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Site-selective imaging in scanning tunneling microscopy of graphite: The nature of site asymmetry

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In the absence of tip-sample mechanical interaction, graphite images show very different behaviors from those of typical images. Contrary to the current interpretation of site asymmetry, where protrusions in images are considered as *B*-site atoms, we have found that one can selectively image *A*- or *B*-site atoms depending on the bias polarity. Furthermore, the corrugation amplitude is extremely small. If measurements are performed under tip-sample mechanical interaction, one observes larger corrugations and in-phase images at opposite polarities. A new interpretation of site asymmetry is proposed.

Graphite is the most popular sample being used for scanning tunneling microscopy (STM) because it is very easy to obtain atomically resolved images with it. It is probably not an exaggeration to say that almost every researcher in the field of STM had experience with this sample. Nevertheless, the understanding of the nature of STM images has been nontrivial and has attracted intensive experimental and theoretical investigations in the past.[1–9] There have been two major issues regarding the understanding of STM images of graphite: the carbon site asymmetry and the anomalously large corrugations. Although these two issues may be considered well understood by now, we have found that the current interpretation of the site asymmetry is questionable and needs to be revised, and the reason is directly linked to the underlying mechanism for the giant corrugations.

The site asymmetry shows that only every other carbon atom appears as a protrusion. At first, it was interpreted that these protrusions correspond to atoms on the *A* site which is the site with another carbon atom lying directly beneath.[3] Primarily due to the theoretical work of Tomanek and Louie,[8] the current interpretation is just the opposite: these protrusions correspond to *B*-site atoms.[10] Based on the electronic structure calculation, Tomanek and Louie have concluded that at typical tunneling biases, atoms on the *B* site have larger contribution to the tunneling current than do those on the *A* site. It was also concluded that this asymmetry is independent of the bias polarity and that it decreases as the bias voltage increases.

The second issue of giant corrugation has been systematically tackled by Soler *et al.*[2] who have shown that strong mechanical interaction (or atomic force interaction) was responsible for the observation of giant corrugations. A reduced mechanical interaction leads to a reduction in the corrugation amplitude. Subsequent investigations by many other researchers have confirmed this point and have built a general consensus of the underlying mechanism for the giant corrugation. However, it is still not clear what the corrugation amplitude should be if the mechanical interaction is absent. In fact, it has been suggested[9] that most of the work reported to date is not free of mechanical interaction including those performed in ultrahigh vacuum (UHV).[3,4]

Although this mechanism of the giant corrugation appears as an independent issue from the site asymmetry, it actually puts the current interpretation of site asymmetry into question: If the typical experimental data are obtained under tip-sample mechanical interaction, then how can one interpret the site-asymmetry data based only on the electronic structure of the sample? The only sensible way is to compare the theory with the experimental data obtained in the absence of tip-sample mechanical interaction. This is exactly what we have done. To our surprise, contrary to the widely accepted interpretation of the site asymmetry, we have found that in absence of tip-sample mechanical interaction, one actually observes the *reversal* of the site asymmetry upon the reversal of the tip bias. In other words, one can selectively image *A*- or *B*-site carbon atoms. Furthermore, the corrugation amplitude is extremely small (always less than 0.1 Å) with a typical value of 0.03–0.05 Å.

Our experiments were performed in a UHV-STM system with a base pressure of 7×10^{-11} Torr or less. We want to emphasize that performing experiments in UHV is a necessary but not sufficient condition for obtaining images without tip-sample mechanical interaction. Many cautious steps were taken to avoid possible contamination and to prevent the tip from touching the sample during the tip-sample approach. To prevent possible contamination, graphite samples were cleaved *in situ*. Tungsten tips were also cleaned *in situ* by using field emission with parameters similar to those used by Becker, Golovchenko, and Swartzentruber.[11] A bare tungsten tip without *in situ* cleaning will inevitably crash the tip into the sample, yielding typical results such as those studied in air. The relative tip movements during the experiments were continuously monitored to assess tip-sample mechanical interactions. Junction characteristics were constantly checked with barrier height measurements.

