Electronic Structures of Superconducting Diamond Films

Diamond, known as a jewel, exhibits outstanding physical properties, e.g., hardness, high thermo-conductivity, a wide band gap, and so on. Slightly doped diamond is a semiconductor and is often called a next generation semiconductor due to these properties that exceed those of other semiconductors [1]. In 2004, a Russian group reported superconductivity in a heavily boron-doped diamond [2]. The observation of the new property in diamond may promote application research for inventing new devices that utilize both the semiconducting and superconducting properties. Even fundamentally, superconductivity in diamond has stimulated a discussion on the origin of the metallic states responsible for the superconductivity [3]. This is because, even though the electric properties of lightly doped semiconductors are understood very well, those in highly doped semiconductors have not been fully understood.

In order to study the electronic structure of heavily boron-doped diamond, we have performed soft X-ray angle-resolved photoemission spectroscopy (SXARPES) for homoepitaxially grown heavily boron-doped (111) diamond films made by a microwave plasma assisted chemical vapor deposition method [4]. SXARPES is a unique experimental method that allows us to determine bulk-sensitive momentum(k)-resolved electronic states, namely electronic bands, of solids, by detecting the kinetic energy and direction of a photoelectron that is emitted from a sample being irradiated with a soft X-ray (Fig. 1). The measurements have been performed at beamline **BL25SU**, using an 825 eV photon energy with energy and angular resolutions of ~250 meV and ±0.1º.

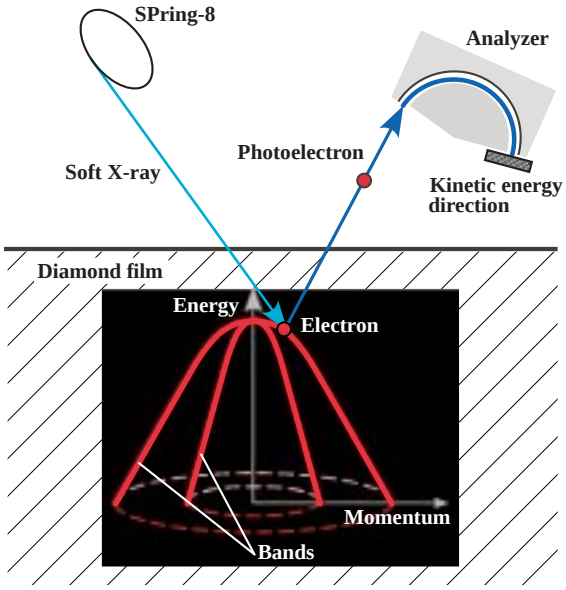

Fig. 1. Schematic illustration of SXARPES measurements.

Some of the physical parameters of three heavily boron-doped diamond films (BDD1, 2 and 3) are listed in Table 1. Figure 2(a) shows a valence band SXARPES intensity map from BDD2 measured along a blue curve in the Brillouin zone (Fig. 2(b)). In the map, higher intensity regions forming several curves correspond to experimentally determined bands. The shape of band dispersions is unique to a particular material (like a fingerprint of a person). Thus, from a comparison with calculated bands for pure diamond, one can find that the electronic structures of diamond retains with heavy boron doping [5].

It is known that the conducting properties of solids are determined by the electronic structures near the Fermi level (E_F), which is the highest occupied energy level. Boron doping dependent SXARPES intensity maps in the vicinity of E_F are shown in Figs. 3(a), 3(b), and 3(c). For BDD1, we clearly see three bands near E_F (1, 2, and 3) and find two bands 1 and 2 that form a parabolic-like dispersion having energy and intensity maxima at k = 0. As the boron concentration increases, the intensity of the top of the parabolic-like

Table 1. Transition temperatures, and boron and carrier concentrations of measured samples. $T_{c,mag.}$, onset of superconducting transition from magnetization measurement, $T_{c,res.}$, onset of superconducting transition from resistivity measurement. $n_{B,SIMS}$, boron concentration determined from secondary ion mass spectroscopy (SIMS). n_{PES}, carrier concentration estimated from present PES studies.

