NEXAFS study of heteroatom-doped hexagonal boron nitride

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Heteroatom doping into two dimensional materials is of interest. It is expected that the nanostructural control by the heteroatom doping leads to tailoring of the electronic and the physical property of two dimensional materials. We are developing a new technique for heteroatom doping by high-energy ion irradiation to the hetero-structure between the two-dimensional material and a thin film containing the heteroatoms intended for doping. In this study, near edge X-ray absorption fine structure (NEXAFS) measurements were conducted for fluorinated hexagonal boron nitride (*h*-BN) which was modified by high-energy ion irradiation.

h-BN was synthesized by conventional thermal chemical vapor deposition on a polycrystalline Cu foil [1]. After the *h*-BN growth, the specimens were introduced to an ultrahigh vacuum chamber and a 100 nm-LiF film was deposited on *h*-BN/Cu. The specimens prepared were then irradiated with 2.4 MeV 63 Cu²⁺ ions at room temperature using a tandem-type accelerator at the Research Institute for Applied Mechanics (RIAM), Kyushu University [2]. After the ion irradiation, the LiF overlayer was removed by water-rinsing.

NEXAFS measurements were conducted at the BL-8 of SR center at Ritsumeikan University. NEXAFS spectra of the irradiated samples were measured in partial electron yield by a microchannel plate detector with retarding grids. The incident angle of SR with respect to the surface plane was set to 30° in order to obtain the detailed information on π^* peaks of the B and N *K*edge spectra.

Figure 1 shows B and N *K*-edge NEXAFS spectra of ion-irradiated LiF/*h*-BN/Cu followed by the removal of the LiF overlayer. The peak **A** is assigned to the excitation of B 1*s* and N 1*s* \rightarrow π^* . The peaks **B** and **C** are assigned to the excitation of B 1*s* and N 1*s* $\rightarrow \sigma^*$. After the ion irradiation, new peaks appeared in the spectra. The peak **A**' at around 398.3 eV in the N *K*edge spectrum is originated from the interatomic interaction between N and Cu [3]. The peak A" (192.1 eV for B and 401 eV for N) can be assigned to the formation of bonding with F [4]. The peak A' appears significantly in the N Kedge spectrum. In contrast, the appearance of the peak A" is remarkable in the B K-edge spectrum. In addition, it should be noted that the finite F 1speak was observed in the XPS spectrum of ionirradiated h-BN/Cu (not shown here). The intensity ratio of the F 1s to N 1s peak amounts 5-7at% fluorination for 10¹⁴ ions/cm² ion irradiated h-BN/Cu. From the results described above we can represent the structural model for the reconstructed h-BN as shown in Fig. 2. Ion irradiation causes the formation of new B-F bonds in *h*-BN, which is consistent with the theoretical prediction [5]. The atomic reconstruction of *h*-BN promotes the interatomic interaction between N and Cu [3].

In conclusion, we have successfully controlled $_{\rm H}^{\rm C}$ the chemical modification of *h*-BN by high-energy ion irradiation of the LiF/*h*-BN/Cu heterostructure. NEXAFS analyses revealed that fluorination of *h*-BN is provided preferentially by the chemical reconstruction of *h*-BN under high-energy ion irradiation. We found that ion irradiation up to 10^{14} ions/cm² causes 5-7at% fluorination of *h*-BN by the formation of B-F bonds.

References

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Fig. 1 (a) B and (b) N *K*-edge NEXAFS spectra of 5×10^{13} and 10^{14} ions/cm² irradiated LiF/*h*-BN/Cu (red and green lines). For comparison, black-marked spectra of pristine LiF/*h*-BN/Cu are also included in the same figures.



Fig. 2 Structure model of fluorinated *h*-BN on Cu.