NEXAFS study of heteroatom-doped hexagonal boron nitride

Shiro Entani[1], Masaru Takizawa[2], Hiroshi Naramoto[1], and Seiji Sakai[1]

1) Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology, Tokai, Ibaraki 319-1195, Japan

2) Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Heteroatom doping into two dimensional materials is of interest. It is expected that the nano-structural 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 $^{63}Cu^{2+}$ 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 micro-channel 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* → π*. The peaks **B** and **C** are assigned to the excitation of B 1*s* and N 1*s* → σ*. 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 K-edge 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 1*s* peak was observed in the XPS spectrum of ion-irradiated *h*-BN/Cu (not shown here). The intensity ratio of the F 1*s* to N 1*s* peak amounts 5-7at% fluorination for 10^{14} ions/cm^2 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].

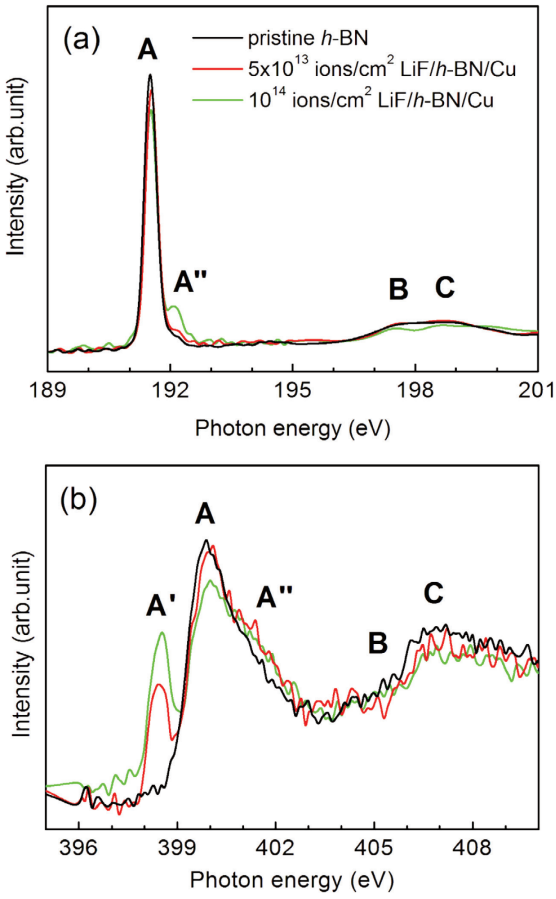

Fig. 1 (a) B and (b) N *K*-edge NEXAFS spectra of 5 × 10^{13} and 10^{14} ions/cm^2 irradiated LiF/*h*-BN/Cu (red and green lines). For comparison, black-marked spectra of pristine LiF/*h*-BN/Cu are also included in the same figures.

In conclusion, we have successfully controlled 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/cm^2 causes 5-7at% fluorination of *h*-BN by the formation of B-F bonds.

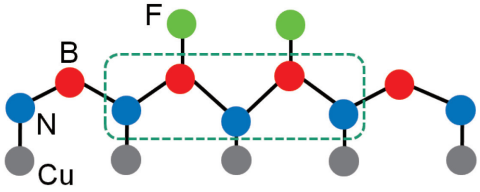

Fig. 2 Structure model of fluorinated *h*-BN on Cu.

References

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