



Enhancement in conductivity of boron doped diamond films deposited by the methanol/acetone/B₂O₃ system



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ABSTRACT

The gaseous boron sources such as trimethylboron and borane have been widely used for boron-doping of diamond film with a high conductivity. Methanol and acetone/B₂O₃/CH₄ (C-B with CH₄) has also been selected as a doping system for its low cost. But the resulting boron-doped diamond (BDD) film exhibited a lower conductivity. The BDD film was deposited by the system of methanol and acetone/B₂O₃ without CH₄ (C-B) and exhibited a higher conductivity and larger carrier concentration. It is found that oxygen plays an important role during the deposition. A large number of vacancies for boron filling can be generated in the diamond film from the CO bonds. The addition of CH₄ decreased the number of oxygen atoms so that fewer vacancies occurred. Enhancement in conductivity results from more boron atoms in the diamond film using the mixed methanol/acetone/B₂O₃ system.

Conductive diamond film that is achieved by doping plays an important role in the field of electrochemistry and neuroscience [1–4]. Owing to the small lattice constant of diamond (3.57 Å), most doping elements would bring about severe lattice distortion and lead to the difficulty of doping [5]. Nevertheless, the boron atoms ($r = 0.85 \text{ \AA}$) served as the acceptor has been become the most successful doping element in p-type diamond film.

During the chemical vapour deposition (CVD) synthesis process, boron can be introduced to the reaction chamber in different ways. Different kinds of boron resources, such as gas (trimethylboron [6,7] and borane [8,9]), liquid (represented by trimethyl borate [10,11]), and solid (boron oxide [12,13]), have been investigated in previous research. Gaseous boron source was the first choice for a gaseous reaction environment with easy control flow rate and high conductivity of the deposited film. However, liquid boron resource was usually utilized due to its low cost and less toxicity. The solid boron source is also cheap and can be volatilized to gas in the chamber during deposition. But it's difficult to control the doping concentration. In addition, boron oxide can also be dissolved in volatile liquids and then carried into the chamber by the gas bubbling with a controllable concentration. But this BDD film exhibited a lower conductivity in the study compared with the film deposited by gaseous boron resources although it is a cheap and controllable way. Moreover, an interesting phenomenon was found that the conductivity and carrier concentration of diamond film decreased with the introduction of CH₄ in this mixed doping process. The reason

based on the influence of oxygen atoms under this system is to be discussed in the present paper.

The microwave plasma CVD technique was employed to investigate the doping mechanism of C-B (C represents methanol and acetone, and V_m: V_a = 1:3; B represents B₂O₃) system. Boron-doping was achieved by hydrogen bubbling the mixed solution, acetone and methanol dissolved B₂O₃, to the reaction chamber. BDD films were grown on the intrinsic Si substrates under conditions of 1400 W microwave power, 4.5 kPa chamber pressure and 6 h deposition time. The B/C ratio of 10000 ppm was the same in both C-B system and C-B with CH₄ system where the number of oxygen atoms decreased because some carbon atoms from the liquid carbon source were replaced by CH₄.

The JSF-7500F field emission scanning electron microscope (JEOL, Japan), LabRAM HR Raman spectrometer (HORIBA, France), Nicolet iS50 Fourier transform infrared spectroscopy (ThermoFisher, US), Hall effect measurements (KEITHLEY, US) were used to characterize the surface morphology, composition, conductivity and carrier concentration of the BDD diamond films as to understand possible mechanisms of doping.

Fig. 1 shows the surface morphology of BDD film obtained from different deposition system. Typical cauliflower-like morphology with large quantities of tiny grains is shown in Fig. 1a. However, as shown in Fig. 1b, the BDD film was grown as micro-grain with 0.5–1 μm diameter after introducing CH₄ to the reaction chamber in C-B system. It may be explained by the decrease in the number of C₂ from liquid carbon

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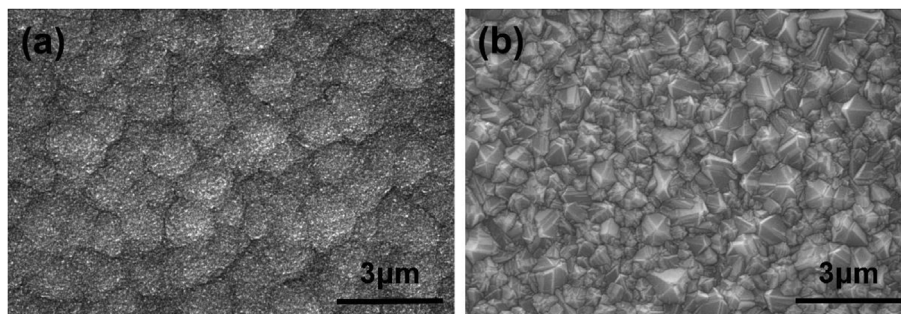


Fig. 1. SEM surface images of the BDD film deposited with different carbon resource: (a) C-B and (B) C-B with CH₄.

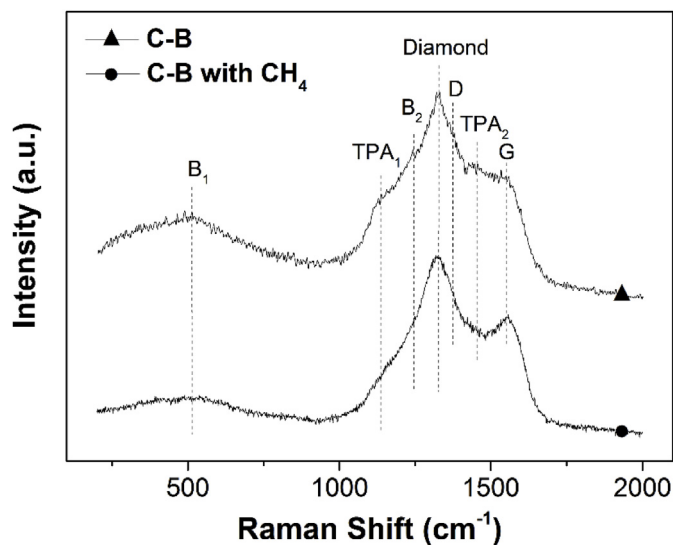


Fig. 2. Raman spectra of film deposited with different carbon resource.

source and oxygen concentration with the introduction of CH₄.

