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Effectiveness of a hot-filament chemical vapor deposition method for preparation of a boron-doped superconducting diamond film with higher superconducting transition temperature

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ABSTRACT

We have investigated the effectiveness of a hot-filament chemical vapor deposition (HFCVD) method for preparation of a boron-doped superconducting diamond film with higher superconducting transition temperature (T_c). A boron-doped superconducting diamond film has been fabricated on a diamond (111) substrate using the HFCVD method, and studied by means of scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and resistivity. The film consists of grains with an average size of 200 mm. Analyses of valence band and boron 1*s* core-level XPS spectra indicate the formation of boron-doped diamond film on the substrate. From the resistivity measurements, the film is found to be a superconductor with onset T_c of 7.1 K. Carrier concentration determined by Hall conductivity measurements is 1.1×10^{21} cm^{-3}. The value of T_c is higher compared with that in boron-doped superconducting diamond films prepared by a commonly used microwave plasma-assisted chemical vapor deposition (MPCVD) method, at the same carrier concentration [A. Kawano et al., Phys. Rev. B 82 (2010) 085318]. The result of higher T_c in the film by the HFCVD method is consistent with the previous one [Wang et al., Diamond Relat. Mater. 15 (2006) 659], suggesting that the HFCVD method is effective for preparation of boron-doped superconducting diamond films showing higher T_c.

1. Introduction

In 2004, Ekimov et al. discovered superconductivity in heavily boron-doped diamond [1]. This new superconductor has attracted much interest as a potential material of high-temperature superconductor. This is because diamond possesses a notably high Debye temperature (2240 K) to which superconducting transition temperature (T_c) is proportional directly [2]. Since the discovery, many researchers have made efforts to attain T_c as high as possible, with developing preparation methods.

The first sample of heavily boron-doped superconducting diamond was synthesized by a high-temperature and high-pressure method [1]. The prepared sample was polycrystalline with carrier concentration of 1.5×10^{21} cm^{-3}, and showed T_c of 4 K. After soon, the superconducting diamond was prepared in the form of film by means of microwave plasma-assisted chemical vapor deposition (MPCVD) [3]. One of the advantages of this method is that a single crystalline film is obtainable. Another advantage is that boron concentration can artificially tune over a wide range. Owing to these advantages, the MPCVD method comes to be used widely for preparation of the boron-doped superconducting diamond film. Kawano et al. and Umezawa et al. fabricated homoepitaxially grown boron-doped diamond films on diamond substrates with changing boron concentration systematically up to about 1×10^{22} cm^{-3} (carrier concentration of ~10^{22} cm^{-3}) by the MPCVD method, and investigated how T_c depends on carrier concentration [4,5]. They revealed that T_c in (111)-oriented films increased with increasing carrier concentration and did not tend to saturate up to $T_c = 8.5$ K (T_c was defined as the temperature where resistivity decreased to 90% of the normal-state resistivity) at attainable maximum carrier concentration. The optimum T_c has not been found yet, because boron cannot be incorporated above 1×10^{22} cm^{-3} in the present doping technology.

Recently, Wang et al. successfully prepared a boron-doped diamond superconducting film by a hot-filament chemical vapor deposition (HFCVD) method [6]. The polycrystalline film was grown on a molybdenum substrate. Onset T_c in the film was 10 K and carrier concentration determined by Hall measurements was 7.3×10^{20} cm^{-3}. It is noteworthy that T_c in this film is higher at relatively lower carrier concentration, compared with the case of homoepitaxial films on

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diamond (111) substrates by the MPCVD method [4]. This fact seems to suggest that the HFCVD method is effective for preparation of superconducting diamond films with higher T_c. The results motivate us to study the superconducting properties, especially to examine the carrier dependence of T_c and reveal maximum T_c in boron-doped superconducting diamond using the film prepared by the HFCVD method. Before such works proceed, it would be beneficial to verify the effectiveness of the HFCVD method for preparation of superconducting diamond films with higher T_c.

