Scanning tunneling microscopy and the electronic and structural properties of intercalated graphite surfaces

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(Received 10 August 1988, revised manuscript received 19 December 1988)

We present a theory of the scanning tunneling microscopy (STM) images of intercalated graphite surfaces. The corrugation amplitude (CA) and carbon-site asymmetry (CSA) are sensitive to the number m of graphite layers covering the first guest layer, to the amount of transferred charge and its distribution, and to the surface subband structure. The CA and CSA can be used to map the stage domains across a freshly cleaved surface. The CSA has a surprising dependence on the charge transfer and on m. We explain the unusual absence of atomic-scale features in the STM images of BiCs-graphite recently reported by Gauthier *et al.* [J. Vac. Sci. Technol. A **6**, 360 (1988)].

The image of a graphite surface obtained with a scanning tunneling microscope (STM) at low bias has some quite remarkable features.[1] Structurally, graphite is very simple, with hexagonal layers of carbon atoms stacked in an *ABAB* sequence. The electron charge density shows only modest variations across the basal surface. However, the tunneling current is strongly depressed over the center of each carbon hexagon, and in addition there is a pronounced asymmetry in the current between adjacent carbon atom sites.[1-7] As was shown by Tersoff,[4] Batra *et al.*,[5] and Tomanek and co-workers,[6,7] the fundamental reason for this behavior is that the STM probes the local electron density of states at the Fermi level. Because the Fermi surface of graphite is very small, the STM image is a reflection of the spatial dependence of the wave functions of just a few electron states. The current "hole" at the center of each hexagon is due to a node in the wave functions of the Fermi electrons,[4] while the asymmetry is a property of the electron eigenstates resulting from the *AB* stacking of the graphite.[5-7] The electronic properties of graphite can be modified systematically by intercalating various guest species into the galleries between the carbon layers. While the physics of graphite intercalation compounds (GIC's) has attracted a great deal of attention in recent years,[8] their surface properties remain largely unexplored. The STM should be an excellent probe for these surfaces, and indeed some interesting experimental work[9,10] has recently begun to appear. But the lack of a theory makes it difficult to interpret much of the data. In this Communication we present calculations of the STM images of GIC surfaces. We show that the corrugation amplitude and the carbon-site asymmetry are sensitive to the charge transfer between the guest and host, to the distribution of the transferred charge among the host layers close to the surface, and to the near-surface band structure. Based on this, it should be possible to use the STM to map out the pattern of stage domains at a GIC surface. Even in the bulk case, there are important unanswered questions about the domain structure and electronic properties of GIC's,[8] which make such surface studies all the more interesting. A surprising prediction of our theory is that in many cases there should be *no* carbon atom asymmetry in the STM image even when the usual *AB* stacking of the graphite layers occurs at the GIC surface, and that the asymmetry should switch on *discontinuously* with decreasing charge transfer. We also present a possible explanation of the remarkable absence of atomic-scale features in the STM images of BiCs-graphite recently reported by Gauthier *et al.*[9]

The characteristic structure of a GIC is represented in Fig. 1, which shows a slice through the crystal perpendicular to the host layers. In a stage n compound (stage 4 in Fig. 1) every nth gallery is occupied by the guest, but the crystal is divided into Daumas-Hérold domains with different galleries being occupied by the guest in adjacent domains.[11] In this article we will discuss surfaces such as the top surface in Fig. 1, where the number m of graphite layers covering the guest layer closest to the surface depends on the particular domain involved. Such surfaces can be prepared by cleaving a GIC sample, and at least in the case of SbCl$_5$-graphite, the surface domain structure appears to be sufficiently stable to be studied in vacuum, according to the high-resolution scanning ion microprobe work of Levi-Setti *et al.*[12] Laguës, Marchand, and Frétigny[13] have suggested that some guest species may tend to segregate towards the surface leading to an in-
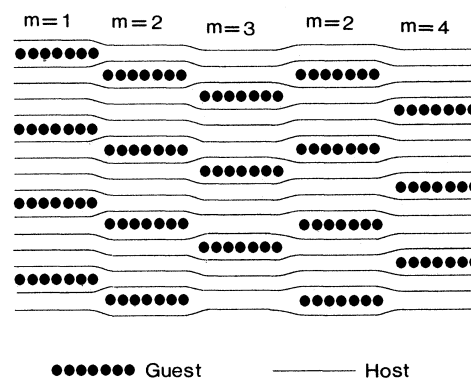

