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Edge state in graphite induced by surface defects

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1 Introduction

Our research interest has been strongly attracted by unique electronic and magnetic properties of sp^2-carbon-based materials. The origins lie in the unconventional electronic structure of graphene described by the massless Dirac equation, and in the spin-polarized localized electronic states at zigzag-shaped edges and atomic-scaled vacancies, which are called edge states. Magnetic properties of edge states have been investigated for graphite nano ribbons, and activated carbon fibers [1,2]. The reduction of edge-state contributions accompanied with heat-induced loop formation between adjacent edges has been observed [1]. For the next advance, we employ HOPG (highly-oriented pyrolytic graphite) with vacancy defects introduced on its surface in order to control the enhancement of edge states by a technique applicable to even single-layer graphene.

2 Experiment

An HOPG sample was fixed on a tantalum substrate and loaded into the chamber maintained in high vacuum (10^{-6} Pa). The Ta substrate was heated to clean the sample by electric current at about 600°C. In order to introduce surface defects to the sample, Ar^+ ions were irradiated at the pressure of 1.0×10^{-4} Pa for 5 minutes with changing the acceleration voltage from 100 V to 3 kV. The carbon K-edge NEXAFS (near-edge x-ray absorption fine-structure) was measured at the soft x-ray beam line BL-7A in the Photon Factory in the Institute of Materials Structure Science. NEXAFS spectra were obtained by a partial electron yield (PEY) mode with an imaging-type microchannel plate detector, which mainly collected the C *KLL* Auger electrons. A total electron yield (TEY) mode was also employed for measurements.

3 Results and Discussion

Figure 1 shows typical C K-edge PEY-mode spectra for HOPG sample before and after 100-eV, 300-eV, and 500-eV Ar^+ irradiation. These spectra are normalized by the edge jump at 370 eV, where the intensity is proportional to the amount of carbons. Pristine sample has intensive features at 285.5 and 292−294 eV which are attributed to the electronic transitions from C 1*s* core state to the π* state and σ* state, respectively. Although 100-eV Ar^+ bombardment can produce single atomic vacancies at the outermost layer of the sample [3], spectral change is not detected. After 300-eV irradiation, however, PEY spectrum shows the significant reductions of the π* and σ* intensities and the low-energy shoulder of the π* peak, while these changes are not noticeable in TEY spectrum (not shown). The additional feature at the region just above the Fermi level of HOPG (284.4 eV) is assigned to the edge state [1,2]. The mean free path of C *KLL* Auger electron is about 8 Å, which corresponds to the thickness of 2 to 3 layers. The presence of edge state peak only in the PEY spectrum indicates that vacancies are produced only within a few layers by 300-eV bombardment. The weakening of the π* and σ* peaks is also in accordance with the partial breaking of the π−network spread on the surface. Higher-energy irradiations enhance the edge-state intensity. The similarity between PEY and TEY spectra evidences the formation of defects at deeper cites.

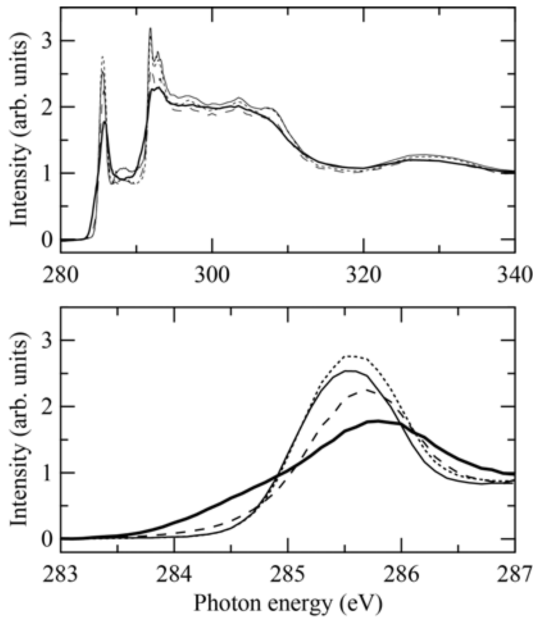

Fig. 1: C K-edge NEXAFS spectra of HOPG before (thin solid curve) and after 100-eV, 300-eV, and 500-eV Ar^+ irradiation (thin dotted, dashed, and thick solid curves, respectively) obtained by PEY mode. The lower figure is the magnification of the upper one in the range of photon energy from 283 to 287 eV, which includes the π* and edge-state features.

References
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