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Observation of a Superconducting Gap in Boron-Doped Diamond by Laser-Excited Photoemission Spectroscopy

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We investigate the temperature (T)-dependent low-energy electronic structure of a boron-doped diamond thin film using ultrahigh resolution laser-excited photoemission spectroscopy. We observe a clear shift of the leading edge below $T = 11$ K, indicative of a superconducting gap opening ($\Delta \sim 0.78$ meV at $T = 4.5$ K). The gap feature is significantly broad and a well-defined quasiparticle peak is lacking even at the lowest temperature of measurement ($=4.5$ K). We discuss our results in terms of disorder effects on the normal state transport and superconductivity in this system.

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Diamond is a very good example of an sp^3 bonded covalent system and has attracted significant attention due to its unique properties. It is the hardest known material and behaves like a typical band insulator with a gap of 5.5 eV. It exhibits high thermal conductivity owing to its high Debye temperature, and is considered important for electronic applications. Boron (B) doping in diamond results in a p -type semiconductor, with the acceptor states displaying an activation energy of 0.37 eV. On increasing the B concentration (n_B), the system undergoes an insulator-metal transition at $n_B^{\text{MI}} \sim 2 \times 10^{20} \text{ cm}^{-3}$. The recent discovery of superconductivity ($T_c \sim 2$ K) in diamond for B concentrations above n_B^{MI} is indeed a striking result [1]. The use of chemical vapor deposition (CVD) as a technique for growing B-doped diamond (BDD) crystals, has resulted in improved sample quality with higher T_c 's [2–6]. This has led to a variety of experimental studies on BDD, with new opportunities for device applications using diamond related materials.

From the theoretical side, several scenarios have been proposed. Band-structure calculations within the virtual crystal approximation (VCA) [7,8] predict that the top of the host diamond valence band at Γ point is shifted above the Fermi level in the metallic region (e.g., 0.61 eV shift for 2.5% hole doping in [8]). The holes at the small pocket around Γ point strongly couple to the optical phonon with ~ 160 meV, and give rise to a BCS-type superconductivity. From experiments, a rigid shift of the valence band and phonon softening at the Γ point have been recently confirmed by angle-resolved photoemission spectroscopy (ARPES) [9] and inelastic x-ray [10] measurements, respectively. These results suggest that the above models are at least qualitatively valid for BDD. Recent supercell cal-

culations point out the importance of the boron site in the structure, which leads to a large local density of states (DOS) at E_F (though smaller than the total DOS of carbon) and modifies the host diamond band by its randomness [11,12]. These calculations also show that the local B-C vibration mode will significantly contribute to the electron-phonon coupling constant λ . In contrast, there is a theoretical report which is entirely based upon the half-filled narrow B-impurity band as schematically realized in the Mott transition picture [13]. This scenario will produce a dirty superconducting (SC) state with an extended s -wave gap due to an exotic pairing interaction, namely, the resonating-valence-bond (RVB) mechanism, derived from strong correlations. In this study, we investigate the low-energy electronic structure of BDD to clarify the characteristics of the superconductivity realized in this doped semiconductor system, by using ultrahigh resolution laser-excited photoemission spectroscopy (PES).

PES measurements were performed using a system constructed with a Scienta R4000 electron analyzer and an ultraviolet ($h\nu = 6.994$ eV) laser for the incident light [14]. The escape depth of the photoelectron in this energy region (i.e., kinetic energy of $2 \sim 3$ eV) attains a large value of ~ 100 Å [15], which enables bulk-sensitive measurements. The base pressure of the chamber was below $\sim 5 \times 10^{-11}$ Torr throughout all the measurements. We annealed the samples before the measurement at 400 °C in a vacuum of $< 10^{-7}$ Torr. This procedure increased the photoelectron intensity near the Fermi level (E_F) by about a factor of 10 times, with no changes in spectral shape. All measurements were performed in an angle-integrated mode. The Fermi level (E_F) of the sample was referred to that of the Au film evaporated on the sample substrate.

The energy resolution was $\Delta E = 0.7$ meV, which we obtained from the Fermi edge of Au as well as that measured for the normal state (13.5 and 15.5 K) of BDD.

