

Electrical properties of boron-doped diamond films after annealing treatment

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Abstract

Trimethylborate ($B(OCH_3)_3$) was used to obtain boron-doped (p-type) polycrystalline diamond thin films on a silicon substrate using microwave plasma-assisted chemical vapor deposition. The effect of the doping agent (trimethylborate) was characterized in terms of electrical properties, and the current–voltage (I – V) characteristics of the boron-doped diamond films using aluminum as contacts at room temperature were examined. A surprising result was that annealing improved the electrical properties of boron-doped diamond films. As the boron concentration increased, the forward current decreased because of the effects of impurity scattering, and the I – V characteristics were still rectified. After the samples were annealed in a helium ambient at 900 °C for 30 min, the I – V characteristics changed: the higher the concentration of boron in the doped diamond films, the more ohmic was the observed behavior. The differences in the I – V characteristics of annealed and non-annealed films were subsequently confirmed by Fourier transform infrared spectroscopy (FTIR), capacitance–voltage (C – V) measurements, and cathodoluminescence (CL) experiments. The results of these experiments demonstrated that the annealing treatment caused boron atoms initially in inactive sites (e.g. interstitial or clustering sites) to be incorporated into substitutional sites. The increase in substitutional boron atoms altered the I – V characteristics of the boron-doped diamond films.

Keywords: Doping p-type; Infrared absorption; Polycrystalline diamond films

1. Introduction

It is well known that diamond films possess semiconductor properties. Because of their large energy gap (5.45 eV), chemical inertness, and temperature stability diamond films are a prospective material for microwave, power and high-speed applications under severe conditions such as high temperature and irradiation environment. In particular, diamond films are also attractive materials for high-frequency and high-power devices because of their large saturation velocity (2.8×10^7 cm s^{-1}) [1], low dielectric constant (5.5), high breakdown field (10^6 – 10^7 V cm^{-1}) [2,3] and high electron and hole mobility (2000 cm² V⁻¹ s⁻¹ and 1800 cm² V⁻¹ s⁻¹ respectively) [4]. To take advantage of these excellent properties, adequate control of doping, in particular by the in-situ method, is required. At present, only polycrystalline diamond films can be deposited on large areas and only p-type doping (by boron) is possible. P-type diamond films presenting good semiconductor properties have been reported [5]. The most common doping procedure for CVD diamond films is to add a boron-containing compound to the reaction atmosphere. Solid, liquid, and gaseous boron-containing compounds such

as diborane (B_2H_6) [6] and boron trioxide (B_2O_3) have been used [7]. In addition, boron doping of diamond films can also be performed by means of ion implantation with boron ion beams followed by annealing for activation of the dopant atoms and recovery of the implantation damage [8]. The effectiveness of doping in polycrystalline CVD diamond by 10^{13} – 10^{16} cm⁻² boron implantation followed by annealing at 800 °C has been studied by $I(V,T)$ measurements [9]. Our previous report [10] demonstrated the use of trimethylborate ($B(OCH_3)_3$) mixed with CH_4 – CO_2 gas mixtures to synthesize good quality, uniformly doped diamond films.

The purpose of the research reported here was to investigate the electrical properties of boron-doped diamond films synthesized by a microwave plasma CVD method using $B(OCH_3)_3$ as a doping source. In order to investigate the effects of annealing on the I – V characteristics of the boron-doped diamond films, the as-deposited diamond films were annealed in helium ambient at 900 °C for 30 min. Fourier transform infrared spectroscopy (FTIR), capacitance–voltage (C – V) measurements, and cathodoluminescence (CL) experiments were used to examine the effects of annealing on boron-doped diamond.

2. Experimental details

The samples used in this work were fabricated by standard microwave-plasma enhanced chemical vapor deposition processes [11]. The experimental conditions are listed in Table 1. N-type Si (100) substrates were scratched using diamond powder (approx. 1–2 mm) to enhance the nucleation density of deposits. The scratched Si substrates were then dipped into a solution of HF:H₂O=1:100 for a few seconds to remove the native oxide of the silicon. A vapor source of trimethylborate was introduced to the CH₄-CO₂ gas mixtures. The flow rate of trimethylborate was varied from 0 to 5 sccm using a mass flow meter.

