Signature of high T_c above 25 K in high quality superconducting diamond

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We have observed zero resistivity above 10 K and an onset of resistivity reduction at 25.2 K in a heavily B-doped diamond film. However, the effective carrier concentration is similar to that of superconducting diamond with a lower T_c . We found that the carrier has a longer mean free path and lifetime than in the previous report, indicating that this highest T_c diamond has better crystallinity compared to that of other superconducting diamond films. In addition, the susceptibility shows a small transition above 20 K in the high quality diamond, suggesting a signature of superconductivity above 20 K. These results strongly suggest that heavier carrier doped defect-free crystalline diamond could give rise to high T_c diamond. © 2015 AIP Publishing LLC.

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Diamond has outstanding physical properties: the hardest known material, a wide band gap, the highest recorded value for thermal conductivity, and a very high Debye temperature. In 2004, Ekimov *et al.* discovered that heavily boron-doped (B-doped) diamond becomes a superconductor around 4 K.¹ Our group controlled the boron concentration and synthesized homoepitaxially grown superconducting diamond films by a chemical vapor deposition (CVD) method.² By CVD method, we found that superconductivity appears when the boron concentration exceeds a critical value of $3.0 \times 10^{20} \text{ cm}^{-3}$ corresponding to a metal-insulator transition³ and its T_c^{zero} increases up to 7.4 K with increasing boron concentration.⁴⁻⁶ We additionally elucidated that the holes formed at the valence band are responsible for the metallic states leading to superconductivity.⁷ The calculations predicted that the hole doping into the valence band induces strong attractive interaction and a rapid increase in T_c with increasing boron concentration.^{8,9} According to the calculations, if substitutional doped boron could be arranged periodically or the degree of disorder is reduced, a T_c of approximately 100 K could be achieved via minimal percent doping.

In this paper, we observed the higher T_c^{zero} above 10 K and onset of resistivity reduction above 25 K in a heavily B-doped diamond film synthesized by a microwave plasma assisted chemical vapor deposition (MPCVD) method. We performed soft x-ray angle-resolved photoemission spectroscopy (ARPES) to investigate the electronic structure of the heavily B-doped diamond. From the band dispersion and the Fermi surface (FS), we found that the carrier concentration is almost the same as the previous report for its T_c of 6.9 K.¹⁰ However, the mean free path and the lifetime of carrier are longer than those previously reported.^{7,10} These results

suggest that the good crystallinity of superconducting diamond results in higher T_c in diamond.

A homoepitaxially grown heavily B-doped single-crystal (111) diamond film was synthesized on a diamond (111) substrate using a MPCVD method as described in Refs. 2–7. Resistivity measurements were carried out using a standard four-probe method in a physical property measurement system (PPMS, Quantum Design). We also confirmed T_c of the film from the magnetic susceptibility by a superconducting quantum interface device (SQUID, Quantum Design).

High-resolution soft x-ray ARPES measurements were performed at BL25SU, Spring-8, on a spectrometer built using a Scienta SES200 electron analyzer. ARPES measurements were performed at 9 K and below $2 \times 10^{-8} \text{ Pa}$. The incident photon energies were set to be 785–875 eV in order to observe the Fermi surface of superconducting diamond. The total energy resolution was set to be 250 meV. E_F of the sample was referenced to that of a Au film which was measured frequently during the experiments. The ARPES measurements were done after annealing at 700 °C under the ultrahigh vacuum to reduce oxygen-related contaminations on the surface.