Figures 1(a) and 1(b) show two images obtained "simultaneously"[12] at opposite tip biases of -0.55 and $+0.55$ V, respectively. "Simultaneous" imaging was achieved by interleaving line scans of the two images resulting in a very small time frame difference of 0.25 sec. Thermal drift (typically <5 Å per min) has been carefully calibrated and corrected for in the final presentation of the to-

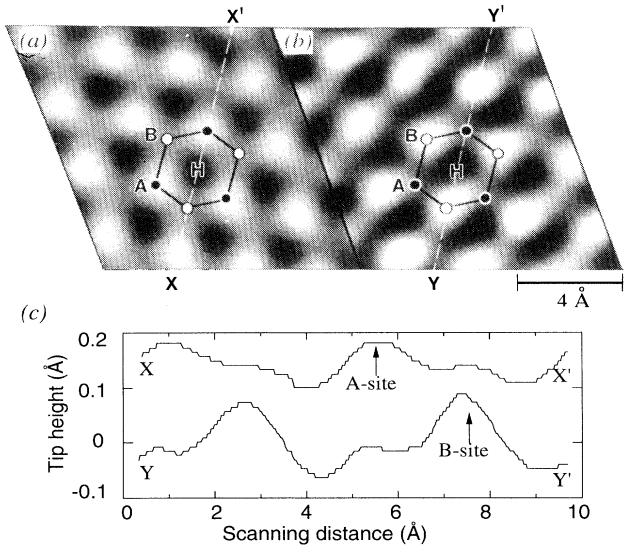

FIG. 1. (a) STM image acquired at a negative tip bias of -0.55 V and a tunneling current of 1 nA. (b) The same image acquired simultaneously at a tip bias of $+0.55$ V. (c) Corrugations along line XX' and YY' in images (a) and (b), respectively. Curve XX' is shifted upward by 0.15 Å for clarity.

pography. Such a low thermal drift rate causes negligible error in the relative positions of the two images. The complementary nature of images 1(a) and 1(b) can be clearly observed with the honeycomb unit cells superimposed on the image. The only uncertainty is to determine which image corresponds to A- (or B-) site atoms. As we will discuss later, image 1(a) shows the A-site atoms and vice versa for image 1(b).

Figure 1(c) shows the cross sections along the same line across images 1(a) (shown as XX') and 1(b) (shown as YY'). This line is chosen to cut through A- and B-site atoms and the center of the honeycomb (labeled as H), thus showing the largest corrugation amplitude in the image. As one can see, even along this line, the corrugation amplitude is extremely weak (≤ 0.1 Å). Furthermore, one observes the *reversal* of the A/B site asymmetry in this pair of cross sections, exemplifying the complementary nature of images 1(a) and 1(b). One might argue that there could exist a tip effect to account for our observation. For example, if the spatial distribution of the filled states of the *tip* differs from that of the empty states, it can result in a phase shift between the filled- and empty-state images. However, since the centers of the honeycomb (label as H) in the two images are aligned, this possibility can be easily ruled out. What we observe is a *reversal* of the site asymmetry instead of a *constant phase shift* in the image.

This behavior of asymmetry reversal at opposite biases has been reproduced several times with different tips and samples. If the tip has been cautiously kept from touching the sample, this behavior can be observed when the tip bias is about 0.5 V or higher, and corrugations of these images are always very small (≤ 0.1 Å) with a typical value of about 0.03–0.05 Å. Interestingly, the extremely small corrugation amplitude is consistent with the recent theoretical calculation of Tersoff and Lang[9] for the tungsten tip. As it turns out, for a reasonable tunneling current (100 pA to 1 nA), we can clearly identify the absence of tip-sample mechanical interaction only when the tip bias is larger than 0.5 V.

Shown in Fig. 2 is a typical measurement of the tip movement (S) as a function of the tip bias (V). Also shown is the measurement of the decay constant, $2\kappa = d\ \ln I/dS$. The reference tip position is arbitrarily chosen to be at a tip voltage of 1.4 V. At this point, $d\ \ln I/dS$ measurement shows a large tunneling barrier (~ 4 eV), indicating good vacuum tunneling characteristics. As one can see, from 1.4 to 0.6 V, the tip movement is roughly linear and changes by only about 1.5 Å. At about 0.5 V, there is a sudden drop by about 1.5 Å. Accompanying this sudden drop, the measured decay constant diminishes, indicating that the vacuum tunneling barrier collapses.[13,14] Below this transition voltage, the tip movement shows strong nonlinear behavior which is similar to that reported by Soler *et al.*[2] Following their analysis, one can conclude that the sample was elastically deformed. In this low bias regime, since deformation of the sample occurs, the measured $d\ \ln I/dS$ has no relevance to the real decay constant of the tunneling probability. Measurements using different tips and samples show similar behavior. The transition voltage from the vacuum tunneling to the elastic deformation regime varies slightly (between 0.5 and 0.6 V), and the amount of tip movement at this transition also varies (1 ± 0.5 Å). However, the site-selective imaging always occurs above the transition voltage. We should also mention that when the bias voltage is larger than 1 V, the corrugation is too weak to be observed.

