

Photoemission Study of Electronic Structure Evolution across the Metal-Insulator Transition of Heavily B-doped Diamond

H. Okazaki,^{1,2} T. Arakane,³ K. Sugawara,⁴ T. Sato,³ T. Takahashi,^{3,4} T. Wakita,^{1,2} M. Hirai,¹ Y. Muraoka,^{1,2} Y. Takano,⁵ S. Ishii,⁵ S. Iriyama,⁶ H. Kawarada,⁶ T. Yokoya^{1,2}

¹*The Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan*

²*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Okayama 700-8530, Japan*

³*Department of Physics, Tohoku University, Sendai 980-8578, Japan*

⁴*WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

⁵*National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan*

⁶*School of Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan*

Abstract

We studied electronic structure evolution of heavily B-doped diamond films across the metal-insulator transition (MIT) by using ultraviolet photoemission spectroscopy (UPS). From high-temperature UPS, which can observe the electronic states near the Fermi level (E_F) up to $\sim 5 k_B T$ (k_B : Boltzmann constant and T : temperature), we observed the carrier concentration dependence of spectral shapes near E_F . From another carrier concentration dependent UPS, we found that the change in the energy position of sp -band of the diamond valence band, which corresponds to the shift of E_F , can be explained by the degenerate semiconductor model, indicating the diamond valence band is responsible for the metallic states for the samples with concentrations above MIT. We discuss a possible electronic structure evolution across MIT.

1. Introduction

In 2004, Ekimov *et al.* reported that heavily boron (B)-doped diamond is a superconductor with the transition temperature of ~ 4 K [1]. Superconductivity arises in heavily B-doped diamond when doping concentration exceeds a critical value ($3.0 \times 10^{20} \text{ cm}^{-3}$) of metal–insulator transition (MIT) [2]. The physical properties of lightly doped semiconductors are described in terms of band structures and impurity levels. However, the electronic structures of heavily doped semiconductors have not been understood very well. Thus, the discovery of superconductivity in heavily B-doped diamond has stimulated fundamental discussion on the origin of the metallic states responsible for the superconductivity: diamond valence band model [3-6] or boron induced impurity band model [7]. Soft x-ray angle-resolved photoemission spectroscopy shows that the valence band dispersions of heavily B-doped diamond clearly cross the Fermi level (E_F), indicating that holes formed at the valence band are responsible for the metallic states leading to superconductivity [8]. However, it is not known how the electronic structure of diamond changes across MIT. Therefore, it is important to directly observe the change in the electronic state across MIT using photoemission spectroscopy in order to further understand the mechanism of the superconductivity.

In this paper, we present photoemission study for investigating the change in the electronic structures across MIT of heavily B-doped superconducting diamond by using high-temperature ultraviolet photoemission spectroscopy (UPS). From the carrier concentration dependence of UPS spectra, we conclude that the change in the electronic state can be explained by the degenerate semiconductor model and the diamond valence band is responsible for the metallic states. We describe a possible electronic structure evolution across MIT.

2. Experimental

Homoepitaxially grown heavily B-doped diamond films were synthesized by a microwave plasma assisted chemical vapor deposition method as described elsewhere [9]. Hall measurements for these films gave hole concentrations (n_h) of 8.4×10^{17} , 3.8×10^{20} , 8.9×10^{20} , and $3.7 \times 10^{21} \text{ cm}^{-3}$,

respectively. T_c 's of the films were confirmed from the onset of the temperature dependence of magnetization measurements down to 2 K, and only the sample with n_h of $3.7 \times 10^{21} \text{ cm}^{-3}$ shows superconductivity with $T_c = 4.5 \text{ K}$.

High-temperature UPS measurements near E_F were performed by a Scienta SES200 electron analyzer. The vacuum pressure of the PES chamber during the measurements at 1000 K is below 1×10^{-9} Torr. The total energy resolution was set to 80 meV at $h\nu = 40.814 \text{ eV}$. UPS measurements for valence band were performed under the same conditions except for sample temperature (room temperature). E_F of the sample was referenced to that of a Mo substrate. Measurements were done after annealing at 1000 K under the ultrahigh vacuum to reduce oxygen-related contaminations on the surface.

