Reconstruction and evaporation at graphene nanoribbon edges

Gun-Do Lee,[1] C. Z. Wang,[2] Euijoon Yoon,[1,3,4] Nong-Moon Hwang,[1,5] and K. M. Ho[2]
[1]*Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea*
[2]*Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[3]*Department of Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Suwon 433-270, Korea*
[4]*WCU Hybrid Materials Program, Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea*
[5]*National Research Laboratory of Charged Nanoparticles, Seoul National University, Seoul 151-742, Korea*
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The reconstruction and evaporation at graphene nanoribbon (GNR) edges are investigated by tight-binding molecular-dynamics simulations and *ab initio* calculations. It is observed that reconstruction through the formation of pentagon-heptagon pairs can take place quickly along the zigzag edge and it is energetically favorable. At very high temperatures, the armchair edge is found to change into a zigzag edge structure, which further accelerates the evaporation of carbon atoms and leads to the formation of carbon linear chains. The evaporation of carbon atoms from both the zigzag and armchair edges is preceded by the formation of heptagon rings, which serve as a gateway for carbon atoms to escape. In the simulation for a GNR armchair-zigzag-armchair junction, carbon atoms are evaporated row by row from the outermost row of the zigzag edge while the armchair edge remains nearly intact. These results can be applied to nanoelectronic devices fabrication through the temperature-controlled edge structure of GNR.

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I. INTRODUCTION

Graphene, a two-dimensional single layer structure composed of carbon atoms has recently become a subject of intensive study due to its peculiar physical properties[1,2] and its potential applications for recent electronic devices.[3–5] In particular, graphene nanoribbons (GNRs) have been reported as a material with a controllable band gap, depending on the edge structure and ribbon width.[6–8] It has also been suggested that zigzag GNRs may be a candidate material for spintronics because they become a half metal when an external field is applied.[9] Because the electronic properties of GNRs are strongly dependent on the edge structure, investigation of the edge structure at the atomic scale has been continually requested in order to understand the interesting electronic features of GNRs. Although many theoretical and experimental efforts have been devoted to elucidating the structure at the edges of GNRs,[10–14] our understanding of the atomic structure and processes at the edges of GNRs is still far from complete. It is also interesting to note that recent experiments have attempted to obtain GNRs with clean edges by trimming the harsh edges using an electric current.[15,16] In these experiments, evaporation of carbon atoms from the edge is observed. Evaporation of carbon atoms from the edge of a hole in graphene during aberration-corrected transmission electron microscopy (TEM) has also been reported.[17] These experiments have stimulated much interest in the reconstruction and evaporation processes at the graphene edge, as an understanding of these processes at the atomic level is essential to controlling the edge structure of GNRs and to obtaining GNRs with clean edges. In this paper, tight-binding molecular-dynamics (TBMD) simulations are performed to investigate the reconstruction and evaporation process of carbon atoms at the edge of graphene.

II. CALCULATIONAL METHOD

The TBMD simulation is performed using the modified environment-dependent TB (EDTB) carbon potential,[18] which was developed from the original EDTB carbon potential.[19] This modified EDTB carbon potential has been successfully applied to the investigation of defects in graphene and has been used to find a structure for double vacancy reconstruction in graphene consisting of triple pentagons and triple heptagons (555-777).[20] Such a double vacancy structure has been confirmed in a recent experiment[17] (see Fig. S1, Ref. 21). In TBMD simulations, the self-consistent calculations are performed by including a Hubbard-U term in TB Hamiltonian to describe correctly charge transfers in carbon atoms of dangling bonds and to prevent unrealistic overestimation of charge transfers.[22] The equations of motions of the atoms are solved by the fifth-order predictor-corrector algorithm with a time step of 1.0 fs. The simulation temperature is controlled via a usual stochastic temperature control algorithm.[23] The supercells in our simulations contain 120 atoms in a six-row zigzag GNR, 108 atoms in a five-row armchair GNR, and 168 atoms in a six-row armchair-zigzag-armchair GNR, and vacuum regions of 30 Å in the y and z directions. *Ab initio* total-energy calculations are also carried out to verify the TBMD results of the formation energies and energy barriers for important configurations and their reconstructions. Those are performed within the local-density approximation using Vienna *ab initio* simulation pack (VASP) code.[24] In the calculation, the basis set contains plane waves up to an energy cutoff of 400 eV, and the structure is relaxed until the force on each atom is less than 0.02 eV/Å. Hydrogen atoms are not included in the simulation cells because under high-temperature conditions ($\geq$1000 °C) for TEM or joule heating by an electric current, the hydrogen atoms dissociate from the edges of the GNRs.

