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Superconductive B-doped nanocrystalline diamond thin films: Electrical transport and Raman spectra
Low-temperature electrical transport in B-doped ultrananocrystalline diamond film

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B-doped ultrananocrystalline diamond (UNCD) films are grown using hot-filament chemical vapor deposition method, and their electrical transport properties varying with temperature are investigated. When the B-doped concentration of UNCD film is low, a step-like increase feature of the resistance is observed with decreasing temperature, reflecting at least three temperature-modified electronic state densities at the Fermi level according to three-dimensional Mott’s variable range hopping transport mechanism, which is very different from that of reported B-doped nanodiamond. With increasing B-doped concentration, a superconductive transformation occurs in the UNCD film and the highest transformation temperature of 5.3 K is observed, which is higher than that reported for superconducting nanodiamond films. In addition, the superconducting coherence length is about 0.63 nm, which breaks a reported theoretical and experimental prediction about ultra-nanoscale diamond’s superconductivity.

Ultrananocrystalline diamond (UNCD) film is a special nanostructured form of diamond film, possessing many excellent properties with several of them actually exceeding those of micro or nanocrystalline forms of diamond films. The UNCD comprises ultra-small diamonds, a few nanometers across with mainly $sp^3$ bonding, embedded in an intergranular carbon that is largely $sp^2$ bonded as demonstrated by the original developers of the UNCD films. The decrease in diamond grain size increases greatly the proportion of grain boundaries in nanodiamond films, resulting in significant improvement in electrical properties. Moreover, the UNCD films with nitrogen incorporated in the grain boundaries have relatively good electronic properties as demonstrated by recent works. It is known that the electrical properties of diamond can be tailored by appropriate doping. Boron (B) atoms can readily substitute C atoms in the diamond lattice providing electrons to the conduction band to yield electrically conductive diamond. For B-doped concentration as low ($n \approx 10^{17} - 10^{19} \text{cm}^{-3}$), the diamond exhibits p-type semiconductivity, while for heavy doped concentration ($n \geq 10^{20} \text{cm}^{-3}$) diamond exhibits metallic conductivity at room temperature, and even superconductivity at low temperature. Thus, UNCD can also be doped by boron to improve its electrical conductivity like micro/nanodiamond. For B-doped micro/nanocrystalline diamond films, their electrical transport properties have been reported widely, and great efforts ensure the improvement in electrical transport properties and superconductivity. Especially, the superconductive transformation temperature of B-doped nanocrystalline diamond film is enhanced from 4 K to 11.4 K by increasing the B-doped concentration up to $3.7 \times 10^{21} \text{cm}^{-3}$, but the nanocrystalline diamond film has still very low superconducting transformation temperature of below 3 K. Similarly, B-doped UNCD film has also showed promising electrical properties but low-temperature electrical transport properties of B-doped UNCD film and the superconductivity in particular are rarely reported so far.

In our work, the low-temperature electrical transport property of B-doped UNCD film is investigated. The B-doped UNCD films with the grain size in the range of 3–6 nm are grown from Ar-rich source gases in hot-filament chemical vapor deposition (HFCVD) system. Different boron concentrations were achieved in UNCD films by controlling the trimethylborate ($\text{B(OCH}_3)_3$) flow rate. The temperature-dependent electrical transport property of B-doped UNCD films is observed by measuring the B-UNCD films resistance as a function of temperature. With increasing B-doped concentrations, low-temperature electrical transport property of B-doped UNCD films has significant changes that a series of superconductivity transformation are identified, among which the highest transformation temperature is 5.3 K, higher than that of reported B-NCD films. In addition, the superconducting coherence length was obtained, but which does not follow the reported prediction by theory and experiment of nanoscale diamond. The work described in this paper shows that UNCD films exhibit different lot temperature properties than microcrystalline diamond (MCD) and NCD films.

