Field emission mechanisms of graphitic nanostructures

Masanuki Arai,1,2∗ Yasuhiro Nakamura,1‡ and Kazuyuki Watanabe1,2†

1 Department of Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
2 CREST, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

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Field emission (FE) and the electronic-states origin of graphitic nanostructures were investigated by first-principles calculations based on time-dependent density-functional theory. We find that the FE current from graphitic ribbons changes remarkably depending on the hydrogen termination and the direction of the applied electric field. Also, the FE current from graphene sheets shows a dramatic increase around vacancy defects. We verified, through the analysis of local electronic structures and energy distributions of emitted electrons, that the dangling-bond (or σ) character is responsible for these results and governs the nature of the FE of graphitic nanostructures.

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I. INTRODUCTION

Recent advances in nanotechnology have made possible the fabrication of a wide variety of nanometer-scale devices using graphitic nanostructures, such as fullerenes, carbon nanotubes, and other carbon-based materials. Among the various applications for these nanostructures, electron field emitters made from carbon allotropes show significant promise for novel electronic devices because they can maintain stable forms under extremely high field-emission (FE) current densities owing to tight covalent-bonds. Chen et al. performed an FE experiment using graphite platelet nanofibers (GPNs) with several thousand graphitic ribbons stacked together like a deck of cards. Wu et al. carried out FE measurements of carbon nanowalls (CNWs), which are nano-graphitized sheets grown perpendicularly on substrates, and pointed out that CNWs are good candidates for nanoscale field emitters as well as carbon nanotubes. For the development of efficient field emitters, examination of FE properties of graphitic nanostructures is interesting and meaningful both from the viewpoint of fundamental science as well as technological applications of the field emitters.

Over the past few years, interesting phenomena in graphitic ribbons have been predicted by theoretical studies. According to theoretical results based on the tight-binding model for the π electrons, zigzag graphitic ribbons are always metallic, while armchair graphitic ribbons are either metallic or insulating depending on the widths of the ribbons. The study also pointed out that zigzag ribbons exhibit specific electronic states, highly localized at the ribbon edges (edge states). This was supported by first-principles calculations based on density-functional theory (DFT). For the edge state, magnetic optical and thermal properties of graphitic ribbons have also been studied theoretically. However, thus far, there have been very few experimental studies of graphitic ribbons.

Recently, the FE of graphitic ribbons was investigated by Tada and Watanabe using the time-dependent density-functional theory (TD-DFT). They found that the dangling-bond states and not the edge states contribute primarily to the FE. They also found that not only evaluation of work functions but also knowledge of local electronic properties, the σ- or π-bonding states, are prerequisite for understanding the microscopic mechanisms of FE properties of covalently-bonded nanostructures. Tada and Watanabe’s results cannot be derived from the conventional Fowler-Nordheim theory for the FE from flat jellium surfaces with the free-electron approximation. With the ultimate goal of complete understanding of microscopic mechanisms of the FE of graphitic nanostructures, in this study, we have investigated the effects of the electric-field direction and vacancy defects on the FE characteristics of graphitic nanostructures by using TD-DFT calculations.

The outline of this paper is as follows. In Sec. II, the computational methods and models used are described. In Sec. III, we present numerical results for the effects of hydrogen (H) termination and the direction of applied electric field on the FE of graphitic ribbons. We also present results for the effect of vacancy defects on the FE of graphene sheets. We conclude with Sec. IV.

II. METHODS AND MODELS

We carried out conventional DFT and TD-DFT calculations to investigate the electronic states and electron emission properties of graphitic ribbons and graphene sheets. TD-DFT has been successfully applied to various non-equilibrium electron dynamics phenomena including FE of carbon nanotubes, graphitic ribbons, covalently-bonded atomic wires, and diamond surfaces. We employed the norm-converging pseudopotentials of NCPS97 based on the Troullier-Martins algorithm and the generalized gradient approximation by Perdew et al. for the exchange-correlation potential. The block Davidson algorithm was adopted to diagonalize the Kohn-Sham Hamiltonian.
matrix. The electronic wave functions were expanded in terms of a plane-wave basis set. In the TD-DFT calculations, the expansion coefficients become time-dependent quantities.

