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Absence of edge states near the 120° corners of zigzag graphene nanoribbonsNguyen Thanh Cuong,^{1,3} Minoru Otani,^{1,3} and Susumu Okada^{2,3}¹*Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan*²*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan*³*Japan Science and Technology Agency, CREST, 7 Gobancho, Chiyoda, Tokyo 102-0076, Japan*

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Based on first-principles total-energy calculations, we studied the energetics and electronic structure of zigzag graphene nanoribbons with nanometer-scale corners. We found that the formation energy of a short zigzag edge with a 120° corner is substantially smaller than that of a straight zigzag edge with an infinite length. We also found that zigzag graphene ribbons with 120° corners are semiconductors for which the band-gap decreases with increasing length between adjacent corners. The edge state is absent for zigzag graphene ribbons with short corner-corner distances, while the edge state emerges for zigzag ribbons that have a corner-corner distance greater than 1.5 nm. The remarkable stability of the 120° corner of the short zigzag edges is in good agreement with the experimental observation of such corners of graphene edges.

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I. INTRODUCTION

Graphene has stimulated intense interest because of its unique structural and electronic properties: a one-atom-thick sheet of hexagonally bonded sp^2 C provides us with the ultimate two-dimensional electron system comprising π electrons and results in two pairs of linear dispersion bands leading to a remarkable carrier mobility of $200\,000\text{ cm}^2/\text{V s}$.¹⁻³ By virtue of these properties, graphene now holds a premier position not only in low-dimensional sciences but also in nanoelectronic engineering.⁴⁻⁷ Imperfections, such as defects, edges, and grain boundaries, decisively affect the electronic properties of graphene. Due to the existence of σ and π electrons, the imperfections result in typical and unusual electron states associated with the imperfections: a point defect leads to dangling-bond states of sigma electrons and localized states associated with the π electrons.⁸ A hydrogenated line imperfection with a zigzag shape (that is, a hydrogen-terminated zigzag edge) leads to peculiar imperfection-induced states around the edge. The electron state is completely localized on atoms with twofold coordination at the zone boundary, while it loses its localized nature as the one-dimensional wave number decreases.⁹⁻¹² Furthermore, it has been demonstrated that the spin polarization occurs at the edge atomic sites and that the polarized spins are ferromagnetically aligned along the edge.^{9,12,13} In sharp contrast, a hydrogenated edge with an armchair shape does not induce such a peculiar edge-localized state. These facts indicate that the control of imperfections in graphene is important for scientific and technological usages of graphene.

Graphene of large area and excellent quality has recently been fabricated by chemical vapor deposition on metal surfaces.¹⁴ However, it has been demonstrated that graphene intrinsically possesses edges with substantial roughness: graphene frequently exhibits zigzag edges with corners with an angle of 120° in transmission electron microscopy images.^{15,16} Furthermore, scanning tunneling microscopy (STM) experiments show that the corners occasionally consist of zigzag edges that are known to be energetically unstable edge conformations.¹⁷ Indeed, early theoretical calculations showed that the edge formation energy of a zigzag edge is larger

by 0.2 eV per edge than that of an armchair edge¹⁸ due to the emergence of the edge state. Furthermore, the higher energy of the zigzag edge induces structural reconstruction to reduce the energy associated with the electron system, albeit with an increase in the lattice energy.^{19,20} For this discrepancy, recently, a theoretical work based on the tight-binding approximation has suggested a clue to explain the emergence of the zigzag edges with corner edges of 120°: the edge states are absent near the 120° corner even though the two edges have a zigzag arrangement, while they emerge with sufficient distance from the corner.²¹ This result suggests that the zigzag edges of graphene possessing 120° corners with a moderately straight region are thermodynamically stable. Besides the 120° corner, a 150° corner has been also observed on graphene edges in experiments.^{22,23} The stability of the 150° corner is ascribed to the small formation energy of the armchair edges of the corner.¹⁸

