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Contamination-mediated deformation of graphite by the scanning tunneling microscope

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We demonstrate that surface deformation mediated by contamination plays a major role in images of graphite obtained by a scanning tunneling microscope in air. Atomic resolution has been obtained with the surface compressed by as much as 100 Å, where abnormally high atomic corrugations, up to 24 Å, are observed. Calculation of the deformation profile reveals that the force necessary to deform the surface must be spread over several thousand square angstroms. The measured deformation is negligible in vacuum with a clean sample and tip, and the corrugation is 0.9 Å.

Graphite has become an increasingly popular substrate for use with the scanning tunneling microscope (STM). It is readily cleaved to give a flat surface that can be imaged in air with atomic resolution[1] and that exhibits a perfect lattice over thousands of angstroms.[2] However, there are a number of well-known puzzling features of graphite viewed by the STM. One peculiarity is that in air the tunneling current is very weakly dependent on the position of the tip in the z direction (normal to the surface). We have obtained atomically resolved images of graphite with the tip progressively displaced over a range of as much as 100 Å. More strikingly, we have observed topographic images in air with a corrugation, i.e., peak-to-peak amplitude, of up to 24 Å. Following Soler, Baro, Garcia, and Rohrer,[3] we explain the large corrugations in terms of an amplification of the tip motion arising from surface deformation. However, in an analysis of the profile of the deformation we show that the tip must press on the surface over a region of several thousand square angstroms. To reconcile the large area over which the force is exerted with the atomic resolution of the images, we propose that the force is mediated by a layer of surface contamination, and that the tunneling is to a miniature tip protruding through the contamination. Progressive cleaning of the surface and tip in ultrahigh vacuum is found to eliminate the deformation, confirming the important role of surface contamination.

There has been some effort to explain why the corrugation of graphite observed in the STM[2-5] is much greater than the hard-sphere estimate of 0.2 Å obtained from helium scattering experiments.[6] Selloni, Carnevali, Tosatti, and Chen,[4] have suggested that variations in the local density of states could account for a corrugation up to 1 Å. Tersoff[5] has pointed out that the unusual electronic band structure of graphite can lead to a corrugation which, depending on tip shape and operating conditions, may be as high as a few angstroms. Following the earlier suggestion of Coombs and Pethica,[7] Soler *et al.*[3] have proposed that the tip elastically deforms the surface to produce an amplification of the corrugation, which they observe to be up to 8 Å on graphite in air. In their model, they propose that the deformation results from a force acting locally over atomic distances.

In our work, we have made extensive studies of freshly cleaved highly oriented pyrolitic graphite (Union Carbide, grade ZYB). We have used both the standard topographic mode, in which the tunneling current is maintained at a fixed value by a feedback loop as the tip is scanned, and the current-imaging mode,[8] in which the tip is scanned at constant height above the surface and the variations in tunneling current constitute the image. We obtain atomically resolved images which, compared with the expected honeycomb structure of the graphite lattice, show a pattern with every other atom suppressed. This asymmetry between atomic sites has been reported by other workers.[2,8] We typically operate at a bias voltage of 10 to 50 mV, but in air we have obtained atomically resolved images with a bias voltage of 1.5 V.

Figure 1 shows the peak-to-peak corrugation amplitude versus tunneling resistance for three values of bias voltage. These data were taken from two-dimensional (2D) topographic images obtained in air. We increased the bias current after each set of five scans, and obtained the corrugation from the 1D scans so produced. Since the resistance decreases with decreasing separation, we see that the corrugation grows as the separation is reduced. At low resistance, the corrugation is as large as 24 Å, although maximum corrugation amplitudes of about 10 Å are more typical. Over the range of tunneling resistance shown in Fig. 1, the tip moved over a distance of roughly 100 Å nor-

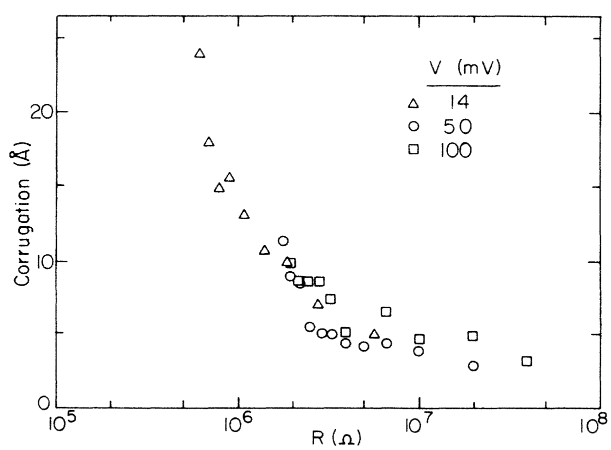

FIG. 1. Topographic corrugation vs tip-to-sample resistance.

mal to the surface. For a clean surface with a work function in the range 5 to 10 eV, the tip should move by only a few angstroms when the resistance is changed over two decades. Thus, our observations provide strong evidence that the surface follows as the tip is retracted, thereby implying that the surface is deformed by the tip.