The BDD sample we used for our measurement was obtained by a microwave plasma-assisted CVD method, which was grown homoepitaxially on an undoped (1 1 1) oriented diamond substrate [5]. The boron concentration determined by the secondary ion mass spectroscopy method is $n_B = 8.4 \times 10^{21} \text{ cm}^{-3}$, which corresponds to B/C ratio of 5%. The carrier density estimated by the Hall coefficient simply assuming $R_H = (n_H e)^{-1}$ is $n_H = 1.3 \times 10^{22} \text{ cm}^{-3}$, which tends to get greater than n_B on increasing the doping level. Such R_H behavior and its relationship with the carrier scattering mechanism is often reported in degenerate semiconductors, which will be discussed in another publication [16]. We show in Fig. 1 the resistivity ρ and magnetization curves for the BDD sample. The SC transition temperature of this sample determined from the Meissner response is $T_c^m = 6.6$ K, as indicated in the inset of Fig. 1(b). The diamagnetic response keeps increasing on lowering temperature (T) down to 2 K without any sign of saturation, reflecting the disordered nature of the super-

conductivity. The resistivity, on the other hand, steeply starts decreasing at 8.2 K and becomes zero at $T_c^{\text{off}} \sim 7$ K. In the inset of Fig. 1(a), the conductivity $\sigma = \rho^{-1}$ is shown. There is another characteristic temperature $T_0 \sim 11$ K where σ starts to deviate from that of the normal state realized under a magnetic field ($H = 9$ T) [17], which will be discussed later.

Indications of the diffusive carrier dynamics in this system can be observed in the normal-state resistivity, which weakly increases on lowering T with the values of $\rho(300 \text{ K}) = 0.59 \text{ m}\Omega \text{ cm}$ (not shown) and $\rho(10 \text{ K}) = 0.68 \text{ m}\Omega \text{ cm}$. In fact, the normal-state conductivity ($H = 9$ T) at $T < 20$ K can be well expressed by $\sigma(T) = \sigma_0 + AT^{1/2}$ with $\sigma_0 = 1435 \Omega^{-1} \text{ cm}^{-1}$ and $A = 11.5 \Omega^{-1} \text{ cm}^{-1} \text{ K}^{-1/2}$, as indicated with a solid curve in Fig. 1(a) inset. Such $T^{1/2}$ behavior is characteristic of a disordered Fermi liquid with long-range Coulomb interaction effect [18,19], which has been often discussed in doped semiconductor systems around the metal-insulator transition (e.g., B-doped Si [20]). Further we estimate the carrier mean free path from $l = \frac{\hbar k_F \tau}{m^*} = \frac{\hbar k_F}{ne^2 \rho}$ and $k_F = (3\pi^2 n)^{1/3}$ in a simple free-electron picture. Substituting $\rho(300 \text{ K})$ and n_B for the carrier density n , we obtain $l = 5.2 \text{ \AA}$ whereas the Hall mobility is $\mu_H = 0.8 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. l is comparable to the cubic lattice parameter $a = 3.57 \text{ \AA}$ [5], indicating that this system is fairly close to the Mott-Ioffe-Regel limit [21]. On the other hand, the SC coherence length of the present BDD sample estimated from the upper critical field H_{c2} is $\xi \sim 60 \text{ \AA} > l$ [5], which classifies it as a dirty superconductor. Here we note that in a lower-doped sample with $n_B = 1.18 \times 10^{21} \text{ cm}^{-3}$ and onset $T_c = 2.78$ K, we obtain $\mu_H = 2.4 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and the estimated value of $l = 5.8 \text{ \AA}$ by using $\rho(300 \text{ K}) = 1.96 \text{ m}\Omega \text{ cm}$ [16]. The clear decrease in mean free path and mobility on increasing boron doping, confirms increase of disorder induced by impurities.

Figure 2 shows the PES of the SC state observed in the BDD sample. With decreasing T from 15.5 K, a slight shift of the spectral edge can be observed below 9.5 K [see the enlarged plot in Fig. 2(b)]. Along with the shift, the spectral shape becomes slightly convex downward at E_F . Such T dependence is indicative of a gap opening at E_F , which is a clear evidence of the mass superconductivity in this sample. Even at the lowest T (4.5 K), however, a considerable amount of DOS at E_F remains and a clear quasi-particle (QP) peak cannot be observed. We tried to estimate the gap value at 4.5 K by fitting the PES using the Dynes function [22] for the DOS represented with the isotropic (s wave) SC gap and the phenomenological broadening parameters Δ and Γ , as $D(E_B, \Delta, \Gamma) = \text{Re}[(E_B - i\Gamma)/\sqrt{(E_B - i\Gamma)^2 - \Delta^2}]$. For the curve fitting, we multiplied the Dynes function with the Fermi-Dirac distribution function, and then convolved it with a Gaussian function corresponding to the energy resolution of $\Delta E = 0.7$ meV. The best-fit result is shown in Fig. 2(c) as the red curve,

