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Graphitic ribbons without hydrogen-termination: Electronic structures and stabilities

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The graphitic ribbons with H termination have been the subject of recent studies, but we investigated the ribbons without H termination using tight-binding and first-principles calculations. The ribbons with armchair edge were found to have phonon frequencies near 2000 cm^{-1} which has been solely ascribed to the one-dimensional carbon allotrope, carbyne. Comparative studies of the formation energies suggest that ribbons will grow more easily in the direction perpendicular to the zigzag edge, consistent with a recent experiment.

The potential of carbon-related materials has long been attracting much attention, because of their flexibility to make both the sp^2 and sp^3 bond networks. After the discovery of low-dimensional materials such as fullerenes and carbon nanotubes, considerable interest has been focused on the exploratory research on the sp^2 network systems. Graphitic ribbon is one of the most simple and fundamental fragments of the sp^2 network. Two types of graphitic ribbons are shown in Fig. 1 schematically, i.e., (a) armchair ribbon and (b) zigzag ribbon with hydrogen (H) termination. Here, the ribbon width parameter $N_a(N_z)$ is defined as the number of dimer lines (number of zigzag lines). According to the tight-binding calculations,[1–4] H-terminated armchair ribbons [Fig. 1(a)] are metallic for $N_a=5,8,11,...,$ and insulating otherwise,[3] while H-terminated zigzag ribbons [Fig. 1(b)] are always metallic independently of the width parameter N_z. This property reminds us of the single-wall carbon nanotubes: Zigzag nanotubes are either metallic or semiconducting depending on their diameter,[5–7] and armchair nanotubes are always metallic independently of its diameter.

Unique to the graphitic ribbons, an almost flat band appears at the Fermi level. This flat band state, called the ''edge state'' by Fujita and co-workers,[1,2] is localized at the ribbon edge and appears independently of the ribbon width. The flat band stems neither from bulk graphite nor from the dangling bonds, but stems from the topology of the π electron networks with a zigzag edge. These tight-binding results[1,2] were supported by first-principles calculations.[8,9] Furthermore, the edge states have been found to be dependent on the stacking of ribbons.[8] The edge state is flat for the *AB* stacking but is not flat for the *AA* stacking.

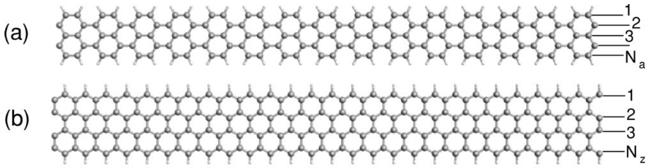

FIG. 1. The schematic view of the armchair ribbon (a) and zigzag ribbon (b) with H termination. Large solid circles indicate carbon atoms and small ones indicate the hydrogen atoms. The width parameter N_a and N_z are defined in the text.

Wakabayashi *et al.*[4] have predicted theoretically that, owing to the edge state, the ribbon will have a paramagnetic susceptibility and the ribbon junction will show a negative magnetoresistance. Some kind of ribbons has already been synthesized experimentally.[10,11] The polyperinaphthalene (PPN), synthesized from the perylenetetracarboxylic dianhydride using heat treatment[10] or pulsed-laser deposition technique,[11] corresponds to an $N_a=5$ armchair ribbon with H termination. Thus we expect that, in the near future, the electronic states of hydrogen-terminated ribbons predicted theoretically will be observed in experiment.

Very recently, however, the ribbons free from H termination have attracted much attention. The dehydrogenated ribbons have been expected to work as a precursor of nanotube or other carbon allotropes. For example, Zhang and Crespi[12] have proposed a mechanism for the nucleation of the nanotube on the basis of double-layered graphitic ribbons. Still, the thermal stability and reactivity of the individual H-free ribbons remain to be investigated. Also, the existence of the dehydrogenated ribbons has not been verified experimentally. Nevertheless we consider that dehydrogenation will not be very difficult when looking at the reasonable stability found from the molecular-dynamics simulations (see below). We would like to emphasize that appearance of the electronic properties found for the H-terminated ribbons is also nontrivial because of existence of the dangling bonds that would induce significant edge reconstruction. It is thus important to do theoretical study and predict properties of the ribbons without H termination.