One can model the mechanism by which deformation leads to amplification as follows.[7] We represent the tip-surface interaction by a spring constant k_t and the restoring force of the graphite lattice by k_g. A change Δs in the tip position produces a change $\Delta d = \Delta s/(1+k_t/k_g)$ in the tip-sample separation. A given change Δd thus requires a correspondingly greater value of Δs, giving rise to an amplification of the corrugation as the tip is moved in and out to maintain a constant tunneling current. Thus, in this model, the increasing corrugation implies that the spring corresponding to the interaction between tip and surface becomes stiffer as it is compressed, that is, the spring is nonlinear.

We have also investigated the dependence of the current modulation on the mean tunneling current I in the current-imaging mode in air. Figure 2 shows the root-mean-square current modulation ΔI obtained from 1D scans as a function of mean current. At the highest currents the 1D scans show atomic features, although the 2D images are of poor quality. At the peak current of 50 nA, the tip has been extended 70 Å toward the surface from its position at 0.5 nA. Over this range, the ratio $\Delta I/I$ is constant, indicating that the relative modulation is independent of the resistance and hence of the tip-sample separation. This result is consistent with the surface deformation model: There is no amplification of the tip motion since the tip is scanned at constant height above the surface, and the compression of the springs is unchanged.

We now briefly discuss the forces required for the amplification process. The elastic deformation and stress distribution arising from a given load applied normal to the surface of an infinite half space of an anisotropic material have been calculated exactly.[9,10] For graphite,[11] a force F in the z direction (c axis) applied uniformly over a disk of radius r produces a maximum deflection $u_0 = 2.4\times10^{-11}F/r$ (mks units). The related "rigid-die" problem of applying a given deformation (as opposed to a given force) to the surface has also been solved for an isotropic material;[10] we have extended this solution to cover the anisotropic case. We model our tip as a paraboloid of the form $\zeta = C\rho^2$, where ρ is the radial distance from the center axis of the tip. This shape has radius of curvature $R = 1/2C$ at the center. Scanning electron microscope pictures of our etched tungsten tips show that this choice is not unreasonable. We take the maximum deformation to be u_0, and assume that for small ρ the deformation profile has the shape of the tip, with no kinks. We find the following surface profile:

$$u(\rho) = u_0 - C\rho^2, \quad \rho < a \ ,$$
$$u(\rho) = (2/\pi)[(u_0 - C\rho^2)\sin^{-1}(a/\rho) + Ca(\rho^2 - a^2)^{1/2}], \quad \rho > a \ ,$$

where $a = [u_0/(2C)]^{1/2} = (u_0 R)^{1/2}$ is the radius over which the surface profile tracks the tip. The model predicts a slowly varying pressure distribution for $\rho \lesssim 0.8a$, with a maximum at $\rho = 0$ of $2\times10^{10}(u_0 C)^{1/2}$ N/m^2. Figures 3(a) and 3(b) show the profiles for a 70-Å deformation, a value that we have achieved at low resistances. The tips shown have $R = 2$ and 500 Å, respectively. In the first case, the tip was chosen to give an atomically small contact area between tip and sample. This tip has an unrealistically small cone angle of 15° over a length of 70 Å. Note that even for such a sharp tip, the contact radius is still 12 Å, and the surface has an unreasonably steep profile. The peak pressure is 1×10^{11} N/m^2 (1 Mbar), and the total force is 3×10^{-7} N, distributed over 300 Å^2. For such large stresses, Hooke's law is not valid, so that the model breaks down and plastic deformation may occur.[12] On the other hand, for $R = 500$ Å, a realistic value for our tips, the deformation profile and the pressure are much more reasonable. Here the total force of 5×10^{-6} N, distributed over an area of 10^5 Å^2, results in a peak pressure of 6×10^9 N/m^2. The peak pressure and the radius of contact vary only as $u_0^{1/2}$; thus for elastic deformations greater than a few angstroms, the force will be distributed over thousands of square angstroms.

Under a large deformation, one might expect a low tip-sample resistance due to the close electrical contact over a large area. This resistance would be dominated by spreading resistance, which we estimate for graphite by extending the analysis of Tinkham, Octavio, and Skocpol[13] for point contacts to an anisotropic material. For a contact

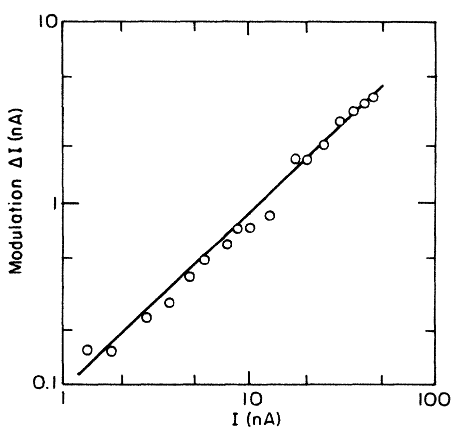

FIG. 2. rms current modulation vs current level in current-imaging mode.