The STM images obtained at the low bias range where the tip-sample mechanical interaction is present show very different behaviors from those obtained in the absence of tip-sample mechanical interaction. Shown in Figs. 3(a) and 3(b) are two STM images obtained simultaneously at ± 0.15 V, respectively. Also shown in Fig. 3(c) are cross sections along the same line across images

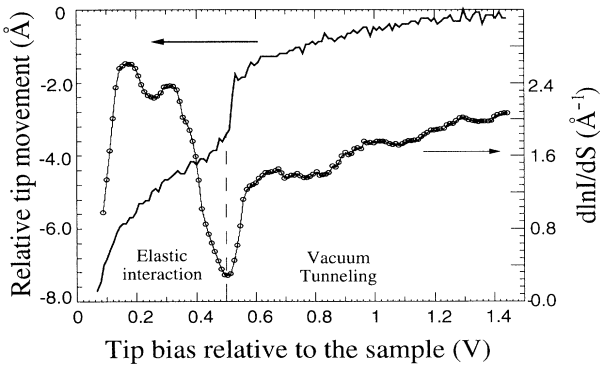

FIG. 2. Measurement of the relative tip movement and $d\ \ln I/dS$, as a function of the tip bias at a constant tunneling current of 1 nA. In this measurement, the relative tip movement was directly recorded from the z-piezovoltage. $d\ \ln I/dS$ was measured by a lock-in amplifier with a z-modulation amplitude of 0.08 Å at a frequency of 1 kHz.

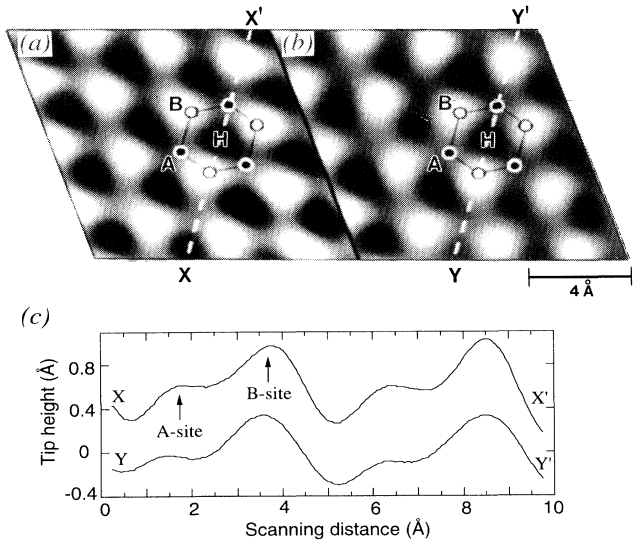

FIG. 3. (a) STM image acquired at a negative tip bias of −0.09 V and a tunneling current of 1 nA. (b) The same image acquired simultaneously at a tip bias of +0.09 V. (c) Corrugations along line XX' and YY' in images (a) and (b), respectively. Curve XX' is shifted upward by 0.6 Å for clarity.