On the other hand, armchair graphene ribbons with corners (chevron shape) have been synthesized by the bottom-up method.²⁴ Furthermore, a previous theoretical study has elucidated that such chevron-shaped graphene nanoribbons possess the peculiar electronic structure depending on their geometry.²⁵ However, detailed energetics and thermodynamic stability of graphene nanoribbons with corners are still unclear. Therefore, in this work, we aim to investigate the energetics and electronic structure of graphene edges with 120° and 150° corners using first-principles total-energy calculations in the framework of the density-functional theory. Our calculations clarify that the formation energies of a zigzag edge of graphene ribbon with a 120° corner are smaller than those of a straight zigzag graphene nanoribbon, indicating the stability of graphene edges with nanometer-scale 120° corners. Moreover, around the apexes of the corners, we found that the edge state is absent, while it appears and increases its localized nature with increasing distance from the apex.

II. COMPUTATIONAL DETAILS

All calculations have been performed based on the density-functional theory^{26,27} as implemented in STATE code.²⁸ We

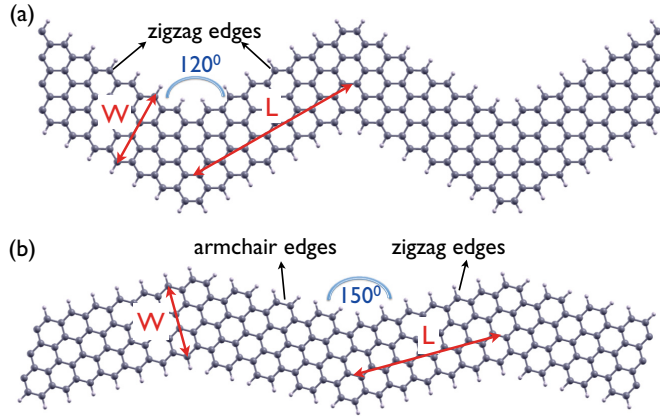


FIG. 1. (Color online) Optimized structures of a graphene ribbon with (a) 120° edge corners and (b) 150° edge corners. The white and black spheres denote the hydrogen and carbon atoms, respectively.

use the local-density approximation to express the exchange-correlation energy of interacting electrons.^{29,30} Note that the spin degree of freedom does not affect the energetics of the geometries of graphene nanoribbons. Ultrasoft pseudopotentials are adopted to describe the electron-ion interaction.³¹ The valence wave functions and charge density are expanded in terms of a plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively. The Brillouin-zone integration is carried out under the uniform k -point mesh technique. The optimal sizes of the k -point meshes for different systems are individually converged, such that the changes in the total energy of the system are reduced by at least 5×10^{-4} Ry. Geometry optimization has been performed for all atoms, until the remaining force acting on the atoms is less than 0.005 Ry/Å. The general direct inversion in the iterative subspace minimization scheme is used for the geometry optimization.

Structural models of graphene edges with corners are shown in Fig. 1. Here we consider graphene nanoribbons with 120° corners [Fig. 1(a)] and with 150° corners [Fig. 1(b)]. In the case of an edge with a 120° corner, the two oblique edges have a zigzag atomic arrangement in which all edge atoms are terminated by hydrogen atoms. On the other hand, in the case of a 150° corner, the oblique edges can have armchair and zigzag atomic arrangements with hydrogen atoms, as shown in Fig. 1(b). Along the x direction, a periodic boundary condition is imposed, while, along the y direction, the graphene ribbon is separated by a 10 -Å vacuum region from its adjacent periodic images. To determine the effects of the width (W) and edge length (L) of the graphene ribbon with corners, we investigate the energetics and electronic structures of various graphene ribbons with corners for widths of 3 – 20 Å and lengths of 5 – 40 Å. To avoid the periodic image errors arising from the slab model, we adopt the effective-screening medium method.^{32,33}