The aim of this paper is to clarify the electronic, vibrational, and structural properties as well as the stabilities of the graphitic ribbons without H termination using the first-principles density-functional calculations and the semiempirical tight-binding molecular-dynamics simulations. We found considerable stability of H-free ribbons even under high-temperature above 2000 K. Strong edge reconstruction of H-free armchair ribbons forming triple bonds was found. This reconstruction caused localized modes of phonon with frequencies around 2000 cm^{-1} similar to those of carbyne: the one-dimensional $-\!(\mathrm{C}\equiv\mathrm{C}-\!)_n$ configuration. The edge reconstruction were also responsible for the wider band gap of the armchair ribbons without H termination than that with H termination. Meanwhile, the electronic structures of H-free zigzag ribbons were found to have both the edge state and the dangling bond state. The edge state here was completely empty contrary to the case of H-terminated ribbons, indicating that the electron doping is necessary for the paramagnetic susceptibility to appear. The bands that crossed the Fermi level were consisting of dangling bonds, which explains why the Peierls instability does not exist despite the one-dimensional structures. We expect that the present findings will be useful for future experimental and theoretical work for graphitic ribbons. In the remainder of this text, we will present details of our computed results and discuss formation of ribbons.

In order to understand the stability of the ribbon structure without H termination, we first performed the tight-binding molecular-dynamics simulations[13] under the constant temperature using Nosé-Hoover thermostat.[14] The H-free $N_a=5$ armchair ribbon and $N_z=4$ zigzag ribbon with length of about 35 Å were chosen for the simulations. When the temperature was less than 2000 K, both the armchair and the zigzag ribbons kept their structure for more than 25 psec. This indicates that the ribbons are sufficiently stable at fairly high temperatures and that H-free ribbons can be generated by heating up hydrogenated ribbons such as PPN.

At higher temperatures some hexagons at the edge became pentagon or heptagon, and hexagonal bonding network were broken at both ends of the ribbon, resulting in a chainlike tail consisting of a few atoms. The temperature at which such change occurs was dependent on the type of the ribbon: 2500 K for the armchair ribbon and 3000 K for the zigzag ribbon. The H-free armchair ribbon was destroyed at 3000 K while the zigzag ribbon kept their structure until 3500 K. Thus the stability at the higher temperatures is quite dependent on the type of ribbons. After the initial structure was destroyed, both ribbons formed one-dimensional chainlike structure, implying the stability of carbyne structure at this temperature.

Next, to investigate the electronic structure and the optimized atomic geometry, we did first-principles calculations based on the density-functional theory within the local-density approximation.[15,16] For the exchange-correlation potential, we used the Ceperley-Alder functional[17] in the parametrization form given by Perdew and Zunger.[18] The plane-wave cutoff energy of 55 Ry and the norm-conserving pseudopotential[19] were used. The calculations were done for infinitely long single-layer ribbons with the width $N_a=5-14$ for the armchair ribbons and $N_z=3-8$ for the zigzag ribbons. Four k points along the ribbon axis in the first Brillouin zone were used for the momentum space integration. To prevent artificial inter-ribbon interactions, individual ribbons were separated by a sufficiently large vacuum region; edge-edge distance and layer-layer distance were taken to be more than 8.0 and 6.3 Å, respectively. The atomic geometry was optimized using Hellmann-Feynman force, and the optimal lattice constant along the ribbon axis was determined by comparing the total energies. The force acting on the individual atom was reduced to less than 10^{-3} Ry/a.u. after the optimization, and corresponding error in the total energy was estimated to be less than 10^{-2} eV in all calculations.

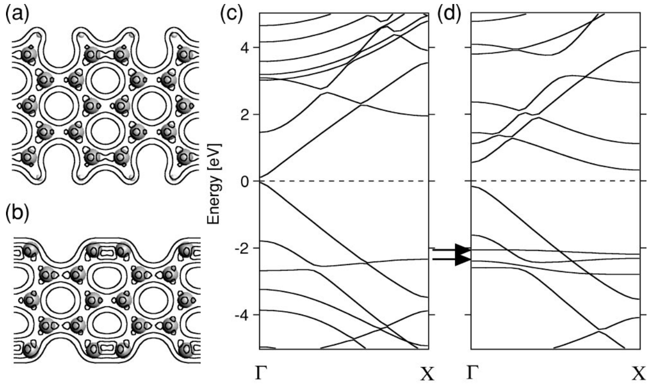

FIG. 2. The total valence charge density of the $N_a=5$ armchair ribbon (a) with H termination and (b) without H termination. The contour spacing is 0.1 electrons/a.u.^{3} and large (small) solid circles represent the position of carbon (hydrogen) atoms. The band dispersion of the same ribbon (c) with H termination and (d) without H termination. The arrows indicate the bands appearing due to the hydrogen extraction.