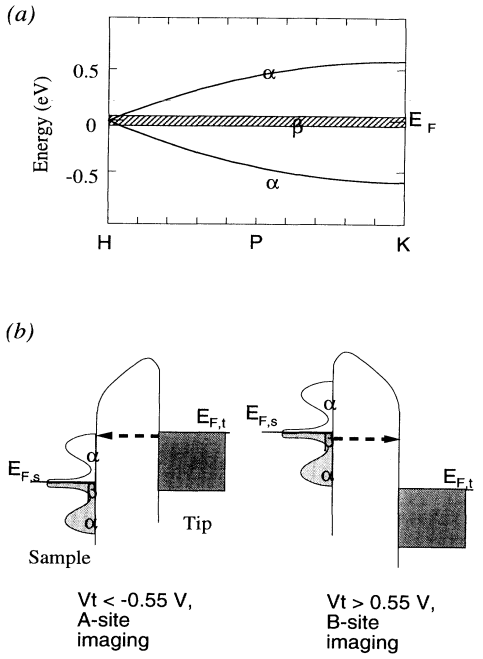

FIG. 4. (a) Band dispersions of electronic states along the vertical line on the corner of the Brillouin zone of hexagonal graphite (after Ref. 8). (b) Schematic diagrams showing the effect of the energy-dependent tunneling probability at a negative tip bias (left), and that a positive tip bias (right). Electronic states with the highest tunneling probability are marked with dashed arrows. The density of states shown in the figure is only a qualitative representation of the one-dimensional density of states near the Brillouin-zone edge.

3(a) and 3(b). One can observe that the corrugations in these two images are much larger (0.3 Å) than those shown in Figs. 1(a) and 1(b). Furthermore, these two images show identical phase. If we operate at even lower voltages and higher tunneling currents, for example, 50 mV and 10 nA, we can observe a much larger corrugation amplitude of 2 Å. However, after such a large deformation of sample, we cannot stabilize the polarity-dependent image (the tip often changes as the polarity is reversed), indicating that the tip may have been irreversibly modified.

The information of tip movement versus tip bias enables us to conclude that images observed in Figs. 1(a) and 1(b) are operated under the condition that the tip and sample are free of mechanical interaction. Under this condition, one always observes very small corrugation amplitude (≤ 0.1 Å) and complementary images at opposite biases. Our observation of the site-asymmetry reversal contradicts the widely accepted interpretation of site asymmetry. The reason that this site-asymmetry reversal has not been reported in the past is probably due to the fact that typical operation parameters inevitably cause tip-sample mechanical interactions. Indeed, our low voltage images obtained with tip-sample mechanical interactions [Figs. 3(a) and 3(b)] show large corrugations and in-phase images at opposite polarities.

Since we have ruled out the possibility of a tip effect to account for the observed reversal of the site asymmetry, the only possibility is that the current interpretation of the site asymmetry is *incorrect*. Here we propose an alternative interpretation. Shown in Fig. 4(a) is the dispersion of the electronic states along the vertical direction at the corner of the Brillouin zone (labeled as H-P-K). The α bands arise from the A-site atoms while the β band arises from the B-site atoms. Dispersion occurs only in the α bands since only A-site atoms have another atom lying directly below whereas the β band is localized near the Fermi level. This results in a higher one-dimensional density of states (predominantly β states) near the Fermi level [shown in Fig. 4(b)]. This is the major reason that Tomanek and Louie have concluded that B-site atoms contribute more to the tunneling current. They further argue that at higher bias (>0.5 V), the contribution of α states should increase, thus reducing the asymmetry. However, their explanation neglects the energy dependence of the tunneling probability.

It has been known that for filled-state imaging, the highest occupied states of the sample see the smallest tunneling barrier (shown as a dashed arrow on the right). In the case of graphite, this corresponds to the β state. On the other hand, for empty-state imaging, the smallest tunneling barrier occurs at the Fermi level of the tip to the highest accessible unoccupied states of the sample which correspond to the α states (shown as a dashed arrow on the left). Thus, the inconsistency between the current interpretation of the site asymmetry and our experimental result can be resolved by including the effect of energy-dependent tunneling probability.

One might also argue that the current interpretation of the site asymmetry is not exactly incorrect, since our low bias images [Figs. 3(a) and 3(b)] are in phase and that the protrusions are B-site atoms. However, the key point

here is that when the tip-sample mechanical interaction is present, one cannot interpret the STM images based on the electronic structure of the sample. The in-phase images at opposite polarities at low bias [Figs. 3(a) and 3(b)] can be attributed to the atomic-force interaction, *not* the electronic density of states of graphite, although the electronic structure can eventually affect the force interaction. In fact, in a recent work by Anselmetti *et al.*[15] who obtained atomic force microscopy (AFM) and STM images of graphite simultaneously, it was found that the AFM and STM images were exactly in phase. Their result is consistent with our interpretation of the low voltage behavior.