III. RESULTS AND DISCUSSION

First, we study the effect of the width of the ribbon by checking the edge formation energy per edge atom as a function of the ribbon width W . The formation energy is calculated by the equation $E_{120}^f = (E_{\text{ribbon}}^{\text{tot}} - E_{\text{graphene}}^{\text{tot}} - n_{\text{H}}\mu_{\text{H}}) / N_{\text{edge}}$,

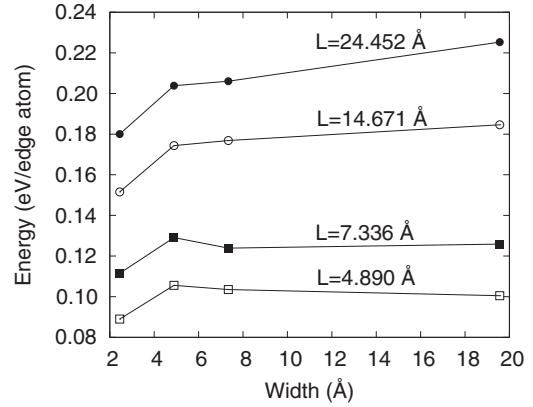


FIG. 2. Formation energy per zigzag edge atom of a graphene ribbon with 120° corners as a function of width W at various edge lengths.

where $E_{\text{ribbon}}^{\text{tot}}$, $E_{\text{graphene}}^{\text{tot}}$, n_{H} , μ_{H} , and N_{edge} are the total energy of the graphene ribbon with 120° corners, the total energy of the bulk graphene, the number of H atoms, the chemical potential of the H atom, and the number of edge carbon atoms, respectively. The chemical potential of the H atom is estimated from the energy difference between the total energies of benzene and graphene. Figure 2 shows the edge formation energy of graphene with 120° corners for various lengths of the oblique edges. For all lengths, the formation energy of the zigzag edge soon converges with increases in the width. For the ribbon that has a width that is wider than 7 Å, the formation energy of the zigzag edge for each length is saturated within a dispersion of about 0.02 eV. Therefore, the ribbons that are 7 -Å wide or wider appropriately simulate the edges with corners in bulk graphene. According to this result, we fixed the width of the ribbon at 7.336 Å for investigation of the length dependence of the edge formation energy and electronic structure of graphene edges with corners.

Figure 3 shows the formation energy of a zigzag edge of graphene nanoribbon with 120° and 150° corners as a function of the length of the oblique edges (L). For the 150° corner, the formation energy is calculated by $E_{150}^f = (E_{\text{ribbon}}^{\text{tot}} - E_{\text{graphene}}^{\text{tot}} - n_{\text{H}}\mu_{\text{H}} - E_a^f N_{a\text{-edge}}) / N_{z\text{-edge}}$, where $E_{\text{ribbon}}^{\text{tot}}$,

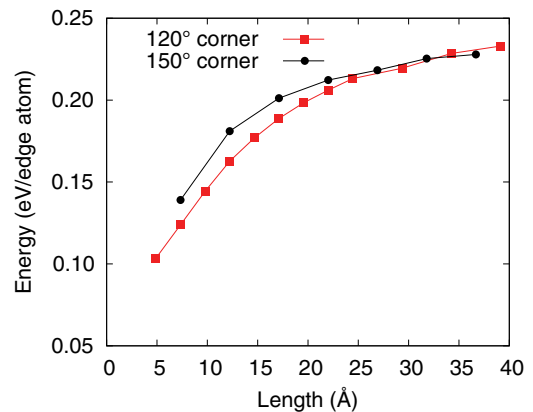


FIG. 3. (Color online) Formation energy per zigzag edge atom of graphene ribbons with 120° corners and 150° corners as a function of edge length L .

