

Electronic structure of a stepped graphite surface

Katsuyoshi Kobayashi

Department of Physics, Faculty of Science, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan
(Received 12 January 1993; revised manuscript received 22 March 1993)

A first-principles band calculation and theoretical simulation of scanning tunneling microscopy and spectroscopy (STM and STS) are performed on a stepped surface of graphite. The calculated band structure and the density of states are similar to those of fullerene tubules. Unlike in fullerene tubules, however, a localized state on the step appears at the Fermi level due to the existence of an edge in the graphite sheet. The calculated STM image shows a triangular lattice structure similar to that of the bulk graphite. However, the positions of the peaks of the tunneling current do not coincide with the atomic sites and shift gradually as they diverge from the step. The calculated STS spectra at a location near the step show a strong peak reflecting the localized state.

I. INTRODUCTION

Scanning tunneling microscopy and spectroscopy (STM and STS) are powerful tools for investigating the atomic and the electronic structures of a surface. Since STM provides direct images of the surface, it can be effectively applied to the study of such aspects of the local structure of the surface as point defects and surface steps, and makes large contributions to the study of the mechanism of crystal growth on an atomic scale. In this paper, we present a theoretical study of a graphite stepped surface performed by first-principles calculations.

Graphite is a prototype layered material and has been studied extensively. In STM experiments, an image of graphite can be easily obtained because of the flatness and the cleanness of the sample over a large area. The STM image of graphite shows a triangular lattice which is different from the honeycomb atomic array of graphite. This is evidence for the fact that we see by STM not the atomic structure but the electronic states of the surface.^{1,2}

There are various anomalous STM images of graphite, which are ascribed to the tip effect,³⁻⁶ the local defect,⁷ the influence of the substrate,⁸⁻¹⁰ etc. It is also reported that anomalous STM images are obtained near the steps of graphite.^{11,12} The STM image of graphite near the step shows a superstructure, and the peaks of the tunneling current shift gradually with distance from the step. However, it is not clear whether the anomalous images are caused by the deformation of the atomic structure near the step or by the distortion in the electronic structure. To clarify the reason for the anomalous images, we performed a band calculation of a graphite stepped surface and calculated the STM image based on the results of the band calculation. In Sec. II, the method of band calculation and the STM simulation are described. The calculated results and discussions are presented in Sec. III. The conclusion is stated in Sec. IV.

II. METHOD OF CALCULATION

A structure model of a graphite stepped surface is shown in Fig. 1. The unit cell is formed of 20 carbon

atoms and two hydrogen atoms. To describe the step, a structure model made with a pile of semi-infinite graphite sheets would be realistic. However, it is difficult to calculate the electronic states of such a structure because of a lack of periodicity. In this paper, a two-dimensional periodic structure with a finite terrace width is assumed instead. If the terrace is wide enough, this is a reasonable model. As will be shown later, the electronic states located near the step decay at the center of the terrace. Therefore, the present terrace width is large enough to investigate the electronic states near the step.

The hydrogen atoms are used to pacify the dangling bonds of the carbon atoms at the edge of the graphite sheet. The C-H bond state is a σ state and does not mix with π states of graphite. Since discussions in this paper are focused on the π states of graphite, the main conclusions do not depend on the type of termination of the dangling bond. Even if the surface is clean and the dangling bond is not pacified, the π states are not affected by the presence of the dangling bond.

Since the σ bond of graphite is strong, the atomic structure and the C-C bond length near the step would

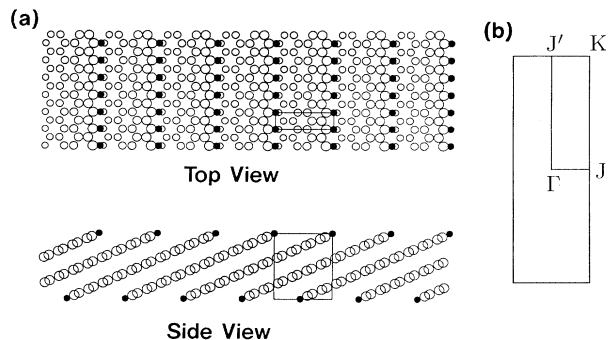


FIG. 1. (a) Atomic-structure model and (b) first Brillouin zone of the stepped graphite surface. The open and closed circles are carbon and hydrogen atoms, respectively. The rectangles in the structure model show the unit cell.

not be drastically different from that of bulk graphite. For simplicity, the C-C bond length and the interlayer spacing are taken to be the same as those of bulk graphite. The C-H bond length is 1.1 Å, which is the C-H bond length of benzene.

The electronic structure is obtained by a first-principles calculation. The band calculation is performed by the $DV\text{-}X\alpha$ method¹³ with the linear combination of atomic orbitals bases. As the basis functions, $1s$, $2s$, and $2p$ orbitals for a carbon atom and $1s$ orbital for a hydrogen atom are used. Each atomic charge is determined self-consistently.

