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Observation of Magnetic Edge-State in Graphene Nanoribbon

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Introduction

Graphene has received attention due to its unique properties. When the size of a graphene sheet is reduced to a few nanometers, other interesting phenomena could be expected due to the growing contribution of the edge [1]. The theoretical and experimental studies showed the presence of a localized non-bonding π state (edge-state) in the zigzag shaped edge regions. In investigating the properties of the nanographene, it is particularly important to confirm the presence of edge-states and their geometrical variations. Here, we pay attention to the graphene nanoribbon. It is because the population of open edges is large for the graphene nanoribbon that makes it a suitable system to investigate the presence of edge-states in nano graphene. In the present study, we have investigated the electronic and magnetic structure of the graphene nanoribbon by NEXAFS and ESR.

Experiment

The CVD grown graphene nanoribbon samples were synthesized by the pyrolysis of an aerosol precursor composed of ferrocene, thiophene, and ethanol. The pristine sample was annealed at 1000, 1500, and 2000 ^{o}C in an Ar atmosphere for each sample to get NR1000, NR1500, and NR2000, respectively. The carbon K-edge NEXAFS was measured at the soft x-ray beam line BL-7A in the Photon Factory in the Institute of Materials Structure Science. A powder sample was mounted on a Ta plate and loaded in to the NEXAFS measurement chamber. NEXAFS spectra were obtained by measuring the sample photocurrent (total electron yield method). ESR measurements were performed in the X-band region with a sample in vacuum at room temperature.

Results

Figure shows the carbon K edge NEXAFS spectra of the pristine graphene nanoribbon (NR), NR1000, NR1500, and NR2000. For the pristine sample, a pre-peak was observed below the π* peak close to the Fermi level. The appearance of the pre-peak indicates the presence of additional electronic states close to the Fermi level, edge state. The intensity of this pre-peak decreased with increasing annealing temperature and disappeared after annealing above 1500 ^{o}C.

The ESR spectrum of NR1500 showed a narrow peak with g = 2.004 ± 0.001. With a further increase in the annealing temperature, NR2000 did not show any significant peak except for a trace of the narrow peak. The narrow peak observed in NR1500 and NR2000 close to the free electron g-value is characteristic of the localized spins of the edge-state. In the case of the graphene nanoribbon, the loop formation commences at an annealing temperature of 1500^{o}C and becomes significant at higher temperatures. Since the edge-state exists at the open edges, there must be a corresponding decrease in the edge-state density with increasing loop formation. The present temperature dependence of the NEXAFS and ESR results confirm the existence of a magnetic edge-state that originates from open nanographene edges.

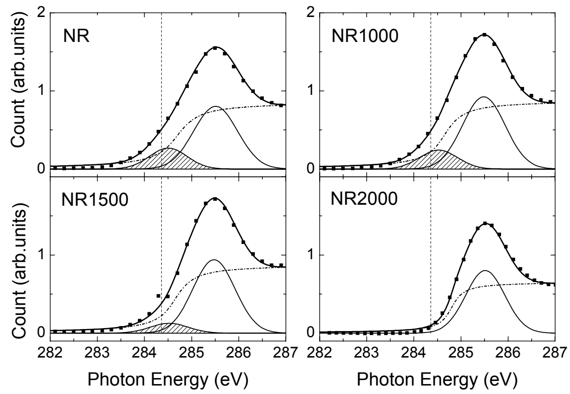

Fig. Carbon K edge NEXAFS spectra of NR, NR1000, NR1500, and NR2000. The deconvolution comprises two Gaussian peaks corresponding to the edge-state (shaded) and the π* state (unshaded), and a step-function (dash-dot curve). The vertical dashed-lines indicate the Fermi level

References

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