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Giant superstructures formed on graphite surface treated with NaOH solutions studied by scanning tunneling microscopy

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Abstract

Giant superstructures with 1.71 and 9.1 nm lattice constants were observed by scanning tunneling microscopy (STM) on the surface of highly oriented pyrolytic graphite (HOPG) treated with NaOH solution. These structures were analyzed by the moiré pattern hypothesis. For both the structures, the orientation angle mismatch of the giant lattices relative to the original atomic lattice of graphite was observed between the theoretical and experimental values. In addition, for the latter structure, the observed boundaries between the superstructural domain and the normal areas were straight, which is different from the theoretically predicted zigzag shape boundary. These discrepancies suggest the existence of some other mechanism responsible for the giant superstructures appearing in graphite intercalation compound surfaces. © 1998 Elsevier Science B.V. All rights reserved.

The graphite (0 0 0 1) surface has been used as a standard sample for scanning tunneling microscopy (STM) study, because of the stability of its surface obtained by cleaving even in air. However, it is also well known that the graphite surface shows various apparent STM images; superstructures appearing near defects [1,2], structures similar to that of macro molecules [3], and so on. More recently, anomalously large scale periodic superstructures have been observed on fresh graphite surfaces [4,5]. The anomalous superstructures have been interpreted by the moiré pattern hypothesis suggested by Kuwabara et al. [4]; Moiré patterns originate from the lattice misorientation introduced by the overlapping of a misoriented top layer of graphite to the underlying graphite single crystal.

On the other hand, graphite is known to form intercalation compounds which have many interesting properties differing from those of the host materials, e.g., superconductivity and low-dimensional conductivity. Among them, alkali-metal graphite intercalation compounds (AM-GIC) have

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been studied widely because of their simplicity in analysis [6,7]. According to STM observations of surface structures of binary and ternary AM-GICs [8–10], in addition to superstructures such as 2×2 and $\sqrt{3}\times\sqrt{3}$, anomalous large scale periodic superstructures, which were similar to the moiré patterns described above, were also observed on the stage-1 AM-GIC (M = Li, K, Rb, Cs) surfaces. Attempts were made to interpret these large scale superstructures as charge density wave (CDW) structures instead of the analysis by the moiré pattern hypothesis, but the origin of the superstructures has not been clarified yet. In order to understand the mechanism of the giant superstructures formed on GIC, it is important to clarify the effect of the intercalants on the host graphite in more detail.

Recently, we found highly oriented pyrolytic graphite (HOPG) treated with NaOH solutions to have an X-ray diffraction pattern characteristic of a stage-8 structure [11]. On this surface, we also observed giant superstructures with 1.71 and 9.1 nm lattice constants in addition to the superstructures of 2×2 and $\sqrt{3}\times\sqrt{3}$ by STM. These giant superstructures appear similar to those previously observed on clean graphite surfaces [4,5]. Since guest materials are separated further in the higher stage GICs compared to the structure of the AM-GICs described above, it must be very useful to analyze the giant superstructures formed on the stage-8 GIC in detail.

In this paper, we present the results of the analysis performed on the giant superstructures appearing on a graphite surface treated with NaOH solution, on the basis of the moiré pattern hypothesis.

Samples were prepared by pouring NaOH aqueous solutions onto freshly cleaved highly oriented pyrolytic graphite (HOPG) surfaces or dipping HOPG crystals into NaOH aqueous solutions. STM was performed in air at room temperature by using Pt/Ir tip. All STM images in this paper are taken in the constant height mode.

Fig. 1 shows STM images of giant superstructures with (a) 1.71 nm and (b) 9.1 nm lattice constants. These giant superstructures have three-fold symmetry like graphite. Similar superstructures were observed on clean graphite surface, as described above, which could be well interpreted as

(a)

(b)

