Atomic-Scale Friction of Monolayer Graphenes with Armchair- and Zigzag-Type Edges During Peeling Process

Naruo Sasaki,* Hideaki Okamoto, and Noriaki Itamura
Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan
Kouji Miura
Department of Physics, Aichi University of Education, Hiroshawa 1, Igayacho, Kariya-shi, Aichi 448-8542, Japan
(Received 27 December 2009; Accepted 28 January 2010; Published 6 March 2010)

We numerically studied the atomic-scale friction of the monolayer graphene sheet during the nanoscale peeling process by molecular mechanics simulation. The zigzag behavior appears twice in the force curve during the surface and line contacts between the graphene sheet and the graphite surface. During the surface contact, the graphene sheet takes the atomic-scale sliding motion, which exhibits the transition from the continuous to the stick-slip sliding particularly for the graphene with the armchair-type free edge. The period of the zigzag structures for the stick-slip motion in the peeling force curve nearly corresponds to the lattice period of the graphite depending on the lattice orientation and the edge structure of graphene. During the line contact, the graphene sheet also takes the stick-slip sliding motion. Comparison between armchair- and zigzag-type free edges reveals the difference of the characteristic atomic-scale sliding of the graphene sheet. These findings indicate the possibility of not only the direct observation of the atomic-scale friction of the graphene sheet at the tip/surface interface but also the identification of the lattice orientation and the edge structure of the graphene sheet. [DOI: 10.1380/ejssnt.2010.105]

Keywords: Peeling; Adhesion; Graphene; Edge effect; Computer simulations; Atomic force microscopy; Stick-slip motion; Tribology

I. INTRODUCTION

The carbon nanostructures such as carbon nanotube (CNT) and graphene have recently attracted great interests as the components of the electronic, magnetic and optical devices. We have so far studied the peeling mechanics of the carbon nanotube (CNT) adsorbed onto the graphite surface both theoretically [1–3] and experimentally [4, 5]. It is clarified that the transition from the line- to the point-contact between the CNT and the graphite surface occurs during the peeling process [1–5]. On the other hand, since the success of its experimental isolation [6], the potential of various application of the graphene has been discussed by many researchers [7, 8]. Therefore the peeling mechanics of the graphene sheet is also very important, which can be regarded as the elementary process of the macroscopic sticky tape such as the gecko-foot-mimic adhesives [9–11], or that of the microscopic extension of the crack in the fracture process.

In our preliminary experiments, we have already succeeded in peeling the multilayered graphene plate with a thickness of several μm by using atomic-force microscopy tip [12]. Here the two-component epoxy resin adhesive is used to bond the graphene plate to the AFM tip. The junction formed between the AFM tip and the graphene should be mechanically rigid enough to measure the elasticity of the graphene sheet during the peeling process. Ahead of experiment, we have theoretically reported the nanoscale peeling behaviors of the monolayer graphene sheet by lifting the center position based on the molecular mechanics simulation [13]. The peeling force curve exhibits the nanoscale change of the graphene shape from the surface to the line contact. However the clear atomic-scale behaviors of the graphene sheet have not been found yet during the peeling process. In this paper, the characteristic atomic-scale sliding behaviors of the graphene sheet are found during both the surface and line contacts in the case of lifting the edge of the graphene sheet. It is clarified that effect of the free edge structure gives the marked influence on the atomic-scale peeling process. These simulated results can indicate the possibility of not only the direct observation of the atomic-scale friction of the graphene sheet at the tip/surface interface but also the identification of the lattice orientation and the edge structure of the graphene sheet.

II. MODEL AND METHOD OF SIMULATION

The same model as that used in the previous work [13] is adopted as illustrated in Fig. 1(a): a rectangular-shaped monolayer graphene sheet with each side of 38 Å × 21 Å comprised of 310 carbon atoms, adsorbed onto the rigid rectangular graphene sheet (which is called, the ‘graphite surface,’ hereafter) with each side of 164 Å × 58 Å comprised of 3536 carbon atoms. The initial position of the graphene is set so that the AB stacking registry between the graphene sheet and the graphite surface is satisfied as shown in Fig. 1(b). The green-colored outermost atoms at the left edge of the graphene sheet are assumed to be attached to the AFM tip apex [Fig. 1(a)], and then they are gradually moved upward along the z direction, parallel to the [0001] axis, by 0.1 Å. In this case, the edge structure is armchair type. First, in Secs. IIIA and IIIB, the atomic-