Band calculations were performed using the first-principles full-potential linearized augmented plane-wave method within local-density approximation. Methodological details follow those used in previous calculations.⁷

To realize high T_c in heavily B-doped diamond, we synthesized homoepitaxially grown heavily B-doped high quality diamond films. The thickness is set to 280 nm, since a cross-section TEM study reported that nearly perfect diamond with substitutional boron can be deposited until a limit of 500 nm on a (111) diamond substrate.¹¹ Figure 1(a) shows the temperature dependent resistivity with a clear superconducting transition around 10 K. The zero resistivity is observed at 10.2 K. In addition, the diamond shows a sharper

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FIG. 1. (a) Temperature dependence of resistivity for heavily B-doped diamond film. (b) Temperature dependence of magnetic susceptibility for both zero-field-cooling (ZFC) and field cooling (FC) processes at a magnetic field of 10 Oe.

superconducting transition than that previously reported,⁴⁻⁶ indicating high quality superconducting diamond. In the temperature dependence of magnetic susceptibility applying 10 Oe, a diamagnetic signal is clearly observed at 10.2 K the same as our observed T_c^{zero} , as shown in Fig. 1(b).

We additionally measured the electronic structure of the heavily B-doped diamond film by soft x-ray ARPES, as shown in Fig. 2(a). The ARPES intensities are plotted with

respect to the binding energy E_B and momentum k . We could measure ARPES spectra including Γ point in Brillouin zone (BZ) using incident photon energy of 835 eV. In Fig. 2(b), the same intensity map is compared with a rigid band shift model of the calculated valence band dispersions for pure diamond and is in good agreement with the calculations. The experimental bandwidth of 23 eV is larger than that of calculated value (21 eV). Thus, the calculated diamond dispersions are energy-enlarged by 10% because of many-body effects on electron-removal energies probed in the photoemission.¹² This is consistent with the previous experimental results for the superconducting (111) diamond films.⁶ The band dispersions near Fermi level (E_F) are plotted in Fig. 2(c). Higher intensity bands show clear dispersions toward E_F and Γ point ($k=0$). These bands clearly cross at E_F , as evident from the sudden reduction of intensity at E_F due to the Fermi-Dirac distribution function, indicating the formation of hole pockets in the top of the diamond-like valence band around Γ point. This result is the same as previously reported.^{7,10} In Fig. 2(d), we compared the experimental intensity map with band structure calculations. The calculated band dispersions were shifted in order to match the Fermi

FIG. 2. (a) ARPES intensity map from heavily B-doped diamond film using incident energy of 835 eV. (b) Comparison of the ARPES intensity map with calculated band dispersions of diamond energy-expanded 10%. (c) ARPES intensity map near E_F . (d) Comparison of the same intensity map of (c) with calculated band dispersions. The calculated band dispersions are shifted by 0.5 eV in order to fit the estimated Fermi momenta from MDC analysis.

FIG. 3. (a) A mapping of ARPES intensities at E_F for incident energy between 785 and 875 eV, together with the experimental Fermi momenta (solid circles) and the calculated FS sheets (solid lines). (b) MDC spectrum at E_F with four Lorentzian functions for the incident energy of 835 eV. Red circles are the experimental data, blue line is the fitting results, and green lines are the Lorentzian functions used for the fitting. The peak positions correspond to k_F .

momenta (k_F). The derivation of k_F is mentioned below. We found that a location of E_F at 0.5 eV below the top of the valence band. The experimental band dispersions and band shift are similar to that of a previous ARPES intensity map, which measured the diamond film with T_c of 6.9 K.¹⁰ From the density of states and the band shift, we estimated the carrier concentration: $n = 3.1 \times 10^{21} \text{ cm}^{-3}$ ($= 1.8\%$).

In Fig. 3(a), the ARPES intensities near E_F for several incident photon energies (785–875 eV) were mapped out in the ΓLUX plane using a free-electron final-state model,⁷ together with the Fermi momenta and the calculated FS based on rigidly shifted diamond valence band. The higher intensity distribution indicates a FS. We can confirm band crossing positions corresponding to k_F from the momentum distribution curves (MDCs) at E_F . To compare the experimental FS with the calculations, we analyzed the MDCs using Lorentzian functions, as shown in Fig. 3(b). Experimental k_F 's were plotted over BZ, together with calculated FS sheets based on the band shift of 0.5 eV. Around Γ point, k_F 's are found to coincide with calculated FS sheets, indicating that the carrier concentration resides in $n = 3.1 \times 10^{21} \text{ cm}^{-3}$. The carrier concentration is close to that of the superconducting diamond film with lower T_c of 6.9 K.¹⁰ However, FS of the highest T_c diamond are clearer than that of previous ARPES study.⁶ A clearer FS is expected when the superconducting diamond has a less disordered crystallinity compared to those

