# Field Emission Patterns Showing Symmetry of Electronic States in Graphene Edges

Noboru Yokoyama, Kazuya Nakakubo, Kohji Iwata, Koji Asaka, Hitoshi Nakahara, and Yahachi Saito*

Department of Quantum Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-8603, Japan

Intriguing field emission microscopy (FEM) images reflecting sub-nanometer sized structures of emitting sites and/or electronic orbitals have been observed from graphene edges. Graphene emitters with free edges (i.e., open edges) show a striped pattern (dubbed as a "lip pattern") consisting of an array of streaked spots (or oval shaped spots); the direction of striation is perpendicular to the graphene sheet, and each stripe is divided into two wings by a central dark band running parallel to the graphene sheet. The dark band may be due to the distractive interference of electrons emitted from π-orbitals with a phase difference of π on either side of the graphene. From the magnification calibration using FEM images of an aluminum cluster with atomic resolution, the spacing of the streaked spots is found to be close to the distance between adjacent carbon atoms aligned along the the zigzag and armchair edges. These observations suggest that the lip pattern reflects the symmetry of π states strongly delocalized at edge atoms.

**Keywords:** graphene, edge, electron emission, field emission, field emission microscopy, electronic orbital, aluminum

* To whom correspondence should be addressed. E-mail: ysaito@nagoya-u.jp, Phone: +81-52-789-4459, Fax: +81-52-789-3703

## 1. Introduction

Nanocarbon materials such as carbon nanotube (CNT) and graphene are potential candidates as excellent field electron emitters because of their geometrical structures with sharp edges, high electrical conductivity, current carrying capability, mechanical robustness, high thermal stability and so on [1-3]. Graphene is now attracting considerable attention as new material with two dimensionality and its peculiar electronic structure [4, 5]. Graphene with finite size has edges self-evidently, and electronic states at the edges exhibit peculiar properties, e.g., localized states depending on the types of edge (zigzag or armchair) [6], and spin polarization (ferromagnetic order) at the zigzag edge [7-9].

Field emission phenomena from graphene have been studied experimentally and theoretically, and effects of edge structures on field emission (FE) have been reported. Yamaguchi et al. [10] reported a streaked pattern in field emission microscopy (FEM) from reduced graphene oxide (rGO), and ascribed the pattern to the interference of electrons emitted from different sites on an edge. Araidai and Watanabe [11] carried out theoretical studies and predicted the contributions of dangling bonds to FE. Li et al. [12] predicted a dragonfly-shaped FEM image of graphene which were obtained by calculation of coherent interference of electrons emitted from π orbitals of the armchair edge.

In our previous FEM study on graphene emitters [13], we have revealed that graphene emitters with open edges gave a streaked pattern in which spots in an array were elongated perpendicular to the array direction and each striation was divided into two wings by a dark band running through the centre of the pattern, while those with closed edges gave a dim (burred) pattern resembling FEM images of capped single-walled CNT [14]. In the present paper, characteristic features of FEM patterns from open edged graphene are carefully examined, and FEM of aluminium (Al) deposited on graphene emitters is also studied. The Al-deposited emitters showed FEM images of a polyhedral Al cluster with atomic resolution. Using the atomically resolved Al image, spacing between the streaked spots in FEM images from open-edged graphene is estimated and the origin of the pattern is discussed.

## 2. Experimental

A piece of graphene is mounted on a tip of a tungsten (W) needle (0.15 mm in dia.) by rubbing its tip on the surface of graphite crystal (HOPG, highly oriented pyrolytic graphite) under a scanning electron microscope by using micro-manipulators. Thus-obtained graphene emitter was multilayered graphene consisting of several to a few tens of layers. The W needle attaching a piece of multilayered graphene was spot-welded to a W filament

(0.15 mm in dia.), which could be used for flash-heating. The assembled emitter was installed to a vacuum chamber for FEM, which was also equipped with a vacuum evaporator to deposit metal on a graphene emitter, as shown in Fig. 1.