*Corresponding author: naru@st.seikei.ac.jp
scale peeling process for the armchair-type edge is discussed. Then, in Sec. III C, the case for zigzag-type edge is also discussed. Effect of the free edge structure gives the marked influences on the atomic-scale peeling process. For each lifting edge height of the graphene sheet \( z \), the total energy \( V_{\text{total}} = V_{\text{cov}} + V_{\text{vdW}} \) is minimized using the conjugate gradient (CG) method [14]. Here the covalent bonding \( V_{\text{cov}} \) [15] and nonbonding energies \( V_{\text{vdW}} \) [16, 17] are considered. Thus the optimized shape of the graphene sheet and the peeling force acting on the lifting left edge, \( F_x \) and \( F_z \), are calculated during the peeling process.

III. RESULTS

A. Nanoscale peeling behavior within \( x-z \) plane

When the left edge of the monolayer graphene sheet is lifted, the shape of the graphene sheet markedly changes during the peeling process within the \( x-z \) plane as illustrated in Figs. 2A-2J, corresponding to Figs. 3(a)A-3(a)J, the vertical force acting on the lifting edge \( F_z \) plotted as a function of the edge height \( z \).

1. Surface-contact region

At first the monolayer graphene sheet takes an initial planar structure parallel to the rigid graphite surface [Fig. 2A: \( z = 0 \) Å], and the vertical force \( F_z \) is zero [Fig. 3(a)A], which means the graphene sheet completely takes the surface contact with the graphite surface. Just after the start of the peeling [Fig. 2B: \( z = 1.1 \) Å], the attractive interaction force \( |F_z| \) becomes the maximum, 0.74 eV/Å [Fig. 3(a)B]. After that the surface contact area gradually decreases as the peeling proceeds [Figs. 2C-2E], where Fig. 3(a) exhibits the atomic-scale zigzag structures [Figs. 3(a)C-E], which will be explained in the section III B.

2. Line-contact region

After the surface contact vanishes, the line contact appears [Fig. 2F]. Here the 'line contact' is defined by the following two criteria: 1) The outermost array of the free edge of the graphene sheet [Fig. 1(b)] receives the averaged repulsive interaction force per one carbon atom from the graphite surface. 2) The second array next to the outermost array [Fig. 1(b)] re-
receives the averaged attractive interaction force per one carbon atom. As illustrated in Fig. 3(b), the edge height \( z = 31.3 \) Å satisfies the above criteria [Fig. 2F]. Here the free edge adsorbed onto the graphite surface is nearly fixed even if the left edge is lifted [Fig. 2E→Fig. 2G: \( z = 33.9 \) Å]. As a result the in-plane bending of the graphene sheet markedly decreases, and \( |F_x| \) decreases to zero [Figs. 3(a)F-G]. After that the free edge slides on the surface until the graphene sheet takes planar structure within the \( y-z \) plane [Fig. 2H: \( z = 37.9 \) Å], where \( |F_x| \) increases again [Fig. 3(a)H].

3. Toward complete peeling Then the graphene sheet is continuously moved upward [Fig. 2I: \( z = 38.0 \) Å → Fig. 2J: \( z = 38.4 \) Å], and is completely peeled from the surface. It is noted the line contact clearly vanishes at \( z = 38.0 \) Å [Fig. 3(b)I]. The attractive interaction force \( |F_x| \) increases to the maximum value [Figs. 3(a)I→J], and then it gradually decreases to zero toward the complete peeling.

B. Atomic-scale sliding within \( x-y \) plane

Fig. 3(a) shows the atomic-scale zigzag structures within the surface- and line-contact regions, which can be explained by the following atomic-scale sliding motions of the graphene sheet within the \( x-y \) plane.

