# *Ab Initio* Study of Field Emission from Graphitic Ribbons

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We have performed first-principles calculations on field emission (FE) from graphitic ribbons within the time-dependent density-functional theory. An important finding is that dangling bond states localized at clean edges are major contributors to FE current. H termination makes the FE current small due to the disappearance of the dangling-bond states. FE is found not to occur from the edge state of a H-terminated zigzag ribbon even when the state is at the Fermi level. The results of the FE current from graphitic ribbons give $\sim 1$ $\mu$A for maximum of FE current from a circular edge of graphitic sheets with $\sim 1$ nm diameter of an open-ended multiwalled carbon nanotube under a high electric field of $\sim 1$ V/Å.

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Carbon nanotubes (CNTs) have been intensively studied in anticipation of their application to novel nanoscale materials and device structures [1]. Among a variety of proposed applications, field emitters [2–5] are predicted as an application to next-generation flat-panel displays because CNTs have intrinsically suitable properties for field emitters, such as high aspect ratio, high mechanical stiffness, chemical inertness, and electrical conductivity. Experimentally, highly enhanced field emission (FE) currents have been observed for open-ended multiwalled carbon nanotubes (MWNTs) and the cause has been attributed to emissions from an atomic chain unraveling from the edge of the nanotubes [6]. Recently, pentagonal shapes have been observed by field emission microscopy (FEM) of capped MWNTs [7].

However, the emission mechanism of CNTs is not understood and these unusual phenomena in FE from CNTs remain to be explained, because the conventional method based on the Wentzel-Kramers-Brillouin (WKB) approximation [8] is not suitable for the analysis of highly inhomogeneous electronic structures caused by the sharp tip ($\sim 1$ nm diameter) with hexagonal and pentagonal carbon atomic structures. Using the scattering formalism, Adessi and Devel calculated the FE currents from single-walled carbon nanotubes (SWNTs) and confirmed the implication of localized states in the emission process [9]. Recently, Han *et al.* calculated FE currents from CNTs by the time-dependent density-functional theory (TD-DFT) for the first time [10].

In this work, we have applied the TD-DFT to the calculation of FE currents from graphitic ribbons. The reasons why FE from graphitic ribbons has been focused on in this study are the following. FE seems to occur from the circular edges of graphitic sheets of open-ended MWNTs [6,11]. It is reasonable to assume that electrons are emitted primarily from the outer sheets among the concentric tubular layers, although little is known about layer-dependent emission properties. Since graphitic ribbons have dangling bonds, $\pi$ bonds, and edge states [12] depending on the type of termination, the study of FE from graphitic ribbons gives a clue to understanding the role of surface electronic states in FE from carbon nanostructures. Further, a very recent experiment of graphitic ribbons grown on a substrate [13] stimulated our interest in FE from graphitic ribbons.

The objectives of this study are to understand the microscopic mechanism of FE from graphitic ribbons based on the electronic band structures, and to clarify the effects of the edge structure and H termination on the value of FE currents.

In the present work, we perform conventional DFT [14,15] and TD-DFT [16,17] calculations in Fourier space to investigate the electronic states and FE from various graphitic ribbons. We used the generalized gradient approximation (GGA) for the exchange-correlation potential [18] and the norm-conserving pseudopotentials of NCPS97 [19] based on the Troullier-Martins algorithm [20]. We expand the electronic wave functions in plane waves up to a kinetic energy of 44 Ry, and choose eleven $\boldsymbol{k}_y$ points along the ribbon axis in the first Brillouin zone. The $x$ and $y$ axes are defined as an inset in Fig. 1. The sizes of the unit cells are 79.8 Å $\times$ 2.49 Å $\times$ 4.99 Å and 76.8 Å $\times$ 4.32 Å $\times$ 4.32 Å for zigzag ribbons and armchair ribbons, respectively.

The systems we investigated in the present study are zigzag ribbons with and without H termination, and armchair ribbons with and without H termination. The H-terminated zigzag and armchair ribbons are shown in Figs. 1(a) and 1(b), respectively. The unit cells are the regions surrounded by the dashed lines. The electric field is applied to the $x$ direction. In the calculation of the time evolution of wave functions in the TD-DFT algorithm, both the Suzuki-Trotter split operator method [21,22] and the fifth-order Taylor expansion method [17] were used. Since the difference in the FE currents obtained by the two methods is negligible and the latter method guarantees the normalization condition on the electron number within an accuracy of $10^{-7}$ for simulation time $t \leq 100$ a.u.