In this work, we prepared a boron-doped superconducting diamond film on a diamond (111) substrate using the HFCVD method and performed the characterization of the film by means of scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and resistivity. We then compared T_c in the film by the HFCVD method with the data obtained from the film by the MPCVD method in order to examine if T_c in the film by the HFCVD method is higher than that by the MPCVD method at the same carrier concentration.

2. Experiment

A boron-doped diamond film was grown on a diamond (111) substrate using the HFCVD method. In our HFCVD apparatus, TaC was used as a filament material. It is much superior to conventional tungsten and tantalum filament for high-temperature use [7]. The diamond substrate was pretreated in an ethanol solution by ultrasonic wave. For film preparation, CH_4 and H_2 were used as reaction gases. Boron species were incorporated into the diamond films during the growth process by bubbling the H_2 gas through the $B(OCH_3)_3$ liquid precursors at room temperature. The flow rate of H_2 bubbles was regarded to be that of boron vapor. The volume flow rates of three gases H_2, CH_4 and H_2 which carries boron species were regulated with mass flow meters to be 190, 2, and 8 sccm, respectively. The total gas pressure was 5000 Pa. The substrate and filament temperature, measured using an optical pyrometer, was 850 °C and 2400 °C, respectively. After deposition of 5 h, the film was cooled under the H_2 gas atmosphere.

The surface morphologies of the boron-doped diamond film was examined with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis using a Hitachi S-4300. The thickness of the film, measured by an optical profilometer using a Zygo NV 7300, was 1 μm. X-ray photoelectron spectroscopy (XPS) measurements were performed at SPring-8 BL27SU. Monochromated X-ray of 1100 eV was used for the measurements and the total energy resolution was 300 meV. Before measurements, the film was annealed in a preparation chamber connected to the spectrometer at 700 °C for 10 min to obtain a clean surface. All the XPS measurements were carried out at 300 K. The Fermi level position was determined by measuring the Fermi edge of gold. Resistivity measurements were carried out using a standard four-point probe method in a Physical Property Measurement System (Quantum Design PPMS). Au wires were attached to the film by silver paste. Carrier concentration was measured by Hall conductivity measurement in the magnetic field range of ±9 T at 300 K.

3. Results and discussion

Fig. 1(a) shows a SEM image of the prepared film. As seen in the figure, the film consists of many grains with an average grain size of 200 nm. By EDX analysis no tantalum is detected in the film, indicating that the filament metal is not incorporated in the film during deposition. Formation of boron-doped diamond in the film is examined by XPS measurements. Fig. 1(b) shows the valence band spectrum of the film. The valence band spectrum shows a three-peak structure: a fairly broad, intense peak located between 15 and 24 eV is mainly due to carbon 2*s* band, a narrower intense peak located at about 11 to 14 eV is mainly due to the mixture of carbon 2*s* and 2*p* bands, and a very broad and decidedly weaker structure, extending from 10 eV to the cutoff energy is mainly due to carbon 2*p* band. The obtained