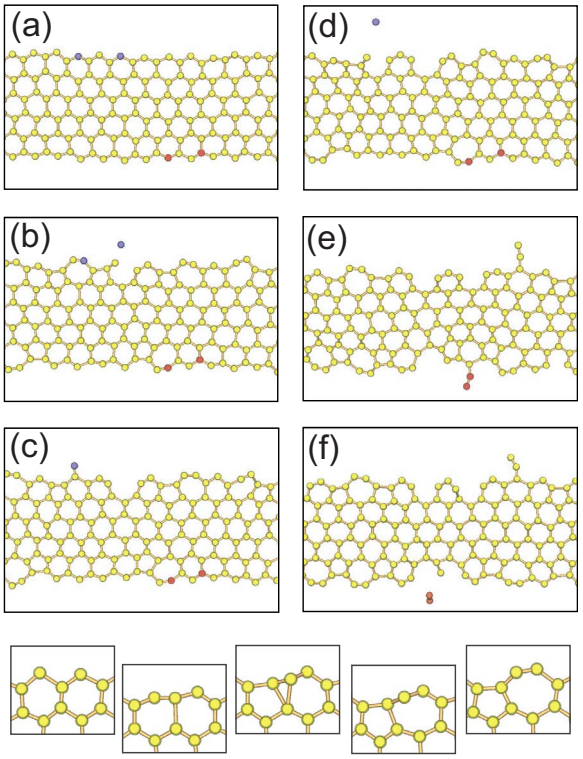

FIG. 1. (Color online) Reconstruction and evaporation of carbon atoms at the edge of a zigzag GNR [(a)–(f)] and reconstruction process of two hexagons into a pentagon-heptagon (5-7) pair (bottom figures) in the TBMD simulation. (a) 0 K (at time $t=0$ ps), (b) ~2800 K($t=44.6$ ps), (c) ~2900 K($t=47.9$ ps), (d) ~2800 K($t=49.5$ ps), (e) ~2800 K($t=123.0$ ps), and (f) ~2900 K($t=124.1$ ps). The gray (blue) color on the top of GNR indicates a carbon atom that is evaporated in the atomic form and the gray (red) colors on the bottom of GNR indicate carbon atoms evaporating in the dimer form.

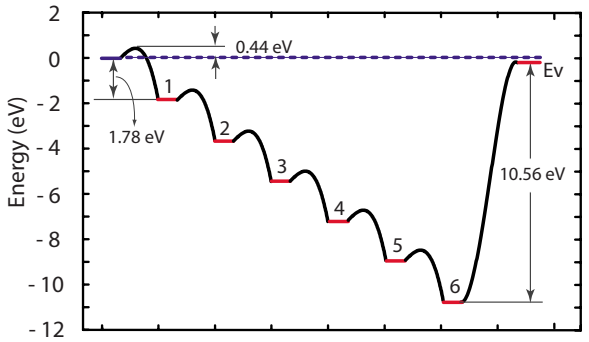

FIG. 2. (Color online) Energy diagram for reconstruction into 5-7 pairs and evaporation of one carbon atom. The abscissa is the total energy relative to the total energy of perfect zigzag edge structure, which is indicated by the dotted (blue) line. The parenthesis indicate reaction coordinates. The solid gray (red) lines indicate the formation of 5-7 pairs and the integer numbers indicate the number of the formed 5-7 pairs. "Ev" indicates the evaporation of one carbon atom from a heptagon.