The as-deposited diamond films were annealed in a helium ambient at 900 °C for 30 min. In an effort to remove any non-diamond surface layer, the diamond films were cleaned in a saturated solution of CrO₃ in H₂SO₄ at 170 °C for 10 min followed by a rinse in a 1:1 boiling solution of H₂O₂ and NH₄OH. The diamond films were then thoroughly cleaned with DI water and dried with a jet of nitrogen gas. Conventional photolithography was used to pattern thin photoresist in a positive mask of circles of various sizes (approx. 7.5 × 10⁻⁴ cm²) on the surface of the diamond films. The patterned samples were hardbaked at 140 °C for 30 min. Aluminum contacts (≈5000 Å) were formed by the lift-off method.

An HP-4145B semiconductor parameter analyzer was used to measure the current–voltage (*I*–*V*) characteristics of the aluminum–diamond contacts. For every experiment, the applied voltage was varied from –10 to 10 V. The maximum operating temperature is 300 °C, achieved by heating the measurement stage.

The infrared absorption characteristics of diamond films were studied using a Nicolet 510 FTIR spectrometer with a Michelson-type interferometer. Infrared data were taken with a resolution of 2 cm⁻¹ over the range 4000–400 cm⁻¹. Free-standing diamond films were produced from as-grown Si (100) substrate by the dissolution of the silicon using a mixture of HF and HNO₃ (3:1) diluted by about 50% using DI water. Infrared spectra recorded by using pellets of free-standing

diamond films compressed with KBr provide better resolution of the boron-doped diamond films.

An IBM PC controlled HP4275 LCR meter was used to measure the capacitance–voltage (*C*–*V*) characteristics of the aluminum–diamond contacts. The calibration of measurement units was executed carefully to reduce the measurement error. A frequency of 1 MHz was used in this work. The doping concentration profile was determined through the following equations [12]:

$$C = \sqrt{\frac{q\epsilon_s N_A}{2(V_{bi} - V)}} = \frac{\epsilon_s}{W}$$

or

$$W = \frac{\epsilon_s}{C}$$

$$N_A = \frac{-1 \times C^3}{q\epsilon_s A^2 (dC/dV)}$$

where ϵ_s is the permittivity of GaAs, N_A is the doping concentration, V_{bi} is the built-in potential and W is the depletion width.

The calculation of the doping profile through the above equations is the so-called depletion approximation. In fact, the doping concentration profile measured from the depletion approximation is the majority carrier concentration profile rather than the doping concentration N_D .

3. Results and discussion

3.1. *I*–*V* characteristics and effects of annealing diamond films

The *I*–*V* characteristics of aluminum contacts on boron-doped polycrystalline diamond films deposited from gas mixtures with different boron concentrations are shown in Fig. 1. To explore the differences in *I*–*V* characteristics, the trimethylborate flow rates used in the experiments were varied from 0.5 to 2 sccm. The *I*–*V* characteristics were obtained by applying a voltage to the Al contact on the diamond film surface while earthing the rear of the Si substrate. Poor rectifying characteristics were obtained as a result of excess reverse leakage current. As the boron concentration increased, the forward current decreased. This deterioration of the forward current may be explained by impurity scattering in the diamond film. For a given temperature, the mobility decreased with increasing impurity concentration because of enhanced impurity scattering [13]. The smaller forward current was due mainly to the smaller hole and electron mobility.

The *I*–*V* characteristics of the as-deposited diamond films deposited with various boron concentrations and

Table 1
Experimental conditions

Microwave power	400 W
Substrate temperature	820 °C (approx.)
Reaction pressure	25 Torr
Gas flow rate	
CO ₂	30 sccm
CH ₄	19.2–22 sccm
B(OCH ₃) ₃	0–5 sccm
Type of substrate	N–Si (100)
Reaction time	1.5 h

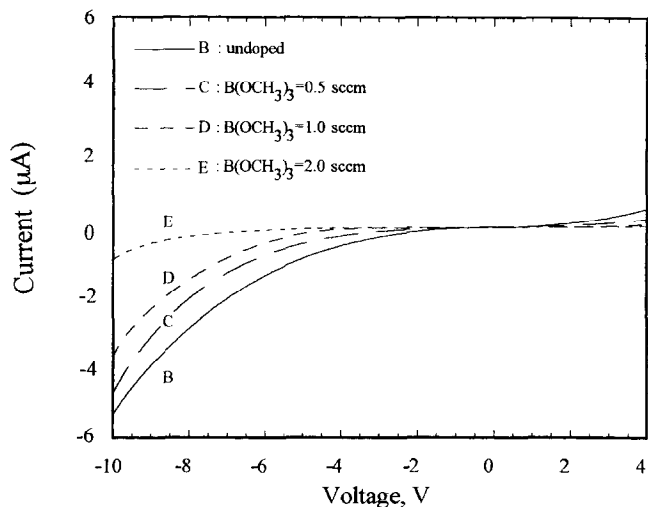


Fig. 1. I - V characteristics of Al contacts to "as-deposited" diamond films with various dopant concentrations.

