

INTERCALATION CHEMISTRY AND ELECTRONIC STRUCTURE OF GRAPHITE-LIKE LAYERED MATERIAL WITH COMPOSITIONS BC_xN ($x \geq 6$)

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Abstract

Graphite-like layered materials with compositions of BC_xN ($x \geq 6$) were prepared by CVD method using acrylonitrile and boron trichloride as starting materials at a temperature in the range of 1470-2070K. Chemical intercalation of Li into the BC_xN prepared at 2070K was observed in $Li^+C_{10}H_8/2$ -MeTHF solution, resulting in formation of the first stage intercalation compound with an interlayer space (d -spacing) of 0.365nm. The BC_6N prepared at 1470K performed electrochemical charge/discharge cycles similar to those of graphite in 1M-LiPF₆/EC+DEC solution. Small contribution of π electrons on their valence and conduction bands was observed for the electronic structures of BC_6N , in comparison with that of graphite, on the basis of X-ray emission and absorption spectroscopy (XES and XAS, respectively). DV-X α molecular orbital calculation for the material was similar to the distributions of bands measured by XES and XAS. Both measured and calculated spectra suggested that the valence band was constructed by C2p with N2p, while a conduction band was made by C2p and B2p. The chemical and electrochemical intercalation of Li into the BC_xN could be explained by the electronic structures.

Introduction

Boron/carbon/nitrogen materials (B/C/N materials) based on the graphite network have been prepared by chemical vapor deposition (CVD) method or solid-gas reaction. Physical and chemical properties of the materials have been investigated and several applications of the materials to energy devices such as secondary Li ion battery have been demonstrated [1]. Investigation of the electronic structure for the materials would be necessary to understand the properties of them and to consider the application of them. In this study, chemical and electrochemical intercalations of alkali metals such as Li into the graphite-like layered materials with compositions of BC_xN ($x \geq 6$) were performed. The electronic structure of the material BC_6N prepared at 1470K was investigated by X-ray emission and absorption spectroscopy (XES and XAS, respectively), being compared with that estimated by DV-X α molecular orbital calculation. The intercalation behaviors were then considered on the basis of electronic structure of BC_6N .

Experimental

Preparation of BC_xN ($x \geq 6$)

Films of the materials BC_xN ($x \geq 6$) were deposited on a carbon susceptor, which was heated by radio-frequency induction, by CVD method using acrylonitrile and boron trichloride as starting materials at a temperature in a range of 1470-2070K.

Intercalation of Li into BC_xN

The chemical intercalation was made in the dry box by a reaction of BC_xN powders with Li-naphthalene complex in THF or 2-MeTHF solution. The chemical intercalation was performed at 300K.

BC_xN powders mixed with acetylene black powders (10wt%) were used as the matrix of electrochemical intercalation of Li. 1M-LiPF₆ in EC (Ethylene carbonate) and DEC (Diethyl carbonate) mixed solvent (50 vol.%) was used as an electrolyte. Lithium metal was used as both counter and reference electrodes. Galvanostatic charge/discharge measurement was performed in a range of 3.00 and 0.01 V vs. Li/Li⁺ with a current density of 100 μ A/cm² at 300K.

XES and XAS measurements

Spectroscopic measurements of the soft X-ray emission and the absorption in the BK, CK and NK regions were performed at the advanced light source (ALS) of the Lawrence Berkeley National Laboratory (LBNL). X-ray emission spectra of the BC_6N prepared at 1470K (BC_6N -1470), together with h-BN, HOPG, and B₂O₃ as references, were measured by using a grating X-ray spectrometer installed in beamline BL-8.0.1. The total-electron-yield (TEY) X-ray absorption spectra of the material BC_6N -1470K were measured in BL-6.3.2 by monitoring the sample photocurrent. In both BL-8.0.1 and BL-6.3.2, the E -vector of the incident synchrotron radiation beams was in the horizontal plane. The samples were rotated around vertical axis, which varied the incident angles and allowed the measurements of angle-resolved X-ray spectra. In the X-ray emission measurements, the emission beam was perpendicular to the incident beam. The used take-off angles were 15, 45 and 75 deg. in the present study. In the X-ray absorption measurements, the used incident angles were 0, 45 and 75 deg.

Results and discussion

Silver metallic films were obtained on the carbon susceptor after the preparation. The composition of the material prepared at 1470K (BC₆N-1470K) was approximately BC₆N, which was detected by the usual combustion method for C, H, N determination and alkali melting followed by ICP emission spectrometry for B. The carbon contents of materials slightly increased with increasing the preparation temperature. Prepared materials had the graphite-like layered structure. The material BC₆N-1470K showed the highest crystallinity among the materials prepared in this study.

Chemical intercalation of Li into the BC_xN prepared at 2070K was observed in Li⁺C₁₀H₈⁻/2-MeTHF solution, resulting in formation of the first stage intercalation compound with an interlayer space (*d*-spacing) of 0.365nm. This value was slightly smaller than that (0.370nm) of first stage graphite intercalation compound (GIC). The material BC₆N-1470K performed electrochemical charge/discharge cycles similar to those of graphite in 1M-LiPF₆/EC+DEC solution.