III. RESULT AND DISCUSSION

Before the TBMD simulation, we relaxed the geometries of the zigzag and armchair GNRs and calculated the formation energies. The formation energy was found to be 1.12 (1.09) eV/Å and 1.41 (1.43) eV/Å for the armchair and zigzag GNRs, respectively, by our tight-binding (*ab initio*) total-energy calculations. These results agree with other *ab initio* calculations in the literature.[11] These results also indicate that the armchair edge is more stable than the perfect zigzag edge without hydrogen passivation. We first performed the TBMD simulation for the zigzag GNR at temperature 2500 K for 24.0 picoseconds (ps) and gradually raised the temperature up to 3000 K for 26.0 ps. After that, the temperature was kept at 3000 K. We found that the zigzag GNR undergoes sequential reconstructions through the formation of pentagon-heptagon (5-7) pairs at the edge, as shown in Fig. 1(b). It has been reported that the reconstruction of the zigzag graphene edge into 5-7 pairs is a self-passivating reconstruction.[11] Our simulation shows that the reconstruction proceeds by bond switching among carbon atoms on the edge of the GNR, as illustrated in the bottom of Fig. 1. We found that the formation of 5-7 pairs stabilizes the edge structure and that the total energy is lowered by 1.51 eV (1.78 eV) on average for generating each 5-7 pair from the perfect zigzag edge in our tight-binding (*ab initio*) calculations. It turns out that the formation energy of a GNR with a reconstructed zigzag 5-7 edge is 1.10 (1.06) eV/Å according to our tight-binding (*ab initio*) calculations, which is slightly lower than that of an armchair GNR. This suggests that the GNR with a reconstructed zigzag 5-7 pair edge is the lowest-energy structure for a GNR without hydrogen passivation. Moreover, the energy barrier for the 5-7 pair reconstruction was also found to be only 0.69 (0.44) eV by our tight-binding (*ab initio*) calculation. Hence, once a 5-7 pair is formed at the zigzag edge, the whole edge should be spontaneously reconstructed into 5-7 pairs. The reconstruction into 5-7 pairs also seems to accelerate the evaporation of carbon atoms in our TBMD simulation. Evaporation of carbon atoms during the process of 5-7 pair formation has been frequently observed at zigzag edges in TEM experiments.[17,25,26] We also investigated the relation between the reconstruction and evaporation of carbon atoms at the zigzag edge by *ab initio* total-energy calculations. From an energetic point of view, because the formation of six 5-7 pairs in the unit cell lowers the total energy by 10.68 eV and the energy required to evaporate one carbon atom from a 5-7 pair is 10.56 eV, as shown in Fig. 2, the formation of six 5-7 pairs at the zigzag edge can ensure the spontaneous evaporation of a carbon atom. In our TBMD simulation, carbon atoms began to evaporate from the edge at a total simulation time of 44.5 ps. The evaporation was often found from the heptagons on the edge of the GNR, as shown in Figs. 1(b)–1(d). The carbon atoms are usually evaporated directly from heptagons. Sometimes flipping of a carbon dimer is also observed on heptagons before a carbon atom is evaporated, as shown in Figs. 1(c) and 1(d). Carbon atoms are also evaporated in the form of dimers as frequently as those in the atomic form. The evaporation of a carbon dimer is usually preceded by the formation of a carbon dimer attached to one of the heptagons at the GNR edge through diffusion of two carbon atoms from two neighboring heptagons, as shown in

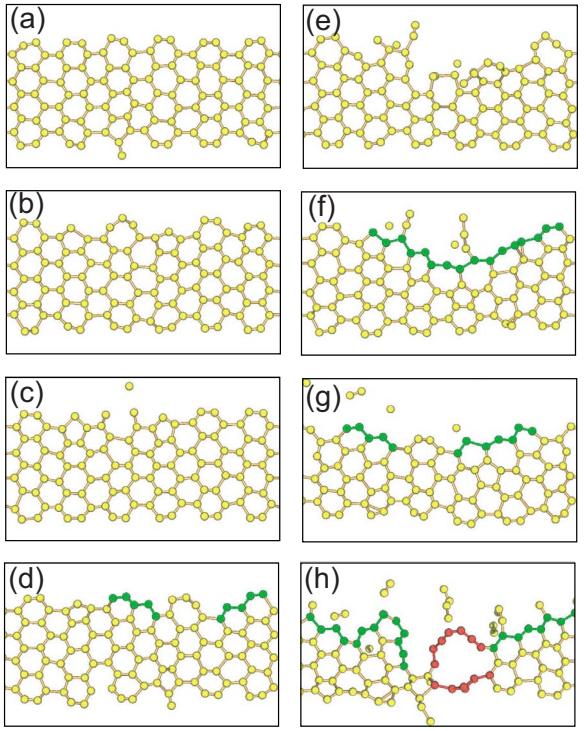

FIG. 3. (Color online) Reconstruction and evaporation of carbon atoms at edge of armchair GNR. (a) ~4100 K(t=9.0 ps), (b) ~4200 K(t=125.1 ps), (c) ~4200 K(t=127.2 ps), (d) ~4700 K(t=137.1 ps), (e) ~4200 K(t=142.9 ps), (f) ~4700 K(t=145.6 ps), (g) ~4300 K(t=151.9 ps), and (h) ~3800 K(t=155.7 ps), t is the elapsed time after the simulation temperature was increased to 4000 K. The dark gray (green) colors indicate the formation of zigzag edges during the simulation and the medium gray (red) colors indicate the formation of carbon linear chains.