1. Surface-contact region During the surface contact region between C and E in Fig. 3(a), \( z - F_z \) curve takes the atomic-scale zigzag structures from I to VII. The zigzag behaviors exhibit the transition from the continuous [Figs. 4(a)I - II] to the sawtooth shapes [Figs. 4(a)III - VII]. First Figs. 4(a)I→II correspond to Figs. 4(b)1→2, which show that the graphene sheet continuously slides passing over the nearest neighboring AB stacking sites with the graphite surface. The trajectories of the graphene sheet exhibit the continuous zigzag paths as shown in
the zigzag behavior of the AB-stacking sites as shown in Fig. 4(c). The period of discrete zigzag paths connecting the nearest neighboring sites result the trajectories of the graphene sheet exhibit the tendency of the decrease of the period and amplitude of the force curve. As a result, the nanoscale peeling process within the graphite surface contact plays quite an important role in electronic properties of graphene, which can be also expected to give influences on the mechanical properties such as the peeling process. Therefore, in this section, the peeling process of the graphene sheet with the ‘zigzag-type’ free edge is discussed. In the simulation, the model obtained by rotating Fig. 1(b) by 30° is used [Fig. 6(a)], and the left zigzag edge is lifted to simulate the peeling process, while the right free edge is zigzag type. As a result, the nanoscale peeling process within the $x$–$y$ plane and the global shape of the force curve [Fig. 6(b)] is similar to that of Figs. 2 and 3, respectively. The qualitative tendency of the decrease of the period and amplitude of the force curve [Figs. 6(b)-I-V] is the similar to that for Figs. 3(a)-I-VII. However the details of the atomic-scale mechanisms of the zigzag edge are clearly different.

C. Edge effect

The free edge of the graphene sheet discussed in the previous section is ‘armchair type.’ However, it is well known that the edge structure plays quite an important role in electronic properties of graphene, which can be also expected to give influences on the mechanical properties such as the peeling process.

Fig. 4(b). Next Figs. 4(a)6→7→8→9→10 correspond to Figs. 4(c)6→7→8→9→10 which show that the graphene sheet takes the zigzag stick-slip motions between the nearest neighboring AB stacking sites. Just before the slip, the graphene sheet deviates quite a little from the AB-stacking site [Fig. 4(c)6: $z = 17.3 \text{ Å}$]. Then it discretely jumps or slips to the neighboring AB-stacking site [Fig. 4(c)7: $z = 17.4 \text{ Å}$]. As the peeling proceeds, the graphene sheet continuously slides quite a little [Fig. 4(c)8: $z = 18.2 \text{ Å}$], then it discretely slips again to the neighboring AB stacking site [Fig. 4(c)9: $z = 18.3 \text{ Å}$]. After that the graphene sheet continuously slides quite a little again [Fig. 4(c)10: $z = 20.1 \text{ Å}$] until the next slip toward the neighboring AB stacking site occurs. As a result the trajectories of the graphene sheet exhibit the discrete zigzag paths connecting the nearest neighboring AB-stacking sites as shown in Fig. 4(c)10. The period of the zigzag behavior of the $F_z$ curve decreases from 3.7 Å to 2.5 Å as shown in Fig. 4(a) as the peeling proceeds. The lattice spacing of the graphite surface, 2.5 Å, appears in the peeling force curve particularly for the stick-slip region.

2. Line-contact region During the line contact region between G and H in Fig. 3(a), $z – F_z$ curve takes another atomic-scale zigzag structures as shown in Fig. 5(a). One of the zigzag behaviors in the force curve [Figs. 5(a)1→2→3] corresponds to the stick-slip sliding motions of the graphene sheet. Here the free edge of the graphene sheet slides with nearly the straight stick-slip motions. One of the carbon atoms on the free edge passes over the carbon-carbon bonds as shown in Figs. 5(b)1 and 3.

FIG. 5: (a) Enlargement of part of the $z – F_z$ curve (Fig. 3(a)) corresponding to the nearly straight stick-slip region during the line contact. (b) The trajectories of the two carbon atoms on the free edge from 1 to 3 indicated in (a).

FIG. 6: (a) Schematic illustration of the initial AB stacking registry of the red-colored graphene sheet with free edge of zigzag-type adsorbed onto the blue-colored graphite surface within the $x$–$y$ plane. (b) The vertical force, $F_z$, acting on the lifting edge, plotted as a function of the lifting edge height $z$ for the graphene with zigzag-type free edge.
During the surface contact, the graphene sheet first takes zigzag [Figs. 7(b)1-6] and then straight stick-slip motions [Figs. 7(c)7-11], passing over the nearest neighboring AB-stacking site along [10\bar{1}0] direction. It is noted, to avoid AA-stacking registry, the graphene sheet takes zigzag slip toward the nearest neighboring AB-stacking site as shown in Fig. 7(b)1!2, although it takes straight slip as shown in Fig. 7(c)7!8. The minimum period of the force curve of 2.9 Å [Fig. 7(a)V] reflects the lattice period of the graphite surface along the [10\bar{1}0] direction, while 2.5 Å for the armchair-type edge [Fig. 4(a)VII] reflects that along the [12\bar{3}0] direction. Thus the edge structure gives the marked effects on the atomic-scale dynamics depending on the lattice orientation of the surface.