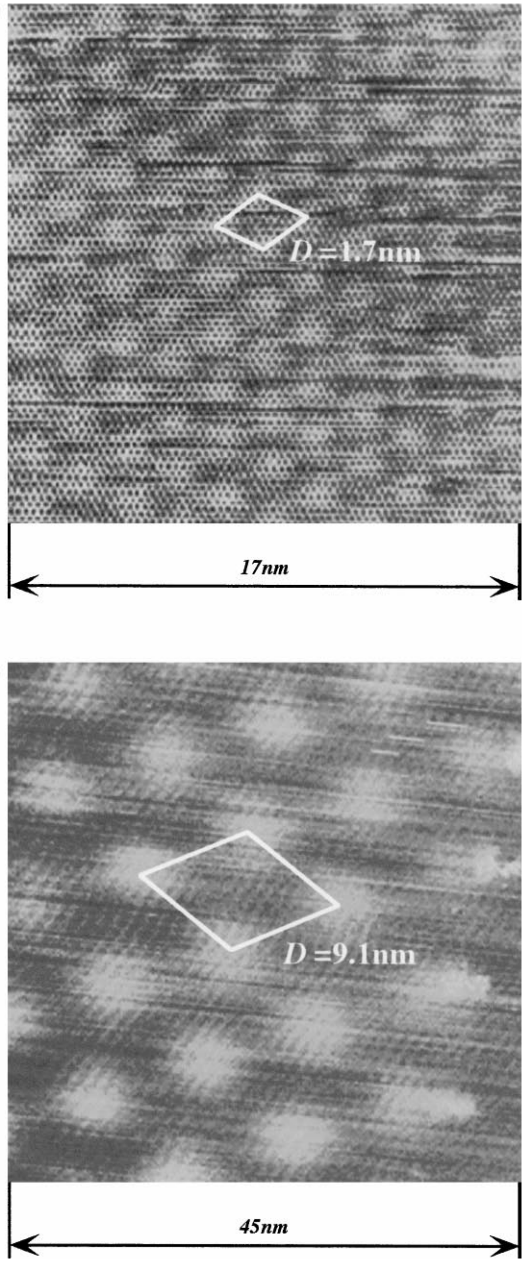

Fig. 1. STM images of giant superstructures with (a) 1.71 nm (sample bias; $V_s = -20$ mV, and tunneling current $I_t = 1.9$ nA) and (b) 9.1 nm lattice constants ($V_s = 30$ mV, $I_t = 0.7$ nA).

moiré patterns [4,5]. Therefore, we apply the moiré pattern hypothesis to the STM images obtained in our work in order to clarify the origin of these superstructures.

By the moiré pattern hypothesis, the period D of the produced Moiré pattern is given by [4]

$$D = d/[2\sin(\theta/2)]\,, \quad (1)$$

where d is the lattice constant of graphite and θ is a rotation angle between the topmost and second graphite layers. Then, the orientation of the giant lattice relative to the atomic lattice of graphite Θ can be given by [5]

$$\Theta = 30^\circ - \theta/2\,. \quad (2)$$

Let us discuss the obtained giant superstructures in Fig. 1 by this method. Magnifications of Fig. 1a and b are shown in Fig. 2a and b, respectively. In addition to the giant superstructure, the graphite lattice could be clearly seen as shown in the figures.

In the case of the giant superstructure shown in Fig. 2a, the period of giant lattice D is 1.71 nm. Substituting the value and $d = 0.245$ nm into Eq. (1), the value of θ becomes $\sim 8.38^\circ$. Therefore, the theoretical value of the orientation Θ of the giant lattice relative to the atomic lattice of graphite can be obtained as 25.81°. On the other hand, the angle obtained experimentally from the STM image in Fig. 2a is 26.6°, which is slightly different from the theoretical value. The observed value in the difference between theory and experiment is small ($\sim 0.8^\circ$), but is within the experimental resolution. Therefore, some other mechanism for this structure is expected supposed to exist beyond the moiré pattern hypothesis.

Next we discuss the structure shown in Fig. 2b. Substituting $D = 9.1$ nm and $d = 0.245$ nm into Eq. (1), we obtain the value of θ as 1.57°, and Θ becomes 29.22° from Eq. (2). However, the observed value of Θ is 27.9°. The angle mismatch ($\sim 1.3^\circ$) is clearly recognized as shown in Fig. 2b, which also suggests the existence of some other mechanism for this structure rather than the moiré pattern. In addition, there are doubts bout the structure of the boundary.

The observed boundary between the giant superstructure and the normal graphite lattice has a straight shape, and both domain boundaries run parallel as shown in Fig. 3a. As is described above, moiré patterns originate from the misorientation

(a)
(b)

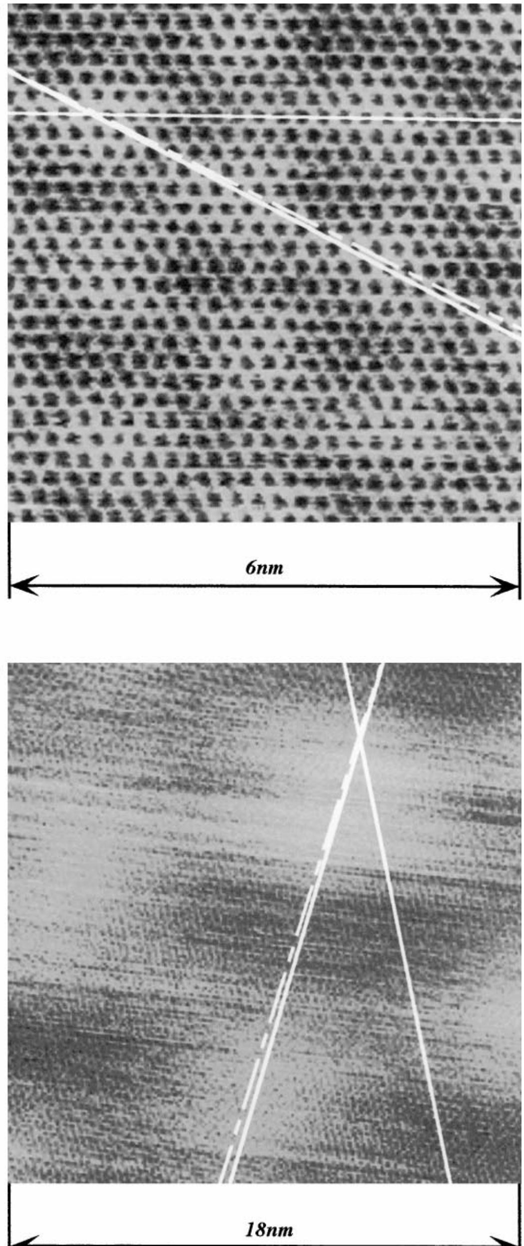

Fig. 2. Magnified STM images of (a) Fig. 1(a) ($V_s = 20$ mV, $I_t = 1.6$ nA), and (b) Fig. 1(b) ($V_s = -20$ mV, $I_t = 0.9$ nA).