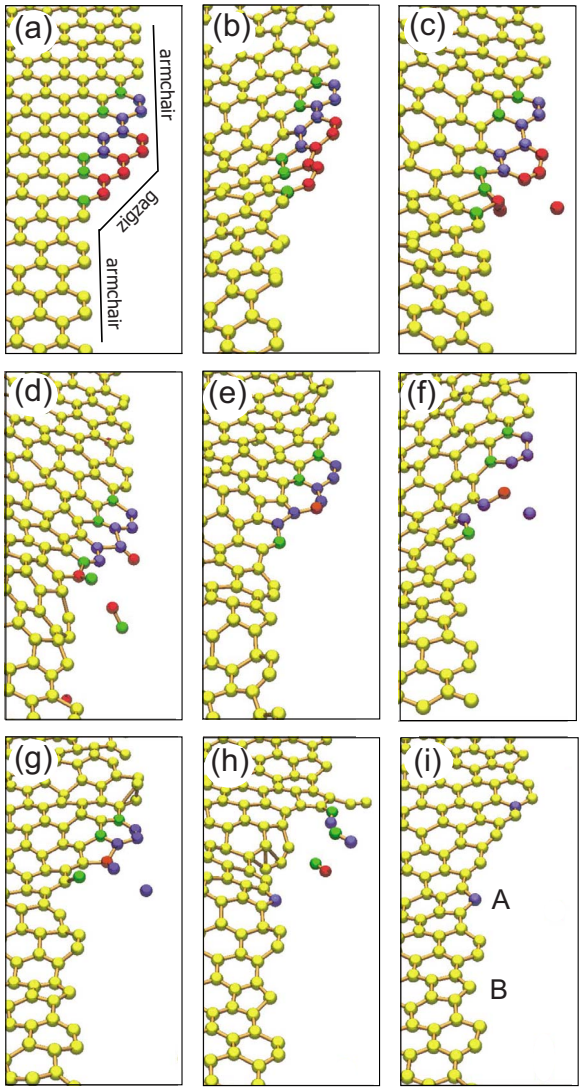

FIG. 4. (Color online) Snapshots from TBMD simulation for a GNR armchair-zigzag-armchair junction. (a) ~0.0 K(t=0.0 ps), (b) ~2800 K(t=32.7.4 ps), (c) ~3300 K(t=99.7 ps), (d) ~3400 K(t=165.0 ps), (e) ~3300 K(t=210.5 ps), (f) ~3600 K(t=234.6 ps), (g) ~3500 K(t=254.4 ps), (h) ~3700 K(t=284.8 ps), and (i) ~3300 K(t=296.1 ps). The dark gray (red and blue) colors indicate carbon atoms on the outermost row and the second outermost row of zigzag edge. The medium gray (green) colors indicate inner carbon atoms to be evaporated during the simulation. See the text for characters in (i).

Figs. 1(e) and 1(f). The energy required to evaporate a carbon dimer from a 5-7 pair was found to be 10.6 eV in our *ab initio* calculation, which is almost the same as that for a carbon atom. From our TBMD simulation and *ab initio* calculation for a zigzag GNR, we can conclude that the formation of heptagons plays a key role in the evaporation of carbon atoms at the zigzag edge of a GNR. TBMD simulations were also performed for an armchair GNR. At a simulation temperature of 3000 K, no reconstruction at the armchair edge was observed during a simulation time of 130 ps. When the temperature was increased to 4000 K, a 90° rotation of a carbon dimer at the edge was observed, as shown in Fig. 3(a). The energy barrier for the flipping of a carbon dimer was found to be 1.84 (2.03) eV and the total energy for the structure with one flipped dimer is higher than that of the perfect armchair edge by 1.81 (2.02) eV in our tight-binding (*ab initio*) calculations. The flipped dimers were observed to quickly return to their original orientation because the energy barrier for restoring the dimer is quite small (~0.03 eV). After the temperature was raised over 4000 K, the armchair edge of the GNR was observed to undergo reconstructions at the simulation times of 25 ps and 125 ps, respectively, in addition to dimer flipping. In this reconstruction, an edge carbon atom diffuses to a neighboring hexagon to form a heptagon, as shown in Fig. 3(b). Similarly to the case of the zigzag GNR, the heptagon plays a role as a gateway for vaporizing carbon atoms, as shown in Fig. 3(c). As more and more carbon atoms are evaporated at the armchair edge through this process, a part of the zigzag edge structure is formed, as shown in Fig. 3(d). Surprisingly, the formation of the zigzag edge accelerates the evaporation of carbon atoms, as shown in Fig. 3(e). As a result of this accelerated evaporation, a longer zigzag edge is formed quickly, as shown in Fig. 3(f). The processes of evaporation and formation of the zigzag edge are repeated as the simulation is continued, as shown in Fig. 3(g). Finally, as shown in Fig. 3(h), linear chains of carbon atoms are generated between zigzag edges,

