Study on the Li and B Co-doped diamond thin film

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Diamond has been paid a lot of attention because of its unique properties, such as hardness, chemical inertness, thermal conductivity, and negative electron affinity. In addition, diamond thin films have unique semiconductor properties, such as wide band-gap (5.45 eV), high breakdown field (10^6–10^7 Vcm^{-1}), and high electron and hole mobilities (2000 cm^2 V^{-1} S^{-1} and 1800 cm^2 V^{-1} S^{-1}, respectively) [1]. To take the advantage of these excellent properties, synthesis of semiconductor diamond films have been extensively studied. The p-type diamond films have been successfully fabricated with boron (B) dopant [1]. The fabrication of the n-type diamond films, however, has not been quite so successful. The nitrogen (N) [2] and phosphorous (P) [3, 4] for n-type diamond films were too deep for donor level. Lithium (Li) [5] and potassium (Na) [6] were proposed as candidate dopants for the n-type because those are much smaller than carbon atoms and can occupy interstitial sites. The doping concentration of Li, however, is too small when it is diffused into a single crystal diamond [7]. Another possibility is co-doping of N and B or hydrogen (H) and P, even though it is not verified with experimental results [8]. In this study, we compared the p-type with B-dopant and the n-type diamond films with the doping of only Li and also the co-doping effect of B and Li was investigated.

The substrate of diamond growth was a silicon (Si) wafer which had ⟨100⟩ orientation, p-type and resistivity of 4–6 Ωcm. The Si wafer was pretreated with 0.5 μm diamond powder to give nucleation sites followed by ultrasonic treatment for 20 min [9]. Diamond films were fabricated on the Si wafer in a Hot Filament Chemical Vaporized Deposition (HFCVD) system. Tungsten filament was used. The filament temperature was 2100 °C during deposition process, measured with optical pyrometer. The substrate temperature was 1000 °C controlled by the distance between the filaments and a substrate [10]. The processing pressure was 30 Torr (hydrogen gas 98%, methane gas 2%) and the deposition time was up to 20 hrs. To increase the dopant density, boron oxide (B_2O_3) powder for B and lithium oxide (Li_2O) powder for Li on a tungsten boat was loaded into the chamber [11, 12]. B_2O_3 powder of 99.5% and Li_2O powder of 99% were made by Johnson Mathey and Junsei Chemical Co. respectively. The diamond film was treated with hydrogen plasma after film deposition in HFCVD process chamber for 5 hrs. The pressure of H_2 gas was 30 Torr, tungsten filament temperature was 2100 °C, and a substrate temperature was 1000 °C.

Microstructure and growth rate were studied with Scanning Electron Microscopy (SEM). For the resistivity measurement of diamond films with four-point-probe, the silicon substrate was fully etched with HF + HNO_3 solution to eliminate effects of silicon substrate. The semiconductor type of diamond films was determined with Hall effect measurements. The dopant concentration in a diamond grain was measured with the Dynamic Secondary Ion Mass Spectrometry (SIMS) at Charles Evans & Associates in U.S.A. A field emission property was measured with the Keithley's Metics system. The distance of the gap—between anode and cathode—was 100 μm. And the area of field emission was 10 mm × 10 mm in vacuum chamber at 2 × 10^{-7} Torr.

Fig. 1 showed the SEM plane view of diamond films. Morphologies are very similar, but the morphology of Fig. 1(c) was rougher, because of H_2 plasma treatment. Also, impurity-doped films' grain size is bigger than undoped films. From the SEM image of cross-sectioned diamond films, the growth thickness was measured and is shown in Fig. 2. Growth rates of doped films were higher than that of undoped film. The previous studies showed the impurity atoms helped to increase the growth rate and the quality of the diamond film [13–15]. Raman spectra were measured at room temperature over the range from 1100 to 1700 cm^{-1} as shown in Fig. 3. There is only one peak at about 1332 cm^{-1}. It shows that the films are of a very high quality diamond [16]. Li doped films had the highest growth rate and highest intensity of diamond peak on Raman spectra.

