Scanning tunneling microscopy and spectroscopy studies of superconducting boron-doped diamond films

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Abstract

We report on scanning tunneling microscopy/spectroscopy (STM/STS) experiments on (1 1 1)-oriented epitaxial films of heavily boron-doped diamond grown by using the microwave plasma-assisted chemical vapor deposition method. STM/STS measurements were performed by \textsuperscript{3}He-refrigerator based STM under ultra-high vacuum. The STM topography on the film surface shows a corrugation (with a typical size of \( \approx 1 \) \textmu m) and grain-like microstructures (\( \approx 5–20\) nm). The tunneling conductance spectra do not show large spatial dependence and superconductivity is observed independent of the surface structures. The tunneling spectra are analyzed by the Dynes function and the superconducting energy gap is estimated to be \( \Delta = 0.87 \text{ meV} \) at \( T = 0.47 \text{ K} \), corresponding to \( 2\Delta/k_B T_c = 3.7 \). The relatively large value of the broadening parameter \( T = 0.38 \text{ meV} \) is discussed in terms of the inelastic electron scattering processes.

Keywords: Scanning tunneling microscopy/spectroscopy; Boron-doped diamond films; Superconductivity; Energy gap

1. Introduction

Lightly boron-doped diamond is a p-type semiconductor with an activation energy of \( \approx 0.37 \text{ eV} \) since boron dopes holes into a shallow acceptor level above the top of the valence band. With increasing boron concentration beyond the critical value \( n_c \approx 2 \times 10^{20} \text{ cm}^{-3} \) for the metal–insulator (MI) transition, the boron-doped diamond shows metallic behavior. Recently, Ekimov et al. \cite{1} discovered superconductivity in the heavily boron-doped diamond synthesized by high-pressure high-temperature (HPHT) method. The superconducting transition temperature \( T_c \) was 2.3–4 K for their polycrystalline bulk samples with the boron concentration \( n \approx 4.9 \times 10^{21} \text{ cm}^{-3} \) (i.e., 2.8\% of the carbon atoms were substituted by boron) \cite{1}. Takano et al. \cite{2,3} reported that (1 1 1)-oriented polycrystalline boron-doped diamond film shows a superconductivity at \( T_c = 4.2–7.4 \text{ K} \); the value is higher than that reported for HPHT diamond \cite{1} and for boron-doped (1 0 0)-oriented single-crystalline diamond films \( (T_c \leq 2.1 \text{ K}) \) \cite{4}. The microwave plasma-assisted chemical vapor deposition (MPCVD) method is a useful technique to control the boron density in a wide range and the doping dependence of \( T_c \) has been studied in MPCVD diamond films \cite{2–5}. In addition to the doping level, the value of \( T_c \) depends on the synthesized process and the orientation of the film growth \cite{5}. In this material, the highest \( T_c \) reached so far is 7.4–11.4 K for (1 1 1)-oriented epitaxial films with \( n \approx 8.4 \times 10^{21} \text{ cm}^{-3} \) \cite{5}. Since the condition is considered to be the underdoped region according to the doping dependence \cite{5}, the value of \( T_c \) may increase more with increasing carrier density to the optimal condition.

In order to understand the electronic structure and the mechanism of the superconductivity in boron-doped diamond, various theoretical proposals \cite{6–10} and experiments \cite{11–14} have been performed. Scanning tunneling microscopy/spectroscopy (STM/STS) is a powerful tool to
detect high-energy-resolution information about the electron local density of states with sub-nanometer spatial resolution. Since the tunneling spectroscopy provides the superconducting gap parameter $\Delta$, the low-energy quasiparticle excitations at the Fermi level, and the electron–phonon coupling strength, the validity of the BCS model can be studied for superconductors in the weak and strong limits. In this paper, we report on low temperature STM/STS experiments on (1 1 1)-oriented epitaxial films of heavily boron-doped diamond. We present the spatial variation of the local density of states and superconducting energy gap structures.

2. Experimental

Heavily boron-doped epitaxial diamond films were grown on the (1 1 1)-oriented type Ib diamond substrates by using the MPCVD method. Details of the thin film growth were described elsewhere [2,3,5]. The superconducting transition temperature was $T_c = 5.4$ K from DC magnetization measurement and the boron concentration was estimated to be $n \approx 6 \times 10^{21}$ cm$^{-3}$ [5]. The boron-doped diamond film was annealed at 450°C in the ultra-high vacuum (UHV) chamber and was inserted into the cold STM head by the transfer rod without breaking vacuum. According to the photoemission spectroscopy [13,14], the annealing procedure is useful to reduce the oxygen/hydrogen contamination at the film surface because the photoelectron intensity increases after annealing.

