First-principles study of edge states of H-terminated graphitic ribbons

Yoshiyuki Miyamoto
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan

Kyoko Nakada* and Mitsutaka Fujita
Institute of Materials Science, University of Tsukuba, Tennodai, Tsukuba 305-8573, Japan
(Received 28 April 1998; revised manuscript received 19 August 1998)

The existence of the edge states of single-layered H-terminated graphitic ribbons predicted by Nakada *et al.* [Phys. Rev. B **54**, 17 954 (1996)] has been confirmed by first-principles calculations within the framework of the local-density approximation and the pseudopotentials. The edge states in cases of stacked ribbons have also been examined, and it has been found that the existence of the edge states is dependent on the stacking manner. This phenomenon can be understood from the electronic structures of *AA*- and *AB*-stacked bulk graphite. [S0163-1829(99)14615-0]

Breakage of translational symmetry of solid states in a certain direction generates localized states. For instance, a cleaved bulk crystal generates surface states that have two-dimensional extensions parallel to the cleaved surface. These surface states originate from the surface dangling bonds located at the Fermi level (E_F). When all surface dangling bonds are terminated, for instance, by hydrogen atoms (H atoms), the surface states move away from E_F and become resonant states of bulk bands. Similarly, one can imagine that localized states are generated when a graphene sheet is cut into graphitic ribbons. Upon the cutting, a graphitic ribbon lacks the original two-dimensional periodic boundaries and the newly generated C-dangling bonds at the ribbon's edge cause localized states at E_F. When all dangling bonds are terminated by H atoms, see Fig. 1(a), their levels should move away from E_F. [Hereafter, the ribbons like Fig. 1(a) are called ''zigzag ribbons.'']

However, it was predicted that the H-terminated graphitic ribbons have peculiar localized states at the ribbons' edges with corresponding energy levels at E_F.[1] These localized states originate from π orbitals of H-terminated C atoms extending normal to the graphitic sheet. These localized states were called edge states. The edge states appear when the wave vectors k along the ribbons are in the region of $2\pi/3<k\leqslant\pi$ in a unit of inverse of a period (2.46 Å). This fact can be analytically derived when only the nearest-neighbor hoppings of π electrons are taken into account,[1] which results in perfect canceling of off-site hoppings of the π orbitals at the H-terminated C sites with k as $2\pi/3<k\leqslant\pi$. Since the localized feature of the edge states is expected to cause remarkable electron-electron correlation, some interesting properties of the zigzag ribbons are expected, e.g., spin polarization, realization of one-dimensional Mott-Hubbard-type insulators, and so on.

This prediction was based on a tight-binding scheme with only nearest-neighbor hoppings, so it should be checked whether the edge states are seen when hopping distance is increased. Indeed, we have an experience of disappearance of the edge state when we artificially introduce the hopping parameter for a long distance. Therefore, a question has arisen as to whether the edge states are obtained by fully self-consistent calculations that express off-site electron hoppings for a reasonable range. Furthermore, the considered structures of the ribbons were restricted in the case of a single layer. On the other hand, stacked layers of ribbons are thought to be more realistic in available samples. The existence of the edge states should therefore be examined for the stacked geometry in which electron hoppings between neighboring layers have to be taken into account.

In this paper, we performed the first-principles band-structure calculation for H-terminated zigzag ribbons within the framework of the local-density approximation (LDA) by using pseudopotentials and the plane-wave basis sets. We have found that the predicted edge states in single-layered ribbons are well reproduced in the present first-principles calculations. Furthermore, we have examined the edge states when the zigzag ribbons are condensed in a manner of the *AA* stacking and the *AB* stacking of the bulk graphite. The edge states can exist only in the case of the *AB* stacking, in which half of the C atoms of one ribbon are located directly above the center of each hexagon on the neighboring ribbons. This fact can be understood from the energy band structure of the *AA*- and *AB*-stacked bulk graphite. In the rest of this paper, details of the computational conditions and the results are shown.

