Laser-excited photoemission spectroscopy study of superconducting boron-doped diamond

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Abstract

We have investigated the low-energy electronic state of boron-doped diamond thin film by the laser-excited photoemission spectroscopy. A clear Fermi-edge is observed for samples doped above the semiconductor–metal boundary, together with the characteristic structures at 150 meV possibly due to the strong electron–lattice coupling effect. In addition, for the superconducting sample, we observed a shift of the leading edge below $T_c$ indicative of a superconducting gap opening. We discuss the electron–lattice coupling and the superconductivity in doped diamond.

1. Introduction

Recently, a striking discovery of the superconductivity was reported in boron-doped diamond [1]. Pure diamond is a typical $sp^3$ covalent system that behaves as a transparent band insulator with a gap of 5.5 eV. By doping boron (B) as an acceptor, the diamond acts as a $p$-type semiconductor and then goes across the insulator–metal (Mott) transition at $n_{MI}^{B} \approx 2 \times 10^{20}$ cm$^{-3}$, accompanied by the superconducting phase [2,3]. There are several theoretical scenarios suggested so far regarding the superconducting mechanism in this compound. One is based on the strong coupling among the doped holes at Brillouin zone center ($\Gamma$-point) and the optical phonon mode arising from the covalency, which is analogous to MgB$_2$ [4,5]. Actually, the small hole-like Fermi sphere and the phonon softening at $\Gamma$-point are recently confirmed by the angle-resolved PES [6] and inelastic X-ray [7] measurements, respectively, which seem to support the above models. On the other hand, there is a theoretical study considering the boron impurity band for its low-energy electronic background, which behaves as a half-filled narrow band near the Mott transition [8]. In this scenario, the strong correlation effect plays the role of the pairing mechanism.

In this study, we investigated the low-energy electronic structure of the B-doped diamond to clarify the characteristics of the superconductivity as well as the nature of the doped carriers. Photoemission spectroscopy (PES) directly probes the occupied density of states, which brings us substantial information for the above purpose. By using the ultrahigh resolution (sub-meV) laser-excited PES, we succeeded in the observation of the superconducting gap below $T_c$. In addition, we found periodic phonon-derived structures in the PES for metallic samples. We discuss our result in terms of the strong electron–lattice coupling in this system.
Table 1
Characterization of the B-doped diamond samples

| Sample | \( n_B \) (cm\(^{-3}\)) | Electrical property | Synthesis          |
|--------|-----------------|--------------------|--------------------|
| BDD1   | \( 3.5 \times 10^{19} \) | Insulating         | HTHP (single)      |
| BDD2   | \( 1.75 \times 10^{20} \) | Weakly insulating  | CVD (poly)         |
| BDD3   | \( 6.53 \times 10^{21} \) | SC, \( T_C = 5 \text{ K} \) | CVD (poly)         |
| BDD4   | \( 8.37 \times 10^{21} \) | SC, \( T_C = 6.6 \text{ K} \) | CVD (single)       |

2. Experiment

The B-doped diamond (BDD) samples we used for our measurement are characterized in Table 1. Here \( T_C \) is the superconducting transition temperature determined by the magnetization measurement. BDD1 is a single crystal grown by high-temperature high-pressure (HTHP) synthesis, and other heavily doped samples are thin films obtained by a microwave plasma-assisted chemical vapor deposition (CVD) method as described elsewhere [9,10]. BDD2–BDD3 are poly-crystalline thin film grown on Si while BDD4 is a single-crystal homo-epitaxially grown on pure diamond (1 1 1) substrate. The boron concentration was determined by the secondary ion mass spectroscopy method. PES measurements were performed using a system constructed with the Scienta R4000 electron analyzer and an ultraviolet \((h\nu = 6.994 \text{ eV})\) laser for the incident light [11]. The temperature was precisely controlled from room temperature down to 4.5 K using a flow-type He liquid refrigerator. The base pressure of the chamber was below 10\(^{-7}\) Torr throughout all the measurements. We annealed the samples before the measurement at 400 °C in the vacuum of \(<10^{-7}\) Torr. This procedure increased the photoelectron intensity near the Fermi level \((E_F)\) for about a factor of 10 times, while not changing the spectral shape. Since we could not catch clear evidence of angle-resolved \((k\text{-dispersed})\) signal for single-crystalline samples, all measurements were performed with an angle-integration mode. The energy resolutions were \(\Delta E\sim 3.7\) and 0.7 meV for respective measurements on \(n_B\)-dependence (BDD1–BDD3) and superconducting gap observation (BDD4). The Fermi level \((E_F)\) of the sample was referred to that of the Au film evaporated on the sample substrate. Raman scattering spectroscopy was performed to obtain phonon spectra for BDD1–BDD3 at room temperature using He–Ne laser (633 nm) as the incident light.