introduced by the overlapping of a misoriented top layer of graphite to the underlying layers, the structure of which is shown schematically in Fig. 3b. In Fig. 3b, a misoriented top layer with a rectangular

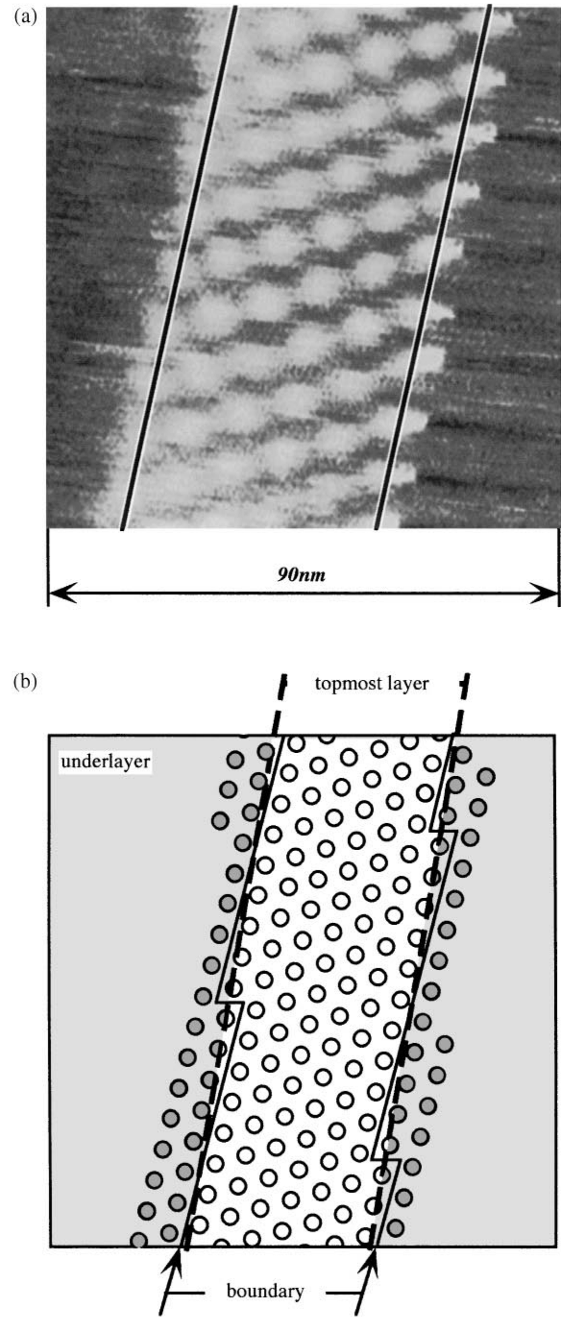

Fig. 3. STM image ($V_s = 30$ mV, $I_t = 0.9$ nA) of the boundary between giant superstructure with 1.71 nm lattice constant and normal graphite lattice (a) and its structural model (b).

shape indicated by dashed boundaries is overlapped to the underlying graphite surface indicated by the large square in the figure. The graphite lattices are not drawn here, and the open circles indicate the giant superstructures which are expected to be observed by STM. The lattice of the superstructure extended to the normal areas at the boundaries are indicated by solid circles in Fig. 3b. When the top layer has a straight boundary, the observed superstructure induced by the moiré pattern must have a zigzag shape at the boundary as indicated by the solid lines in Fig. 3b. In fact, according to the previous report on the STM image of a moiré pattern, the observed boundary between a superstructure and the normal graphite structure had a zigzag shape similar to that in Fig. 3b [4]. Therefore, from the results of the angle mismatch and the difference in the boundary structures between the theory and experiment, the moiré pattern hypothesis is not suitable for the analysis of the giant superstructure in this case, too.

The obtained results in our work suggest the existence of some other mechanism for the formation of the observed giant superstructures on GIC; some interaction between the intercalants, and the host graphite may result in the structures. In order to understand the relationship between the characteristic properties of GIC and the giant superstructures, further experiments and theoretical studies are necessary.

In conclusion, giant superstructures with 1.71 and 9.1 nm lattice constants were observed by STM on the surface of HOPG treated with NaOH solution. Analysis by the Moiré pattern hypothesis could not explain the structures comprehensively. Some other mechanism must be introduced to understand the giant superstructures on GIC.

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