  

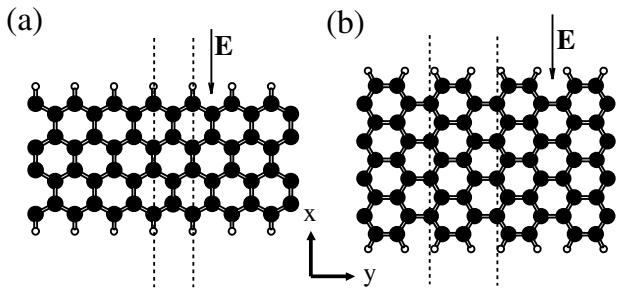


FIG. 1. Structures of (a) a zigzag and (b) an armchair ribbon with H terminations. Small open circles and large closed circles are hydrogen atoms and carbon atoms, respectively. Unit cells are the regions surrounded by the dashed lines. The sizes of the unit cells are 79.8 Å × 2.49 Å × 4.99 Å and 76.8 Å × 4.32 Å × 4.32 Å for zigzag ribbons and armchair ribbons, respectively. Electrons are emitted from the upper edges of the ribbons in electric fields $E$ indicated by arrows.

(2.4 fs), we employed the latter scheme to save computational time in this study. The time step for the integration is 0.05 a.u. We evaluate the FE currents from graphitic ribbons in an electric field of 1.0 V/Å. The method of evaluating the FE current from the time-dependent electron emission is as follows. First, we determine the ground states of atomic and electronic structures of graphitic ribbons using the conventional DFT in a zero electric field. Second, the electric field is switched on and increased to 1.0 V/Å linearly until $t = 25$ a.u. using the TD-DFT scheme to calculate the time evolution of the wave functions. The electric field is fixed at 1.0 V/Å after a time of 25 a.u. (0.6 fs). This technique is found to be very useful in stabilizing the time evolution of wave functions. Finally, the value of the FE current is evaluated from the linear slope of the curve of the number of emitted electrons as a function of time.

The band structures as a function of wave number ($\boldsymbol{k}_y$) are shown for the clean zigzag ribbon (without H termination) in Fig. 2(a) and for the H-terminated zigzag ribbon in Fig. 2(b). The characteristic features are the same as those obtained in another study based on the DFT, except for some fine structures caused by the different size of the unit cell and/or types of stacking of graphitic ribbons [23,24]. The edge state, which has been discussed in detail by Nakada *et al.* [12] is seen above the Fermi level in Fig. 2(a) and on the Fermi level in Fig. 2(b) near $X$ points.

In Fig. 3, we present the result of the time evolution of electron numbers ($N_e$) emitted toward the vacuum from the upper edge of the H-terminated zigzag ribbon in a field of 1.0 V/Å. The broken and dotted curves refer to the $N_e$ from the states with a dot and a triangle at $\Gamma$ point in Fig. 2(b), respectively. These two $\sigma$ states are main contributors to the FE current at $\Gamma$ point, because the wave functions have large amplitudes at the hydrogen atoms on the edge. The $N_e$ from the other states are negligible, as seen from the curves close to zero. Electrons begin to leak from the edge of the graphitic ribbon around $t =$

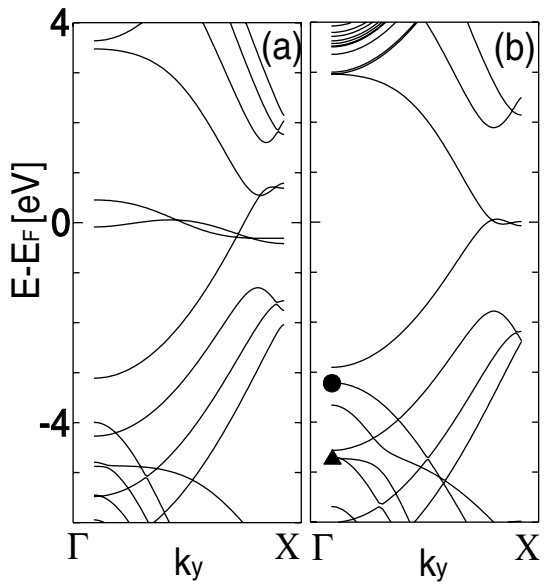


FIG. 2. Band structures of (a) a clean zigzag ribbon and (b) a H-terminated zigzag ribbon as a function of wave number $\boldsymbol{k}_y$.

20 a.u. (0.5 fs) and increase linearly in number with time. After $t = 60$ a.u. (1.4 fs), the $N_e$ deviates from the linear curve due to the interference between the outgoing and reflected waves. This is a clear artifact caused by the high potential barrier of sawtooth-type electric-field potential in vacuum [upper end of the unit cell is not shown in Fig. 1(a)]. This phenomenon has already been seen in the previous study [10]. Therefore, we evaluate the value of the FE current from the linear slope in the time region of 45 a.u. (1.1 fs) $\leq t \leq$ 55 a.u. (1.3 fs).