H extraction from the armchair ribbons led to formation of the stronger bonding as can be seen by the change in the charge density accumulated between dimer atoms at the edge in Figs. 2(a) and 2(b). Strong edge reconstruction occurred and the bond length between dimer atoms reduced from 1.38 to 1.23 Å, which is close to the triple bond of acetylene (1.20 Å). Looking at the similarities in the bondlength and the charge density, the bond may be identified as a triple bond. We found that this triple bond was formed for all the armchair ribbons investigated $(5\leqslant N_a\leqslant 14)$. The triple bond formation has also been predicted for a graphite flake at the armchair type edge,[20] but corresponding electronic structure has not been discussed. We next show the band structures of the present ribbons.

The band dispersion of the $N_a=5$ armchair ribbon with and without H termination are shown in Figs. 2(c) and 2(d), respectively. For all the ribbons with N_a between 5 and 14, the band gap became wider upon the H extraction and then all the H-free armchair ribbons became insulating. It is an interesting property of the armchair ribbons because many materials usually decrease the band gap when termination of the dangling bonds are removed, e.g., solid surfaces. Of course a graphene sheet is semimetallic, so the ribbon's band gap will disappear for very large N_a. The arrows in Fig. 2(d) indicate the bands which appear owing to the H extraction. The wave-function character of these states was found similar to the dangling bonds. Though they are a few eV below the Fermi level, we expect that these occupied states would play an important role in chemical reaction with approaching hydrocarbons making the ribbons highly reactive.

To identify the triple bond at the edge of the armchair

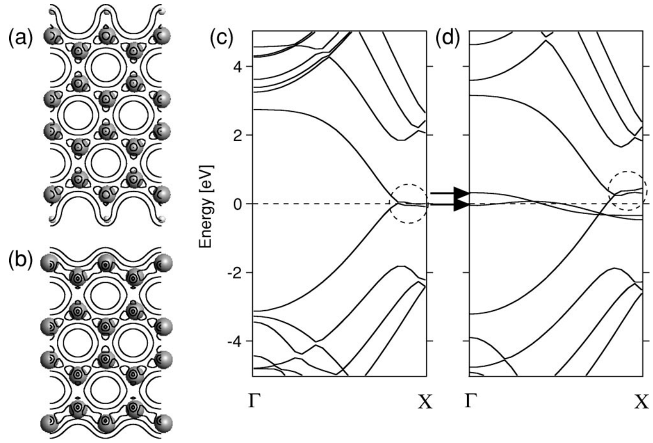

FIG. 3. The total valence charge density of the $N_z=4$ armchair ribbon (a) with H termination and (b) without H termination. The contour spacing is the same in Fig. 2. The band dispersion of the same ribbon (c) with H termination and (d) without H termination. The arrows indicate the bands appearing due to the hydrogen extraction. The circle with dotted line indicate the edge state.

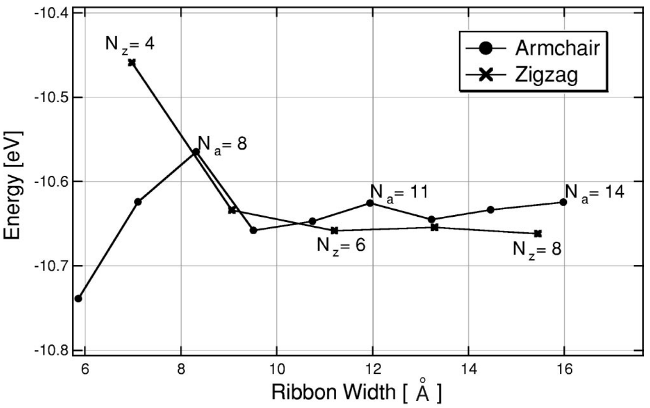

FIG. 4. The formation energy for the armchair ribbons (solid circles) and zigzag ribbons (crosses) as a function of ribbon width. N_a (N_z) are ribbon width parameters for armchair ribbons (zigzag ribbons) as shown in Fig. 1. See text for the definitions of the formation energy.

ribbons experimentally, the vibrational frequencies can be one of the key information. We then calculated the vibrational frequencies at the Γ point for an armchair ribbon within the harmonic approximation by diagonalizing the dynamical matrices obtained from computed Hellmann-Feynman forces. The highest two vibrational frequencies corresponded to the C≡C stretching mode on both edges of the ribbon with antiphase (2000 cm^{-1}) and with in-phase (1976 cm^{-1}), respectively. This indicates an appearance of the specific Raman shift at these frequencies. These frequencies are quite higher than the typical frequency for graphite, which is located at about 1590 cm^{-1} (G band), indicating that the formation of the armchair ribbons would be detected experimentally by observing Raman spectra. The reason why such high frequencies appeared is due to the formation of the strong triple bond.