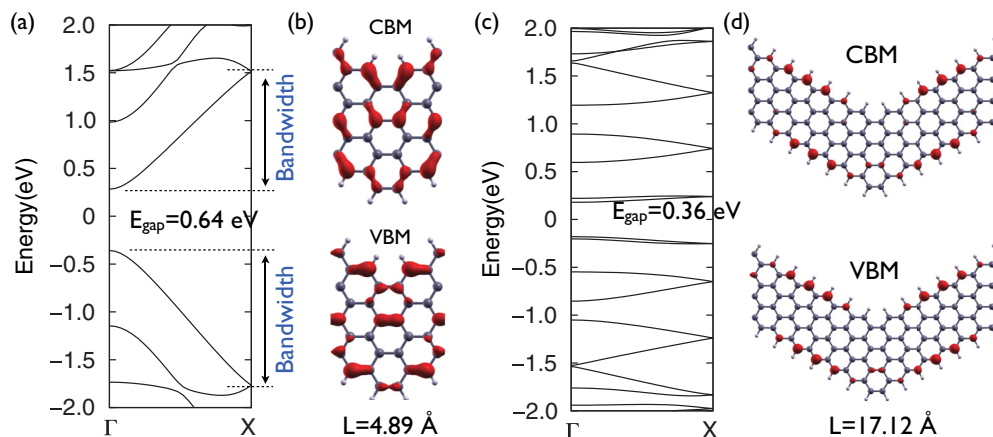


FIG. 4. (Color online) (a, c) Electronic energy bands and (b, d) wave-function distribution (red color region) of valence-band maximum (VBM) and conduction-band minimum (CBM) states at the Γ point of a graphene ribbon with 120° corners at $L = 4.89 \text{ \AA}$, $W = 7.336 \text{ \AA}$ and at $L = 17.12 \text{ \AA}$, $W = 7.336 \text{ \AA}$. Energy is measured from the midgap point of the system. The white and black spheres denote hydrogen and carbon atoms, respectively.

$E_{\text{graphene}}^{\text{tot}}$, n_{H} , μ_{H} , E_{a}^{f} , $N_{\text{a-edge}}$, and $N_{\text{z-edge}}$ are the total energy of the graphene ribbon with 150° corner, the total energy of the bulk graphene, the number of H atoms, the chemical potential of the H atom, the formation energy of the armchair edge, the number of atoms situated at an armchair edge, and the number of atoms situated at a zigzag edge, respectively. The formation energy of an armchair edge (E_{a}^{f}) is 0.1 eV, as estimated for a graphene armchair ribbon.¹⁸ By using the above equation, we can extract the formation energy of a zigzag edge in a graphene ribbon with 150° corners. We find that the formation energy monotonically increases with increasing oblique edge length (L). For the long edges, we find that the formation energy is about 0.2 eV per zigzag edge atom irrespective of the corner angle. In sharp contrast, for the short edge region, we find that the formation energy of the 120° corner is slightly smaller than that of the 150° corner. Indeed, the edge formation energies of both of the corners are smaller than those of the straight zigzag edge¹⁸ for the short oblique-edge region. This result indicates that the zigzag edges with corners are energetically stable, which explains why they are observed in STM experiments under usual conditions. Furthermore, corners are essential for and intrinsic

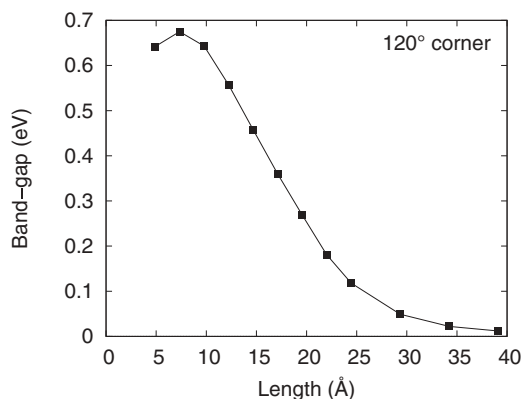


FIG. 5. Energy gap of a graphene ribbon with 120° corners as a function of edge length L .

to the edges of graphene. Note that the energetic stability of the edge shape in a real situation strongly depends on the additional external conditions, such as metal substrate and impurity atoms or molecules. Therefore, further investigations are expected. As described below, the length dependence of the formation energy of graphene with corners is ascribed to the electronic structure of the zigzag edges. It is well known that the zigzag edge possesses an edge-localized state at the Fermi energy leading to the large formation energy.¹⁸

