The effect of interstitial clusters and vacancies on the scanning tunneling microscopy image of graphite

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Abstract

Making use of the tight-binding Green's function technique, we have calculated the scanning tunneling microscopy (STM) images of graphite with surface and sub-surface defects, while taking into account the relaxation of the lattice due to defects. We have demonstrated that two different physical mechanisms may result in the formation of hillocks in the STM images: buckling of the graphite surface due to interstitials between the uppermost graphite layers; and the enhancement of the electron density of states close to the Fermi energy on the carbon atoms in the vicinity of vacancies. Our results indicate that small hillocks may originate both from the interstitial clusters and from the vacancies. By contrast, however, large hillocks in excess of 10 Å in diameter can be caused only by interstitial clusters. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Scanning tunneling microscopy (STM) is a powerful tool for investigating surfaces with defects inasmuch as it gives real-space images of surfaces with atomic resolution. Radiational defects near the surface profoundly effect STM images of graphite. Appearances of hillock-like features in STM images of graphite after irradiation with noble gas ions have been reported repeatedly [1–8].

These hillocks (or bumps or protrusions), which reveal themselves as a substantial increase in the tunneling current, have an average lateral diameter of from several Å up to tens of Å, with the typical height of hillocks constituting 1–5 Å. Since these

structures have never been observed on graphite surfaces free of defects, they are associated with defects created by incident ions near the surface.

Despite numerous studies, however, the actual nature of hillock-like features remains controversial. Hillocks may result from local buckling of the surface due to internal stresses induced by subsurface defects [1,2] and — more specifically — by carbon interstitial clusters between the graphitic layers [3,4,9], that is, within the framework of this assumption the hillocks can be interpreted topographically.

Recent molecular dynamics (MD) simulations [9,10] provide evidence in favor of this interpretation. It has been demonstrated that ion irradiation of graphite may result in the formation of interstitial clusters under the graphite surface and in the buckling of the surface layer.

The physical mechanism for interstitial cluster

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formation is proposed in [10]. The interstitials created by ion impact lie predominantly between graphite layers [9] and have a high mobility parallel to the layers. At the same time, as has been shown in [10] by the MD method, an interstitial stretches the graphite lattice within its vicinity, with other interstitials in that same interlayer region tending to be attracted to the stretched region. Thus, due to the minimization of the total buckling of the graphite layers, the formation of interstitial clusters lowers the deformation energy, as compared to the case of interstitials being spatially separated.

A different interpretation [6] of hillock-shaped features is that the surface atomic vacancy is seen as a protrusion in STM images of graphite because of the vacancy-induced enhancement of an electron density corresponding to the states close to the Fermi energy (E_F) on the carbon atoms near the vacancy. Inasmuch as STM probes only some of the electronic states of the sample within a certain energy range near E_F determined by the bias voltage V_{bias}, the enhancement of electron density leads to an increase in the tunneling current. Real geometry of the surface remains practically flat.

It should also be noted that the hillocks may be explained by incident ions trapped near the graphite surface [7], but, in many cases (e.g. in the case of incident ions with high energy), the formation of hillocks seems to be associated with carbon atoms only. Adsorbate effects are believed [6] to be either absent or relatively negligible. Therefore, we restrict our consideration only to cases of carbon interstitials and vacancies.

The lack of a clear understanding of the nature of the hillocks may be due in part to the comparatively small number of theoretical works on the subject. The effect of lattice vacancies on the STM image of graphite was studied in Refs.[11,12] by the tight-binding (TB) molecular orbital method and in Ref. [13] using the first-principles plane wave formalism. The results of simulations support

the interpretation that vacancies may lead to the formation of hillocks.

However, we are not aware of any theoretical works dealing with the simulation of the STM images of graphite in the presence of interstitials near the surface.

In this paper, we simulate the STM images of the graphite surface having defects such as interstitials and vacancies making use of Green's function calculations based on the TB model. Our main goal is to clarify whether the vacancies and interstitial clusters under the graphite surface result in the formation of protrusions in the STM images.

2. Computational details

In general, in our simulations we adopt the technique used in Ref. [14]. To describe the graphite electronic structure, we employ the parametrization of the TB Hamiltonian for carbon systems proposed in Ref. [15]. Since the density of states near E_F in graphite is determined by p-states perpendicular to the graphite layers [14,16], we take into consideration only $2p_z$ electrons. The tip was modeled as the final atom of a semi-infinite, one-dimensional chain. To the first order in the tip–surface interaction, the tunneling current I as a function of the tip coordinates in the (x, y) plane (parallel to the graphite surface) and the tip height h may be written as follows [14]:

$$I(x, y, h) = \frac{2\pi e}{\hbar} \int_{E_F - eV_{bias}}^{E_F} \sum_i |V_i(x, y, h)|^2$$
$$\times \rho_{tip}(E)\rho_{surf}(r_i, E)\,dE, \qquad (1)$$

where V is the tip–surface matrix element, the sum over i runs over graphite surface sites effected by the tip, $\rho_{surf}(E)$ and $\rho_{tip}(E)$ are the local densities of states (LDOS) of the non-interacting surface and tip, respectively.