Figure 1(right) shows TEY X-ray absorption spectra in the CK region of the material BC₆N-1470K. This figure suggests a conduction band of the material. By comparison between of the spectra in Fig.1 (right) and the calculated DOS spectra, the peak at lower energies (285-286eV) attributes to an unoccupied π* orbital, while the peaks at higher energies attributes to an unoccupied σ* orbital. The relative intensity of the unoccupied π* orbital increased with increasing the incident angle, indicating that the *ab* plane of the structure oriented parallel to the surface of film. The relative intensity of unoccupied π* orbital even in the high incident angle was smaller than that of graphite. Other XAS spectra in the BK and NK regions as well as the spectra in Fig.1 (right) were considerably different from those of graphite and h-BN, suggesting that hybridization of orbital among boron, carbon and nitrogen in the structure.

Figure 1(left) shows X-ray emission spectra in the CK region of the material BC₆N-1470K. This figure suggests a valence band of the material. The shoulder at higher energies (281-282eV) attributes to an occupied π orbital, while the peak at lower energies attributes to an unoccupied σ orbital. The relative intensity of the occupied π orbital decreased with increasing the take-off angle, which also indicated the anisotropic nature of the film described above. Unlike X-ray absorption spectra, the shapes of X-ray emission spectra (Fig.1-left) are rather similar to those of graphite. The relative intensity of occupied π orbital even in the low take-off angle was smaller than that of graphite. XES and XAS studies, therefore, suggested that small contribution of π electrons on their valence and conduction bands was observed for the electronic structures of BC₆N, in comparison with that of graphite.

DV-Xα molecular orbital calculation for the material could explain the distributions of bands measured by XES and XAS. The calculated spectra of BC₆N indicated that the valence band was mainly composed of C2p and N2p orbital, while the conduction band was made of C2p and B2p orbital. Almost no band gap was observed between the valence and conduction bands of BC₆N, according to the measured and calculated spectra.

The overlapping of bands and the existence of occupied π and unoccupied π* orbital could explain that the intercalation behavior of BC₆N was basically similar to that of graphite. ESCA study for the intercalation compounds of Li_yBC_xN, which was prepared by the chemical method, suggested that nitrogen in the BC_xN strongly interact with the intercalated Li. The *d*-spacing of first stage compound Li_yBC_xN slightly smaller than that of first stage GIC (LiC₆) could be explained by the strong interaction between the host BC_xN and the intercalated Li.

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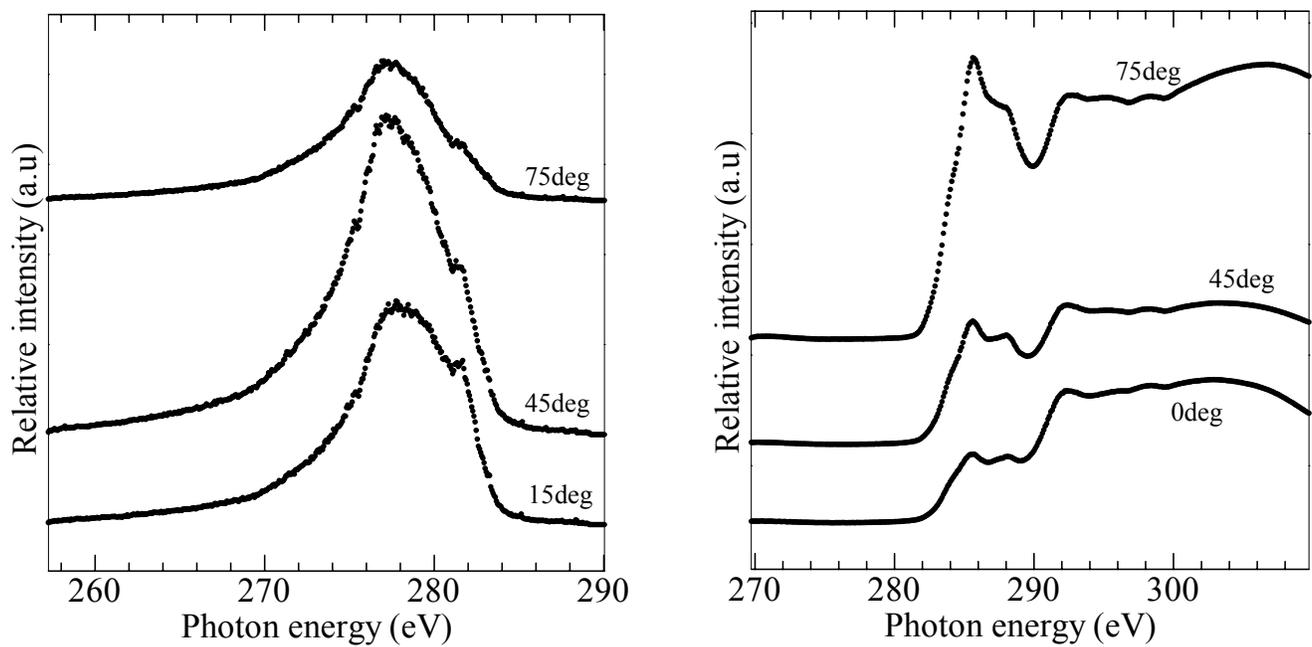


Figure 1. X-ray emission spectra (left) and TEY X-ray absorption spectra (right) in the CK region of BC₆N film. Take-off angles (left) and incident angles (right) are indicated in the figures.