3. Results and discussion

Fig. 1 shows the photoemission spectra at 4 K for samples BDD1–BDD3. For BDD1, which is still highly insulating, the measurement was performed at room temperature to avoid the effect of charging caused by the loss of electrons. Since the normalization of spectral intensity is difficult solely in this energy region, we simply normalized them at the binding energy of 0.6 eV in Fig. 1.

The PES for BDD1 shows long tail-like states indicative of disordered \(p\)-type semiconductor, without any evidence of Fermi edge. For BDD2, which is just on the verge of the insulator–metal transition \((n_B^\text{MI}\sim 2 \times 10^{20} \text{ cm}^{-3})\), we already observe a small Fermi edge. To show the appearance of the Fermi edge more clearly, the PES near \(E_F\) for BDD1-2 are enlarged and plotted on the upside of Fig. 1. The emergence of the Fermi-edge shows the degenerate metallic property for samples with \(n_B\gtrsim n_B^\text{MI}\). The resistivity shows that BDD2 still behaves as a weak insulator, which may be attributed to the sample inhomogeneity or localization effect. We note that in any of the PES for BDD1–BDD3, there is no indication of a narrow impurity band (or any in-gap state) near the Fermi level, which is discernible separately from the valence band. The rapid increase of intensity in a wide-energy region on increasing \(n_B\) seems to be naturally understood as the result of the rigid band chemical potential shift of \(\Delta\mu\sim 0.2 \text{ eV}\) across the insulator–metal transition observed in a recent angular-resolved PES study [6].

In addition to the Fermi edge, we also recognize some characteristic features at around \(E_B = 150\), 300, and 450 meV for BDD2–BDD3. Apparently, it has a certain periodicity denoted as \((150 \times n) \text{ meV} (n = 1, 2, 3, \ldots)\). Such a periodic structure brings us about the possibility of phonon satellites arising from strong electron–lattice coupling in this hole-doped diamond system. They are actually observed in the case for H\(_2\) molecule \((\text{H}_2 \rightarrow \text{H}_2^+)\) photoemission spectrum [12], the “0-0” peak at \(E_0\) and the satellites at \(E = E_0 – n\omega_0\) with the characteristic energy of the oscillator \(\omega_0\). The “0-0” peak corresponds to a transition between the ground states of the neutral and of the ionized system, while the satellites reflect the transitions.
to vibrationally excited states. Recently, the anomalously broad spectral shape in the valence band (angle-resolved) PES observed in various transition metal oxides, including high-$T_c$ cuprates, are also discussed in terms of the broadening effect arising from the strong electron–phonon coupling [13,14]. This is the first case, however, that such lattice-derived oscillation is actually observed in the valence band PES.

It is well known that there are optical phonon branches in the non-doped diamond corresponding to the bond stretching vibration mode, which are triply degenerate at $I$-point ($Q = 0$) with energy of 164 meV [15]. It gives rise to an unique Raman-allowed optical phonon mode ($A_g$). In Fig. 2, we show the PES of BDD3 together with the phonon spectra obtained by Raman scattering spectroscopy measurement. For the Raman spectrum of undoped diamond (broken curve), an intense 1-phonon peak is observed at 164 meV as mentioned above. The broad feature at around 300 meV corresponds to the 2-phonon spectrum [16]. At the first glance, the energy positions of the step-like feature in PES and the 1-phonon peak structure in Raman spectra show a good correspondence with each other. In BDD3, new features around 60 and 150 meV appear in Raman spectrum. Though fairly well studied till now, their origins are not yet fully clarified [17]. Here we focus on the boron-doping effect on the 1-phonon peak at 164 meV. We can recognize it becomes rapidly broad and asymmetric with softening, as shown in Fig. 3. They are indicative of Fano-type resonance [17], which tends to appear when a discrete energy state like an optical phonon couples to conductive carriers. A recent inelastic X-ray scattering study also reports the characteristic phonon softening ($\sim 7$ meV) and broadening (FWHM $\sim 17$ meV) on increasing $n_B$, mainly observed in the optical phonon dispersion at around $I$-point [7]. These results indicate the strong coupling of doped holes to the optical phonon which is qualitatively expected in VCA numerical calculations [4,5]. Such scenario may also account for our results. At the same time, however, we cannot rule out the possibility of carriers strongly coupling to the B–C local vibration mode, which is expected to be important in the supercell calculations [18,19]. To discuss the local mode in B-doped diamond, more experimental studies seem to be necessary in future works.