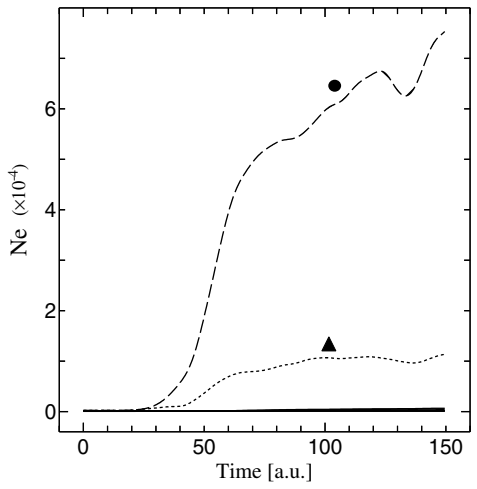


FIG. 3. Time evolution of electron numbers at $\Gamma$ point in Fig. 2(b) emitted from H-terminated zigzag ribbon into the vacuum. Total number of electrons in the unit cell is normalized to one in this case. The electric field is increased to 1.0 V/Å linearly until $t = 25$ a.u. (0.6 fs) and fixed as 1.0 V/Å after $t = 25$ a.u.. Dashed line and dotted line refer the electron numbers from the states marked with the dot and triangle in Fig. 2(b), respectively.

Now we have the values of FE currents as a function of wave number $\boldsymbol{k}_y$ by summing the currents from each state at each $\boldsymbol{k}_y$ obtained above. The results for zigzag ribbons are given in Fig. 4(a). There are two important findings regarding this result. One is that the FE current from the clean (without H termination) zigzag ribbon (solid line) is larger than that from the H-terminated zigzag ribbon (dashed line). The dominant part of the FE current from the clean zigzag ribbon comes from the dangling-bond states at the Fermi level [Fig. 2(a)]. The dangling-bond states do not exist in the H-terminated zigzag ribbon but the $\pi$ state remains [Fig. 2(b)]. Since localized states such as dangling-bond states were found to significantly react with the electric field from the previous studies [25–27], the present result enables us to confirm that the dangling-bond states essentially contribute to FE from clean graphitic ribbons.

The other important property is that the current decreases as $\boldsymbol{k}_y$ increases from $\Gamma$ to $X$ points. This feature initially appears to contradict the dispersions of the occupied band in Fig. 2(b). Here, we recall that the kinetic energy of electrons in the direction of the applied field is essentially responsible for electron tunneling into the vacuum [8]. Therefore, we define the energy eigenvalue $\varepsilon_x^i$ as

$$\varepsilon_x^i = \langle \phi_{\boldsymbol{k}_y}^i | (\boldsymbol{G}_x^2 + V_{\text{eff}}) | \phi_{\boldsymbol{k}_y}^i \rangle , \tag{1}$$

$$\phi_{\boldsymbol{k}_y}^i(r) = \sum_{\boldsymbol{G}} C_{\boldsymbol{k}_y,\boldsymbol{G}}^i \exp[i(\boldsymbol{k}_y + \boldsymbol{G}) \cdot \boldsymbol{r}], \tag{2}$$

where $i$ and $\boldsymbol{G}$ are the band index and reciprocal lattice vector, respectively. $\phi_{\boldsymbol{k}_y}^i$ and $V_{\text{eff}}$ are the wave function and effective potential of the Kohn-Sham Hamiltonian [14], respectively. $\varepsilon_x^i$ of the highest occupied band ($\pi$ state) of Fig. 2(b) is given in Fig. 4(b). $\varepsilon_x^i$ has a larger value at the $\Gamma$ point than at the $X$ point, indicating that the tunneling probability of electrons is higher from the former point than the latter one. As a result, electron emissions from the *edge state* do not occur even though it is on the Fermi level.

The currents emitted from four graphitic ribbons in an electric field of 1.0 V/Å are presented as a function of energy in Fig. 5. A large peak at the Fermi level of the clean zigzag ribbon (solid line) in Fig. 5(a) comes from the dangling-bond states in Fig. 2(a). On the other hand, the highest peak of the H-terminated zigzag ribbon (broken line) comes mainly from the state marked by a dot at the $\Gamma$ point in Fig. 2(b). These properties of the energy distribution also appear in armchair ribbons, as shown in Fig. 5(b), except that the highest peak position of the clean armchair ribbon (solid line) is shifted down from the Fermi level and the distribution for the H-terminated armchair ribbon (dashed line) is more extended than for the H-terminated zigzag ribbon. The highest peak (solid line) at 2.5 eV below the Fermi level also comes from the dangling-bond states [24], and the extended distribution is due to separated bands at the $\Gamma$ point, although the energy band structures of armchair ribbons are not shown in this paper.