After evacuating the FEM chamber down to 5.0 x $10^{-7}$ Pa, the graphene emitter was flash-heated to desorb molecules before FE measurement. FEM patterns on an observation screen were recorded by a digital camera. The distance between the tip of a graphene emitter and a screen for FEM observation was about 40 mm. When Al was deposited on the graphene, the emitter assembly was rotated to face it to the evaporation source. After the deposition of Al, the emitter was again faced to the observation screen without exposure to air.

### 3. FEM patterns from a clean graphene emitter

A time sequential series of FEM patterns from a graphene emitter and the corresponding time trace of emission current under a constant voltage of 690 V are shown in Figs. 2 (a) and (b), respectively. Except for the beginning of FE, the FEM images manifest features characteristic to graphene emitters, i.e., striated (or oval) spots are aligned parallel with each other, and a dark line (node) running perpendicular to the direction of striated spots is found at the centre of the pattern (see Fig. 2 (c)). Thus, the pattern has a mirror symmetry with respect to the dark line. The direction of the dark line (node) is parallel to the graphene plane [13]. The experimental pattern as a whole looks like a lip. With the elapse of time, the size of the lip pattern is extended with the increase of the number of striated spots, the emission current being concurrently increased even under the constant voltage. A possible cause of the pattern growth and the emission current increase is the extension of electron-emitting area which is brought about by evaporation of contamination or adsorbed molecules covering the graphene edge due to the temperature rise caused by Joule heating, as illustrated in Fig. 3.

Theoretically, taking into account only π orbitals, Li et al. predicted a dragonfly-shaped FEM patterns from a graphene emitter [12]. In their predicted patterns, the central node (dark line) parallel to the graphene plane is reproduced, which is due to the destructive interference of electron waves emitted from π-orbitals which have two lobes with the phase difference π on either side of the graphene plane. However, consideration of only π orbitals for the interpretation of experimental FEM patterns is inadequate since unoccupied states are filled by electrons when the graphene is negatively biased for FE experiment. So, emission from electronic states originating from π* and σ* orbitals have to be taken into account. Electronic states called interlayer states existing above Fermi level, which accommodate electrons in the formation of alkali-metal graphite intercalation compounds

[15, 16], may also play an important role in FE.

The origin of the arrayed oval spots, on the other hand, is not clear. Yamaguchi et al. [10] ascribed the array of streaked spots in their experimental FEM pattern from rGO to an interference of electrons emitted from a few emission sites, but the appearance of their FEM patterns is different from the present one. We consider that each oval spot in our FEM may corresponds to respective emission site along the graphene edge. More specifically, we conjecture that each oval spot originates from respective π orbital which has high density of states at each carbon atom on the graphene edge. Supporting evidences are presented in the next two sections describing FEM images of an adsorbed molecule and an Al cluster on the graphene emitter with atomic resolution.

In the present interpretation of FEM patterns, we postulate that these emission patterns came from a single sheet of graphene even though multi-layered graphene was used as the emitter. The reason of the postulation is as follows. Graphite has the ABAB stacking sequence, thus atom positons in adjacent layers being shifted with each other. Therefore, the edges of the multi-layered graphene are indented layer by layer. An electron microscopy study on edges of several-layered graphene [17] has shown the presence of offsets between the edges of two adjacent layer, and the distances between edges of adjacent layers have been measured to be 0.34 nm and 0.37 nm for zigzag and armchair edges. So, we expect that the lip patterns originate from an effectively single layer of graphene.

## 4. FEM of adsorbates on a graphene edge

After a prolonged observation of FEM pattern, residual gas molecules adsorb on graphene emitter as has been observed for CNT emitters [18, 19]. Figure 4 shows FEM patterns from a graphene emitter before and after the adsorption of residual gas molecules. Bright spots indicated by arrows in Fig. 4 (b) suggests the presence of an adsorbed molecule. When molecules adsorb on the graphene emitter, electron emission is enhanced through the molecule as observed in CNT emitters [18, 19]. The molecular species is not identified in this case, though it is possibly a hydrogen molecule because hydrogen is the most abundant residual gas species in the ultra-high vacuum. The size of the bright spot originating from an adsorbate is similar to the width of each striated spot, indicating that the origin of each striated spot has a size comparable with that of the molecule.