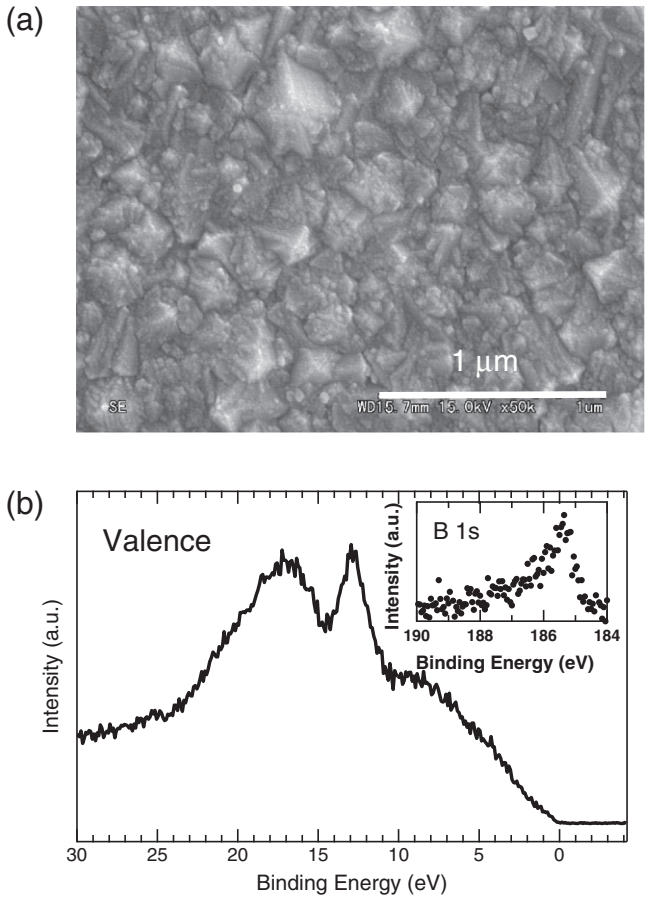

Fig. 1. (a) SEM image of a boron-doped diamond film grown on a diamond (111) substrate. (b) Valence band spectrum of a boron-doped diamond film on a diamond (111) substrate taken at the photon energy of 1100 eV. Inset shows boron 1*s* core-level spectrum of a boron-doped diamond film on a diamond (111) substrate taken at the photon energy of 1100 eV.

spectrum is in good agreement with that of diamond bulk sample reported previously [8]. Inset of Fig. 1(b) displays the XPS spectrum of boron 1*s* core-level for the prepared film. The spectrum shows a peak structure around the binding energy of 185.4 eV. This structure corresponds to a signal from substitutionally doped boron atoms [9], indicating that boron atoms are incorporated in the film. The XPS measurements of valence band and B 1*s* core-level find that boron-doped diamond is formed in the film on the diamond (111) substrate.

Fig. 2(a) shows the temperature dependence of resistivity of the boron-doped diamond film on the diamond (111) substrate. The resistivity increases gradually with decreasing temperature from room temperature. This behavior does not display the metallic-like behavior, which suggests a relatively low carrier concentration of the film. The resistivity begins to drop rapidly near 7.1 K (onset T_c) and reaches an immeasurably small value at around 3.8 K, as shown in Fig. 2(b). The resistivity measurement clearly shows that the present diamond film is a superconductor. This is the first observation of superconductivity for a boron-doped diamond film grown on a diamond substrate prepared by the HFCVD method. The carrier concentration of the superconducting film is determined from Hall conductivity measurements to be 1.1×10^{21} cm^{-3} at room temperature.

Fig. 3 shows the plot of T_c against carrier concentration for the present film. The data obtained from heavily boron-doped diamond films on diamond (111) substrates by the MPCVD method is plotted in the same figure for comparison [4]. Another data from the previous film by the HFCVD method is also added [6]. T_c is defined as the temperature where resistivity decreases to 90% of the normal-state resistivity. It is clearly shown in the figure that T_c in the present film is higher