We evaluate the total FE currents (in units of $\mu$A/nm) from the four graphitic ribbons stated above in an electric field of 1.0 V/Å and list the results in Table I. The FE current is influenced much more by the condition of the edges, i.e., clean or H-terminated, than by the structural difference, i.e., zigzag or armchair type. We estimate the FE current from a circular edge of graphitic sheet with ~1 nm diameter of an open-ended MWNT under a high field of ~1 V/Å to be ~1 $\mu$A using those from the graphitic ribbons in Table I, if the edge structure of graphitic sheets of an open-ended MWNT is regarded to be approximately the same as that of the graphitic ribbons. The order of magnitude of the result is compatible with the observed results [5]. The emission current is not expected to monotonically increase above ~1 $\mu$A as the tube diameter increases (a few tens of nm), because the field enhancement at the edge of the nanotube decreases as the aspect ratio decreases [28].

Finally, we discuss how the dangling-bond states localized at the edge of the nanotubes behave in the typical FE environment. The edges of graphitic ribbons in free space

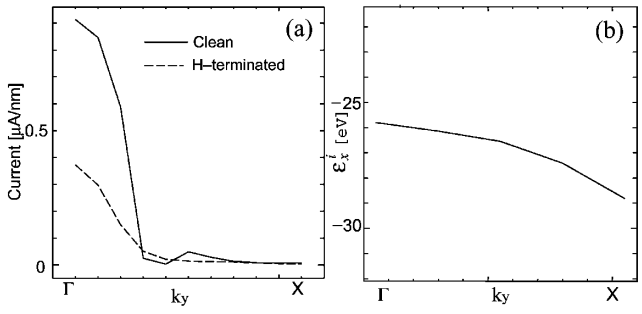


FIG. 4. (a) FE currents from clean (solid line) and H-terminated (broken line) zigzag ribbons as a function of wave number $\boldsymbol{k}_y$. (b) The energy eigenvalue $\varepsilon_x^i$ [the definition is given in Eqs. (1) and (2)] of the highest occupied band ($\pi$ state) of H-terminated zigzag ribbon in Fig. 2(b) as a function of $\boldsymbol{k}_y$.

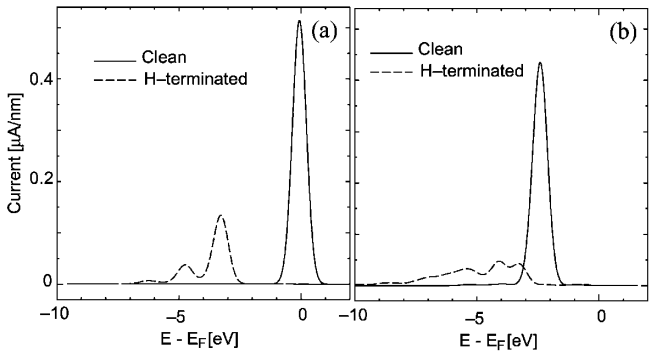


FIG. 5. Energy distributions of electrons emitted from (a) a zigzag ribbon and (b) an armchair ribbon in a field of 1.0 V/Å.

TABLE I. FE currents [$\mu$A/nm] in an electric field of 1.0 V/Å.

| Type | Clean | H-terminated |
|---|---|---|
| Zigzag | 0.369 | 0.137 |
| Armchair | 0.320 | 0.144 |

are possibly reactive [24] and the dangling-bond states will disappear upon hydrogen or oxygen termination. Even though such chemical species are adsorbed to the edges, they are predicted to evaporate rather easily due to emission currents. As a result, dangling-bond states remain stable in FE. Of course, the calculation of forces exerting on adsorbed atoms will be required to check whether the adsorbates evaporate owing to the emission current.

In conclusion, the dangling-bond states localized at edges of clean zigzag and clean armchair ribbons are the main source of the FE current. Thus, the FE current from H-terminated graphitic ribbons significantly decreases due to the disappearance of the dangling-bond states. The edge states unique to the zigzag ribbons do not contribute to FE even though they are at the Fermi level. We obtain reasonable values for FE currents from the circular edges of graphitic sheets of open-ended MWNTs from the present results of FE current from graphitic ribbons.

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