The Raman spectra of two BDD films excited by the 632-nm laser are shown in Fig. 2. There are seven peaks marked as diamond mode, D mode, G mode, trans-polyacetylene modes (TPA₁ and TPA₂) [14], B-induced disorder mode (B₁ and B₂). Diamond mode in Fig. 2 indicated a well-formed crystal with the peak at 1331–1333 cm⁻¹. The higher relative intensity of TPA₁ and TPA₂ in C-B curve illustrated a higher TPA content and smaller grain. B₁ and B₂, which were located around 500 cm⁻¹ and 1200 cm⁻¹ respectively, might be caused by phonon scattering at boron-induced structural modifications [15]. The C-B sample was performed a heavier boron-doping because the relative intensity of 500 cm⁻¹ feature increased with shift to lower wave number compared with the C-B with CH₄ sample. G mode located in 1550 cm⁻¹ corresponds to bond stretching of sp² in graphite and the intensity would be reduced by doping with boron [16]. The higher G mode intensity in C-B with CH₄ system reflected that the lower doping level and the dilution of oxygen weakened the etching process of graphite.

Fourier transform infrared spectroscopy (FTIR) is an effective method for evaluating the substitutional doping in a diamond and the result of two kinds of diamond is shown in Fig. 3. The resultant spectra recorded in the reflection mode (ATR) with a curved baseline. The peak located at 1300 cm⁻¹ can be attributed to the doping of boron in diamond. With regard to pure diamond, the one-phonon vibrations located in the region of 1000–1350 cm⁻¹ are inactive. Meanwhile, it would appear as a peak of 1280 cm⁻¹ in the IR absorption spectrum of BDD [17]. The peaks in the region about 2350 cm⁻¹ are caused by carbon dioxide. Peaks in the region of 1000–1500 cm⁻¹ and 1650–1850 cm⁻¹ can be interpreted as vibrations of the oxygen groups with a single C–O bond and double bond C=O. The larger intensity of B-related and C=O

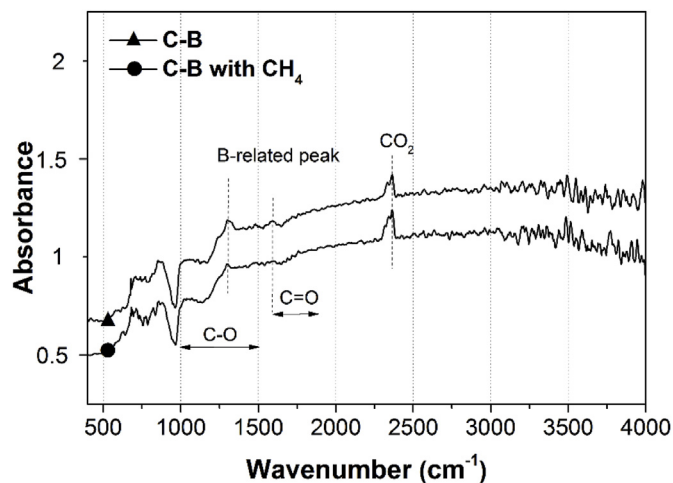


Fig. 3. FT-IR spectra of BDD deposited by C-B and C-B with CH₄ system.

peak in C-B system indicated a heavier boron doping compared with the C-B with CH₄ system. This result is in coincidence with the Raman test mentioned above. Because of the large amount of boron atoms located in the outermost surface of C-B film, there were fewer dangling bonds for adsorbing of CO₂ [18] and brought about a weaker CO₂ absorbance peak.

Hall effect measurement was performed on BDD film which was grown on 10 × 10 mm intrinsic Si substrates. As shown in Table 1, there is a higher conductivity of 37.87 S cm⁻¹ and carrier concentration of 9.62 × 10¹⁸ cm⁻³ for boron-doping diamond film based on C-B system. However, there is a decrease in the conductivity (σ) and the Hall carrier concentration (n_{Hall}) with respect to the introduction of CH₄. It suggests that the introduction of CH₄ weakened the doping of boron atoms.

It is known that oxygen atoms can improve film quality by selectively etching the non-diamond phase [19]. However, few studies concerned about the role of oxygen atoms in the deposition process of BDD. In the C-B and C-B with CH₄ system, the concentration of oxygen is large even higher than that of the boron. A competitive process took place between carbothermal oxidation reaction of diamond and oxygen etching of non-diamond phase. But in BDD film, the etching resistance of oxygen was enhanced because of the higher B–C bond energy and the fewer dangling bond [18]. The higher oxygen concentration indicated

Table 1

The electrical properties of two kind of BDD film measured by Hall effect at room temperature of 300 K.

| Sample | R _s (Ω/□) | σ (S/cm) | μ (cm ² /Vs) | n (cm ⁻³) |
|--------------------------|----------------------|----------|-------------------------|-------------------------|
| C-B | 66.00 | 37.87 | 24.61 | 9.62 × 10 ¹⁸ |
| C-B with CH ₄ | 112.89 | 21.82 | 22.16 | 6.16 × 10 ¹⁸ |

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