3. Results and discussion

Figure 1(a) shows the valence band spectra from heavily B-doped diamond films at 1000 K. The intensities of these spectra are normalized with the area of valence band spectra. These spectra show monotonous decrease of intensities toward E_F without any anomaly, implying that impurity states might not be located around E_F . With increasing hole concentration, these spectra show increase of intensities at E_F . There is negligible intensity at E_F in the lowest concentration ($8.4 \times 10^{17} \text{ cm}^{-3}$) sample. The intensity at E_F for the sample with concentration near MIT ($3.8 \times 10^{20} \text{ cm}^{-3}$) increases, and it further increases with increasing hole concentration.

In Fig. 1(b), in order to see the change of electronic structure even above E_F , we divided the valence band spectra by the Fermi-Dirac (FD) distribution function at 1000 K, which is convoluted with a Gaussian with the instrumental resolution (80meV) [10]. The Boltzmann tail of the FD function, which comes from the thermal excitation of electrons near E_F , is drowned by the background intensity above E_F around $\sim 5 k_B T$ (k_B : Boltzmann constant and T : temperature). Since this procedure takes away FD function from UPS spectra, we obtained the density of states (DOS) including unoccupied level. Here is obtained the DOS up to about - 0.4 eV binding energy. In the

lowest concentration ($8.4 \times 10^{17} \text{ cm}^{-3}$) sample, there is negligible intensity region below and above E_F , consistent with the fact that diamond with carrier concentration much less than MIT is in semiconducting states. In the middle concentration ($3.8 \times 10^{20} \text{ cm}^{-3}$) sample, which is very close to MIT, there is a minimum of DOS near E_F and increase from E_F to - 0.4 eV. The increase of DOS above E_F may be a part of impurity states. In the highest concentration ($3.7 \times 10^{21} \text{ cm}^{-3}$) sample, the intensity at E_F is the highest in all spectra and decreases toward - 0.2 eV with almost constant intensity from - 0.2 to - 0.4 eV. This result indicates that the diamond valence band is responsible for metallic state in carrier concentration over MIT. With increasing hole concentration, E_F may gradually approaches the valence band of diamond and move away from impurity states. The possible coincidence of the energy positions of the minimum of DOS and E_F observed for the heavily B-doped diamond with hole concentration near MIT may be important for understanding MIT in diamond. In order to establish this behavior, further study is worth trying.

In order to estimate the hole concentration dependence of E_F shift, we investigated the energy positions of *sp*-band that forms a peak in the valence band spectrum of diamond [11]. Figure 2(a) shows lower binding energy shift of *sp*-band with increasing hole concentration, which seems consistent with the shift of those spectra in Fig. 1. This indicates that the change of electronic structure of diamond can be explained by the simple rigid band shift. This result is in line with the ARPES results [8]. Considering the simple rigid band shift, the shift of the peak positions corresponds to the shift of E_F . This indicates that E_F gradually shifts toward the valence band of diamond with increasing hole concentration. In Fig. 2(b), the shift of the peak position is compared with that of the calculated chemical potential position against valence band maximum in degenerate semiconductor [12] of each concentration. Here we superimposed the calculated value to the experimental energy shift for the sample near MIT. The value of the peak shift for samples over MIT is in good agreement with that of a simple degenerate semiconductor model. This result shows that E_F shift of heavily B-doped diamond can be explained by a simple degenerate semiconductor model in which the valence band near E_F is not remarkably disturbed by the impurity states except

near the band edge. Thus, we found that the electronic structure near E_F with the concentration over MIT can be explained by the undisturbed valence band of pristine diamond in the first approximation.