	BDD1	BDD2	BDD3
	Nonsuperconducting (T > 1.7 K)	$T_{c,res.}$ ~ 2.5 K	$T_{c,mag.}$ ~ 7.0 K
	2.88×10^{20}	1.18×10^{21}	8.37×10^{21}
		6.6×10^{20}	1.9×10^{21}

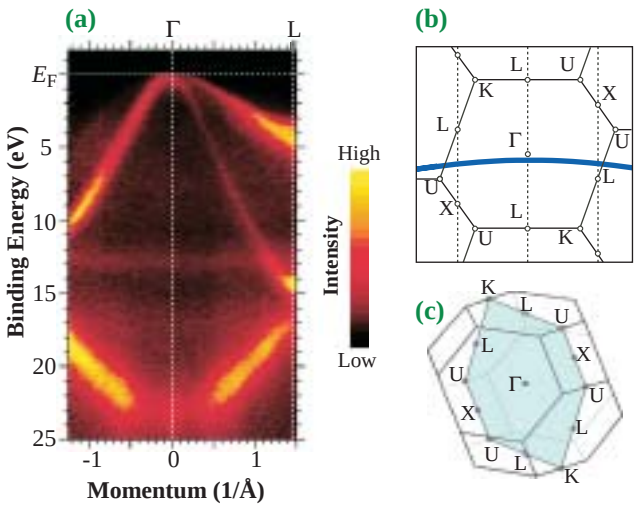

Fig. 2. **(a)** Valence band SXARPES intensity map of heavily boron-doped diamond film measured along a blue curve in two-dimensional Brillouin zone of diamond **(b)**, which is a slice (sky blue plane) of three-dimensional Brillouin zone **(c)**.

band decreases and, consequently, the intensity maps of BDD2 and 3 show local minima at k = 0 near E_F. For BDD3, the top of the parabolic-like band appears to be terminated, which is indicative of introducing holes into the top of the valence band. From comparisons with calculated band dispersions, the locations of E_F with respect to the top of the valence band were estimated to be 0.2 ± 0.1 eV for BDD2 and 0.4 ± 0.2 eV for BDD3 [5]. The systematic shift of E_F indicates increasing carrier numbers as a function of boron concentration. From a simple analysis of the observed data, the concentration of carriers can be also estimated (n_{PES}, in Table 1).

The doping-dependent SXARPES has shown that occupied electronic structures are consistent with the diamond bands and E_F shifts systematic with respect to the valence band. These results indicate that holes in the diamond bands play an essential role for the metallic properties of the heavily boron-doped diamond superconductor, and also provide a foundation for the possible development of diamond-based devices. Moreover, the present study demonstrates the usefulness and reliability of SXARPES for studying electronic structures of new materials. We hope that this study promotes further SXARPES works on various types of materials at SPring-8 in the near future.

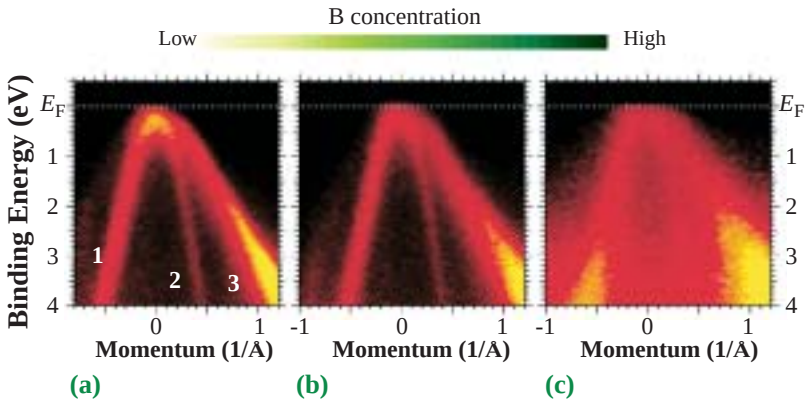

Fig. 3. **(a)-(c)** Near $_F$ SXARPES intensity maps of heavily boron-doped diamond fims with different boron concentrations.

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