At this point, it is interesting to point out that Raman peak at around 2000 cm^{-1} is typical of carbyne.[21] This Raman peak has been often interpreted by the stretching mode of a linear carbon chain with alternating carbon-carbon triple and single bonds (polyyne structure). However, the structure of carbyne has not been confirmed due to the lack of large enough carbyne single crystal. Here, we found that the bond alternation $\leftarrow\!\mathrm{C}\equiv\mathrm{C}\!\rightarrow$ occurs not only to a linear chain structure but also to the H-free armchair ribbons, which also support the specific Raman shift at around 2000 cm^{-1}. Therefore, the H-free armchair ribbons can be a new model for carbyne.

For the zigzag ribbons, there was no significant structural change at the edge of the ribbon due to the H extraction, where the bond length between adjacent edge atoms reduced slightly from 1.40 to 1.38 Å, and corresponding change in the charge density was tiny [see Figs. 3(a) and 3(b)]. The band structure of $N_z=4$ zigzag ribbon with and without H termination are shown in Figs. 3(c) and 3(d), respectively. The band structures near the Fermi level are very similar to each other except for the extra two bands existing for the H-free ribbon. Note that the edge state, indicated by a circle in Fig. 3(c), survives after the H extraction as shown in Fig. 3(d) and coexists with the states originated from the dangling bond [see the bands indicated by the arrow in Fig. 3(d)]. The edge state is located about 0.2 eV above the Fermi level, indicating that one needs to dope electrons in order for the peculiar properties related to the edge state[3,4] to appear. The coexistence of the edge state and dangling bond state is explained by little interaction between them, since their orbitals are geometrically orthogonal to each other. Even for other zigzag ribbons ($3\leqslant N_a\leqslant 8$), essentially the same properties were seen and the two bands related to the edge state became flatter for wide ribbons around the X point, as had been also mentioned for H-terminated zigzag ribbons.[3] It is interesting to point out that the zigzag ribbons were not subject to the Peierls instability in spite of their one-dimensional metallic nature. In order for the Peierls distortion to occur, sufficiently large energy should be gained by opening the energy gap. The states crossing the Fermi level correspond to the dangling bond states and the edge state. Considering that the Peierls transition should be accompanied by lattice distortion in the direction along the ribbon's axis,[22] both the dangling bond states and the edge state extending normal to the ribbon's axis would not be able to open an energy gap by such distortion. Therefore, the energy gain of the gap opening would not be able to compensate the loss in energy due to the lattice distortion. Note that the Peierls instability of H-terminated zigzag ribbons has been also denied by theoretical investigation.[3]

The formation energies for the armchair ribbon and the zigzag ribbon have much information about the growth and the stability of ribbons. Thus, we estimated the corresponding quantities for zigzag ribbons and armchair ribbons. Figure 4 shows the formation energy, which is defined as the energy to make width N ribbon from $N-1$ ribbon by adding C_2 dimer: $E(N)-[E(N-1)+E(C_2)]$, where N represents N_a or N_z. The solid circles (crosses) indicate the formation energy for the armchair (zigzag) ribbons. The energy curve of armchair ribbons indicates the triple periodicity with respect to N_a while that of the zigzag ribbons exponentially decreases. These zigzag shapes of energy curve coincide with the triple periodicity of band gap predicted for H-terminated armchair ribbons.[3] Comparing the formation energies, we found that the zigzag ribbons are slightly easier to widen than armchair ribbons when the width is large enough, while the edge energy of armchair ribbons is lower than that of zigzag ribbons.[20] In other words, the zigzag edge is less stable and more reactive compared to the armchair edge. If the relative reactivity of the zigzag edge generally holds for other sp^2 network systems, we will be able to do some predictions: single-crystal graphite plates would grow anisotropically perpendicular to the zigzag edge, which is consistent with the recent experiment by Badzian.[23] Similarly, we can expect that the edge of the zigzag nanotube will be more reactive compared to that of the armchair nanotube and the difference in the reactivity will play an important role in the relative speed of growth.[24] We expect that the present theoretical results will be useful for further experimental works.

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