Figure 4 shows the electronic structures of graphene ribbons with 120° corners with lengths of $L = 4.89$ and 17.12 \AA , in the form of the squared magnitudes of the wave functions associated with the valence-band maximum (VBM) and those associated with the conduction-band minimum (CBM). In both cases, the ribbons are semiconductors with a finite direct energy gap at the Γ point. The calculated gap energies are 0.64 and 0.36 eV for $L = 4.89$ and 17.12 \AA , respectively. The energy gap strongly depends on the length of the oblique edges. The gap monotonically decreases and approaches zero

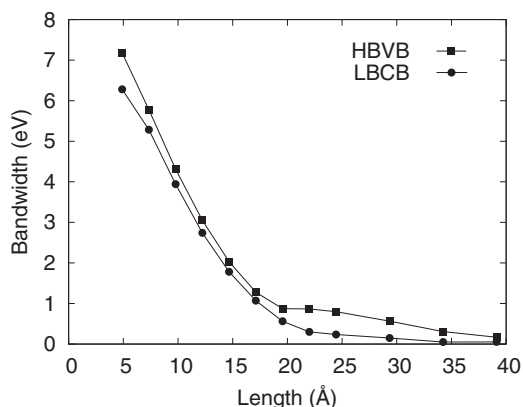


FIG. 6. Bandwidths of the highest branch of the valence band (HBVB) and the lowest branch of the conduction band (LBCB) of a graphene ribbon with 120° corners as a function of edge length L . The bandwidth is normalized by the length of the Brillouin zone due to the difference in the lattice parameter.

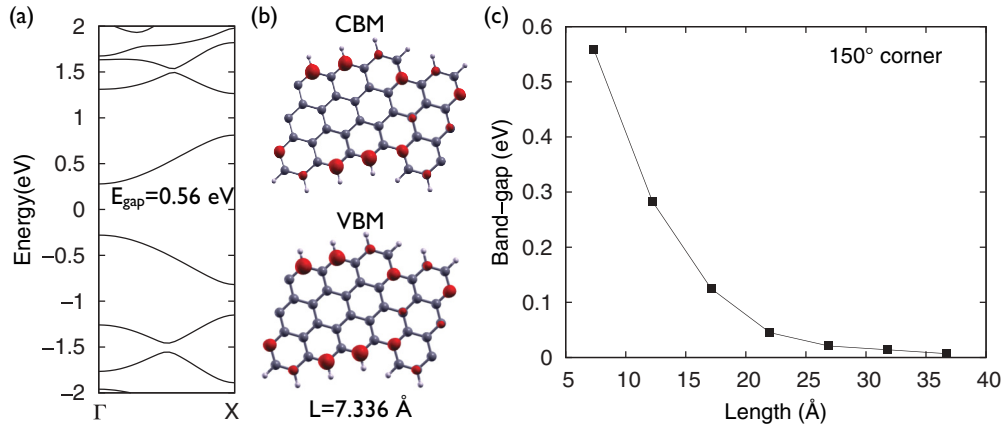


FIG. 7. (Color online) (a) Electronic energy band and (b) wave-function distribution (red color region) of the valence-band maximum (VBM) and conduction-band minimum (CBM) states at the Γ point of a graphene ribbon with 150° corners at $L = 7.336 \text{ \AA}$, $W = 7.336 \text{ \AA}$. Energy is measured from the midgap point of the system. The white and black spheres denote hydrogen and carbon atoms, respectively. (c) Energy gap of a graphene ribbon with 150° corners as a function of edge length L .

as the length of the zigzag edge increases, as shown in Fig. 5. These results agree well with experiments and with theoretical results in which an infinitely long zigzag graphene ribbon exhibits metallic electronic properties.^{34,35}