a constant annealing temperature of 900 °C in helium ambient for 30 min are shown in Fig. 2. After the annealing treatment, there was no deterioration in the I - V characteristics of the undoped diamond films. For the boron-doped diamond film ($B(OCH_3)_3 = 2$ sccm), the leakage current for the 10 V forward voltage increased by a factor of 2 and deterioration in the rectifying characteristics was observed. Increasing the $B(OCH_3)_3$ flow to 5 sccm caused the diamond films to exhibit more ohmic behavior. We are interested in the differences in the I - V characteristics of the boron-doped diamond films caused by annealing prior to metallization. We speculated that the annealing would cause boron atoms doped into the diamond films and located in inactive sites (e.g. interstitial and clustering

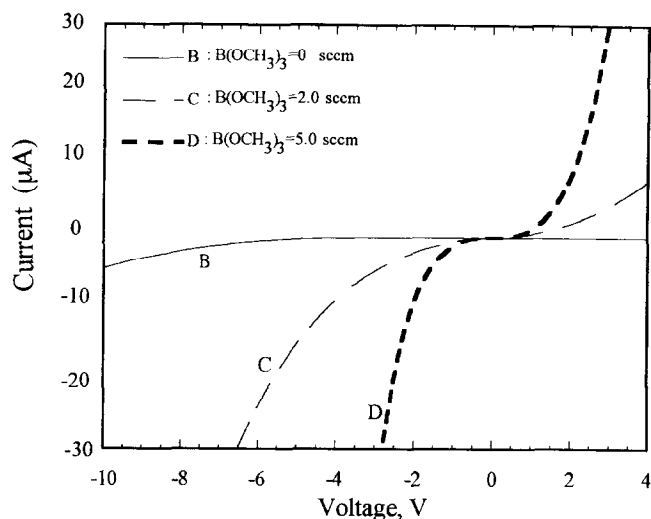


Fig. 2. I - V characteristics of Al contacts to "as-deposited" diamond films with various dopant concentrations after 900 °C annealing treatment.

sites) to be incorporated into substitutional sites in the films. The increase in the number of substitutional boron atoms would then change the I - V characteristics of the boron-doped diamond films because of the tunnelling effect. This hypothesis was examined in our FTIR and CL experiments from the viewpoint of bonding behavior, carrier concentration, and CL emission intensity.

3.2. FTIR analysis of diamond films

FTIR experiments were carried out to examine the difference in the bonding behavior of boron atoms in the diamond films that resulted from annealing in helium ambient at 900 °C for 30 min.

To more clearly resolve the absorption due to the incorporation of boron in the lattice of the diamond films, spectra were taken from samples compressed with free-standing diamond films and dry KBr powder. As shown in Fig. 3(a), a broad band was detected in the region of 3000–3500 cm^{-1} due to O–H stretching vibrations of molecular water physisorbed on the surface of the diamond or diamond–KBr pellets. A peak due to O–H bending vibrations was also found at 1650 cm^{-1} . This result suggests that the diamond surface readily adsorbs atmospheric water on the polar carbonyl groups [14]. The weaker band appearing at 2450 cm^{-1} was identified as the O=C=O stretching vibrations band. This means that a small amount of CO_2 was physically adsorbed onto the sample surface from the atmosphere. A sharp peak at 1380 cm^{-1} and a small peak at around 2980 cm^{-1} were due to bending and stretching vibration bonding of C–H, respectively. The peaks at 620, 1180 and 1360 cm^{-1} were due to boron present in the boron-doped diamond films. These well-known bands have been defined as the O–B–O vibration [15] and B–H deformation bands [16].

When the diamond films were annealed and then compressed with KBr powder into transparent pellets,

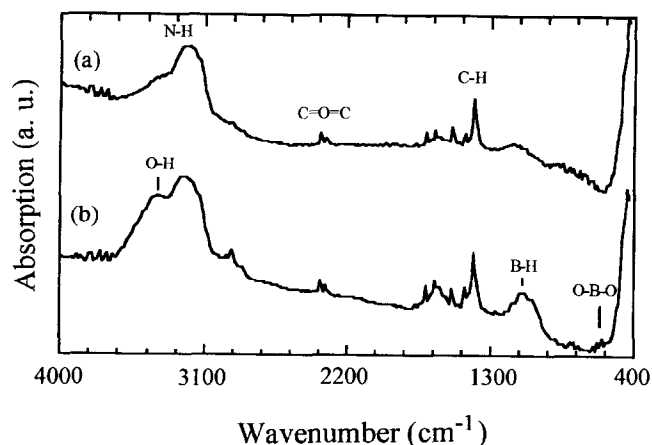


Fig. 3. Infrared absorption spectra of pellets formed from diamond films compressed with KBr powder. The doped diamond films were deposited using $CO_2 = 30$ sccm mixed with $CH_4 = 19.2$ sccm, $B(OCH_3)_3 = 2$ sccm (a) as-deposited (b) after annealing.