## 5. FEM of Al on graphene; Atomic resolution image of Al cluster

Al was deposited onto the graphene emitter after measuring FE from a clean graphene.

Figures 5 (a) and (b) show FEM patterns from a clean graphene emitter and Al-deposited one, respectively. Mean thickness of deposited Al was 5.9 nm.

Before the Al deposition, the lip pattern characteristic of graphene with free edges was observed. By the deposition of Al, as shown in Fig. 5 (b), a spotty pattern, in which spots are arranged in 4-fold and 6-fold symmetries, appeared. Similar patterns like this have been observed for Al-deposited CNT emitters. The contrast of the spotty pattern is reminiscent of the structure of an atom cluster with a shape of cubo-octahedron, which is a crystal form characteristic of face-centered cubic metals. A structure model of the Al cluster is shown in Fig. 5 (c). Four bright spots observed in the upper part of the Al image correspond to four corners of a (100) surface. Below the (100) face, a hexagonal shape, corresponding to a (111) face, the corners of which are manifested by bright spots. Since the electric field concentrates at locally protruding atoms which are located at the corners and the edges, tunneling probability of electrons at these atoms is significantly high. Therefore, only atoms at the corners and edges are highlighted, which is the same phenomena observed in field ion microscope (FIM) of a metal tip. The possibility of attaining the atomic resolution in FEM for a protrusion or atomic cluster on CNT emitters has been discussed in our previous paper [20]. The discussion on the possible observation of atomic images in FEM is considered to hold for graphene emitters.

The distance between neighboring atoms along the edge of the (111) surface of Al is 0.286 nm when the lattice constant in the cluster is kept the same as that of bulk Al. Using this interatomic distance as a measure of the magnification of these FEM images, the spacing between adjacent streaked spots for clean graphene emitters is estimated to be in a range between 0.14 and 0.23 nm, being consistent with the inference derived from the size of an adsorbed molecule in the previous section. The derived distances of 0.14 and 0.23 nm in the lip pattern are very close to the C-C bond length (0.144 nm) and the distance between the outermost carbon atoms at the zigzag edge (0.249 nm), respectively, as shown in Fig. 6. The quantitative estimation of the image size in FEM patterns indicates that the streaked spots correspond to emission sites with atomic size, and strongly supports our conjecture that the lip patterns reflect the symmetries of π orbitals localized at the graphene edge.

## 6. Concluding Remarks

We have shown that the FEM images called “lip patterns” observed for open-ended graphene originate from emission sites with atomic scale and is indicative of the symmetry of π electrons at the edge of graphene. Another possible origin may be emission of electrons from the interlayer state of graphene [15, 16] which is filled by supplying

electrons to the graphene (application of negative voltage to graphene for FE donates electrons to it) and has a spatially periodic charge density. In order to confirm the conjecture on the origin of the lip pattern, further studies including field ion microscopy (FIM), which uses helium or neon ions as imaging particles with higher spatial resolution than FEM, are required. Measurement of spin polarizability of electrons emitted from graphene edges are also an intriguing study not only for revealing the electron emission sites but also for developing a novel spin-polarized electron source, since it is predicted that electron spins on the zigzag edge are ferro-magnetically ordered [21, 22].

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**References**


[1] W. A. de Heer, A. Châtelain, D. Ugarte, *Nature* **1995**; *270*, 1179.

[2] A. G. Rinzler, J. H. Hafner, P. Nilolaev, L. Lou, S. G. Kim, D. Tománek, P. Nordlander, D. T. Colbert, R. E. Smalley, *Science* **1995**; *269*, 1550.

[3] Y. Saito, *Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*, Wiley-VCH, Weinheim, **2010**.

[4] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**; *6*, 183.

[5] A. H. C. Neto, R. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys*. **2009**; *81*, 109.

[6] M. Fujita, K. Wakabayashi, K. Nakada, K. Kasukabe, *J. Phys. Soc. Jpn*. **1996**; *65*, 1920.

[7] G. Z. Magda, et al. *Nature* **2014**; *514*, 608.

[8] O. V. Yazyev, et al. *Phys. Rev. B* **2011**; *84*, 115406.