The STM image and the STS spectrum are calculated by the following formula:^{14,15}

$$I(\mathbf{r}; V) = \int_{E_F}^{E_F + eV} dE \rho(\mathbf{r}; E), \quad (1)$$

where $\rho(\mathbf{r}; E)$ is the local density of states of the surface defined as

$$\rho(\mathbf{r}; E) = \sum_i |\Psi_i(\mathbf{r})|^2 \delta(E - E_i). \quad (2)$$

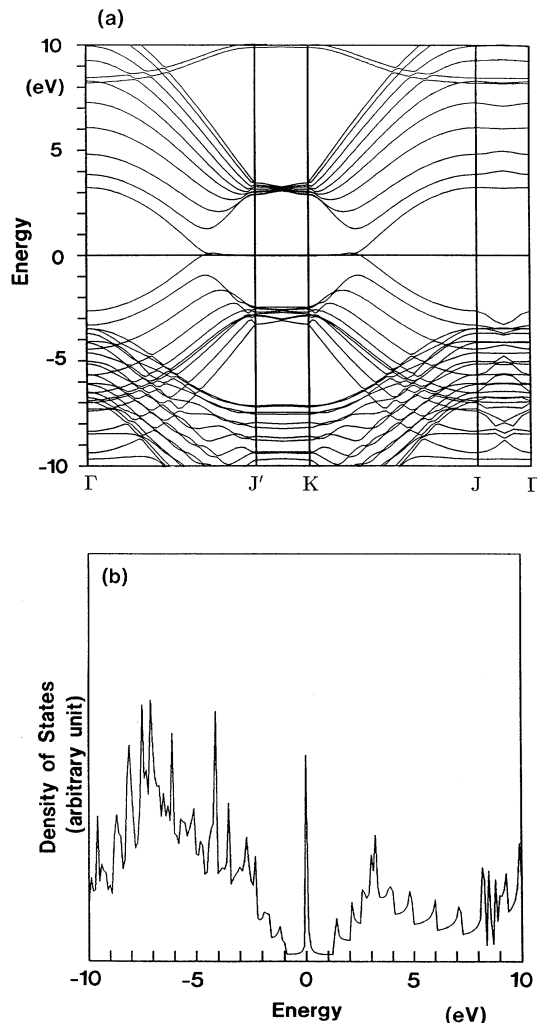


FIG. 2. (a) Calculated band structure and (b) density of states of the stepped graphite surface.

In the above, $\Psi_i(\mathbf{r})$ is a wave function of the surface with energy E_i , and E_F is the Fermi energy. The tunneling current depends on both the applied bias voltage V and the tip position \mathbf{r} .

III. CALCULATED RESULTS AND DISCUSSION

The calculated band structure and the density of states (DOS) are shown in Fig. 2. The DOS of the graphite stepped surface is a superposition of those of the one-dimensional bands. The envelope of the DOS corresponds to that of the π bands of bulk graphite. These features are similar to the band structures of the fullerene tubules.¹⁶⁻¹⁹

However, the electronic structure near the Fermi level is quite different. In the case of the fullerene tubules, two bands near the Fermi level either cross linearly at the Fermi level or do not cross, and the crossing depends on the way the tube is made by rounding a graphite sheet. As the result, the fullerene tubule is either a metal with a constant DOS in the vicinity of the Fermi level or a semiconductor with a band gap which decreases as the radius of the tubule increases.

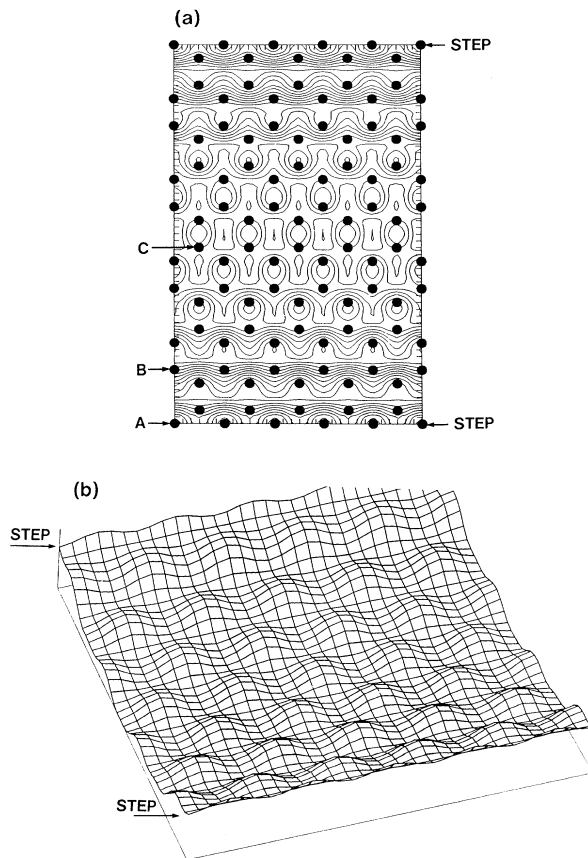


FIG. 3. Calculated STM image of the stepped graphite surface. (a) A contour map and (b) a three-dimensional expression of the tunneling current are shown. The closed circles in (a) show the position of the carbon atoms. The tip bias voltage and the position are -1.0 eV and 2.6 Å above the graphite surface, respectively.