The B-doped UNCD thick films were grown using HFCVD method on silicon substrates. The substrate surface was seeded with nanocrystalline diamond particles via the immersion of the substrate in an ultrasonic bath containing a solution of nanocrystalline diamond particles in methanol. The hydrogen gas flow is separated into two gas flowing tubes, one inserted directly into the film growth chamber and the other passing though the liquid $\text{B(OCH}_3)_3$ precursor container at room temperature. The hydrogen/$\text{B(OCH}_3)_3$ mixed gas was introduced into the film growth chamber. The flow rates of argon, hydrogen, methane, and the hydrogen mixed with $\text{B(OCH}_3)_3$ were controlled at 90, 8, 1, and x sccm, and here, x varied from 0 to 6. The total pressure in the reaction cavity was 2 kPa. And the substrates temperature was about

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650 °C, controlled by the filament current and the cooling water system. At the beginning of the HFCVD process, an assisted voltage was applied between the substrate and filament with the value of 250 V, with the substrate is biased negatively with respect to the filament. During growth process, the formation of the plasma produced a great deal of C\textsuperscript{+} ions, and these C\textsuperscript{+} ions were accelerated towards the substrate promoting the nucleation under applied negative bias.\textsuperscript{11} The large nucleation density favors the growth of UNCD films. The surface morphologies of UNCD films were analyzed with scanning electron microscope (SEM). Raman analysis with a 532 nm wavelength laser is used to determine the chemical bonds in the UNCD film. The conductivity and the carrier concentration were measured with a physical property measurement system (PPMS), and the measured temperature is varied from 300 K to 1.9 K during the measurements.

Figure 1(a) shows the SEM images of B-doped UNCD film with a thickness of 1.2 μm and a growth rate of about 240 nm/h, displaying distinctly the surface morphology of UNCD films. We can observe that the UNCD particles assemble together to form big clusters so that the clusters are connected to the film, and the diameter of clusters is estimated to be 150–200 nm. Figures 1(b) and 1(c) display the images of high resolution transmission electron microscopy (HRTEM) of the UNCD film sample, and a dotted line frame marked in the Fig. 1(c) is enlarged to Fig. 1(c) with a higher resolution. From Fig. 1(c), we can discern easily the distribution of a single ultrananocrystalline of diamond along the arrow, and these separated crystalline grains have a size range of 3–6 nm, indicating that our as-prepared UNCD films possess a very fine ultrananocrystalline grains with sub-10 nm in size to correspond to the typical characteristic of UNCD. This ultra-small grain size in UNCD is practically independent of the film thickness because of the continuous re-nucleation during film growth. The UNCD is composed of grain boundaries exceeding 10% of the total volume fraction and this leads to a great proportion of non-diamond or disordered carbon in the films.

The further characterization of UNCD films were given with Raman spectrum, as shown in Fig. 1(d). There are four characteristics in the spectrum: (1) the zone-center phonon band of diamond at 1345 cm\textsuperscript{-1}, (2) the appearance of band centered at 1150 cm\textsuperscript{-1} relative to NCD, (3) the interesting bands centered at about 460 and 1200 cm\textsuperscript{-1}, and (4) the fluorescence background of the Raman spectrum. Raman reveals the chemical bonding of the carbon atoms. In Fig. 1(d), the band at 1550 cm\textsuperscript{-1} is corresponding to G band. The peak around 1345 cm\textsuperscript{-1} is corresponding to the diamond sp\textsuperscript{3} bonding and the peak at 1550 cm\textsuperscript{-1} reveals the sp\textsuperscript{2} bonding of carbon atoms mainly in the grain boundaries. The appearance of band centered at 1150 cm\textsuperscript{-1} is supposed to come from the transpolyacetylene of the NCD surface,\textsuperscript{12} which is the main feature of NCD. The broad peak at about 460 cm\textsuperscript{-1} and 1200 cm\textsuperscript{-1} may correlate with the phonon scattering at boron-induced structure modifications or with boron-related electronic transitions and Raman scattering by phonons away from the center of Brillouin zone.\textsuperscript{13} And the presence of the wide package centered at 460 cm\textsuperscript{-1} may be correlate with the superconductivity properties of diamond.\textsuperscript{14} The fluorescence background of the Raman spectrum is related to the largely existence of amorphous carbon around the UNCD surface. In addition, the 521 cm\textsuperscript{-1} peak comes from the silicon substrate.