First, we determined the ground states of atomic and electronic structures by using conventional DFT in a zero electric field. Next, we applied an electric field of 10 V/\text{nm} and calculated the time evolution of the wave functions by applying the TD-DFT scheme. Then, wave functions with higher energies start to contribute to FE. The KS Hamiltonian is updated by a new electron density at each time step, and a part of the dynamical screening effect and some electron correlation effects are automatically taken into account in this calculations. It is noted that the simulation time should not exceed a certain time because the emitted electrons bounce back from the unit-cell boundaries. However, within a simulation time \( t \leq 150 \ \text{a.u.} \) (3.6 fs), such reflection does not occur. In this calculation of the time evolution of wave functions, we have adopted the seventh-order Taylor expansion method.\footnote{The Taylor expansion method cannot guarantee the unitarity condition, although this method has computational simplicity. The Suzuki-Trotter type split-operator method would be more accurate and reliable for long time simulations because this method ensures the unitarity condition for the time evolution. The Taylor expansion method, however, guarantees the normalization condition for the electron number with an accuracy of 10^{-6} for our simulation time. Moreover, the computational time for the Taylor expansion method is much shorter than that for the Suzuki-Trotter expansion method. Therefore, we have employed the Taylor expansion method in this study. Finally, we counted the number of electrons tunneling into a large vacuum region by summing the squares of the coefficients at each time step and obtained a curve of the electron number as a function of time. The value of the FE current was evaluated from the linear slope in the curve.}

The systems we investigated in this study are zigzag graphitic ribbons with and without H termination and graphene sheets with and without a vacancy defect, as shown in Fig. 1. Since the effect of edge states on the FE is interesting, we chose the zigzag ribbons in the present calculations. The \( x \) and \( y \) axes are defined as shown in Fig. 1. The unit cell sizes for the graphitic ribbons are \( 79.8 \ \text{Å} \times 2.49 \ \text{Å} \times 4.99 \ \text{Å} \) and \( 14.8 \ \text{Å} \times 2.49 \ \text{Å} \times 88.6 \ \text{Å} \), when electric fields are applied parallel (\( \parallel \)) and perpendicular (\( \perp \)) to the ribbons, respectively. The widths of the graphitic ribbon in Fig. 1(a) and (b) are 9.12 Å and 7.10 Å, respectively. The size of the unit cell for the graphene sheets is \( 8.52 \ \text{Å} \times 7.38 \ \text{Å} \times 85.2 \ \text{Å} \). The cutoff energies for the calculations for graphitic ribbons and graphene sheets are 45 Ry and 34 Ry, respectively. We chose 10 \( k_x \) points in the first Brillouin zone for the graphitic ribbons and 16 points in the \( k_x-k_y \) plane in the first Brillouin zone for the graphene sheets for the determination of the ground-state electronic and atomic structures. The atomic structure around the vacancy defect of the graphene sheet was noticeably deformed, as seen in Fig. 1(d).

III. RESULTS AND DISCUSSIONS

A. Direction of electric field

We begin with a brief review of a prior study\footnote{We now describe the results for the FE of the zigzag ribbon in the perpendicular field, \( E_{\perp} \). The energy distributions of the FE current and the corresponding electronic distributions are given by solid lines in Fig. 2. For the H-terminated ribbon (Fig. 2(a)), FE currents are emitted from the \( \pi \) states at the edge, as expected, although no prominent peaks appear, compared to the energy distribution curve for the parallel field, \( E_{\parallel} \) (broken line in Fig. 2(a)). For the clean ribbon (Fig. 2(b)), however, a sharp peak originating from the DB state appears, similar to the case for the parallel field, \( E_{\parallel} \). Negligibly small contributions of the \( \pi \) states to the total FE current are found in the energy distributions. The direction of electronic distribution of the DB state in the upper right panel in Fig. 2(b) is \textit{not} parallel to the perpendicular field, \( E_{\perp} \). It follows from this result that the DB state contributes to the FE even when the direction of}
the electronic distribution is not parallel to the direction of the electric field.

Here, it is important to clarify why π states cannot be the main source of the FE even when π orbitals extend along the applied electric field, \( E_{\perp} \). Figure 4 shows the equipotential surface of the clean ribbon on the plane perpendicular to the ribbon sheet (inset) and electrostatic potential energy curves along the direction of the perpendicular field, \( E_{\perp} \). It becomes apparent from the equipotential surface that the electric field becomes negligibly small due to the screening effect in the center of the ribbon. Therefore, electrons are not emitted from the center region of the ribbon. On the other hand, the electric field is enhanced at the edges of the ribbon, as seen from the equipotential surface, and thus electrons are emitted mainly from the edges. We focus on the three electrostatic potential energy curves drawn along the lines corresponding to the three positions in the inset of Figure 4. The slope of the potential curve around the origin of the horizontal axis is the strength of the local electric field around the edge atoms along the direction of the perpendicular field, \( E_{\perp} \). The direction of the local field of curve 1, where the DB orbital exists, is parallel to the applied field, \( E_{\perp} \). However, the direction of the field for curve 3, where π orbitals protrude, becomes opposite to that of the applied field. Consequently, electrons cannot be emitted from the π orbitals even when the π orbitals are parallel to the applied field. The electrostatic potential energy curves of the H-terminated ribbon also show similar features as the clean ribbon.