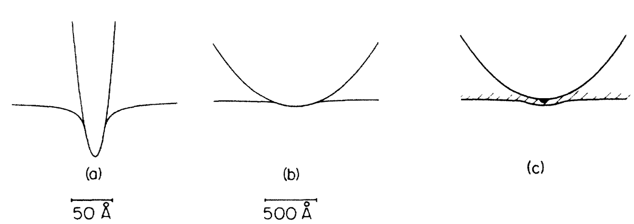

FIG. 3. Surface profile for a 70-Å deformation with force applied by tips with radii (a) $R = 2$ Å, and (b) $R = 500$ Å; (c) shows the contamination model, with a miniature tip providing the tunneling path.

radius of 200 Å, as in Fig. 3(b), we find a spreading resistance of less than 2 kΩ. This is significantly less than the 1 MΩ observed in air with the tip extended 70 Å.

To reconcile the large area of mechanical contact with the high observed resistance we propose that a layer of contamination acts to cushion the tip and transmit the force to the surface. To explain the atomic resolution images, we further propose that the tunneling occurs from a miniature tip protruding from the end of the tip through the contamination [Fig. 3(c)]. Since Sonnenfeld and Hansma[14] have recently shown that the STM can operate with atomic resolution on graphite in water, it is entirely plausible that all images of graphite in air are obtained through a surface layer of water or other contaminant.

To investigate the role of surface contamination, we have measured the variation of the current I with tip position s under a variety of conditions. All the measurements were taken on a flat region on which we first obtained high-quality images of the graphite structure. While scanning laterally to obtain a value of s averaged over several atomic positions, we disengaged the feedback loop and ramped the voltage to the z drive up and back. The voltage was kept constant, and the current was measured as a function of tip position s. Figure 4(a) shows I vs s for graphite in air. We speculate that the strong hysteresis was due to an expulsion of material from the gap between tip and sample as they were pressed together. We obtained Fig. 4(b) after transferring the sample into a vacuum of 3×10^{-10} Torr, and Fig. 4(c) after the sample was subsequently heated to 1000 °C for 1 h in the ultrahigh vacuum system. Finally, to obtain Fig. 4(d) we cleaned the tungsten tunneling tip by field emission at 500 V to a gold surface and scanned the cleaned graphite surface without breaking vacuum. The hysteresis disappeared as the sample was cleaned. Even more striking is the steepening of the I-s curves as the sample and tip became progressively cleaner. In (a), the current increased to 300 nA over roughly 100 Å, while in (d) it increased to 300 nA over only 1 Å. These results imply that both surface and tip are contaminated in air, and as the graphite surface and tungsten tip were progressively cleaned the tendency of the surface to follow the displacement of the tip was greatly reduced. Under clean conditions, we observed a topographic corrugation of 0.9 Å at 120 mV bias voltage and 20 nA tunneling current, in contrast to the 5 Å corrugation observed in air under the same bias conditions. These results provide strong evidence that significant distortion of the surface occurs only when there is a layer of contamination available to transmit the force from the tip.

In conclusion, the fact that one can observe atomic corrugations when the tip is displaced over a distance as large as 100 Å provides strong evidence that the tip deforms the surface in air.[3,7] However, a simple model for the deformation suggests that the forces are not localized to atomic dimensions as proposed by Soler *et al.*,[3] but rather extend laterally over many hundreds of angstroms. In air, we believe the force is transmitted to the surface via a contamination layer; as the surface, and finally the tip, are progressively cleaned, the deformation of the surface becomes negligible. It is known that the graphite surface adsorbs a variety of gases, and must be baked to remove them.[15] The nature of the contamination on graphite in our experiments is presently under investigation. One implication of our results is in the determination of the effective barrier height ϕ from measurement of the current I as a function of s from the well-known Wentzel-Kramens-Brillouin expression $I \propto \exp\{[-\phi/(1\ \text{eV})]^{1/2}\ s/(1\ \text{Å})\}$. Clearly, if the surface follows the tip position, an anomalously low value for barrier height will be obtained; this mechanism could thus explain the low barrier heights obtained for graphite and other materials in air, where contamination may be present.[7] Finally, one might expect deformation of the surface by the STM tip to be an important problem for a variety of systems, including biological materials.

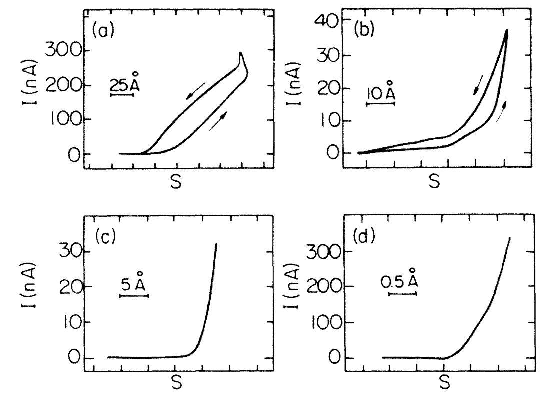

FIG. 4. Current I vs tip position s for graphite (a) in air, (b) in ultrahigh vacuum, (c) in ultrahigh vacuum with heated sample, and (d) with tip cleaned also by field emission.

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