STM/STS measurements were performed by $^3$He-refrigerator based STM (UNISOKU, USM-1300SD2) at several temperatures under UHV ($P \sim 10^{-10}$ Torr) condition. The STM/STS can be operated at temperature down to $\sim 0.47$ K at the sample stage when the condensed $^3$He achieves a base temperature of $\leq 0.3$ K. The $^3$He-refrigerator using the charcoal pump can keep the sample stage at 0.47 K for about 48 h before recondensation is needed. A mechanically sharpened Pt–Ir wire was used as the STM tip, which was approached perpendicular to the (1 1 1) surface of boron-doped diamond film. The differential tunneling spectra were obtained either by numerically differentiating the current ($I$)-voltage ($V$) curves or directly by using the lock-in amplifier; the two methods yield similar results. The typical tunneling parameters for STS measurements were $V = 5–10$ mV and $I = 5–100$ pA for the set sample bias and the current, respectively. The coarse $x$–$y$ stage of the STM tip, which can be driven by shear piezo elements, is used for macroscopic positioning of the tip over the sample, so the scanning area with high quality surface can be selected macroscopically for STM/STS measurements.

3. Results and discussion

For the natural surface of the boron-doped diamond films, it was difficult to stabilize the tunneling condition during STM/STS measurements because of the unstable surface character of as-grown thin films. After thermal annealing, however, we have succeeded in making the stable tunneling junction at low temperatures and in obtaining the reproducible STM/STS results as shown below. Fig. 1(a) shows the typical STM topographic image of the (1 1 1)-oriented epitaxial film ($\#B70$) of heavily boron-doped diamond measured in constant current mode at 4.2 K. The film surface shows a corrugation with a typical size of $\sim 1$ μm and grain-like microstructures covering over the entire surface of thin films. The size of the fine microstructure is 5–20 nm. Fig. 1(b) shows the topographic image on the center of Fig. 1(a) with a higher resolution at 0.47 K. The flat surface shows the weak but regular modulation with an atomic scale, which becomes remarkable in the film after thermal annealing. However, the atomic arrangement is not clear enough to distinguish the diamond lattice structure from other possibility, such as the reconstructed surface and the existence of the adsorbed hydrocarbons. Further development of the surface treatment and STM measurements is necessary to make this point clear.

Fig. 1. STM topographic images of the (1 1 1)-oriented epitaxial film ($\#B70$) of heavily boron-doped diamond. (a) $V = 600$ mV, $I = 0.1$ nA, $T = 4.2$ K. (b) $V = 100$ mV, $I = 0.1$ nA, $T = 0.47$ K.
In order to confirm the quality of the tunneling junction for spectroscopic measurements, we have measured the dependence of the tunneling spectra on the distance between the tip and film surface by changing the magnitude of the junction resistance $R_t$ at the same point [the center position of Fig. 1(b)]. Fig. 2 shows a series of the tunneling spectra normalized at $V = 5\, \text{mV}$ for different values of $R_t = 0.1, 0.2, 0.4, 0.6, 0.8, 1.2\, \text{G\Omega}$ at 0.47 K. The whole data exhibit characteristic features of the superconductivity, such as a suppression of the tunneling conductance near the zero bias and the coherence peak. As shown in Fig. 2, the shape of the tunneling spectra is independent of the junction resistance. The results indicate that our measurement is clean vacuum tunneling spectroscopy and the tip does not perturb the electronic state of the film surface.

We have performed STS measurements to study the spatial dependence of the superconducting properties. Fig. 3(a) shows the topographic image for STS measurements at 0.47 K. The STS data shown in Fig. 3(b) are taken at the points from A to J marked in Fig. 3(a). The tunneling spectra show the superconducting energy gap $2\Delta$, the broad coherence peak, and the symmetric conductance with a flat background at $V > \Delta$. In addition, the zero-bias conductance shows relatively high value, which is about $35\% \pm 10\%$ of the normal background, contrary to the BCS expression of the density of states without any broadening parameter. These features are reproducible at different tunneling resistance $R_t$ (see Fig. 2) and at different locations on the film surface in the scanning area of $200 \times 200\, \text{nm}^2$ (see Fig. 3). Since the tunneling conductance spectra are independent of the microstructures, the superconducting order parameter is not suppressed locally by defect structures, stoichiometry changes or impurities but homogeneously distributes in the wide range beyond the Ginzburg-Landau coherence length $\xi_{\text{GL}} \approx 6.9 - 15\, \text{nm}$ [1–4].