The resistivity of as-grown UNCD films was measured by the I-V measurement using the four-probe method, and their carrier concentration was determined by Hall-effect measurement with a current of 10 mA and extra magnetic field of 0.1 T at room temperature. Hence, the carrier concentration of the total UNCD film was calculated to obtain the average value.

Fig. 2 shows the electrical resistance of B-doped UNCD films grown with the flow rate of hydrogen mixed with B(OCH\textsubscript{3})\textsubscript{3} as a function of temperature (R-T) at zero magnetic fields, and different flow rates are corresponding to different B-doped concentrations. When the B-doped concentration is low, the UNCD films show a temperature-depended electrical property without any superconductive transition, as shown in Fig. 2(a). We observe that in the temperature range of 300–175 K for the samples with the flow rate of 2.5–3 sccm and 300–270 K for sample with the flow rate of 2 sccm, the resistance is decreased with the reduction of temperature, that is, a positive value of $\partial R/\partial T$ is expected for metallic transport property.\textsuperscript{15} But when the temperature is below 270 K for the sample with flow rate of 2 sccm and 175 K for samples with flow rate of 2.5 sccm–3 sccm, the resistance shows step-like jumps increasing feature with the decrease of temperature down to 2 K, corresponded resistance jumps occur at about 250 K, 175 K, 125 K, and 50 K, respectively.

This first decrease and then step-like increase feature of resistance with decreasing temperature indicate a change of electric transport mechanism. Here, the resistance jumped increasing feature with decreasing temperature can be explained by three-dimensional Mott’s variable range hopping (3D-VRH) transport theory.\textsuperscript{16} The 3D-VRH transport process is generally expressed by using Mott’s conduction mode as $R(T) = R_0 \exp[(T_0/T)^{d+1}]$. Here, $R_0$ is a material
parameter, and $T_0$ is a temperature scale defined by electronic states density $N(E_F)$ at the Fermi level $E_F$, and $T$ is the working temperature.\cite{17} According to the above mechanism, the resistance increases with decreasing temperature. In disordered system like B-doped UNCD, there exists the possibility of electrons hopping (phonon-assisted tunneling) between local states in the vicinity of the Fermi level, and the average hopping distance is increased with the increase in temperature. For VRH transport model, $\ln[R(T)]$ is proportional to $T^{-1/4}$, and $d$ is the hopping parameter, depending on the dimensionality of the system and the hopping distance, where $d = 3$ for three-dimensional system of UNCD.\cite{15,17} Fig. 2(b) shows the $\ln[R(T)]$ versus $T^{-1/4}$ curve, corresponding to Fig. 2(a), and a linear relation of $\ln[R(T)]$ versus $T^{-1/4}$ indicates that the 3D-VRH mechanism is applicable to interpret the electronic transport properties of B-doped UNCD. In addition, the different slopes in different temperature regions shown in Fig. 2(b) are due to the different values of $T_0$, which reflects at least three temperature-modified electronic states density $N(E_F)$ at the Fermi level $E_F$. This phenomenon not found in the B-NCD, being probably related to the surface state energy level quantization caused by the grain size great reduction in UNCD. But, as we see, a more thorough interpretation needs further study.

Figs. 2(c) and 2(d) show the R-T curves of heavily doped UNCD films, corresponding to the mixed hydrogen/B(OCH$_3$)$_3$ flow rate of 3.5, 4, 4.5 sccm, showing completely different electric transport properties. When the flow rate reaches to 3.5 sccm, the UNCD films begin to exhibit the superconductivity at the low temperature range, and a corresponding carrier concentration is calculated to be about $8.7 \times 10^{17}$ cm$^{-3}$. With the flow rate increasing to 4.5 sccm with a higher carrier concentration of $1.3 \times 10^{18}$ cm$^{-3}$, a better superconductivity of UNCD film is observed. However, this concentration is still two orders of magnitude lower than that reported for microdiamond films. This is may be related to the abundant grains in UNCD films. Due to the inevitable randomness of the positions and orientations of UNCD particles, there are vast lattice mismatch existing between neighboring grains. Therefore, the grain boundaries are abundant in disordered $sp^2$ and $sp^3$ phases. In these boundaries, boron atoms act as deep-level impurities without contributing to mobile charge carriers in electrical transport.\cite{18–21} When the carrier concentration reaches to $1.3 \times 10^{18}$ cm$^{-3}$, the UNCD film exhibits the maximum superconductivity transformation temperature in our experiments. With temperature decreasing, the resistance begins to drop rapidly at the temperature of 5.3 K, corresponding to the onset of superconductivity transformation. And when the temperature drops to 4.4 K, the resistance reaches an immeasurably small value, corresponding to the offset temperature of superconductivity transformation. This transformation temperature (5.3 K) is much larger than that of reported B-doped NCD films.