The resistivity and the Hall coefficient are shown in the Table I. Co-doped film with H_2 treatment showed

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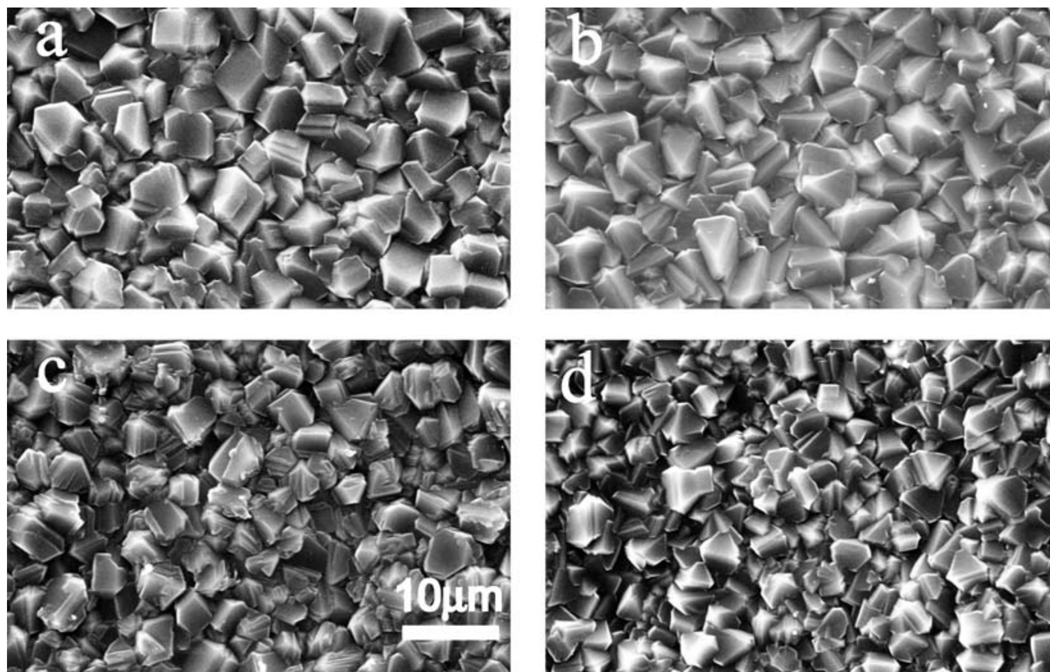

Figure 1 SEM micrographs of plane view of diamond films after 20 hrs; (a) a boron-doped diamond film (b) a lithium-doped diamond film (c) a boron and lithium co-doped diamond film after hydrogen plasma treatment for 5 hrs and (d) undoped diamond film.

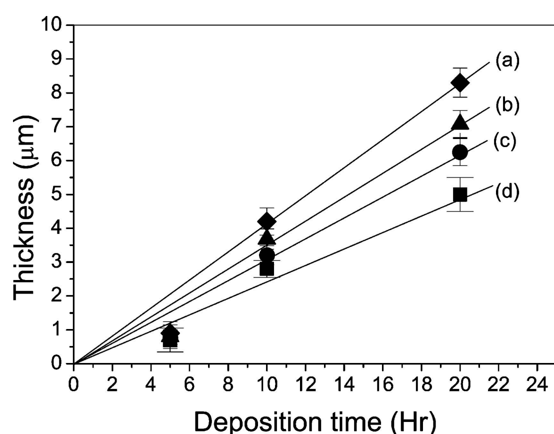

Figure 2 The growth rate of diamond film; with (a) doping only Li, (b) co-doping Li and B followed by hydrogen treatment for 5 hrs, (c) doping only B, and (d) undoped.

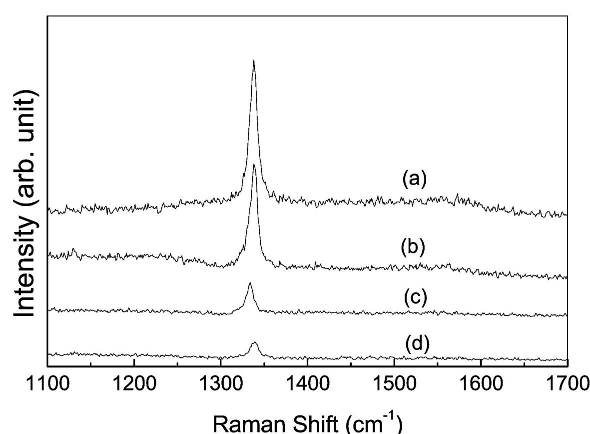

Figure 3 The Raman spectra of diamond films with (a) only Li doping, (b) only B doping, (c) Li and B doping followed by hydrogen treatment for 5 hrs and (d) undoped.

negative sign and so this film seems to be the n-type semiconductor and has low resistivity. Resistivity of lithium-doped diamond films with H_2 treatment was about 22 Ωcm. The resistivity was a little improved as compared to that of a diamond film without H_2 treatment. In the case of co-doped films, the resistivity after H_2 treatment was greatly improved, as shown in Table I. Even though there are many reports that H_2 plasma treatment formed dangling bonds on the surface of diamond films [15, 17], the mechanism is not yet fully understood in the co-doped film.