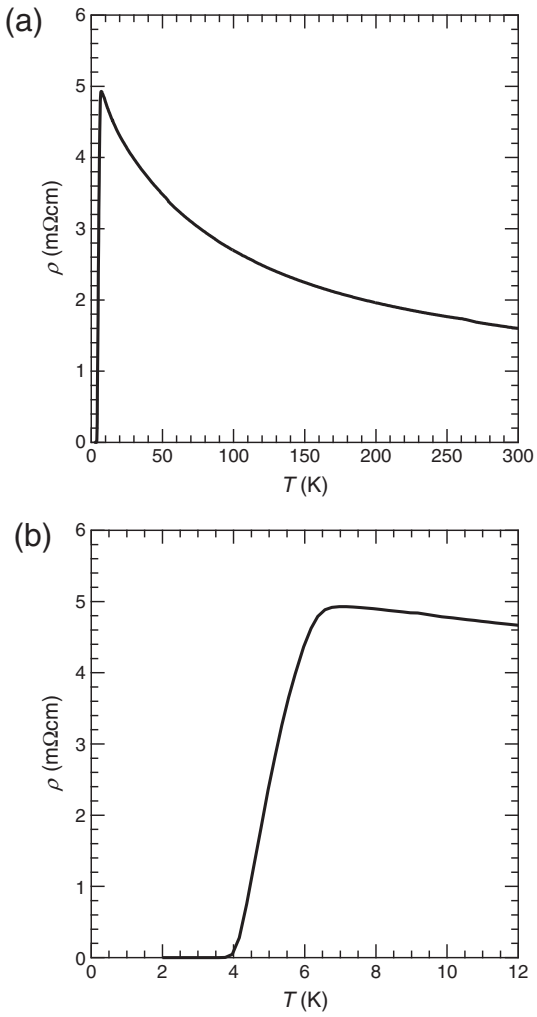

Fig. 2. (a) Temperature dependence of resistivity for a boron-doped diamond film on a diamond (111) substrate. (b) Temperature dependence of resistivity for a boron-doped diamond film on a diamond (111) substrate near T_c.

compared with that in the film by MPCVD method at the same carrier concentration. The result of higher T_c in the film by the HFCVD method is consistent with the previous one by Wang et al. [6], and thus strongly suggests that HFCVD method is effective for preparation of boron-doped superconducting diamond films with higher T_c.

The present result offers us a significant issue to be solved: why is T_c in the film by the HFCVD method higher than that by the MPCVD method at the same carrier concentration? One may think about the possibility of incorporation of tantalum into the film and the effect that the tantalum may have on the superconductive properties. Boron doping was done with trimethyl borate which contains substantial quantities of oxygen. This oxygen will form water vapor and will also oxidize the filament material and form both Ta_2O_5 (melting point about 1870 °C) and hydrates which may be volatile at 2400 °C filament temperatures. As such they may be incorporated into the diamond at levels similar to those seen for tungsten when tungsten filaments are used. EDX is only sensitive to levels of about $10^{20}\,cm^{-3}$ so there may be substantial quantities of tantalum in the diamond film which were undetected. In order to answer these questions, further study is necessary to be done. We intend to characterize the film by a more accurate analytical technique such as secondary ion mass spectrometry (SIMS) in order to examine the possibility of incorporation of tantalum into the film. Also, we are now planning to switch to a non oxygen containing boron source from trimethyl borate to prevent uncontrolled interactions with the filament, and to study how the

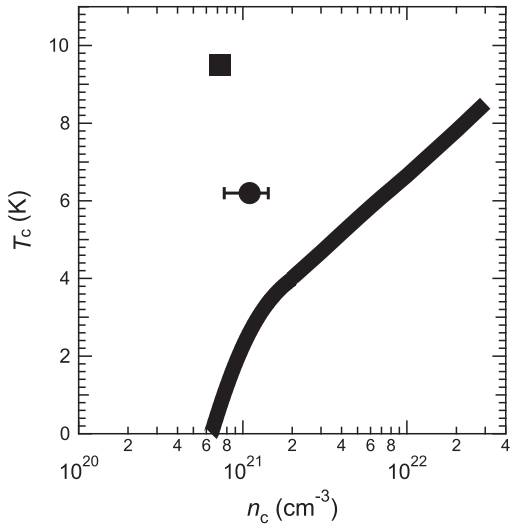

Fig. 3. T_c plotted against carrier concentration for a boron-doped diamond film on a diamond (111) substrate (closed circle), together with the data obtained from boron-doped superconducting diamond films on diamond (111) substrates by the MPCVD method (bold line) for comparison [4]. T_c in the previously reported film by the HFCVD method is also added (closed square) [6].

superconducting property changes for the film prepared using such a boron source. The obtained results will provide information related to the metal contamination from the filament.

In conclusion, we have fabricated a boron-doped superconducting diamond film grown on a diamond (111) substrate using the HFCVD method. The film consists of many grains with an average size of 200 mm. Formation of boron-doped diamond film is confirmed by X-ray photoemission spectroscopy measurements. From the transport measurements, it is found that the film is a superconductor with onset T_c of 7.1 K. The carrier concentration determined by Hall conductivity measurements is $1.1\times10^{21}\,cm^{-3}$. T_c in the present film is higher than that in the boron-doped superconducting diamond films prepared by the widely used MPCVD method at the same carrier concentration. This result is consistent with the previous one, suggesting that the HFCVD method is effective for preparation of boron-doped superconducting diamond films showing higher T_c.

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