FIG. 1. Schematic representation of stage order and domain structure in a stage-4 GIC.

creased guest concentration in the first subsurface gallery, while the opposite effect may occur for other guests. Our theory applies also to such systems, as well as to graphite monolayers and multilayers on clean metal surfaces. In our calculations we assume that the stacking sequence of graphite layers, where it is *not interrupted* by the presence of a *guest layer*, is the usual graphitic *ABAB* sequence. This is known to be correct in the bulk case for most staged GIC's.[8] In this stacking there are two kinds of carbon atom sites: α sites which are adjacent to carbon atom sites in the neighboring graphite layer(s), and β sites which are adjacent to the (vacant) centers of the carbon hexagons in the neighboring layers.

Our starting point is the result of Tersoff and Hamann,[14] that at low bias voltages, for a simple s-wave model of the STM tip, the tunneling current is proportional to the local density of states at the Fermi energy E_F which is given by

$$\rho(\mathbf{r},E_F) = \sum_{kn} |\Psi_{kn}(\mathbf{r})|^2 \delta(E_{kn} - E_F) ,$$

where $\mathbf{r}$ is the center of curvature of the tip and Ψ_{kn} and E_{kn} are the electron eigenstates and energy eigenvalues of the sample. The STM image in the constant-current mode represents a contour of constant $\rho(\mathbf{r},E_F)$.

To calculate $\rho(\mathbf{r},E_F)$ we use a modification of the tight-binding model of Blinowski and co-workers.[15] The model of Blinowski and co-workers has been used successfully to describe the bulk electronic properties of staged GIC's for the larger guest species. We note that simple tight-binding models are known to be capable of describing the main features of the STM image of pristine graphite.[7] Our calculations reproduce the results of the published first-principles calculations of the STM images of multilayer slabs of pristine graphite[5] as well as of graphite monolayers[4] with reasonable accuracy. For example, we find an asymmetry of ~ 0.6–0.7 Å between the α and β sites of a four-layer slab of pristine graphite in constant current mode, which is close to the 0.5 Å found by Batra *et al.*[5] under similar conditions using a self-consistent pseudopotential method.

Our tight-binding Hamiltonian H includes the matrix elements γ_0 of H between the carbon $2p_z$ orbitals on nearest-neighbor atoms within each graphite layer, and also the matrix elements γ_1 between the orbitals of nearest-neighbor α atoms on adjacent graphite layers. We take $\gamma_0 = 2.51$ eV and $\gamma_1 = 0.377$ eV.[16] All matrix elements between graphite layers separated by a guest layer and between graphite and guest are neglected. The electrons (holes) which are transferred to the graphite from the donor (acceptor) guest screen the charged guest layers, and their concentration is highest in the graphite layers closest to the guest. Because of the unusual band structure of the graphite the screening is nonexponential, with the screening charge density and the associated potential decaying roughly as a power of the distance from the closest guest layer.[17] We find the STM images to be sensitive to the quantity and distribution of the transferred charge. We treat this effect by including in the tight-binding Hamiltonian site-diagonal matrix elements Δ_j that represent the average potential energy of an

electron in graphite layer j, which is due to the self-consistent screened potential. (Thus, in our model the presence of the intercalate is felt only through its influence on the site-diagonal Hamiltonian matrix elements, and on the number of electrons present.) In their model of the bulk electronic structure, Blinowski and co-workers[15] treat the matrix elements Δ_j phenomenologically, but we calculate them by solving numerically the nonlinear self-consistent Thomas-Fermi equations of Safran and Hamann,[17] for a semi-infinite GIC with appropriate surface boundary conditions. We remark that the energetics of staging is also very sensitive to the distribution of the transferred charge, and calculations based on the Safran-Hamann Thomas-Fermi theory agree quite well with experimental measurements of the staging phase diagram.[8,17,18] Having found the matrix elements of the tight-binding Hamiltonian of the m surface graphite layers, we diagonalize the Hamiltonian and then evaluate $\rho(\mathbf{r},E_F)$ using Herman-Skillman tight-binding carbon orbitals.[19]