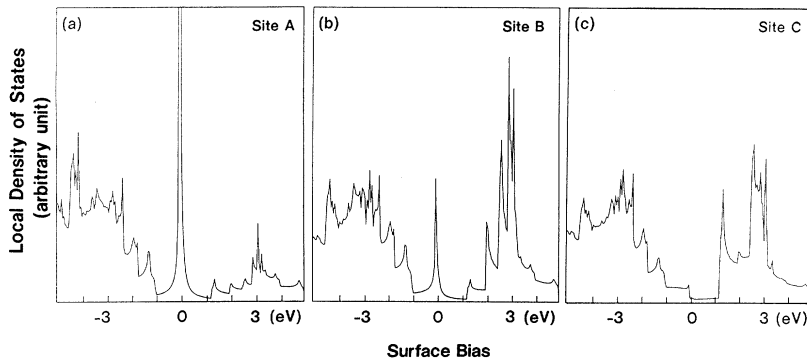


FIG. 4. Calculated STS spectra of the stepped graphite surface. The tip is located 2.6 Å above the carbon sites *A*, *B*, and *C* indicated in Fig. 3.

On the other hand, the two bands of the graphite stepped surface touch without any dispersion near the Fermi level and the DOS diverges at the Fermi level. This is due to the existence of a localized state near the step, caused by the cut of the graphite sheet at the step. The reason is as follows.

The wave function of bulk graphite at the Fermi level is described by three waves at the *K* point in the Brillouin zone. However, the wave function of the step consists of only two waves because of the cut in the graphite sheet. By a simple tight-binding calculation, it can be shown that the phase factor of the two waves compensate each other near the *K* point and the wave function becomes localized on the atoms of the step.

This localized state is similar to the step-induced localized state on the Si(100) surface.²⁰ However, the former is different from the latter which is a Tamm state. For a Tamm state to exist, the on-site potential at the step must be strong enough. In the present case, on-site potential is not needed. Therefore, the localized state at the graphite step is not a Tamm state.

Due to the localized state, the STM image of graphite near the step is quite different from that in the terrace. In Fig. 3, the calculated STM is shown. The tip bias voltage and the position are +1.0 V and 2.6 Å above the graphite surface, respectively. The STM image of graphite near the step shows a triangular lattice similar to that of the terrace. However, the peak positions of the image shift gradually with distance from the step. Near the step, the peaks in the STM image are located at the atomic sites. On the terrace, however, the peaks are located at the center of the two atoms. The gradual shift of the peaks of the tunneling current coincides with the experiment.¹¹

For the bias voltage within about ± 1 eV, averages of the tunneling current over the direction parallel to the step have a peak at the step and decrease with distance from the step. This reflects the fact that the localized state is the main component of the tunneling current near the Fermi level. This can be clearly demonstrated by the STS spectra. In Fig. 4, the STS spectra at the points *A*, *B*, *C* indicated in Fig. 3 are shown. At the step, the STS spectrum has a divergently large peak at the Fermi level, which decreases with distance from the step. The spectrum at a point far from the step converges with that of

bulk graphite. To obtain exactly the same spectrum as that of the bulk, a large unit cell is needed along the direction perpendicular to the step, where the energy difference of the π bands is negligibly small.

It may not be easy to observe the localized state in STS because the appearance of the localized state depends on the orientation of the step. A simple tight-binding calculation shows that if the orientation is rotated by 30°, the localized state does not appear and the electronic structure near the step is similar to that of the bulk. Moreover, experimental steps are not periodic but random. These may be the reasons why the localized state near the graphite step has not yet been reported. In the future, advances in the technology of microfabrication will enable us to make an ideal step and observe it.

IV. CONCLUSION

A first-principles band calculation is performed on the stepped surface of graphite. The calculated band structure and the density of states are similar to those of the fullerene tubules. The difference from the fullerene tubules is the existence of a localized state at the Fermi level, which is caused by the cut of a graphite sheet and localized near the step.

Based on the band calculation, the STM image and the STS spectra are also calculated. The STM image shows a triangular lattice structure similar to bulk graphite. Unlike the bulk graphite, however, the positions of the peak in the tunneling current shift gradually with distance from the step. The STS spectra near the step show a strong peak at the Fermi level, reflecting the localized state.

ACKNOWLEDGMENTS

The author thanks S. Schmidt for reading the manuscript. The numerical calculations were performed by the HITAC S-820 computer system at the Computer Center of the University of Tokyo and the Institute for Molecular Science. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Crystal Growth Mechanism in Atomic Scale" No. 213, from the Ministry of Education, Science and Culture, Japan.

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