infrared absorption spectra of the annealed films were as shown in Fig. 3(b). After annealing, the spectra of the diamond films contained significant bands in the region of $2800\text{--}2980\text{ cm}^{-1}$, which can be ascribed to C–H stretching vibrations of sp^3 hybridized bonding. This indicates that the annealing caused hydrogen atoms present in the diamond films to migrate from inactive to active sites and bond with carbon atoms.

3.3. Carrier concentration measured by CL measurement

Cathodoluminescence spectroscopy were used to examine the difference between the boron atoms in annealed and non-annealed diamond films. The CL spectrum of undoped diamond film shows a main emission peak at 2.8 eV. For the boron-doped diamond films, the emission peaks were located at 2.35–2.40 eV and the intensity was higher than that of undoped diamond films. The variation of the emission band between 2.0–3.5 eV can be explained directly by the distance between D–A pairs [17]. The increase in the CL intensity at 2.4 eV can be explained by the increase of substitutional boron, which becomes an acceptor in the D–A pair recombinations. As shown in Fig. 4, the intensity of CL at 2.4 eV increased dramatically after annealing was performed. From the change in the intensity of CL at 2.4 eV, it appears that the amount of substitutional boron in the boron-doped diamond films increased because of the annealing treatment. The number of substitutional boron atoms increased, resulting in an increase in the CL intensity at 2.4 eV after annealing. This result confirmed again that inactive boron atoms were activated and the I – V characteristics of the boron-

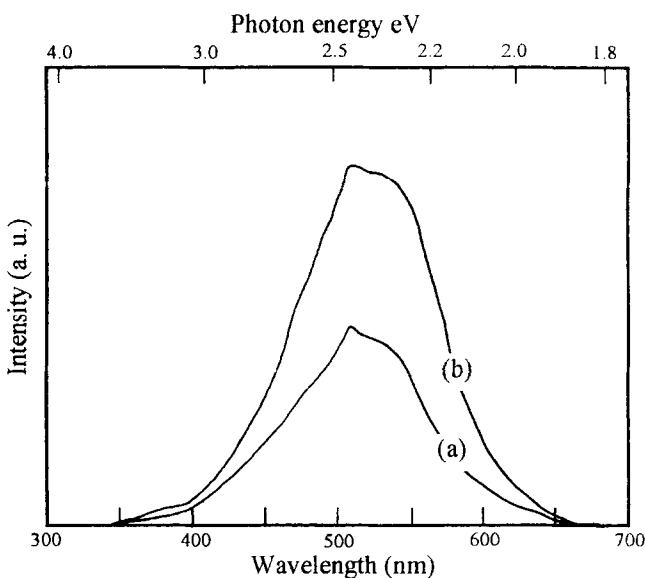


Fig. 4. CL spectra of diamond films deposited using $\text{CH}_4/\text{CO}_2 = 19.2/30$ sccm and $\text{B}(\text{OCH}_3)_3 = 2$ sccm: (a) as-deposited and (b) after annealing treatment.

doped diamond films were altered by the annealing treatment.

3.4. Carrier concentration measured by C–V method

The C–V curves of the Al–diamond contacts were performed (not shown here) with boron concentration equal to 3.8% in the gas phase. Assuming the dielectric constant ϵ ($= 5.7 \epsilon_0$) is uniform over the entire film, the depth W from the surface is given by ϵ/C . Inserting experimental values in the expressions in W and N_A , we can derive the depth profile of the activated boron concentration beneath the Al electrode, as shown Fig. 5 and Fig. 6. Fig. 5 shows the depth profile of carrier concentrations in the boron-doped diamond film ($B = 3.8\%$) before the annealing treatment. It is interesting to compare the mean N_A values obtained from the

