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Edge States of Graphene Revealed by Field Emission Microscopy

Introduction

Electronic states at graphene edges exhibit peculiar properties, e.g., localized states depending on the edge types (zigzag or armchair), and spin polarization (ferromagnetic order) at zigzag edge [1]. Field emission microscopy (FEM) images of open graphene edges show a striped pattern (or "lip pattern") consisting of an array of streaked 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 [2]. The "lip pattern" is considered to reflect the symmetry of π orbitals at a graphene edge. Field ion microscopy (FIM) images, complementary to FEM, of the graphene edges gave unoccupied π orbitals with higher spatial resolution. We also tried to measure spin-polarization of field-emitted electrons and obtained for the first time an evidence of the spin polarized states at edge of graphene.

FEM and FIM of Graphene Edge

Both FEM and FIM measurements were carried out using the same graphene edge. Typical FEM and FIM images of the same graphene emitter are shown in Figs. 1 (a) and (b), respectively. The FEM image (Fig. 1 (a)) exhibits a "lip pattern" characteristic to a graphene edge; array of two lobes elongated perpendicular to a graphene plane. The corresponding FIM image (Fig. 1 (b)) reveals more detailed structures because of higher spatial resolution; each streak in FEM is resolved into a pair of spots. The FIM image was taken using Ne as imaging gas. The direction of a line joining paired spots in FIM is perpendicular to the graphene plane, being similar to the case of FEM where streaks in FEM are elongated in the direction perpendicular to the graphene plane. Both of the FEM and FIM patterns show a mirror symmetry with a mirror plane along the central dark band (parallel to the graphene plane). Based on our previous studies on FEM of carbon emitters [2], the spacing between adjacent streaks in FEM and FIM is presumed to correspond with that of carbon atoms at the graphene edge. The image of paired bright spots extending to both sides of a graphene plane are considered to be formed by Ne atoms ionized in proximate to an unoccupied π*-orbital at the edge. Thus, the FIM pattern is interpreted to represent a spatial distribution of the unoccupied edge states.

Spin Polarization of Electrons Emitted from Graphene edge

Spin polarization measurements of field-emitted from graphene edges were measured by the Mott spin polarization analyzer [3]. The direction of spin at the edge of the graphene was identified by measuring each spin component of field emitted electrons for 20 minutes at low temperature and room temperature. The present result is the first demonstration of spin polarization of electrons at graphene edges by using field emission method. Abrupt decreases in the spin polarization as a function of time may result in the adsorption of hydrogen, which is the main residual gas in the UHV chamber. Although the type of termination of graphene edge by hydrogen, i.e., adsorption of molecular or atomic hydrogen, is not identified, atomic hydrogen adsorption causes a reduction in magnetic moment per dangling bond of 1.3 μ_B for the clean edges by 1 μ_B [4].

The electron emission characteristics before and after the measurement in this study also suggest hydrogen adsorption on the edges.

References

[1] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. 65 (1996) 1920
[2] N. Yokoyama, K. Nakakubo, K. Iwata, K. Asaka, H. Nakahara, Y. Saito, Surf. Interface Anal. 48 (2016) 1217
[3] S. Nagai H. Sakakibara, K. Hata, M. Okada, H. Mimura, Ultramicroscopy 111 (2011) 405
[4] K. Tada, J. Haruyama, H.X. Yang, M. Chshiev, T. Matsui, and H. Fukuyama, Phys. Rev. Lett. 107 (2011) 217203

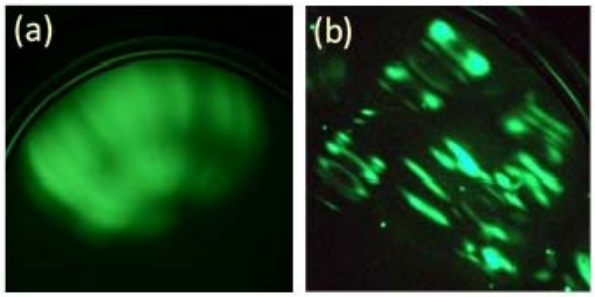

Figure 1: (a) FEM and (b) FIM images of a graphene.