In conclusion, our STM studies of graphite performed under the condition free of tip-sample mechanical interaction have revealed the nature of the site asymmetry in STM images of graphite. In contrast to the current interpretation of the site asymmetry, we have found that selective imaging of A- or B-site atoms can be achieved by reversing the bias polarity with the tip bias >0.5 V. Furthermore, the corrugation amplitude of STM images in the absence of the mechanical interaction is extremely small with a typical amplitude of 0.03–0.05 Å. At a smaller bias range (between -0.2 to 0.2 V), mechanical interaction is inevitable, resulting in a larger corrugation amplitude and in-phase images at opposite polarities.

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[13]A diminishing tunneling barrier naturally leads to a sudden drop in the tip movement. When $d\ln I/dS \approx 0$, ΔS causes virtually no change in current, namely, a constant current is maintained even when there is a large change in S.

[14]In principle, $\kappa=(2m\phi/\hbar^2+k_\parallel^2)^{1/2}$. Thus, $d\ln I/dS$ should reflect an enhancement of κ as the tip samples the states near the Brillouin-zone edge. While this effect has been observed in Si(111)2×1 (Ref. 12), we observe only a weak effect which shows as a small peak near a tip bias of 0.65 V. Our interpretation is that as the effect of large $k_\parallel$ starts playing a role, the tip-sample distance inevitably decreases to a point that the image potential substantially reduces the vacuum barrier. This may also explain why the enhancement of κ has not been observed in layered compounds where this effect is supposed to be the largest. For example, in the case of $NbSe_2$ studied by Hess *et al.* [J. Vac. Sci. Technol. A **8**, 451 (1990)], only a moderate barrier height of 1.5 eV was reported despite the fact that the electronic states being sampled are near the Brillouin-zone edge.

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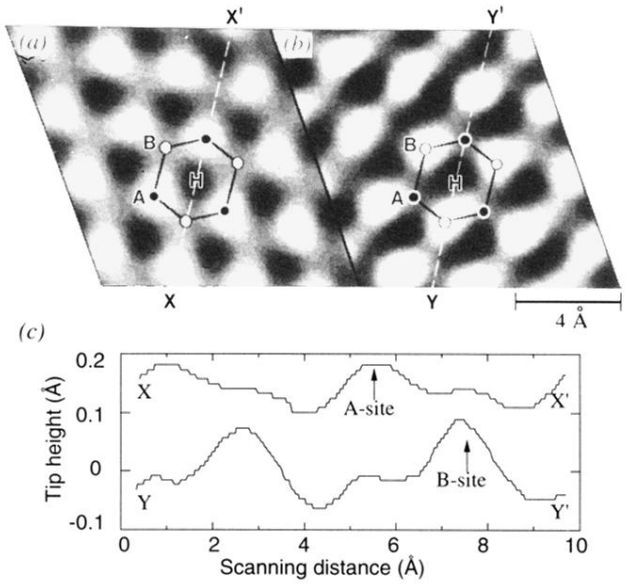

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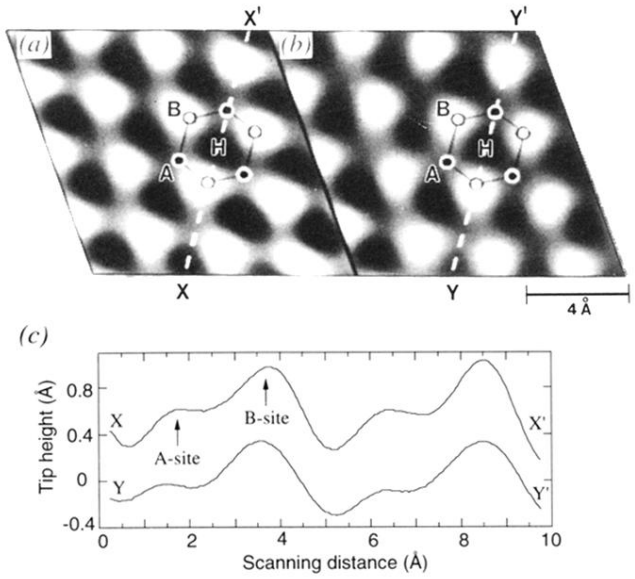

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