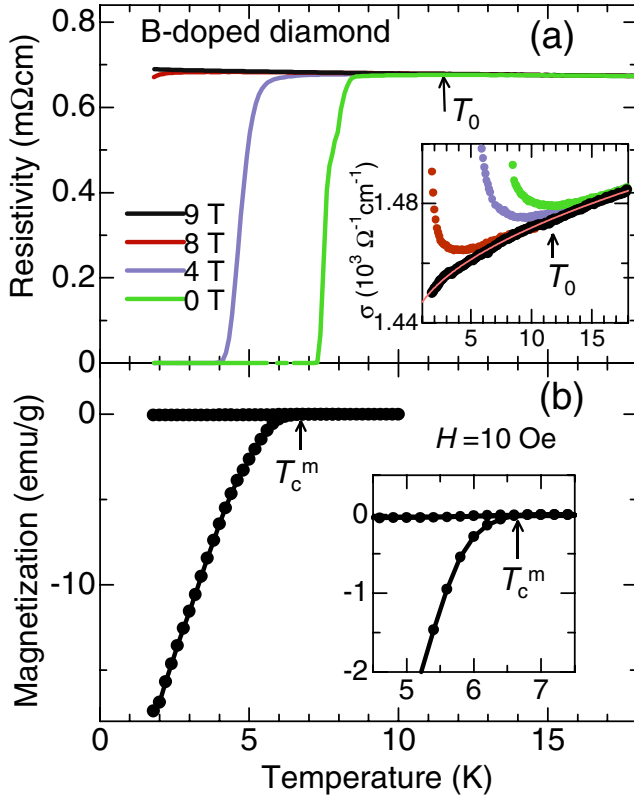


FIG. 1 (color online). (a) T dependence of the resistivity ρ in BDD. The inset shows the conductivity $\sigma = \rho^{-1}$ with the power law fit (solid curve) to the normal-state ($H = 9$ T) data. (b) T dependence of the magnetization with inset showing the magnification of the region near the SC transition. T_0 shows the temperature where σ starts to deviate from that of the normal-state behavior, whereas T_c^m represents the onset temperature of the Meissner response.

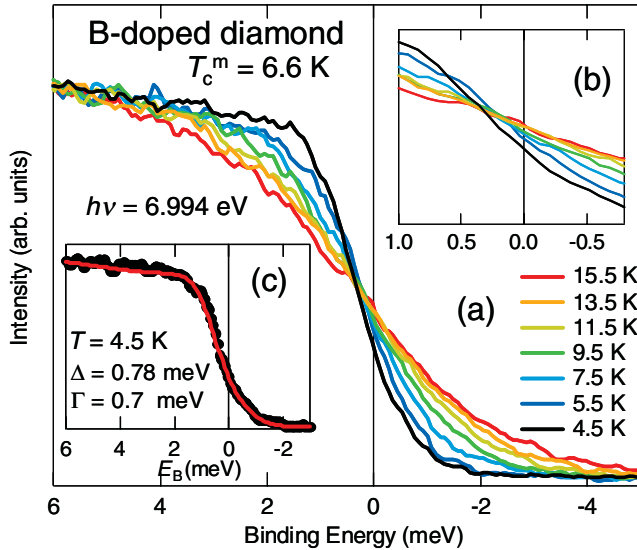


FIG. 2 (color). T dependence of the ultrahigh resolution PES in BDD (a). Enlarged plot around E_F is shown in (b). (c) shows the PES at 4.5 K indicated together with the fitting result.