Fig. 1. Constant current mode of operation of STM: (a) Variation in tip height h for a scan across x, y on the graphite surface near a ten-interstitial cluster at a current of 4 nA and $V_{bias}=0.08$ V. (b) The contour map of (a). ●, Positions of carbon atoms in the surface layer; ■, carbon atoms in the interstitial cluster.

a

h, Å
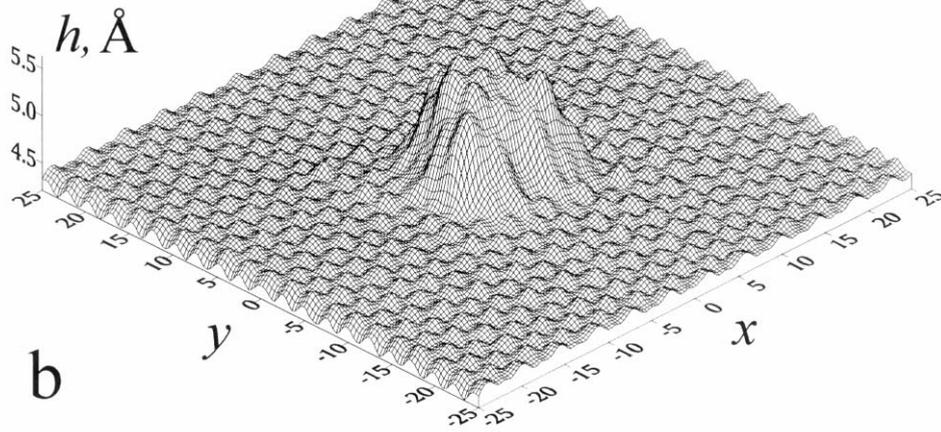
b
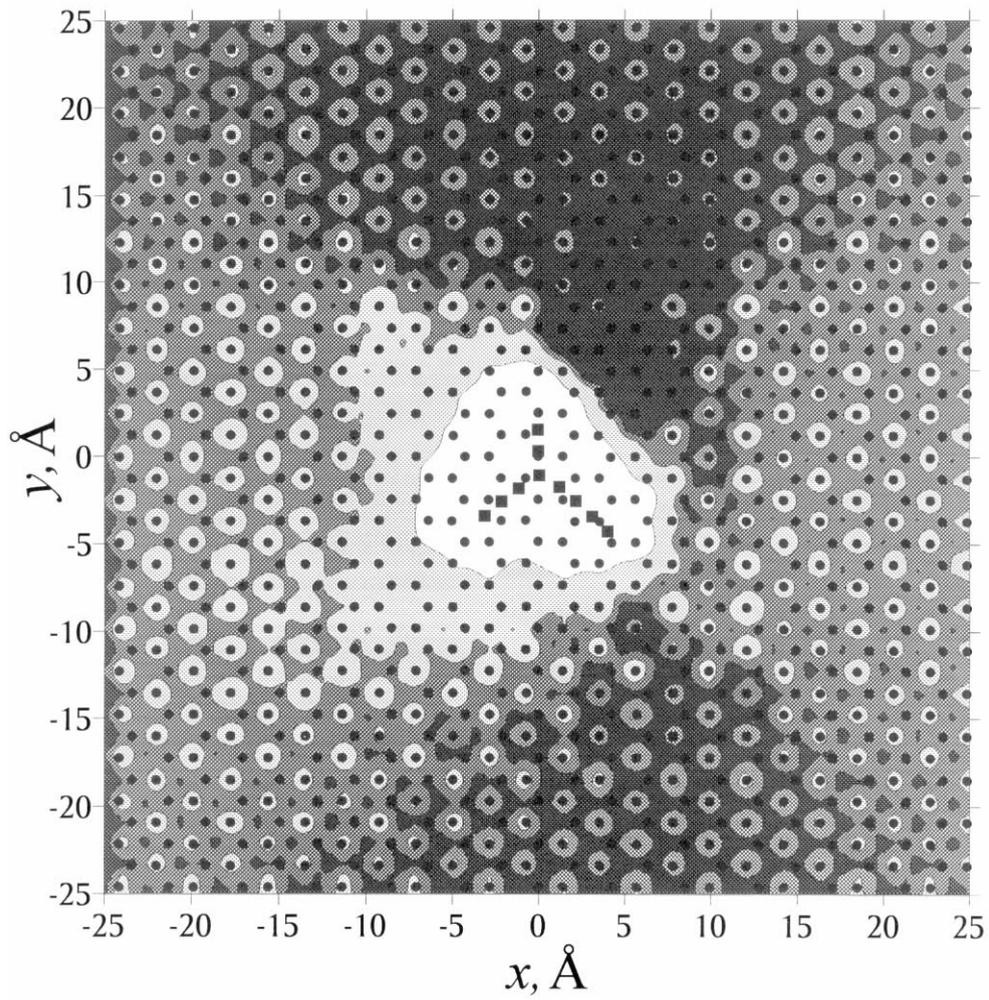
To account for the deformation of the graphite lattice near the defects, the MD method was employed. Details of calculations are given in Ref. [10]. Graphite was modeled by the crystallite consisting of six graphite layers, each composed of 1096 atoms. Crystallites with different numbers of atoms were also used, but the results proved to be practically independent of the crystallite size. Interstitials were initially distributed randomly over the crystallite between the uppermost layers. Ten initial variants were considered for each number of interstitials. The tunneling current was calculated after the relaxation of the lattice and interstitial cluster formation due to deformation interaction.

