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Formation of fullerene-like structure by B and N doping in graphite

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Introduction

As a recent report that B- and N-doped carbon electrodes improved catalytic activity, doping of boron and nitrogen are often used modify properties of carbon materials. [1] However, structure of B- and N-doped carbon has not been clarified well because of complicated chemical bonding between B, C, and N atoms, and the active center is still controversial. To study local structures around B and N dopants, we analyzed polarization dependence of NEXAFS spectroscopy and found distorted planner structure. Fullerene-like structure is proposed for the distorted planner structure.

Experimental

The experiments were performed at the BL-11A station. Doping was performed by ion implantation. Fragment ions of borazine ($B_3N_3H_6$) were implanted in highly oriented pyrolytic graphite (HOPG) with an acceleration energy of 3 keV. HOPG was annealed at 500 or 800 C˚ during the implantation. Sample preparation and NEXAFS measurements were carried out in a vacuum chamber to avoid contamination in atmosphere. NEXAFS spectra were measured at various incidence angles of x-ray to analyze polarization dependence.

Results and discussion

Figure 1 shows an example of polarization dependence of B and N K-edge NEXAFS spectra in three-dimensional figures. Spectra measured at incidence angles of 20˚ and 90˚ are shown as solid and dotted curves below the 3D spectra. Broken lines indicate energies of π^* peaks of hexagonal boron nitride (*h*-BN).

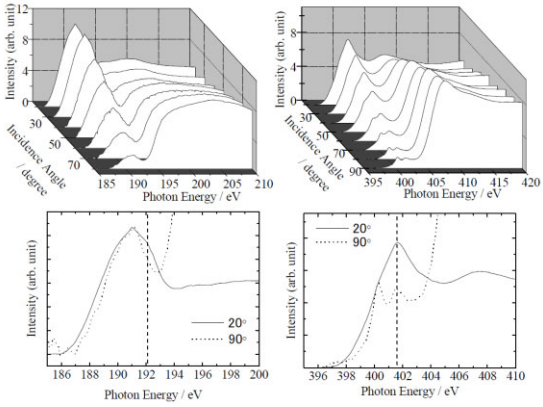

Fig. 1. B and N K-edge NEXAFS spectra of B- and N-doped graphite.

Both B and N K-edge spectra showed graphite-like polarization dependence, which means that B and N atoms have sp^2 configuration and that peaks enhanced at grazing angles are assigned to out-of-plane transitions to π^* states. Furthermore, close inspection showed existence of multiple components in the π^* peaks which have different polarization dependences. Solid curves showed larger intensity than broken curves at the π^* peak of *h*-BN. This means that other π^* peaks have smaller polarization dependence than the π^* peak of *h*-BN, and decrease of polarization dependence suggests distortion of planner configuration.

We propose fullerene-like structure which consists of hexagons and pentagons as the origin of the distorted planner configuration. It has been reported that N doping induces formation of pentagon in graphite matrix [2,3]. Based on the precedent works, B and N substitution effect on structural stability was compared. Molecular orbital calculations clarified difference of heat of formation between graphite structure and fullerene-like structure decreased for B- and N-substituted clusters. This means that pentagon formation is promoted by B and N substitution in graphite. *h*-BN has only graphite-like configuration, and molecular orbital (MO) vectors of π^* states of *h*-BN prone to align to surface normal reflecting orientation of HOPG. On the other hand, if pentagons are formed around dopants, MO vectors of π* states of B-C-N moiety lose specific alignment by the buckled structure. Since frontier orbital is strongly localized around pentagon sites as shown in figure 2, fullerene-like structure is interesting as an active center of catalytic activity.

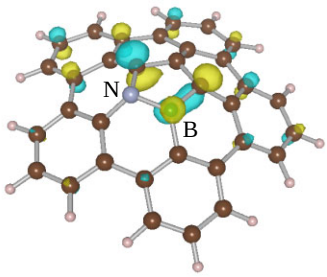

Fig.2. A model of B- and N-doped fullerene-like

References

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