[9] M. Golor, T. C. Lang, S. Wessel, *Phys. Rev. B* **2013**; *84*, 155441.

[10] H. Yamaguchi, K. Murakami, G. Eda, T. Fujita, P. Guan, W. Wang, C. Gong, J. Boisse, S. Miller, M. Acik, K. Cho, Y. J. Chabal, M. Chen, F. Wakaya, M. Takai, M. Chhowalla, *ACS Nano* **2011**; *5*, 4945.

[11] M. Araidai, Y. Nakamura, K. Watanabe, *Phys. Rev. B* **2004**; *70*, 245410.

[12] Z. Li, N. Xu and H. J. Kreuzer, *Phys. Rev. B* **2012**; *85*, 115427.

[13] K. Nakakubo, K. Asaka, H. Nakahara, Y. Saito, *Appl. Phys. Exp*. **2012**; *5*, 055101.

[14] Y. Saito, Y. Tsujimoto, A. Koshio, F. Kokai, *Appl. Phys. Lett.* **2007**; *90*, 213108.

[15] M. Posternak, A. Baldereschi, A. J. Freeman, E. Wimmer, M. Weinert, *Phys. Rev. Lett.* **1983**; *50*, 761.

[16] T. Enoki, M. Suzuki, M. Endo, *Graphite Intercalation Compounds and Applications*, Oxford University Press, New York, **2003**, Chap. 5.

[17] X. Jia, M. Hofmann, V. Meunier, B. G. Sumpter, J. C. -Dergado, J. M. R. -Herrera, Y. –P. Hsieh, , A. Reina, J. Kong, M. Terrones, M. S. Dresselhous, *Science* **2009**; *323*, 1701.

[18] K. Hata, A. Takakura, Y. Saito, *Surface Sci*. **2001**; *490*, 296.

[19] Y. Saito, *Coord. Chem. Rev*. **2009**; *253*, 2912.

[20] Y. Saito, T. Matsukawa, K. Asaka, H. Nakahara, *J. Vacuum Sci. Tech. B* **2010**; *28*, C2A5.

[21] M. Fujita, K. Wakabayashi, K. Nakada, K. Kusakabe, *J. Phys. Soc. Jpn.* **1996**; *65*, 1920.

[22] Y. –W. Son, M. L. Cohen, S. G. Louie, *Nature* **2006**; *444*, 347.

Figure captions

Fig.1 FEM apparatus.

Fig.2 (a) Time sequential series of FEM patterns from a graphene emitter without adsorbates, and (b) the corresponding time trace of emission current under constant voltage. (c) Enlarged FEM pattern at the time 10 sec, explaining striated spots and a dark line (node).

Fig.3 Schematics illustrating the increase in the emission area. (a) At the initial state of electron emission, and (b) the state giving the lip pattern.

Fig.4 FEM patterns from a graphene emitter (a) before and (b) after the adsorption of a residual gas molecule. A bright spot indicated by an arrow in (b) suggests the presence of an adsorbed molecule. The scales in the figures show the size on the observation screen.

Fig. 5 FEM pattern from (a) a clean graphene emitter, and (b) Al-deposited one. Mean thickness of deposited Al was 5.9 nm. (c) Structure model of the Al cluster with the cubo-octahedral shape.

Fig. 6 Structure of graphene edge.