Based on these experimental results, we present following schematic picture for the evolution of the electronic structure for B-doped diamond with hole concentration across MIT, as shown in Fig. 3. In much lower concentration than MIT, the electronic structure of diamond can be explained by the valence band of pristine diamond only, since there is negligible intensity region near E_F and diamond is not metallic yet, as shown in Fig. 3(a). In carrier concentration near MIT, there is minimum intensity near E_F and increase from E_F to -0.4 eV, indicating that the impurity state is much away from E_F , as shown in Fig. 3(b). In addition, E_F position is in the valence band different from that of the diamond with much lower carrier concentration and can be explained by the simple degenerate semiconductor model, indicating that E_F relocates in the undisturbed valence band. In larger concentration than MIT, which shows the superconductivity, E_F additionally shifts in the valence band by more doping and can be also explained by the simple degenerate semiconductor model. Moreover, its electronic structure near E_F can be described by the valence band stemmed from pristine diamond only since there is monotonous decrease toward -0.4 eV with no anomaly, as shown in Fig. 3(c). These results indicate that E_F relocates in the diamond valence band in the concentration over MIT and holes are formed at the diamond valence band, which are responsible for the metallic states with superconductivity [1,2], as well as the results of ARPES study [8].

4. Conclusions

We studied electronic structure evolution of B-doped diamond across the MIT by using UPS. From high-temperature UPS, we observed the carrier concentration dependence of spectral shapes near E_F . From carrier concentration dependent UPS, we found that the shift of E_F can be explained by the degenerate semiconductor model, indicating the diamond valence band is responsible for the metallic states for the samples with concentrations above MIT. We discussed the possible electronic

structure evolution across MIT.

Acknowledgements

This work was supported partly by a Grant-in-Aid for Scientific Research of the Ministry of Education, Culture, Sports, Science and Technology, Japan (20340091).

Figure captions

Fig. 1. (a) Hole concentration dependence of valence band spectra near E_F at 1000 K from B-doped diamond. (b) Hole concentration dependence of valence band spectra divided by the FD function, which is convoluted with a Gaussian with the instrumental resolution.

Fig. 2. (a) Hole concentration dependence of peak position of sp -band of B-doped diamond. (b) A comparison of the energy shift induced by hole doping. Circles show the shift of the sp -band peak position, corresponding to E_F shift, of B-doped diamond. Triangles show calculated chemical potential positions against the top of valence band in a degenerate semiconductor [11].

Fig. 3. Experimentally-inferred electronic structure evolution of heavily B-doped diamond with B doping. A schematic picture of the electronic structure of diamond (a) with carrier concentration much less than MIT, (b) with carrier concentration near MIT, and (c) with carrier concentration more than MIT. In (b), further B-doping leads to acceptor impurity states near the top of the valence band.

References

- [1] E. A. Ekimov *et al.*, Nature **428**, 542 (2004).
- [2] Y. Takano *et al.*, Diamond Relat. Mater. **14**, 1936 (2005); Y. Takano *et al.*, J. Phys.: Condens. Matter **21**, 253201 (2009).

- [3] L. Boeri, J. Kortus and O.K. Andersen, Phys. Rev. Lett. **93**, 237002 (2004).
- [4] K.-W. Lee and W.E. Pickett, Phys. Rev. Lett. **93**, 237003 (2004).
- [5] X. Blase et al., Phys. Rev. Lett. **93**, 237004 (2004).
- [6] H.J. Xiang et al., Phys. Rev. B **70**, 212504 (2004).
- [7] G. Baskaran, J. Supercond. Nov. Magn. **21**, 45 (2008).
- [8] T. Yokoya *et al.*, Nature **438**, 647 (2005); H. Okazaki *et al.*, J. Phys. Chem. Solids **69**, 2978 (2008).
- [9] Y. Takano *et al.*, Appl. Phys. Lett. **85**, 2851 (2004).
- [10] T. Greber *et al.*, Phys. Rev. B **79**, 4465 (1997).
- [11] J.J. Pireaux and R. Caudano, Phys. Rev. B **15**, 2242 (1977).
- [12] C. Kittel and H. Kroemer, Thermal Physics (W. H. Freeman and Company, San Francisco and London, 1980).