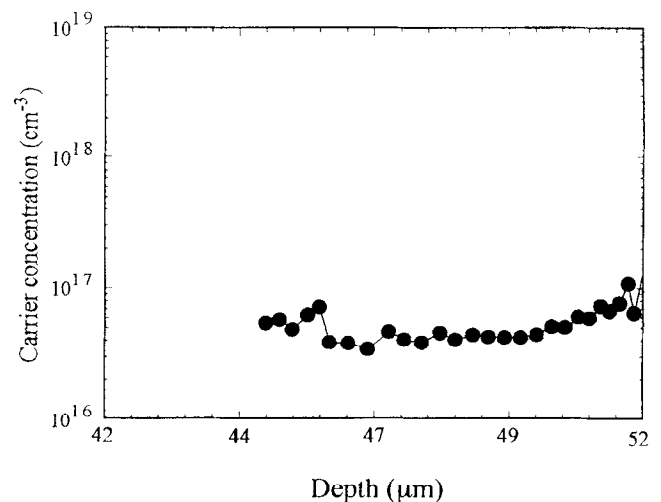


Fig. 5. Carrier concentration of boron-doped diamond film using $\text{CH}_4/\text{CO}_2 = 19.2/30$ sccm and $\text{B}(\text{OCH}_3)_3 = 2$ sccm.

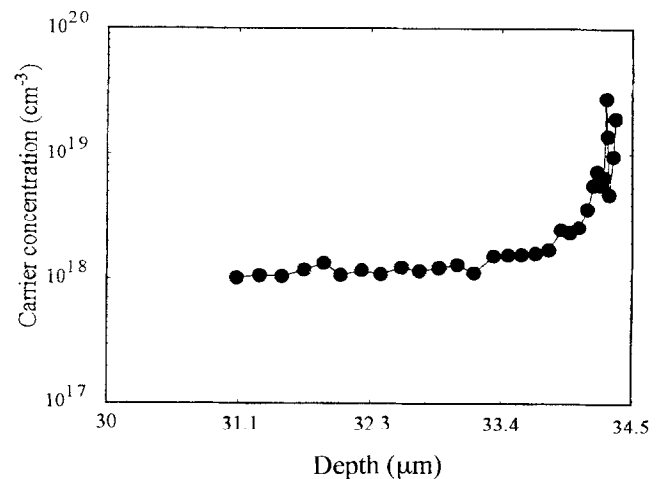


Fig. 6. Carrier concentration of boron-doped diamond film using $\text{CH}_4/\text{CO}_2 = 19.2/30$ sccm and $\text{B}(\text{OCH}_3)_3 = 2$ sccm diamond film at $900\text{ }^\circ\text{C}$ with annealing treatment.

depletion approximation measurement, representing a selected region about $0.4\ \mu\text{m}$ in depth, with those obtained previously from SIMS measurement. The boron concentration derived from the $B=3.8\%$ diamond films using depletion approximation is $6 \times 10^{16}\ \text{cm}^{-3}$ and that obtained using SIMS measurement is $2.2 \times 10^{20}\ \text{cm}^{-3}$. It is apparent that the SIMS measurement overestimates the value of the boron concentration by a factor of almost 4. We believe the SIMS measurement detected the quantity of the boron atoms in the diamond films. These boron atoms perhaps located at the substitutional, interstitial, or clustering sites in the diamond films. Unlike the SIMS technique, the depletion approximation technique directly measures the number of charges in the depletion layer. As a result, it is reasonable for there to be a difference between these two values.

Fig. 6 shows the depth profile of the annealed boron-doped diamond film using the depletion approximation technique. It is evident that the depth distribution of carriers is uniform in the region of $0.31\ \mu\text{m}$ to $0.345\ \mu\text{m}$. The carrier concentration in the annealed boron-doped diamond film is about $1 \times 10^{18}\ \text{cm}^{-3}$, which is almost two orders of magnitude larger than the value for the non-annealed diamond film. This large increase in the amount of carriers probably results from the large number of acceptors. In the boron-doped diamond films, boron atoms are the dominant acceptors, and the number of acceptors increases after annealing.

4. Conclusions

At room temperature, the I – V characteristics of boron-doped diamond films using aluminum as contacts exhibited rectifying behavior. As the boron concentration increased, the forward current decreased, owing to impurity scattering and rectifying behavior. After the samples were annealed in a helium ambient of $900\ ^\circ\text{C}$ for 30 min, the I – V characteristics changed: the higher the boron concentration in the doped diamond films, the more ohmic behavior they presented. CL measurements confirmed that the intensity at $2.4\ \text{eV}$ increased

after the annealing treatment was performed. These data indicate that more substitutional boron atoms were obtained as a result of annealing and that annealing altered the I – V characteristics of the boron-doped diamond films.

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