We have performed the band-structure calculations within the LDA in which the exchange correlation energy of many-body electrons are treated as a functional form[2] of the charge density, which was fitted to the numerical results of electron gas.[3] To express effects of $1s$ core electrons of C atoms on valence electrons, the norm conserving nonlocal pseudopotentials are generated by using a scheme of soft core radius.[4] Only the s components are used as the nonlocal part. While for the H atoms, the local pseudopotential formed as $1/r\Sigma_i^2 C_i erf(r/rc_i)$ is used with r being a distance from proton. The present parameters are 1.0519 and -0.0519 for C_1 and C_2, 0.207 02 bohr and 0.399 93 bohr for rc_1 and rc_2, respectively. A cutoff energy of 40 Ry is used for plane-wave expansion of valence wave functions. To mimic a situation of an isolated zigzag ribbon, we adopted three-dimensional repeating cells in which individual ribbons

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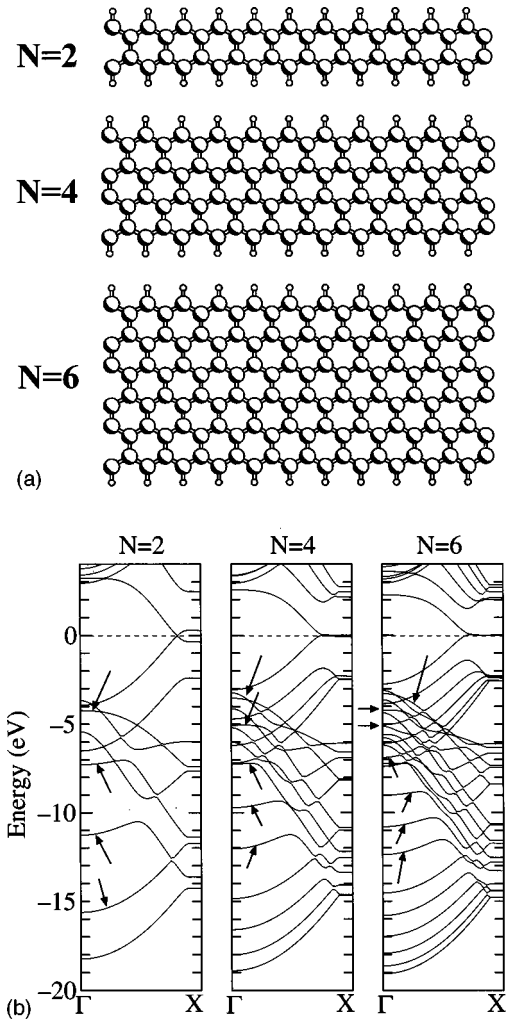

FIG. 1. (a) Atomic geometry of a zigzag ribbon ($N=2\sim6$) terminated by H atoms. Shaded circles denote carbon atoms while smaller circles denote hydrogen atoms. (b) Band structure of the corresponding geometry ($N=2\sim6$). The positions of E_F are set as 0 eV indicated by dotted lines. Arrows indicate the states having localized C–H σ characters.

are separated by a vacuum region. In the adopted vacuum region, the intervals among the ribbons are kept as 8.5 Å and 6 Å for edge-edge and layer-layer distances, respectively. These intervals have been found to be enough to prevent artificial interribbon interactions.[5] As for the k-point sampling for the momentum space integration, nine k points in the wedge of the first Brillouin zone (BZ) are used. According to the calculated Hellmann-Feynman forces, the atomic geometry is optimized to achieve the total-energy minimum within a restriction of the planar configuration of the ribbon.[6] However, the geometry optimization is found not to considerably change the atomic structure from the ideal one, i.e., a perfect honeycomb pattern with C–C length of 1.42 Å and H terminations with C–H length of 1.01 Å. Indeed the C–C bond lengths are shortened only by 0.02 Å at the H-terminated site. Therefore, a qualitative feature of electronic structure is less sensitive to the geometry optimization.

Figure 1(b) shows band structures of zigzag ribbons in Fig. 1(a). The width of each ribbon corresponds to $2\sim6$ arrays of zigzag C–C chains. We call this width $N=2\sim6$ according to Ref. 1. A remarkable feature in the band structure of a ribbon with $N=6$ is that two bands meet at the k vector beyond two thirds on the way from Γ to X in the first BZ, where $\Gamma=0$ and $X=\pi/a$ with $a=2.46$ Å (ribbon's period). Then these bands become nearly flat up to $k=X$, and the location of E_F corresponds to these flatbands. While in the thinner ribbons ($N=2\sim4$), flatbands are not seen. Those ribbons are too narrow to separate the edge states penetrating from both edges. The nearly flatbands seen in the ribbon with $N=6$ suggest that the electron transfer of longer ranges gives no remarkable effect for wider ribbons. These results are qualitatively the same as that obtained in the tight-binding calculations.[1]

Next, the wave function's character of the flatbands in the case of $N=6$ has been investigated. We have calculated the overlap between the atomic valence wave functions of each C site and the Bloch wave functions of the flatbands. The Bloch wave functions have their maximum amplitude at the π orbitals of H-terminated C sites, and the second maximum amplitude is located at second neighbor C sites. Again, these features agree well with the former tight-binding calculations.[1] From these wave function's characters, these flatbands shown in Fig. 1(b) with $N=6$ can be attributed to the edge states.