with the parameters $\Delta = 0.78$ meV and $\Gamma = 0.7$ meV. We note that Γ is remarkably large, $\Gamma \approx \Delta$, which accounts for the large DOS at E_F and the hardly recognizable QP peak. Because of the observed spectral shape, it is impossible at present to discuss the SC gap symmetry, whether it is simple s wave or not, solely from our result. However, we can still estimate the reduced gap $\Delta(0)/k_B T_c$ from our result at the lowest T , i.e., $\Delta(4.5 \text{ K}) = 0.78$ meV, by simply assuming the BCS-like T dependence of $\Delta(T)$. If we take $T_c = T_c^m = 6.6$ K, we obtain a $\Delta(0)/k_B T_c = 1.78$ with $\Delta(0) = 1.01$ meV. This is close to the typical value for weakly coupled BCS superconductors. The result suggests that the Δ we observe is consistent for weak-coupling regime superconductivity with $T_c = T_c^m$, the temperature at which superconductivity shows up in the volume-sensitive magnetization.

To confirm the evolution of the gap structure itself, we show in Fig. 3 the PES symmetrized at E_F to remove effects due to the spectral cutoff by the Fermi-Dirac distribution. It is now clearly recognized that the intensity at E_F starts to decrease and gradually forms a gap below 9.5 K. Also, in the symmetrized PES which represents the DOS, we cannot discern a well-defined QP peak and the gap structure is fairly diffuse. This result is in striking contrast to that of a scanning tunneling spectroscopy (STS) study on a (1 0 0) CVD thin film with $T_c = 1.9$ K and $n_B = 1.9 \times 10^{21} \text{ cm}^{-3}$ [23], where a SC gap spectrum with well-defined QP peaks ($\Delta = 0.285$ meV and $\Gamma = 255 \text{ mK} = 0.022$ meV at $T = 70 \text{ mK}$) is observed. Furthermore, its T dependence is in accord with the weak-coupling BCS gap function with $\Delta(0) = 1.74 k_B T_c$. On the other hand, another very recent STS result on a (1 1 1) CVD thin film with $n_B = 6 \times 10^{21} \text{ cm}^{-3}$ and $T_c^m = 5.4$ K shows a broad SC gap spectrum fairly similar to ours with $\Delta = 0.87$ meV and $\Gamma = 0.38$ meV at 0.47 K

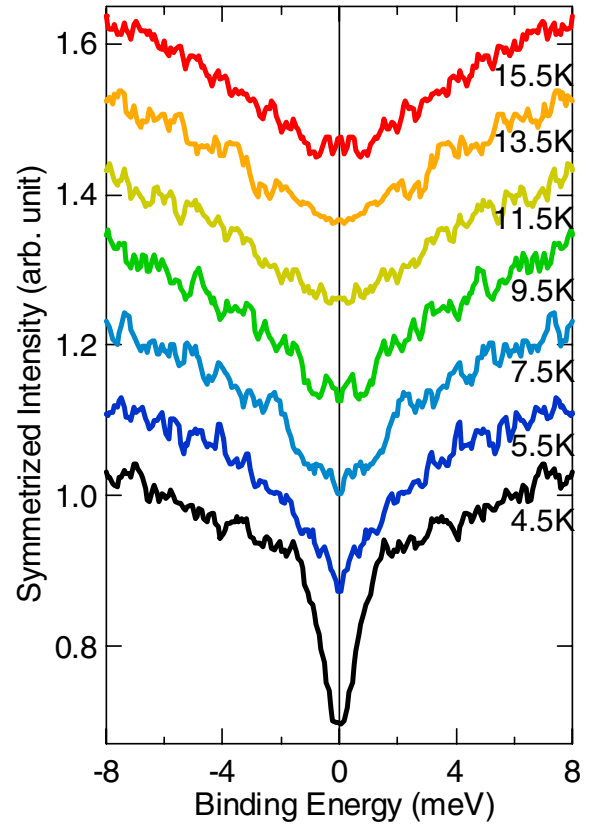


FIG. 3 (color online). T dependence of PES in BDD symmetrized at E_F to exclude the Fermi-Dirac cutoff.