By analyzing the distributions of the wave functions of VBM and CBM for graphene ribbons with 120° corners, we find an interesting edge length dependence of its localization nature: for the short length region $L = 4.89 \text{ \AA}$, we find that the wave functions of the VBM and CBM states exhibit the usual π character and are extended through all carbon atoms as shown in Fig. 4(b). In sharp contrast, with increasing edge length, the wave functions associated with the VBM and CBM states exhibit a localized nature and are mainly distributed at edge atomic sites [Fig. 4(d)], as in the case of the conventional edge state in zigzag graphene ribbons.^{9–11} Indeed, VBM and CBM states around the Γ point exhibit the flat-band nature for the ribbon with long edge lengths [see Fig. 4(c)], as does the edge state of the graphene ribbon with straight edges. Furthermore, we find that the localized edge state does not appear near the corner, as shown in Fig. 4(d). It has been demonstrated that the interference of the edge states between two zigzag edges near the corner suppresses the distribution at the apex of the corner. The suppression of the edge state decreases the formation energy of zigzag edges with short flat edges, as shown in Fig. 3.

The appearance of the localized edge state on graphene edges is strongly correlated with the flatness of the electron states just below and above the fundamental gap. We calculate the bandwidth of the highest branch of the valence band (HBVB) and the lowest branch of the conduction band (LBCB) of a graphene ribbon with 120° corners. Figure 6 shows the bandwidth of the HBVB and the LBCB as a function of the corner-corner separation. It should be noted that the bandwidth is normalized by the length of the Brillouin zone due to the difference in the lattice parameter. We find that the bandwidth dramatically decreases with increasing corner-corner length and converges at around a length of 15 \AA . Indeed, the wave functions of the VBM and CBM analyses show that the localized edge state only appears when the

corner-corner length L is larger than 15 \AA (see Figs. S1–S6 in the supplemental material for more detail³⁶). Thus, the edge-localized states of graphene ribbon with 120° corners emerge in the flat region of the zigzag when the length is larger than 15 \AA .

Finally, it is worth investigating the detailed electronic structure of graphene edges that have a different corner angle. Figure 7(a) shows the electronic structure of the graphene ribbon with 150° corners for a ribbon width and an edge length of 7.366 and 7.366 \AA , respectively. The ribbon with 150° corners is also a semiconductor with a direct band gap of 0.56 eV , similar to the graphene ribbon with 120° corners. Furthermore, the gap monotonically decreases with increasing edge length [Fig. 7(c)]. On the other hand, the wave functions associated with the VBM and CBM in graphene ribbons with 150° corners exhibit different characteristics than those obtained in graphene ribbons with 120° corners. As shown in Fig. 7(b), the wave functions of these states are clearly distributed along the edge atoms, which are situated at the zigzag edges for ribbons of any edge length (also see Figs. S7–S9³⁶). The emergence of the edge-localized state may explain the physical origin of the higher edge energy of the 150° corners with respect to the 120° corners for the short edge length region. This is because, as discussed above, the ribbons with short edge regions and 120° corners do not possess the edge-localized nonbonding states.

IV. CONCLUSION

We investigated the energetics and electronic structures of graphene edges with 120° corners using first-principles total-energy calculations in the framework of the density-functional theory. We found that the formation energy of a zigzag edge in a graphene ribbon with 120° corners is smaller than that of the straight zigzag edge for a short oblique-edge region. This result suggests that the zigzag edges of graphene possessing 120° corners with a moderately straight region are thermodynamically stable. On the other hand, it is necessary to investigate the effects of additional external

conditions, such as metal substrate and impurity atoms or molecules on the energetic stability of graphene edge shape for fully determining the epitaxial graphene on metal surfaces. In addition, we found that the graphene ribbons with 120° corners are semiconductors for which the band gap decreases with increasing corner-corner length of the zigzag edges. Moreover, around the corner of the zigzag graphene ribbon, the edge-localized states are absent for short corner-corner lengths, while the edge state emerges along the zigzag edges for lengths greater than 15 Å. This unusual length dependence

of the edge state is not found, however, in the case of the 150° corner of the graphene ribbon.

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