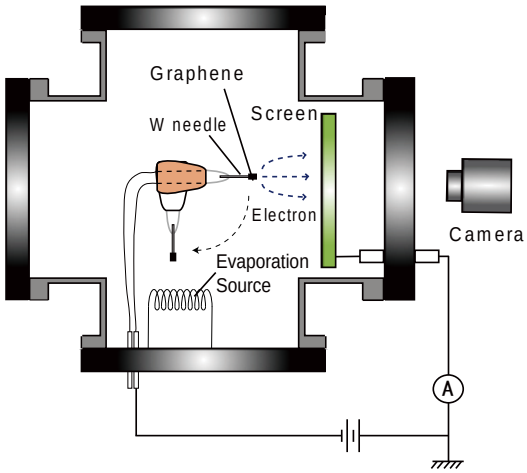
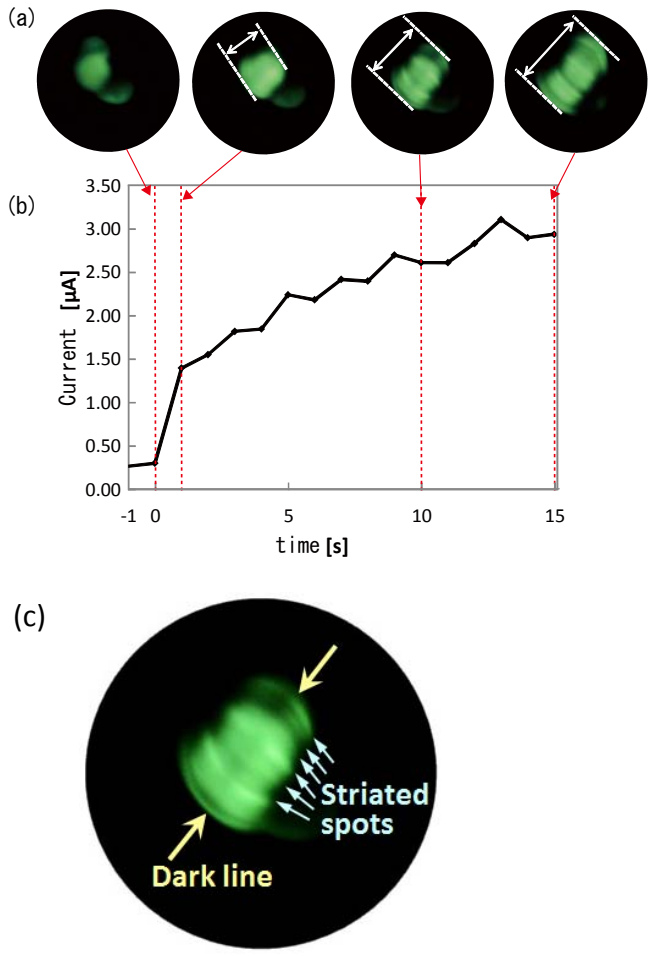

Graphene
W needle
Screen
Electron
Camera
Evaporation
Source
A

Fig.1


(a)
(b)
Current [μA]
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-1
0
5
10
15
time [s]