which are also in excellent agreement with experimental observations of linear chains.[25,27] On the other hand, the armchair line on the bottom edge of the GNR is quite stable, although the top edge of the GNR is almost fully evaporated due to the formation of the zigzag edge structure. The simulation result shows that the armchair edge is much more stable than the perfect zigzag edge under structural reconstruction. Evaporation of carbon atoms at the armchair edge can only be observed at a simulation time of 63 ps and a temperature of 4000 K, while at the zigzag edge, evaporation of carbon atoms is observed at a shorter simulation time (45 ps) and a much lower temperature (2800 K). From our TBMD simulations, it is also obvious that the perfect zigzag without hydrogen passivation is the edge structure of local minimum energy and easily reconstructed into the 5-7 zigzag edge. At high temperature, the perfect zigzag edge is very fast evaporated because it is metastable and sometimes, it could happen directly, not via the reconstruction into the 5-7 zigzag edge. Due to the rapid evaporation of the outermost row from zigzag edges, the second outermost row still keeps the perfect zigzag edge structure. These processes are repeated and the perfect zigzag edges are frequently observed and, accordingly those seem to be very stable in experiment.[17] However, as a matter of fact, the perfect zigzag edge is metastable and very active for the evaporation of edge carbon atoms. As we mentioned in high-temperature TBMD simulation for the armchair GNR, the accelerated evaporation of edge carbon atoms is observed after the formation of zigzag edges. We also performed the TBMD simulation for a GNR consisting of armchair-zigzag-armchair junction, as shown in Fig. 4. In the simulation, we found that evaporation at the zigzag edge section is much faster than that at the armchair edge sections. During the first 20 ps, the simulation temperature was kept at 2500 K. After a simulation time of 8.8 ps, carbon dimers were frequently found to flip back and forth at the armchair edge sections, but no reconstruction was observed. In order to observe the reconstruction and evaporation of carbon atoms, the temperature was raised up to 3500 K. At a simulation time of 32.5 ps, the formation of a 5-7 pair was observed at the zigzag edge section, as shown in Fig. 4(b). The evaporation of one carbon atom was observed from the 5-7 pair on the zigzag edge at 99.7 ps, as shown in Fig. 4(c). Carbon atoms were sometimes found to evaporate in the form of a dimer, as shown in Fig. 4(d). Carbon atoms on the outermost row of the zigzag edge were evaporated one by one until the outermost row of the zigzag edge was almost fully evaporated, as shown in Fig. 4(e). After the evaporation of the outermost row, carbon atoms were also observed to evaporate one by one at 234.7 ps, 254.1 ps, and 269.1 ps, respectively, and two dimers were evaporated simultaneously at 284.6 ps, as shown in Fig. 4(h). Finally, two outermost carbon rows on the zigzag edge almost disappeared from the junction by the sequential evaporation of carbon atoms, as shown in Fig. 4(i). On the other hand, evaporation of carbon atoms from the armchair edges was not observed during the simulation time. On the armchair edge, some carbon atoms were found to leave the pentagon rings, as indicated by "A" and "B" in Fig. 4(i). These moving atoms were not evaporated but diffused to fill the vacancies near the zigzag edge that were generated by the evaporation of carbon atoms. The TBMD simulation results for the GNR consisting of armchair-zigzag-armchair junction demonstrate that the fabrication of armchair GNR is attainable by vaporizing zigzag edges from GNRs of harsh edges. On the other hand, in the high-temperature TBMD simulation for armchair GNR, the formation of zigzag edges is frequently observed even though those are easily evaporated. These results provide useful insights into the way for temperature-controlled edge structures which can be applied to nanoelectronic device fabrication

IV. SUMMARY

We have performed TBMD simulations and *ab initio* calculations to study the reconstruction and evaporation of carbon atoms at the edges of GNRs. We observed that the zigzag edge is reconstructed very quickly into a zigzag 5-7 pair edge, which is energetically favorable. On the zigzag and armchair edges, the evaporation of carbon atoms is preceded by the formation of heptagon rings that work as a gateway for carbon atoms to escape. In the TBMD simulation of an armchair GNR, the formation of the zigzag edge at very high temperature accelerates the evaporation of carbon atoms, and finally, linear carbon chains are formed between the patches of the zigzag edge. In the TBMD simulation of a GNR containing armchair-zigzag-armchair junctions, the carbon atoms were found to evaporate in a row-by-row fashion from the outermost zigzag edge region, while the structure at the armchair edge region remained almost intact.

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