Finally, we can summarize the FE properties of zigzag graphitic ribbons. We list the values of the FE currents from the two type of ribbons, H-termination and clean, in electric fields along two directions (\( E_{\parallel} \) or \( E_{\perp} \)) in Table I. The DB orbital is the main source of the FE from the clean ribbon in both electric field directions. The DB state disappears upon H-termination and thus the σ orbitals and the π orbitals become emitting sources in the parallel and perpendicular electric fields, although the contributions of the π orbitals are negligible.

| Type of termination | \( E_{\parallel} \) | \( E_{\perp} \) |
|---------------------|-----------------|-----------------|
| Clean               | 0.37            | 0.10            |
| H-termination       | 0.14            | 0.06            |

IV. CONCLUSIONS

The FE and the electronic-states origins of graphitic nanostructures were investigated by first-principles calculations based on TD-DFT. We found that the character of the local electronic states responsible for FE changes and thus the FE current varies, depending on the conditions of hydrogen termination and the direction of the electric field. The DB states are predominant sources for the FE because the electronic orbitals tend to appear at the edges and protrude along the direction of the electric field in vacuum. High FE currents from the edges of the graphene sheets of CNWs9 which are in parallel to the electric field, have been observed. Thus, the present study can provide a theoretical interpretation for the features observed in the experiment. We naturally expect that a similar property will be observed in the FE of GPNs.9 It is interesting to note that the direction of electronic-orbitals has been found to remarkably influence the ionization rate of atoms in strong laser fields.

Substantially enhanced emission current from the atomic vacancy sites in the graphene sheet confirms the essential contribution of the DB states to the FE from graphitic nanostructures. The π states, however, contribute minimally to the FE even when the electronic orbitals project along the direction of the electric field because the electric-field strength tends to decrease substantially in the region of the π orbitals, i.e., owing to a screening effect.

These findings are remarkable reflecting the covalent-bond character. The results emphasize the need for first-principles studies taking into account the geometric and electronic structures of field emitters towards better un-
derstanding of FE mechanisms, and for the design of nanoscale graphitic field emitters.

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* Electronic address: j1204701@ed.kagu.tus.ac.jp
† Present address: Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
‡ Electronic address: kazuyuki@rs.kagu.tus.ac.jp
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FIG. 1: Top views of graphitic ribbons (a) with and (b) without hydrogen (H) termination and graphene sheets (c) without and (d) with a vacancy defect in the unit cell. Gray circles are carbon atoms and the small black dots in (a) are H atoms. Dashed straight lines denote boundaries of the unit cells and a dashed circle in (d) denotes a vacancy defect.

FIG. 2: Energy distribution of the FE current for (a) the H-terminated ribbon and (b) the clean ribbon. The vacuum level is chosen for the origin of the energy. On the right side of each panel, electronic distributions causing the peaks are shown by blue clouds with carbon atoms (white spheres) and H atoms (white dots). The broken and solid lines denote the results in a parallel ($E_{//}$) and perpendicular ($E_{\perp}$) electric field, respectively.

FIG. 3: Schematic diagram of electron orbitals (gray clouds) of a clean graphitic ribbon around the right edge (side view). $E_{//}$ and $E_{\perp}$ denote the applied electric fields parallel and perpendicular to the ribbon, respectively. DB represents a dangling bond.

FIG. 4: The electrostatic potential energy as a function of the position from the ribbon sheet. The plane on which the ribbon lies is chosen to be the origin of the horizontal axis. The inset shows the equipotential surface of the clean ribbon from a lateral view in the perpendicular field, $E_{\perp}$. Electrons are emitted from the ribbon into the upper region. The lines 1, 2 and 3 are 1.2 Å, 0.6 Å and 0 Å away from the right edge atom of the ribbon.

FIG. 5: FE images of the graphene (a) without and (b) with a vacancy defect. The distance between the FE image plane and the graphene is 4.9 Å. The FE current density around the vacancy is about 22 times larger than that from the other regions.
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