TABLE I Hall measurement and resistivity results of diamond films

Specimen	Hall coefficient (cm^3/C)	Resistivity (Ωcm)
LiB(H2)[a]	-2.974×10^{-2}	0.01–0.02
Li	−158.26	37–45
B	5×10^{-3}	0.01–0.02

[a]LiB(H_2): Co-doping with Li and B followed by hydrogen plasma treatment.

The doping level of boron and lithium are shown in the dynamic SIMS results of Fig. 4. In the case of B-doped diamond film, the B concentration is about 10^{20} atoms/cm^3 (Fig. 4a) whereas Fig. 4b shows the lithium level is about 10^{16} atoms/cm^3 and also that it decreases from the surface to the interior of the film. The co-doped film results are shown in Fig. 4c. The lithium level is more uniform from the surface to the interior of the diamond, 10^{18} atoms/cm^3, and the boron level is almost the same as (a), i.e., 10^{20} atoms/cm^3. From this result, the co-doped process helped to improve the stable doping level of Li in diamond films.

Field emission results are shown in Fig. 5. B-doped diamond film and hydrogen treated co-doped film, were compared with filed emission characteristics. A field emission phenomenon is analyzed with

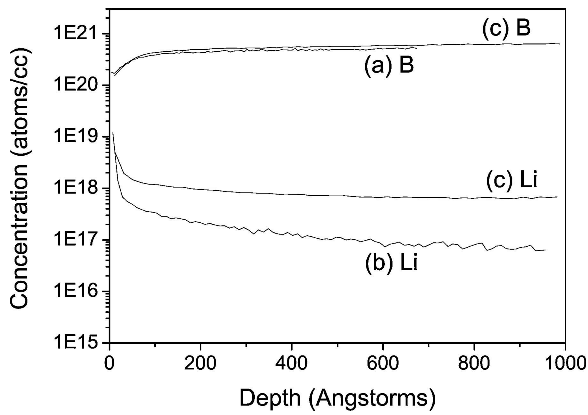

Figure 4 Dynamic SIMS results with (a) boron doped (b) lithium doped (c) co-doping of Li and B followed by hydrogen plasma treatment diamond films.

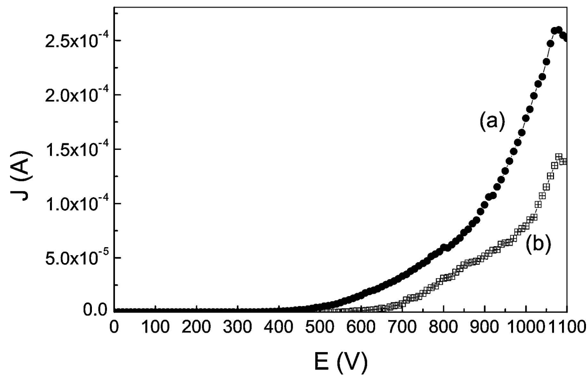

Figure 5 Field emission properties of the diamond films with (a) co-doping of Li and B followed by hydrogen plasma treatment, and (b) doping of B.

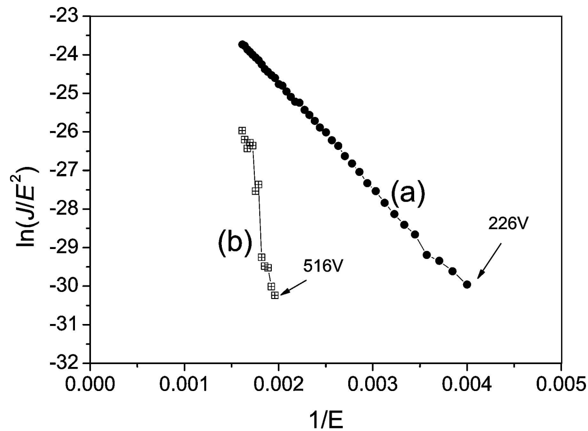

Figure 6 Fowler–Nordheim plot of the diamond films in Fig. 5 (a) with co-doping of Li and B with hydrogen plasma treatment and (b) doping of B.

Fowler–Nordheim equation,

$$J = aE^2 \exp\left(\frac{-b\phi^{3/2}}{E}\right)$$

where a and b are constant, J is the electron current density, E is the applied electric field, and ϕ is the work function of the emitter, i.e., diamond film [18, 19]. The field emission current density of B-doped diamond film was 1.43×10^{-4} A/cm^2 at 1080 V and that of co-doped film was 2.59×10^{-4} A/cm^2 at 1080 V. From Fig. 6, the emission turn-on voltage of co-doped film was 226 V but that of B-doped film was 516 V with 100 μm gap. From the result, the co-doped film's field emission characteristics were much better than the B-doped film.

Li and B co-doped process helped the high doping of Li in diamond and also H_2 plasma treatment increased the electronic performance of the diamond film.

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