During the line contact, the difference between the armchair- and zigzag-type edge is enhanced. Fig. 8(a) reflects the zigzag stick-slip motion of the graphene sheet [Figs. 8(b)1-9] unlike nearly the straight stick-slip motion [Figs. 4(b)1-3]. Important point of the line-contact sliding is that each carbon atom on the free edge takes stick-slip motion between the nearest neighboring six-membered rings. When each atom is located on the hollow site of the six-membered ring, the graphene sheet does not deform along the y direction [Figs. 8(b)1, 4-5, and 8-9]. However, when each atom is located a little far from the hollow site or near the carbon bond, the graphene sheet bends along the y direction to decrease the total interaction energy [Figs. 8(b)2-3 and 6-7]. Thus, in the case of the zigzag-type edge, collective motion of the single carbon atom on the free edge nearly dominates the graphene mechanics together with its deformation. On the other hand, for the armchair-type edge, collective motion of the single carbon bond is dominant.

IV. DISCUSSIONS AND CONCLUSIONS

In this paper the atomic-scale sliding motion of the monolayer graphene sheet during the peeling process...
The period becomes the lattice spacing along [10\bar{1}0] direction. (b) The graphite surface along [12\bar{3}0] direction, particularly for the stick-slip region corresponds to the lattice spacing of the peeling force curve parallel to the zigzag structures of the peeling force curve with the same period of about several Å have been also observed by our preliminary experiments using the multilayered graphene, which will be reported elsewhere [12]. Of course, if the number of the peeled graphene sheets is reduced, the direct comparison between the present simulation and the experiment will become possible. Another interesting point is that the behavior of the lateral force curve $(F_x(z))$ is qualitatively the same as that of the vertical force curve $(F_z(z))$ during the surface contact as shown in Fig. 9(b). Therefore it can be said that the peeling force curve, $F_z(z)$, directly reflects the atomic-scale friction force, $F_x(z)$, which decreases to $0.019 \text{ eV/Å} \approx 30 \text{ pN}$ for $z = 27.8 \text{ Å}$ [Fig. 9(b)]. This ultralow friction force, $F_x$, is derived from the superlubricity at the interface between the graphene sheet and the graphite surface [18–20].

Furthermore effect of the edge structure on the peeling process is clarified by comparison of the free edge between the armchair- and zigzag-types. The atomic-scale structure of the force curve during the surface contact reflects the lattice spacing of the graphite surface. So the period of the atomic-scale structure of the force curve can tell us the atomic-scale lattice orientation and structure of the free edge of graphene. Such information can be used for the control of the electronic properties of the graphene sheet adsorbed onto the substrate. Therefore this paper indicates the possibility of the identification of the lattice orientation and the edge structure of the graphene sheet.

The peeling process discussed in this paper is closely related to the atomic-scale wear of the graphite and the graphene tip formation in the friction force microscopy [21]. When the tip is pushed onto the surface for less than the critical tip height, the outermost graphene layer is attached to the FFM tip, which results in the formation of the graphene tip. In that case, the graphene sheet takes the surface contact with the second layer graphene, and it takes the two-dimensional stick-slip motion. However it is difficult to observe directly the stick-slip motion during the scan process, due to the very small gap between the FFM tip and the graphite surface. On the other hand, if the peeling process is used, it can be expected that the contact at the AFM tip/graphite interface has a wider space to be observed directly by ex. Transmission Electron Microscopy (TEM). This paper indicates the possibility of a direct observation of the stick-slip motion of the graphene sheet, that’s to say, the elementary process of the atomic-scale friction or superlubricity which occurs at the tip/graphite surface interface.

### Acknowledgments

This research was supported by a Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (No. 20360022). This work was also supported by the Ministry of Education, Culture, Sports, Science and Technology through a Grant-in-Aid for Building Strategic Research Infrastructures.
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