Recently, a global superconductivity mechanism in B-doped NCD films related to the phase locking between different superconducting grains was proposed, which is different from that in B-doped MCD films but is equally suitable for B-doped UNCD film.\cite{22,23} On account of such mechanism, the B-doped UNCD film can be considered as a large resistor network composed of superconducting grains connected though a large network of grain boundary resistors, phase locking between the superconducting order parameters of neighboring grains generates a weak junction with current tunneling through atomically narrow grain boundary, forming Josephson junction. As a complex of abundance of Josephson junctions induced by numerous smaller superconducting grains, UNCD film will undergo superconducting transition slowly.\cite{24–26}

Fig. 3(a) shows the influence of a gradually increasing external magnetic field on the resistance of the UNCD film dependence of temperature when the carrier concentration is
1.3 × 10^{18}\text{ cm}^{-3}. With the magnetic field increasing, the superconductivity transformation temperature gradually drops. From Fig. 3(b), we can deduce the dependence of critical magnetic field $H_{c2}(T)$ on temperature $T$. The corresponding $T = 0$ critical field $H_{c2}(0)$ is estimated to be about 8.5 T, larger than the estimated one (2.1 T) according to the standard relationship for a dirty type-II superconductor: $H_{c2}(0) = -0.69T_{c}dH_{c2}(T)/dT$.\textsuperscript{27} The low $H_{c2}$ may be related to Ginzburg–Landau coherence length ($\xi$). According to the BCS theory, $\xi$ accords with the relation: $\xi(T) = \left[H_{c2}(0)/2\pi^{1/2}T\right]^{1/2}$. Figure 3(c) gives the coherence length of B-doped UNCD film depended on the temperature. When temperature is 0 K, the coherence length $\xi(0)$ is estimated to be 0.63 nm.

According to reported experimental data and theory,\textsuperscript{24} when diamond crystal size is less than 18 nm, the coherence length will be reduced to zero and thus the diamond will become no-superconducting, meaning that it is impossible for B-doped UNCD to possess superconductivity. However, here, we are still testing superconductivity of B-doped UNCD with the grain size of 3–6 nm, and moreover superconducting transition temperature is several times higher than that of B-doped NCD. Although obtained coherence length is smaller than that of the reported B-doped NCD, but it does not reduce to zero, being still in line with the trend of B-doped NCD superconductivity. The only explanation is that, when the diamond size is small to a certain extent (such as sub-10 nm), the linear relationship between the reciprocal of the particle size (1/D) and Ginzburg-Landau coherence length $\xi$ ($T$) is no longer applicable, this may be due to the quantum size effect caused by UNCD’s ultrasmall nanosize particles.

In conclusion, we have grown B-doped UNCD films with 3–6 nm grain size using HFCVD method, and find their low-temperature electrical transports have some nontraditional characteristics which is different from that of NCD and MCD due to ultra-nanosize effect. With decreasing temperature, low-doped UNCD shows at least three temperature-modified electronic states density at the Fermi level due to the surface state energy level quantization caused by great reduction of the grain size in UNCD. Importantly, a series of superconducting transformation with the highest transformation temperature of 5.3 K are observed with increasing B-doped concentrations for the first time in the B-doped UNCD, and a superconducting coherence length of 0.6 nm is obtained to prove the fact that when diamond crystal size is sub-10 nm, the superconductivity still remains. This work makes up the gap of low-temperature electrical property of UNCD and gives a further understanding about the electrical transport and superconductivity mechanism of B-doped diamond.

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