The existence of the edge states in single-layered graphitic ribbons has thus been confirmed by performing the first-principles calculations. One can consider that the edge states may have the Fermi instability since there should be a sharp peak of the density of states at E_F. However, a theoretical investigation based on the Su-Schrieffer-Heeger (SSH) model[7] denied this possibility. Since there are no serious discrepancies in the results for hydrocarbon systems between SSH model and the first-principles calculation, we expect that the Fermi instability will also be denied in LDA calculations.

In addition to the existence of the edge state, one may be interested in the influence of hydrogen 1s states on the electronic structure, which can be expected to cause hybridization with C–C σ orbital. We have found that there are several eigenstates having C–H σ characters. The states with considerable amplitudes at the C–H bonds are denoted by arrows in Fig. 1(b). On the other hand, the C–H σ^* (antibonding) states are found far above E_F, which are out of the scale in Fig. 1(b). These C–H σ^* states have no contribution for the conducting properties of the ribbons since the energy levels are away from E_F by more than 5 eV. They also have no influence on the edge state since the orbitals of C–H σ and σ^* extend parallel to the ribbon while those of the edge states (π orbitals) extend normal to the ribbon.

Our next interest is whether the edge states can be seen in stacked layers of the zigzag ribbons. From practical viewpoints, realization of a single layer of the zigzag ribbon is rather hard compared to that of a multilayered sample. We have performed band-structure calculations of the stacked ribbons by assuming the AA- and the AB-stacking geometries. In the AA stacking, all C atoms of one ribbon are located directly above all C atoms on the neighboring ribbons, while in the AB stacking, half of C atoms of one ribbon are located directly above the center of each hexagon of

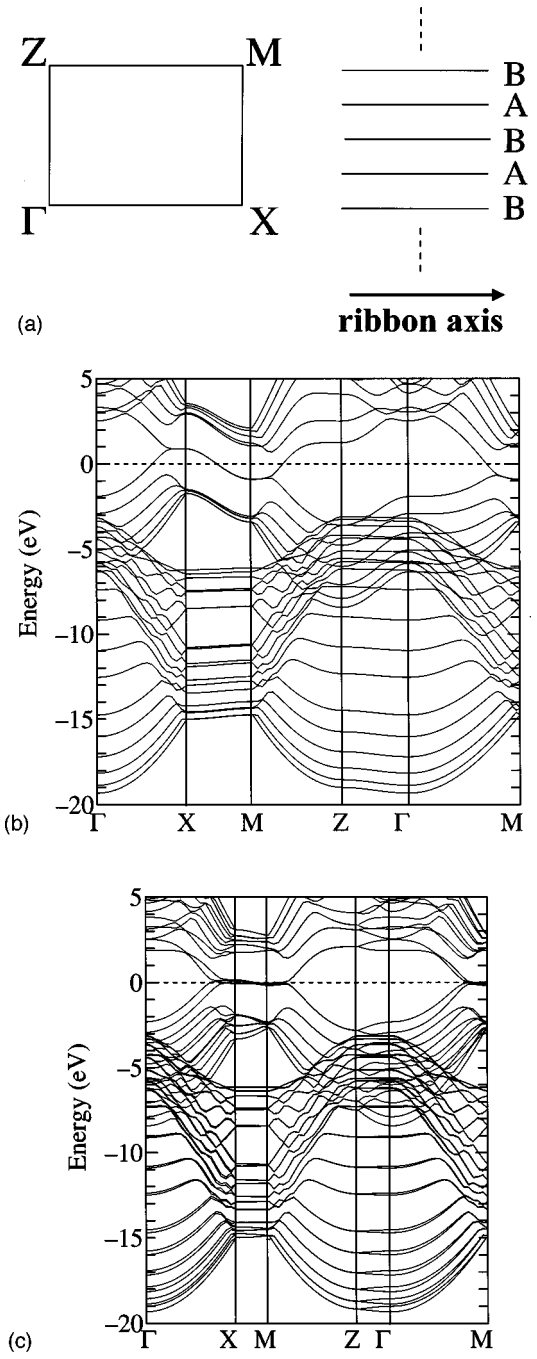

FIG. 2. (a) The first Brillouin zone of *AB*-stacked zigzag ribbons with $N=6$ and corresponding directions in real space. Γ-*X* and *Z*-*M* lines are along the ribbon's axis while Γ-*Z* and *X*-*M* lines are along the stacking direction. (b) Band structures of *AA*- and (c) *AB*-stacked ribbons with $N=6$. The positions E_F are set as 0 eV shown as dotted lines.