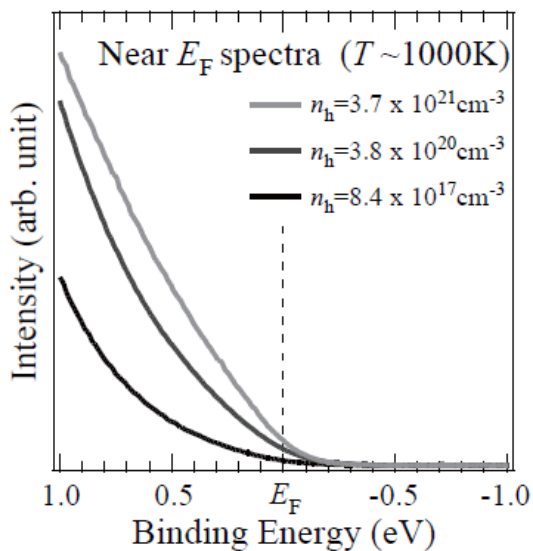


Fig. 1(a)

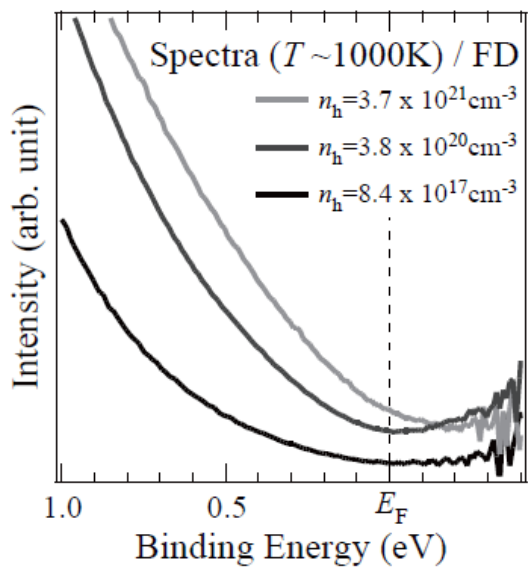


Fig. 1(b)

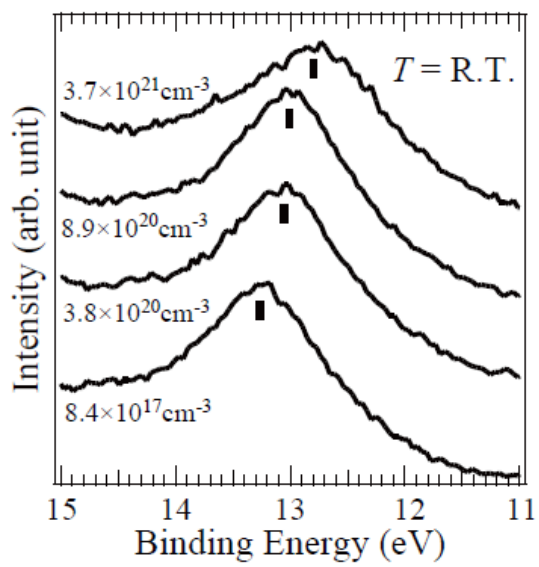


Fig. 2(a)

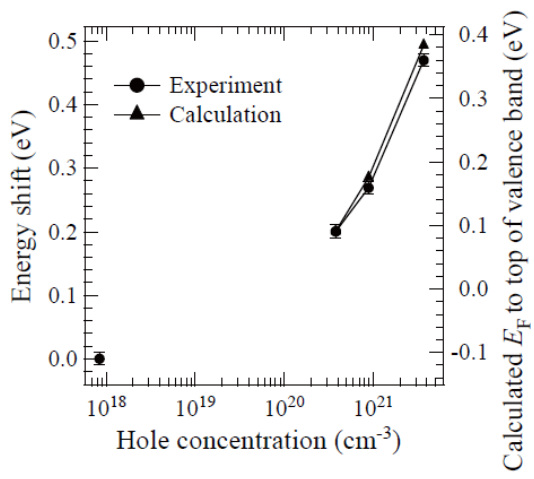


Fig. 2(b)

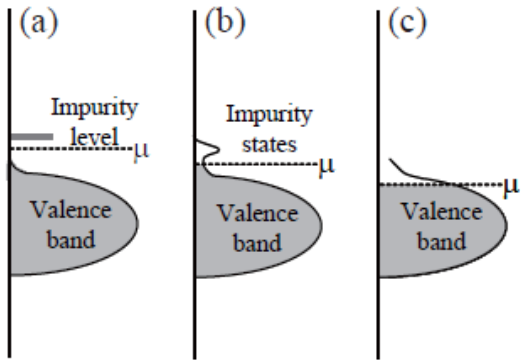


Fig. 3