

## Electronic states of superconducting boron-doped diamond by soft x-rays absorption and emission spectroscopy

Jin NAKAMURA\*<sup>1</sup>

<sup>1</sup>Univ. Electro-Commun. Chofugaoka, Chofu, Tokyo 182-8585, Japan

### Introduction

Since the discovery of superconductivity in heavily boron doped diamond (BDD)[1], a large number of experimental and theoretical studies have been performed[2]. From a theoretical viewpoint, character of hole states created by p-type dopant boron is still controversial: a rigid band like state or an impurity band. In the former model, the origin of the superconductivity of BDD might be based on conventional BCS model. On the other hand, in the latter case, a strong electron correlation will be important. From the experimental viewpoint, Yokoya et al. have measured ARPES using homo-epitaxially growth BDD and maintained that the result follows the rigid band model[3]. But the observed chemical shift is considerably smaller than the theoretical expectation. Furthermore, Umezawa et al., have pointed out a different boron concentration dependence on superconducting transition temperature ( $T_c$ ) between (100) and (111) oriented BDD samples[4].

In order to clarify the character of hole states of BDD, soft x-rays absorption (XAS) and emission spectra (XES) near B- and C-K edges were measured for the superconducting and non-superconducting BDD specimens[5]. The result shows clear hole states in XAS spectrum and almost no chemical shift, i.e., it does not follow the simple rigid band model. But the energy resolution of the previous experiment is not enough to discuss the small chemical shift of about 0.5 eV. In this report, results of high-resolution B- and C-K XAS and XES measurements are presented.

### Experimental

Homo-epitaxially growth BDD samples were synthesized on (111) and (100) oriented single crystalline diamond substrates by MPCVD method.[4] The values of  $T_c$  of heavily doped BDD samples are 7.0 and 2.8 K for (111) and (100) samples, respectively. The boron concentration ( $n_b$ ) of these two samples are 6% estimated from SIMS measurement. The other lightly doped (111) and (100) BDD samples,  $n_b \sim 0.7\%$ , do not show superconductivity above 2 K. The XAS and XES measurements were performed at BL-19B and 2C of KEK-PF. An excitation photon energy was about 400 eV for both B- and C-K XES measurements in order to get a maximum count rate at the fluorescence spectrometer. Then the present XES is incoherent spectrum. The energy resolutions were about 0.3 eV for both B- and C-K XES, and to about 0.2 and 0.3 eV for B- and C-K XAS measurements, respectively.

### Results and discussions

C-K XAS spectra of superconducting BDD show clear hole states. There are two characteristic peaks at around 283 and 284 eV. The small peak at 283 eV will be attributed to a hole state of carbon neighboring to dopant boron, because C 1s core level of carbon atom surrounding  $C_2B$  will be shallow compared with that surrounding  $C_3$  (ideal  $sp^3$  configuration). Because of this core shifted small component, it is hard to discuss whether a small chemical shift of main hole state peak at 284 eV exists or not. In (100) sample, an extra in-gap state at about 286 eV was observed. B-K XAS spectrum of lightly doped (111) sample shows clear hole state at 185 eV, but in (100) sample, this peaks shift higher energy side of about 1 eV and shows large in-gap states. In heavily doped BDD samples, both spectra are similar to each other with broaden 185 eV peak and in-gap states.

The overall feature of C-K XES spectra of all samples is same with that of non-doped diamond. The threshold at higher energy side corresponding to the energy of valence band maximum in non-doped diamond, shows no clear shift upon boron concentration. In lightly doped BDD samples, a small difference between (111) and (100) samples, but it disappears in heavily doped BDD samples. B-K XES spectra show same tendency with C-K XES spectra, but the difference between (111) and (100) samples is more remarkable in lightly doped samples. It suggests that there are two boron sites with different electronic structures and the prefer site synthesized on (111) substrate must play an important role of the superconductivity of boron doped diamond.

### Acknowledgement

I would like to thank Prof. T. Oguchi for theoretical band calculations. This work was partially funded by MST Japan.

### References

- [1] E.A. Ekimov et al., *Nature*, **428**, 542 (2004).
- [2] L. Boeri et al., *Phys. Rev. Lett.*, **93**, 23002 (2004), K.W. Lee and W.E. Pickett, *Phys. Rev. Lett.*, **93**, 23003 (2004), G. Baskaran, cond-mat/0404286.
- [3] T. Yokoya et al., *Nature*, **438**, 647 (2005).
- [4] H. Umezawa et al., cond-mat/0503303.
- [5] J. Nakamura et al., *Phys. Rev. B*, **70**, 245111 (2004), J. Nakamura et al., unpublished.

\* jin@pc.uec.ac.jp