the neighboring ribbons. The interlayer distance is assumed to be 3.34 Å, which is the same as that of the graphite.

Here we must comment on the LDA approach in describing the interlayer interaction of graphite. It is widely thought that the graphite interlayer interaction is dominated by the van der Waals interaction. If this is the case, the LDA calculation fails to express the graphite interlayer interaction and (maybe) the electronic band dispersion along the stacking direction. However, Schabel and Martins[8] showed that the application of the LDA and pseudopotentials scheme for the *AB*-stacked graphite gives reasonable values of interlayer binding energy, the optimum distance, and the compressibility, each of which agrees well with the experimental values cited in Ref. 8. Furthermore, the calculated band structure (including the dispersion along the stacking direction) was found to be consistent with the photoemission data, which are also cited in Ref. 8. Since the absolute value of the interlayer binding energy is tiny (few tens meV per atom), there still remains an argument for the numerical accuracy in energetics. On the other hand, there are no serious problems of the LDA in describing energy-band structures of stacked graphite as far as we know. We have confirmed that our present computational condition well reproduced the band structures shown in Ref. 8 as well as Ref. 9. We therefore believe that the band dispersion of the stacked ribbons is also well described within the LDA scheme. Our present cutoff energy is not so high as the previous one,[8] so instead of the optimization of the interlayer distance we have just adjusted the ideal interlayer distance of 3.34 Å.

The band dispersion of stacked ribbons becomes two dimensional in directions along the ribbon and along the stacking. Figure 2(a) shows the two-dimensional BZ and the related directions in real space. (Only the case of the *AB* stacking is shown here.) The calculated band structures for *AA*- and *AB*-stacked ribbons are shown in Figs. 2(b) and 2(c), respectively. The assumed width of the ribbons is $N=6$ in both cases. The flatbands located at E_F are seen only in the case of the *AB* stacking.

We again investigated the wave function's character of these nearly flatbands seen in the *AB*-stacked ribbons and found the similarity to the edge state of a single layer of a zigzag ribbon. In the *AB*-stacked ribbons, the edge states are individually localized on the edge of either each *A* layer or each *B* layer. There are no remarkable electron hoppings between the edge states of *A* and *B* layers despite extension of the corresponding wave functions normal to each layer. However, this fact is not so surprising when we compare the present results with that of the *AB*-stacked graphite bulk,[8,9] which also has very small band dispersion around E_F along K-H line of the BZ (in the direction of the stacking). As mentioned before, the *AB* stacking allows half of C atoms to be neighbored to the center of each hexagon in the stacking direction. The edge state of a single ribbon is essentially characterized by a nonbonding orbital (π electrons) whose amplitude is mainly distributed at the H-terminated edge sites and their second neighbors. Remember that such C sites are located either above the center of the hexagon in the neighboring ribbon or directly above the nodal site of the neighboring ribbon. The interlayer hoppings of the π electrons on those sites are thus suppressed, which results in the very small dispersion near E_F. While in the case of the *AA* stacking, all C atoms of one layer are located directly above all C atoms on the neighboring layers, which allows the π-electron hoppings in the direction of the stacking, so appearance of the flatbands is inhibited.

From the present results, we conclude that the edge states exist in both single and *AB*-stacked H-terminated graphite ribbons. These states are expected to be detected by scanning tunneling microscopy (STM). We would like to point out here that the substrate without electron levels near E_F should

be chosen in STM measurement in order to prevent hybridization between the edge states and the substrate states near E_F. If the hybridization takes place, the localized nature of the edge states might be destroyed.

The authors acknowledge M. Saito for his comments and suggestions on this paper. All calculations were done by using the SX4 Supercomputer System at the NEC Tsukuba Research Laboratories.

*Present address: College of Science and Engineering, Aoyama Gakuin University, 1-1 Morinosato-Aoyama, Atsugi, 243-0123 Japan.

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