3. Results and discussion

We have calculated the STM images of the graphite surface near both a single interstitial as well as clusters composed of two to ten interstitials. Fig. 1a shows an isometric plot of the variation in the tip height h for a scan across (x, y) near a ten-interstitial cluster on the graphite surface at a current of 4 nA and $V_{bias} = 0.08$ V. Fig. 1b depicts a contour map corresponding to Fig. 1a and simulating the STM image. A dramatic protrusion above the interstitial cluster is evident. This hillock is due to a graphite surface buckling (~ 1 Å) which results in a corresponding growth of V and in an increase in the tunneling current. The graphite LDOS does not change substantially near the cluster. The positions of maxima and minima of the tip height near the cluster correspond to those in the defect-free case (in graphite every second atom is observable due to electronic effects [16]). Slight anisotropy in the corrugation (~ 0.05 Å) near the cluster is associated with the non-uniform distribution of electron density because of the anisotropic form of the interstitial cluster, see Fig. 1b.

Hillock-like features were observed for all clusters, but the height and lateral diameter of protrusions were dependent on the number of interstitials in the cluster N_{int} as well as on the cluster shape. The average diameter of hillocks $\bar{d}$ as a function of N_{int} is shown in Fig. 2. It is seen that $\bar{d}$ increases
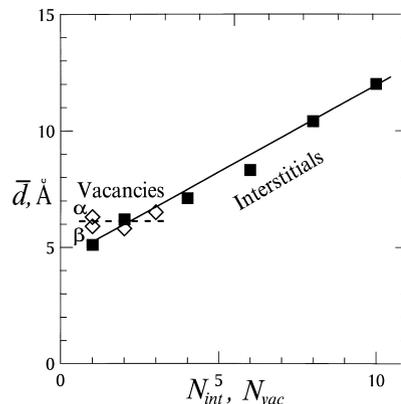
Fig. 2. The average diameter $\bar{d}$ of the hillock as a function of the number of interstitials and vacancies in the system.

linearly with N_{int}. The average height also grows with N_{int}, but rather slowly ($\bar{h} = 1$ Å for $N_{int} = 1$ and $\bar{h} = 1.5$ Å for $N_{int} = 10$), which may be associated with the two-dimensional character of interstitial clusters.

Let us proceed to the effect of vacancies on the STM image. Fig. 3 shows the variation in the tip height h for a scan on the graphite surface near a single vacancy positioned on the β surface site (there is no atom below the β site in the second graphite layer). The tunneling current and V_{bias} were the same as in the case of interstitials. As follows from Fig. 3 and although real geometry remains flat, the vacancy results in the formation of a hillock with a height of ~ 0.8 Å. The increase in h is governed by the enhancement of the LDOS at E_F on the atoms in the immediate vicinity of the vacancy, which is in agreement with the results of Refs. [11,12].

The superstructure (SS) $\sqrt{3} \times 3\sqrt{3}R30°$ is seen in the image. The SS was also evident in our calculated images near single interstitials. Similar SS were experimentally imaged next to some hillocks in Refs. [1,2]. Our calculations confirm the interpretation [17,18] that these SS are actually a purely electronic effect due to point defects and are not indicative of any surface reconstruction. Note that SS are absent in Fig. 1 since interstitial clusters result in a long-range perturbation of the lattice.