Full details of our calculations and a systematic survey of the results will be published elsewhere. Here we will discuss some representative cases. In Fig. 2 we show the calculated constant-current STM profiles for a typical acceptor GIC, stage-4 $SbCl_5$-graphite, with stoichiometry $SbCl_5C_{14\times4}$ and charge transfer coefficient $f = 0.31$.[20] We chose $SbCl_5$-graphite because of the previous experimental observation of the surface domain structure in that system.[12] The results for a stage-4 alkali-metal donor GIC with stoichiometry $MC_{6\times4}$ and $f = 1$ are shown in Fig. 3. $MC_{6\times4}$ was chosen since it corresponds to a donor GIC with a high areal density of transferred charge. Among
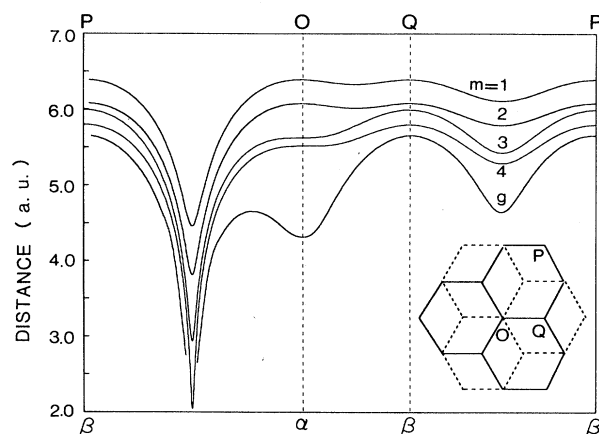

FIG. 2. Calculated constant-current STM profiles for stage-4 $SbCl_5$-graphite surfaces (curves 1–4 correspond to $m = 1$–4 graphite layers covering the top guest layer as in Fig. 1), and for a four-layer slab of pristine graphite (curve g). For curve g the Fermi energy was taken to be 0.0258 eV to reflect in a rough way the thermal broadening of the Fermi surface as discussed in Ref. 5. The scans shown are along PO-QO-QP in the inset. Inset: Structure of the surface graphite layer (solid hexagons), and (for cases $m = 2$, 3, 4) of the first subsurface graphite layer (dashed hexagons). The corrugation amplitudes shown here decrease by about 10% when the average tip separation is increased by 2.5 a.u.

alkali-metal GIC's only Li-graphite has equilibrium phases with *bulk* stoichiometry of $MC_{6 \times n}$ at ambient pressures, the other alkali metals being more dilute. However, guest concentrations as high as MC_6 in the first subsurface gallery have been reported for the other alkali metals.[13] While the results shown are for stage-4 compounds, the calculated profiles are very insensitive to the bulk stage, and reflect mainly the number of graphite layers covering the guest layer closest to the surface, the in-plane density of that guest layer and f. Thus, the results are also representative of other bulk stages with similar in-plane densities.

In Figs. 2 and 3, the vertical axis represents the distance from the center of curvature of the tip to the plane containing the carbon nuclei in the surface-graphite layer. The horizontal axis stands for the surface coordinate. Curves 1, 2, 3, and 4 in each figure correspond to $m = 1, 2, 3$, and 4 graphite layers at the surface covering the top guest layer as in Fig. 1. Curve g, shown for comparison, is the result for a four-layer slab of pristine graphite. The scanning path across the surface is along the line *PO-OQ-QP* as defined in the inset of Fig. 2. The points labeled α and β on the horizontal axis mark the locations of the α and β atoms of the surface-graphite layer. The five curves in each figure correspond to the same tunneling current, but the current was chosen to be somewhat larger in Fig. 3 than in Fig. 2. No corrections for finite instrumental resolution are included.

A striking feature of the STM profiles shown in Figs. 2 and 3 is the marked reduction in the strength of the depression at the center of the carbon hexagon upon intercalation. This is due to the fact that the Fermi surface of the graphite is greatly expanded by the carriers transferred from the guest so that the wave functions of the Fermi electrons no longer have an exact node at the hexagon center, in agreement with Tersoff.[4] The increase in the strength of the depression as the number of host layers m between the first guest layer and the surface increases can be understood qualitatively as an effect of the screening of the guest layer by the transferred charge:
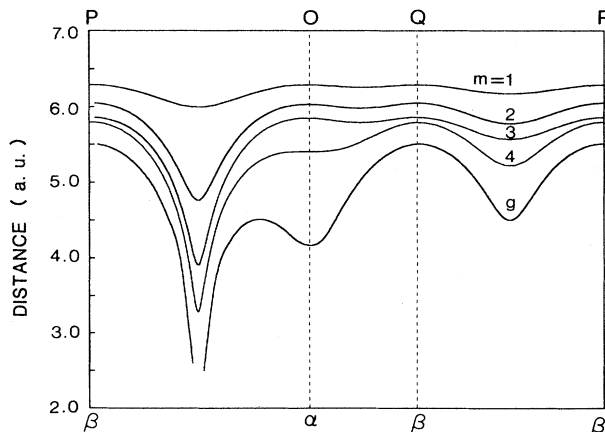

FIG. 3. Calculated constant-current STM profiles for stage-4 $MC_{6 \times 4}$ alkali-metal–graphite surfaces and for pristine graphite. Notation as in Fig. 2.