TABLE I. Mean free path l , lifetime τ , T_c , and carrier concentration n estimated from the present and previous ARPES results.^{7,10} For Ref. 10, we calculated l and τ from the previous results.

	l (Å)	τ (fs)	T_c (K)	n (cm^{-3})	Reference
Present	11.6	3.8	10.2	3.1×10^{21}	...
Previous I	7.6	3.1	6.9	2.8×10^{21}	7
Previous II	5.3	2.8	7.0	1.9×10^{21}	10

previously reported. We estimated the mean free path l and the carrier lifetime τ from the full-width half maximum of the Lorentzian for MDC to be 11.6 Å and 3.8 fs, respectively. Here, a comparison with other superconducting diamond samples is important. Table I shows the comparison of the present results with previous ARPES results.^{7,10} Previous I shows heavier carrier than Previous II in spite of having a similar T_c . Since previous reports show an estimated error of the carrier concentration, these diamond samples probably have almost the same carrier density. In contrast, present results show little error because of the clearer FS. From the table, we found that l and τ are longer than those of previous results, which present good crystallinity of the highest T_c diamond. The results indicate that higher T_c originates from good crystallinity as the calculations predicted.^{8,9}

Moreover, we observed a signature of high T_c in this high quality diamond around 25 K. Figure 4(a) shows the temperature dependence of resistivity under a magnetic field. We observed the separation between the resistivities above 20 K and estimated the onset of transition to be at a value of 25.2 K, which is the highest transition temperature reported so far.^{2,5} The onset is gradually shifted to lower temperatures with increasing magnetic field. In addition, we observed a small transition around 25 K close to the onset in the resistivity, as shown in Fig. 4(b), suggesting that a very small fraction shows the superconductivity. If the onset is T_c^{on} , the upper critical field (H_{c2}) is determined to be 30.1 T from the linear extrapolation of the field dependent T_c^{on} , as shown in Fig. 4(c). Assuming that the superconductivity in heavily B-doped diamond is in the dirty limit, the upper critical field H_{c2} is estimated to be 21.0 T using the equation $H = H_{c2}^{\text{WHH}} (1 - (T/T_c)^{1.5})$. We also estimated the irreversible field (H_{irr}) to be at a value of 13.0 T. These values are also the highest H_{c2} and H_{irr} reported so far.⁵ The signature of higher T_c may

FIG. 4. (a) Comparison of temperature dependence of resistivity between 0 T and 7 T. The broken line corresponds to T_c^{on} . (b) Extended view of smoothed susceptibility around 25 K of Fig. 1(b). (c) The magnetic field dependence of T_c^{on} and T_c^{zero} .

be attributed only to better crystallinity or a combination of better crystallinity and partially heavier carrier density. On the other hand, the high temperature superconductivity may also arise at the interface by the correlation between the carrier in B-doped diamond side and the phonon of the pure diamond substrate side with higher frequency than that of heavily B-doped diamond. The signature above 20 K should be already reported if the small high T_c region arises as a consequence of only partially heavier carrier density or only the interface effect. Thus, we expect that the good crystallinity is important for the small high T_c region.

The present results demonstrate that a high quality heavily B-doped diamond film shows superconductivity with the highest T_c^{zero} reported so far. Since this diamond film shows clearer FS and longer mean free path and carrier lifetime but has a similar carrier density to previous diamond film with T_c of 6.9 K, less crystal disorder induces higher T_c . Additionally, we observed the signature of a transition around 25 K in both the resistivity and the susceptibility. These results suggest that high T_c diamond could be produced through a perfect crystalline diamond with higher carrier density.

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