Qualitatively similar results were obtained for the vacancies in the α positions, divacancies, and
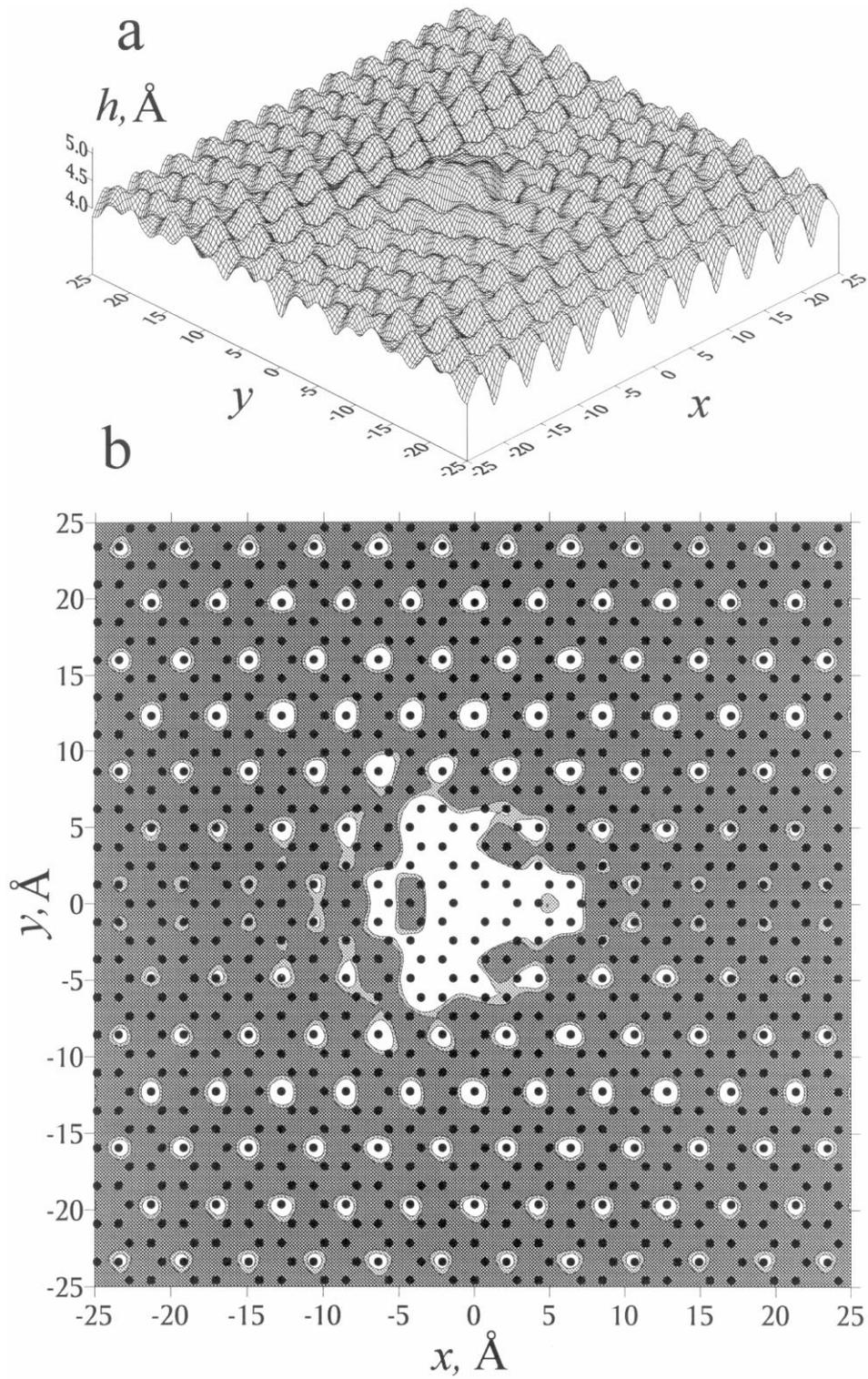
Fig. 3. The same as in Fig. 1, but for a single vacancy.

trivacancies. The lateral size of the vacancy-induced hillock depends slightly on the number of vacancies in the system, see Fig. 2. Therefore, our results indicate that large, experimentally-observed hillocks exceeding 10 Å in diameter can be caused only by the interstitial clusters.

4. Conclusions

In summary, we have calculated the STM images of graphite having surface and sub-surface defects. Two different physical mechanisms may give rise to the appearance of hillocks in the STM images: buckling of the graphite surface due to interstitials between the uppermost graphite sheets; and the enhancement of the partial charge density of states on the carbon atoms near vacancies. Small hillocks (<10 Å in diameter) may originate from both the interstitial clusters and vacancies. However, large hillocks (>10 Å) may be caused only by interstitial clusters. Thus, our results confirm the mechanism [10] of interstitial cluster formation in the irradiated graphite due to deformation interaction.

Acknowledgements

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