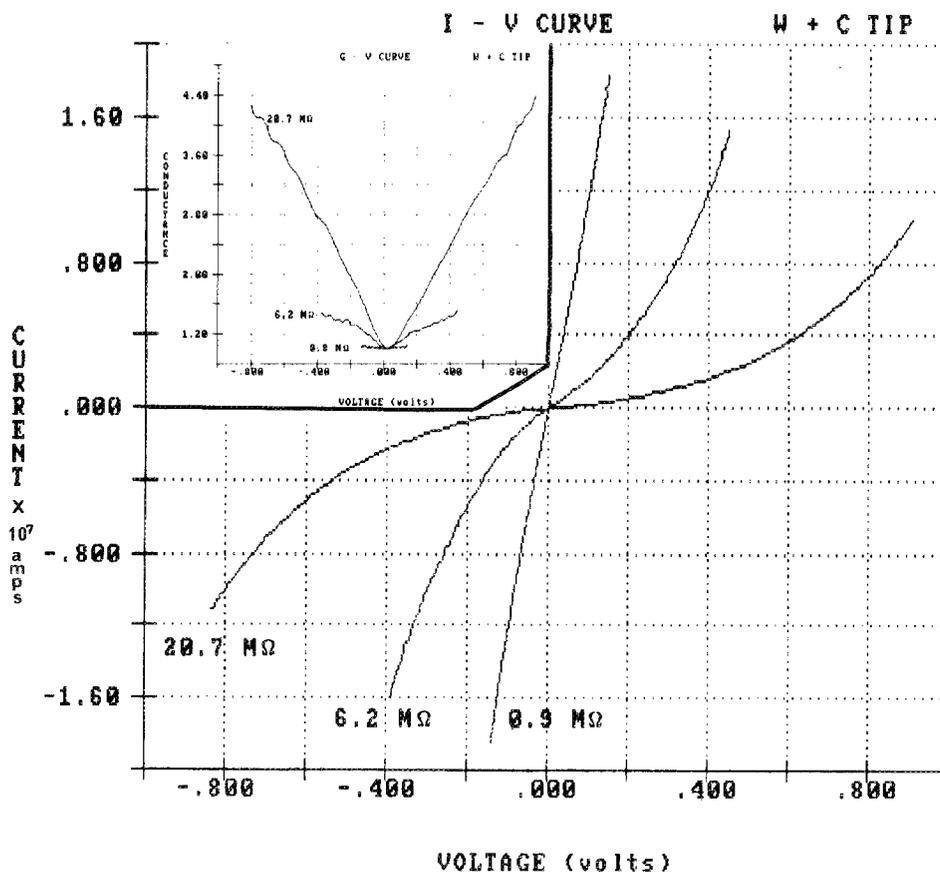


FIG. 3. Current-voltage ($I-V$) curves for a graphite-coated tungsten tip and HOPG sample at zero-bias resistances of 20.7, 6.2, and 0.9 M Ω . The inset shows the conductance-voltage ($G-V$) curves obtained by numerically differentiating the $I-V$ data. The $G-V$ curves have been smoothed and normalized.

voltages. The curve at 6.2 M Ω is broader.

Conventional metal-insulator-metal (MIM) junctions and tunneling theory show parabolic conductance spectra.¹⁹ The nonparabolic nature of these spectra suggests that the conduction mechanism is not simply vacuum tunneling. If the tip and surface were in contact, the shape of the conductance spectra would be altered considerably. Tip-sample contact may also explain the low R_0 values observed.

IV. CONCLUSION

In our experiments, we use tunneling voltages (V_T) and tunneling currents (I_T) comparable to those reported by other investigators.^{3,4,7} We find an exceptionally large Δz range for these V_T and I_T values. Because the apparent tip motion has little or negligible effect on the current, V_T and I_T can be stabilized without the use of feedback. As a result, HOPG is easily imaged and routinely gives atomic resolution. Atomic resolution remains over a large range of Δz and R_0 values which is inconsistent with conventional MIM or STM tunneling theory.

The I - V spectra observed are also inconsistent with MIM and STM theory. I - V spectra are linear over large ranges of Δz and images can be obtained even when part of the tip is in Ohmic contact. Direct contact between tip and sample or contact through a contamination layer provides a conduction mechanism in addition to the exponential tunneling mechanism responsible for STM imaging. The enhanced conductance introduces an increasingly large background current at increased Δz resulting in less image contrast. The graphite or graphite-coated tips may provide more surface area for contact with the HOPG to give higher mechanical and electrical stability leading to quieter, more stable tunneling currents and easily reproduced atomic images. The alignment of graphite planes upon tip-surface contact seems likely and would support Pethica's suggestion of sliding planes. Furthermore, multiple tunneling tips are probably responsible for images without the expected hexagonal or trigonal symmetry. Finally, we can image HOPG without feedback control of the vertical tip position. Our observations indicate that the use of HOPG for testing and calibration of STM instrumentation may be misleading.

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