In the low temperature region much below $T_c$, the differential conductance $(dI/dV)$ spectra provide a direct information on the local density of states of quasiparticles $N(E, \mathbf{r})$ and consequently on the superconductor gap structure. Here, $E$ is the energy of quasiparticles and $\mathbf{r}$ is the position of the STM tip on the film surface (i.e., the measured point). The tunneling spectrum can be analyzed by using the modified BCS expression for the superconducting density of states [15,16]:

$$N(E, \Gamma) \propto \left| \text{Re} \left( \frac{E - i\Gamma}{\sqrt{(E - i\Gamma)^2 - \Delta^2}} \right) \right|, \quad (1)$$

where the phenomenological broadening parameter $\Gamma$ accounts for the pair breaking effects. Fig. 4 shows the experimental tunneling conductance spectrum (open...
circles) and calculated conductance (solid line) using the Dynes function [Eq. (1)]. The best fit to the experimental data yields the parameters $\Delta = 0.87\text{meV}$ and $\Gamma = 0.38\text{meV}$ at $T = 0.47\text{K}$ (i.e., $t = T/T_c = 0.087$). The value of $\Delta$ in this study is consistent with that in recent experiments by the laser-excited photoemission spectroscopy for MPCVD diamond film ($\Delta = 0.78\text{meV}$ at $4\text{K}$) [14] and by STM/STS for polycrystalline bulk diamond ($\Delta = 0.8-1.0\text{meV}$ at $0.5\text{K}$) [17]. With the measured value of $T_c = 5.4\text{K}$ we obtain the BCS ratio $2\Delta/k_BT_c = 3.7$; the value is somewhat larger than the theoretical value $2\Delta/k_BT_c = 3.53$ for a weak coupling BCS superconductor, but is much smaller than that of the strong coupling superconductors such as Pb ($2\Delta/k_BT_c = 4.3-4.7$) [18] and MgB$_2$ ($2\Delta/k_BT_c = 4.5$) [19].

The tunneling spectra observed in this study indicate the broad coherence peak, the high zero bias conductance and the relatively large value of $\Gamma$. Although the results are completely different from the recently reported STM/STS study on the (001)-oriented MPCVD diamond film ($T_c = 1.9\text{K}$, $n \sim 1.9 \times 10^{21}\text{cm}^{-3}$) [20], where the tunneling spectrum is described by the weak-coupling BCS expression without broadening parameter $\Gamma$, the photoemission experiment on the (1 1 1)-oriented MPCVD diamond film ($T_c = 7-10\text{K}$) [14] is consistent with our results. The large value of $\Gamma$ cannot be explained in terms of the thermal broadening effect, because our STM/STS experiments have been performed at low temperatures ($t = 0.087 \ll 1$) in this study. Consequently, the alternative mechanism of the pair breaking effect is needed as the origin of the low energy excitations. Dynes et al. [16] suggested that the lifetime broadening of the energy gap edge is due to the inelastic scattering of electrons and this effect is enhanced in the disordered thin film near the MI transition; the situation may be similar to that of heavily boron-doped diamond films.

The disorder introduced by the boron doping is a possible origin of the pair breaking centers; in this case, the different tunneling spectra between (001)- and (1 1 1)-oriented diamond films result from the different boron concentration and the different growth mode [5]. With increasing boron concentration, the value of $T_c$ increases because of the carrier doping, however, the introduction of the boron into the diamond produces the disorder that enhances inelastic electron scattering. Umezawa et al. [5] have pointed out that boron–boron pairs, which distort the diamond lattice locally, are easily formed during (1 1 1)-growth rather than (001)-growth. Considering the intrinsic disorder by the heavy boron doping, the characteristic feature of the tunneling spectra with ungapped excitations in the (1 1 1)-oriented diamond film can be understood in terms of the inelastic electron scattering. This scenario is supported by the experimental results of the large resistivity $\rho \sim 2.5\text{m}\Omega\text{cm}$ near $T_c$ [3,11] and the short electronic mean-free path $l = \hbar v_F/(\pi e)^2 \sim 0.34\text{nm} < \xi_{GL}$ [11] in superconducting boron-doped diamond. These results indicate that the quasiparticles experience significant scattering and the pair breaking creates amount of excitations within the gap, which enhances the zero bias conductance.

4. Summary

We have performed STM/STS experiments on (1 1 1) -oriented epitaxial films of heavily boron-doped diamond grown by using the MPCVD method. The STM topography on the film surface shows a corrugation (with a typical size of $\sim 1\mu\text{m}$) and grain-like microstructures ($\sim 5-20\text{nm}$). The tunneling conductance spectra do not show the spatial dependence and superconductivity is observed independent of the microstructures. At temperatures much below $T_c$ (i.e., $t = 0.087$), the superconducting energy gap is $\Delta = 0.87\text{meV}$ which corresponds to $2\Delta/k_BT_c = 3.7$. Considering the intrinsic disorder by the heavy boron doping, the characteristic features of the tunneling spectra, which show the broad coherence peak, the high zero bias conductance and the large value of $\Gamma$, can be explained in terms of the inelastic electron scattering.

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