The further the surface graphite layer is from the guest layer the less the free carrier density at the surface and the more the STM image resembles pristine graphite. The depression in the profile is weaker for a given value of m in Fig. 3 than in Fig. 2 for two reasons; (a) there is a higher density of transferred charge in the former case and (b) the form of the electron eigenfunction at the Fermi surface is different for electrons and holes and also depends on the self-consistent potentials Δ_j in such a way that the corrugations are weaker for donors than for acceptors even when the magnitude of the transferred charge is the same.

The combination of these effects is so strong when there is only one graphite layer covering the alkali-metal guest (curve $m = 1$, Fig. 3) that the STM image is predicted to be nearly featureless on the atomic scale. Thus, we are able to explain the quite remarkable absence of atomic scale features in the STM image of BiCs-graphite reported recently by Gauthier *et al.*,[9] if as was noted by those authors, there is a high concentration of Cs in the first subsurface gallery of their samples due to segregation effects.[9]

The behavior of the asymmetry between the α and β carbon sites is very interesting. There is no hint of any asymmetry for $m = 1$ or 2 in Fig. 2 or for $m = 1, 2$, or 3 in Fig. 3. This is a surprise since bilayers and trilayers of AB stacked pristine graphite display a strong asymmetry. Recently, Tomanek and Louie[7] have pointed out that in stage-1 alkali-metal GIC's, which have AA stacking, there should be no carbon atom asymmetry since the asymmetry is linked to AB stacking. Here we predict that the asymmetry should be absent for small numbers of graphite layers covering the first guest layer, even for AB stacking. The asymmetry appears abruptly at $m = 3$ in Fig. 2 and at $m = 4$ in Fig. 3 but is weaker than in pristine graphite. It changes only slightly from $m = 3$ to $m = 4$ in Fig. 2. This is quite different from the behavior of the corrugation hole at the center of the carbon hexagon which never disappears totally and grows *smoothly* with increasing m. We find that the finite asymmetry appears *discontinuously* with decreasing charge transfer at fixed $m > 1$, when the highest electron (deepest hole) surface subband is emptied of carriers. This band is parabolic at its extremum, which implies that (in two dimensions) it has a nearly constant density of states. Thus, its contribution to the tunneling current (which strongly favors the α site) switches off discontinuously as it empties, which explains how it is possible for the asymmetry to be a discontinuous function of the Fermi level. While the overall trend is towards higher asymmetry with increasing m, exceptions can occur, as in Fig. 2, where the asymmetry *decreases* slightly from $m = 3$ to $m = 4$. The reason is that the different surface subbands contribute differently to the asymmetry strength, so that their number of character and the location of the Fermi level *relative* to them are all important and *change* with m. It is clear that careful asymmetry measurements would be very interesting.

An excellent way to test our predictions experimentally would be to map out the surface domain structure of a freshly cleaved staged GIC, since different domains with different m values should have differing corrugation

strengths and carbon atom site asymmetries, as well as having their surfaces offset vertically from each other[11] because of the bends in the graphite layers at the domain walls.

In conclusion, we have developed a theory of the STM images of the surfaces of staged graphite intercalation compounds. Our predictions should stimulate further experimental and theoretical work in this interesting new area of surface science. Such studies will also help to clarify some currently controversial issues about the bulk properties of intercalation compounds.

Note added. Since this paper was submitted for publication, a pseudopotential calculation for stage-1 LiC_6 has been published by A. Selloni, C. D. Chen, and E. Tosatti [Phys. Scr. **38**, 297 (1988)]. Their calculated corrugation is in good agreement with ours for the case of MC_6, lending support to the validity of our model. They also find that superlattice effects on the corrugation amplitude (due to the in-plane intercalate periodicity being different from that of the graphite) are small, justifying the omission of these from our model.

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