Now we show the PES of the superconducting state observed in a homoepitaxially grown single-crystalline B-doped diamond thin-film BDD4 (Fig. 4). The superconducting transition of this sample observed in the magnetization measurement is fairly broad with the onset transition temperature $T_c = 6.6$ K. On decreasing temperature from 15 K, a slight shift of the spectral edge can be observed in Fig. 4. Such temperature dependence is indicative of a gap opening at $E_F$, which is a clear evidence of the bulk superconductivity in this sample. Even at the lowest temperature 4.5 K, nevertheless, quasiparticle peak is hardly recognizable. We tried to estimate the gap value by fitting the PES using the Dynes function represented with the superconducting gap and broadening parameters.
\( A \) and \( \Gamma \) [20], as
\[
D(E_B, A, \Gamma) = \text{Re} \frac{E_B - i\Gamma}{\sqrt{(E_B - i\Gamma)^2 - \Delta^2}}.
\]

The best-fitted result is shown in Fig. 4 as the solid curve, with the parameters \( \Delta = 0.78 \text{ meV} \) and \( \Gamma = 0.7 \text{ meV} \). We note that \( \Gamma \) is remarkably large; \( \Gamma \approx A \), which is already not suitable for applying the Dynes function. This is in contrast to the previously reported scanning tunneling spectroscopy (STS) study, where a BCS-type weak-coupling superconducting gap spectrum (\( 2\Delta_0 = 3.5k_B T_c \)) with well defined quasiparticle peaks is observed in CVD (1 1 1) thin film with \( T_c = 1.9 \text{ K} \) [21]. Very recently reported STS results on (1 1 1) thin film, on the other hand, exhibits a broad superconducting gap feature fairly alike to that of our PES measurement [22]. This discrepancy among (1 0 0) and (1 1 1) thin films may be explained by the sample inhomogeneity which is reported to become serious in (1 1 1) thin films, particularly in the heavily B-doped region [23]. Further investigation with more homogeneous sample remains to be elucidated in future works. Finally, we estimate the reduced gap from our PES result. We obtain from \( \Delta(4.5 \text{ K}) = 0.78 \text{ meV} \) and \( T_c = 6.6 \text{ K} \) that \( \Delta_0 = 1.78k_B T_c \) with \( \Delta_0 = 1.01 \text{ meV} \). Thus, \( \Delta \) must be representing the rough average of the local superconducting gap in the laser spot area, i.e. several hundreds micron in diameter, which is well related in a weak-coupling regime with \( T_c \) possibly reflecting the percolation temperature of the superconducting current in this sample.

4. Summary

In conclusion, we have performed a ultrahigh resolution photoemission spectroscopy measurement to elucidate the near-\( E_F \) electronic structure of boron-doped diamond. For the highly doped samples with \( n_h \gtrsim n_h^\text{M} \) (insulator–metal transition), we observed the appearance of a clear Fermi-edge indicating the degenerate metallic quality. In such metallic samples, characteristic phonon features at \( \sim 150 \times n \text{ meV} \) are recognized. It indicates the importance of the strong electron–phonon coupling in this system. Regarding the superconducting state, we observed the formation of the superconducting gap below \( T_c \). Possibly due to the disorder effect, a clear quasiparticle peak is not discernible even at 4.5 K. The dominant size of the gap, though under an uncertainty due to the lack of quasiparticle peak, is estimated to be about \( \Delta = 0.78 \text{ meV} \) at 4.5 K.

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