[24]. Both measurements report that the STS spectra reflecting the local DOS show very little spatial dependence over the sample surfaces, which should rule out the possibility of mesoscopic (nanoscale) modification of the SC state in these samples. The discrepancy among the results on (1 0 0) and (1 1 1) samples may be explained by the difference in n_B . We note that on increasing n_B , the carrier mobility tends to get lower, reflecting the disorder induced by random boron doping. Recent supercell calculations carried out for the random alloy case of BDD [8], and ARPES [9] results, also show that the lifetime of the carriers becomes shorter with higher n_B . It indicates the dirtiness of the electronic structure in high- n_B samples, which gives rise to the SC gap with large Γ as observed in (1 1 1) samples. A very recent infrared reflectivity study has also concluded that BDD behaves like a dirty BCS superconductor [25]. Another possibility is the extrinsic sample inhomogeneity which is known to be greater in (1 1 1) samples. It is actually reported that there are two structural phases with slightly different lattice constants in (1 1 1) samples when n_B and T_c become high ($T_c^m > 6$ K) [16]. Since the lattice constant of a heavily doped BDD is greater than that of undoped ones by about 0.5%, there is tendency towards a uniaxially expanded phase near the substrate and an isotropically relaxed phase away from the substrate. Although, how exactly these two phases coexist in BDD thin films is still under investigation,

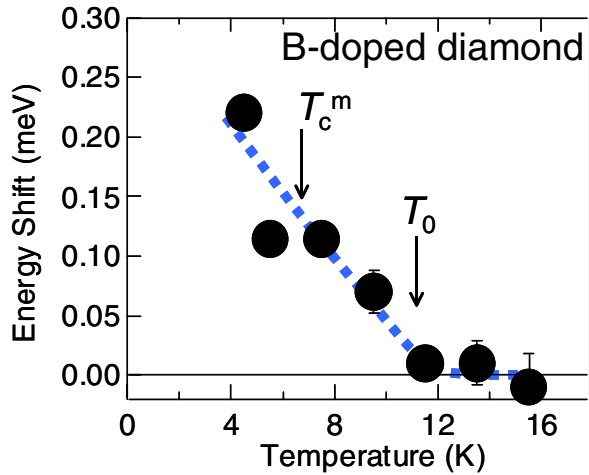


FIG. 4 (color online). T dependence observed in the energy shift of the leading edge in PES, which should reflect that of the SC gap. T_0 and T_c^m indicate the characteristic temperatures observed in resistivity and magnetization, respectively. The broken curve is merely a guide for the eyes.

such local inhomogeneity may account for the line shape of the observed SC gap structure.

Now we discuss the T dependence of the SC gap in this sample. Since it is very difficult to get accurate gap values by fitting these rather featureless spectra for all T , we simply estimated the energy shift of the leading edge in PES (Fig. 2) as a measure of the gap. Its T dependence is shown in Fig. 4. The T dependence resembles that of the Meissner response, which increases monotonically on decreasing T , as shown in Fig. 1(b). The onset T of gap evolution at around $T_0 \sim 11$ K, however, is apparently higher than that of the magnetization, $T_c^m = 6.6$ K. Looking back at the conductivity curve in Fig. 1(a) inset, we find a characteristic behavior at around T_0 . At T_0 , the conductivity starts to deviate from that of the normal state. While the conductivity and gaplike anomalies above T_c^m can possibly arise from a pseudogap effect as observed in underdoped high- T_c cuprates, it is not considered to be dominant since magnetic field quenches the conductivity anomaly. Such a deviation may be reflecting the inhomogeneous conductivity near T_c , with T_0 attributed to the onset of the local SC transition and $T_c^{\text{off}} \sim 7$ K to the temperature of bulk supercurrent percolation. If this is the case, our PES result is suggestive of its high sensitivity for probing the local superconducting state with high T_c . At the same time, it shows the potential for development of a diamond superconductor with $T_c \sim 11$ K consisting purely of the local “high- T_c ” phase. More precise investigations on (1 0 0) and (1 1 1) samples with the least extrinsic properties, including angle-resolved studies, would be instructive and are highly desired.

In conclusion, we have performed an ultrahigh resolution photoemission spectroscopy measurement to elucidate the near- E_F electronic structure of the superconducting boron-doped diamond with $T_c^m = 6.6$ K. We observed a

gradual formation of the superconducting gap below $T_0 \sim 11$ K, the temperature at which the deviation of the resistivity from the normal state is observed. The normal-state conductivity provides evidence of diffusive carrier dynamics, typical of a disordered Fermi liquid with long-range Coulomb interactions. Although the PES spectrum lacks a quasiparticle peak, the dominant size of the gap is estimated to be about $\Delta = 0.78$ meV at 4.5 K. Its broad spectral shape and T dependence indicate that the superconductivity in this system is strongly affected by randomness and/or inhomogeneity introduced by boron doping.

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