(c)
Striated spots
Dark line

Fig. 2

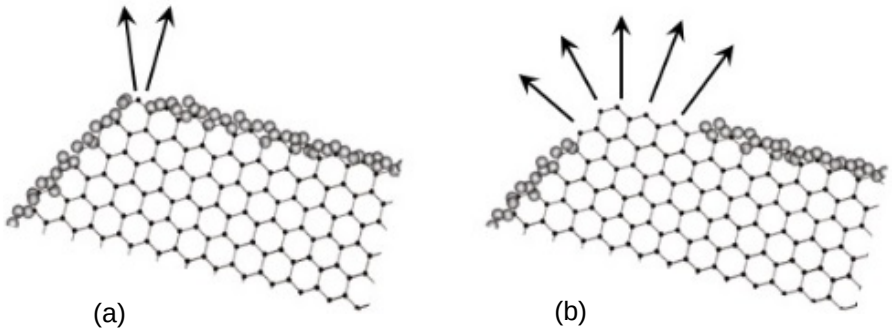



Fig. 3

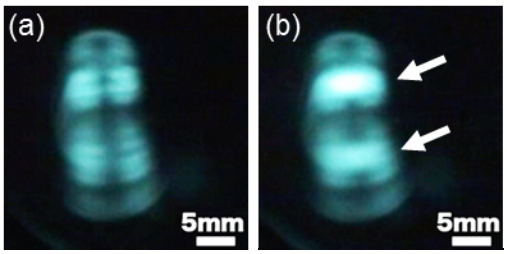



Fig. 4

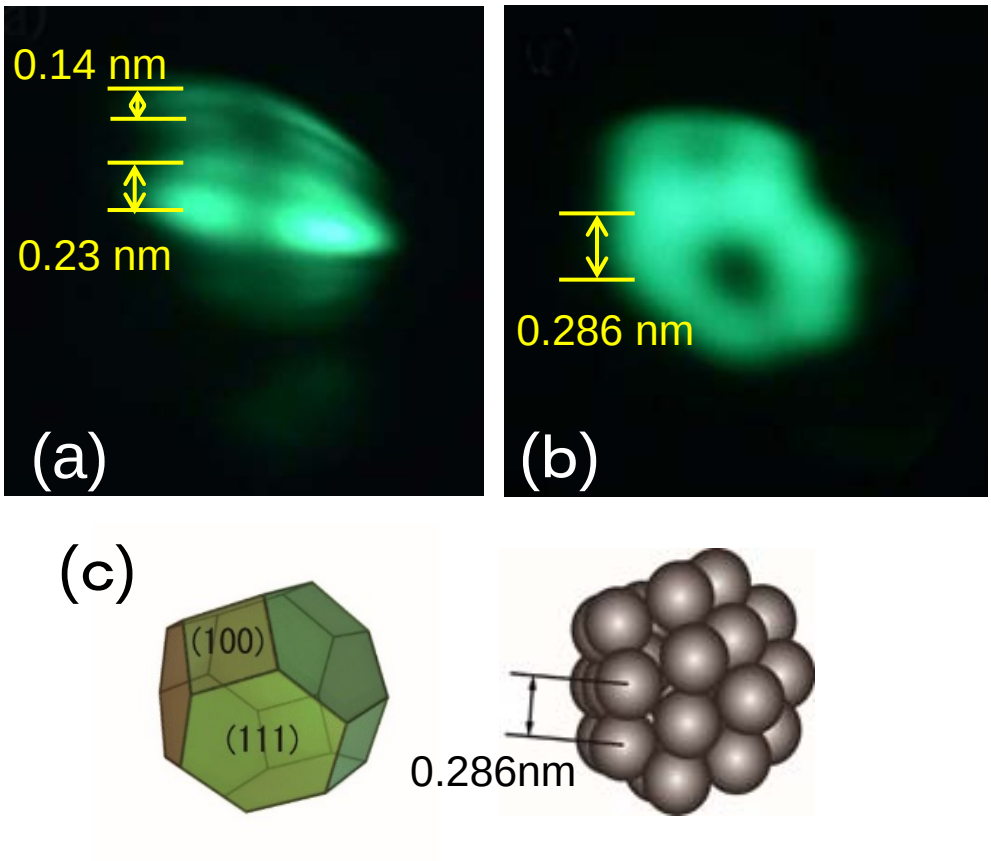



Fig. 5

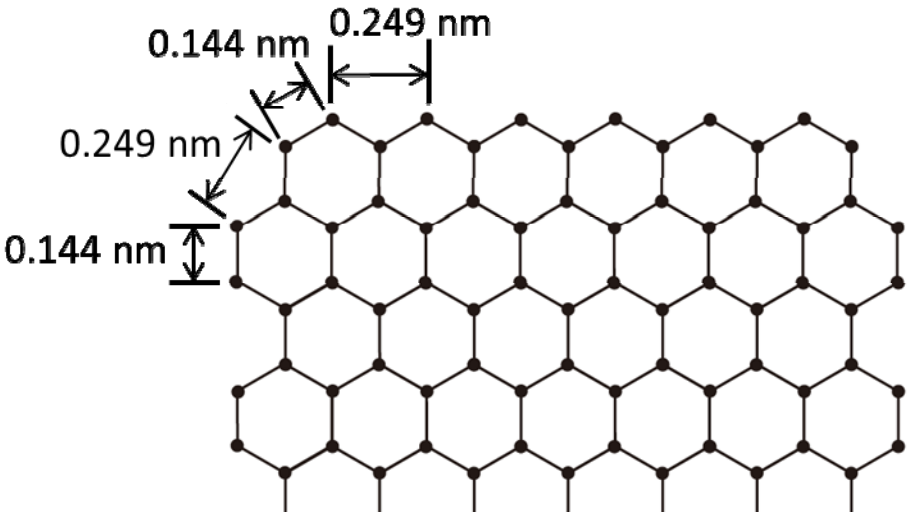



Fig. 6