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LETTER TO THE EDITOR

Plasma-immersion ion-processed boron-doped diamond-like carbon films

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Abstract. Boron-doped diamond-like carbon (DLC) was prepared using an inductive radio-frequency Ar + C_2H_2 + B_2H_6 plasma-immersion ion-processing (PIIP) technique. The novel results show that B incorporation reduces the stress and that low-energy Ar-ion impingement suppresses the increase of the amount of hydrogen in the B-doped DLC film. An optimal combination of higher hardness, 24.6–28 GPa, and reduced stress was reached in DLC film doped with 4 to 10 at.% B. An increase in the sp^3 carbon and sp^3 CH bonding in the DLC films was found with B doping and was correlated with the enhancement of the properties.

Dielectric films of amorphous hydrogenated diamond-like carbon (a-C:H DLC or DLC) have been shown to have high hardness, and interesting electrical and optical properties [1, 2]. These properties depend strongly on the chemical bonding and the amount of hydrogen incorporated in the DLC films [3–5]. It is possible to modify the optical and electrical properties of DLC films by doping with boron (B), silicon (Si), or nitrogen (N) by using the gas of diborane (B_2H_6) [5], silane (SiH_4) [2], or nitrogen (N_2) [6], respectively. These chemical modifications can be performed using either plasma or ion beam techniques. Recently, there has been increased interest in the preparation and structural characterization of B-doped DLC films as the B doping promotes an increase in the hopping conductivity [1, 5], and improves the field-emission characteristics of planar DLC field-emission arrays [7]. It has been argued that B doping suppresses the formation of sp^2 graphitic clusters and increases both the sp^3 bonding and the hydrogen content in the DLC films [8], and thus changes the electrical and optical properties [1, 5]. However, no investigation on the influence of B doping on the hardness and residual stress in DLC films, to the best of our knowledge, has been presented yet.

In this letter we present the first results on the investigation of the structure, hardness, and stress with B dopant in DLC films prepared by plasma-immersion ion-processing (PIIP) deposition. The PIIP technique, using radio-frequency (RF) inductive plasma sources, provides a unique non-line-of-sight deposition process that produces hard and adherent coatings on substrates with complicated shapes without the need for substrate heating [9]. In PIIP deposition, a dc-pulsed negative bias is applied to the sample stage and the positive ions are attracted from the plasma to bombard the growing films. The low-energy ion bombardment promotes the formation of DLC films with improved sp^3 bonding, high hardness ($\geqslant$30 GPa), high density (2.8–3.1 g cm^{-3}), and good optical properties (an optical gap of $\sim$2 eV) [10–12]. The use of two inductive RF plasma sources at low pressure during PIIP applications makes it easy to apply doping during DLC growth by the plasma decomposition of doping gases such as nitrogen, diborane, and silane [9]. In this study, B doping is executed in a controlled way by alternating the flow ratios of C_2H_2 gas to B_2H_6 gas during PIIP depositions.

The preparation of B-doped DLC films on silicon (100) (380 μm thick) and molybdenum (Mo) sheet (200 μm thick) was performed using a RF plasma which was generated from a mixture reactant of Ar + C_2H_2 + B_2H_6 gases. The bipolar negative dc-pulse bias applied to the substrates was produced by an insulated-gate transistor solid-state modulator [9]. A duty cycle of 20%, produced at a pulse width of 20 μs and a frequency of 10 kHz, was maintained during all deposition processing. Prior to film deposition, the substrates were subjected to Ar^+ sputter cleaning using a -600 V pulsed bias and an incident dose of $\sim 7 \times 10^{17}$ cm^{-2} to remove surface contaminants or oxides. The transition from surface sputtering to DLC deposition was accomplished by slowly adding C_2H_2 + B_2H_6 to the existing inductive Ar plasma. This action usually takes 3–5 minutes to achieve the desired Ar + C_2H_2 + B_2H_6 plasma, and also promotes better adhesion of the DLC film to the substrates. A total gas flow of C_2H_2 + B_2H_6 was maintained over a range of 6–8 sccm and an Ar flow was fixed at 12 sccm. In addition, a RF power of 400 W and a working pressure of 0.1 Pa were kept constant during all deposition. Additional details for PIIP deposition of DLC films have been reported elsewhere [10, 12]. DLC films with different B dopants were synthesized by either adjusting the reactive-gas flow ratio of B_2H_6 to C_2H_2 ($F_{B_2H_6}/F_{C_2H_2}$) from 0 to 1.67 while keeping a pulse bias of -150 V constant, or varying the pulse bias from -70 to -800 V at a fixed gas flow ratio of $F_{B_2H_6}/F_{C_2H_2} = 1$. The growth rate of DLC films was found to vary in a range of 0.9–1.3 nm min^{-1}, depending on the deposition conditions. The thicknesses of the DLC films used in this study were between 120 and 280 nm, as measured by a surface profilometer.

The experimental procedures used for the measurements of the hardness and stress of the DLC films are the same as those in the previous work [10]. The B-dopant and carbon contents in the DLC film deposited on Mo sheet and Si(100) were measured by Rutherford backscattering spectrometry (RBS) using 2 MeV $^4He^+$-ion and resonant-ion backscattering spectrometries (RIBS) at 6.66 MeV $^4He^{2+}$ [13]. The hydrogen content was obtained by elastic recoil detection (ERD) measurement with a 75° beam-incidence angle to the surface normal. Figure 1 shows a typical RIBS spectrum acquired using a 60° beam-incidence angle to the surface normal, which characterizes the existence of C and B in the 9.6 at.% B-doped DLC film deposited at a pulsed-bias voltage of -150 V and a gas flow ratio $F_{B_2H_6}/F_{C_2H_2} = 1$. The RBS spectrum of DLC films on channelled Si(100) and the RIBS spectrum (7.6 MeV, $^4He^{++}$) on Mo sheet (not shown here) indicated a negligible amount of oxygen contamination. The inset in figure 1 is the ERD spectrum showing a uniform hydrogen (H) distribution in the DLC film. The RBS, IRBS, and ERD spectra were analysed using RUMP simulations to determine the B, C, and H content in the DLC films [14]. The argon content was found to be less than 3 at.% in all deposited DLC films. The film density, estimated from the composition and film thickness obtained, varied in a range 1.68–2.57 g cm^{-3}, depending on the deposition parameters.

Figure 2 shows the interrelationship of the hardness and stress (a) with the B and H contents (b), as a function of gas flow ratio, $F_{B_2H_6}/F_{C_2H_2}$. These films were deposited at a pulse-bias voltage of -150 V and $F_{B_2H_6} + F_{C_2H_2} = 6$ sccm. It can be seen that the DLC films without B doping (e.g., $F_{B_2H_6}/F_{C_2H_2} = 0$ and $F_{C_2H_2} = 4$ sccm) exhibit a hardness of about 29.2 GPa, a compressive stress of -6.8 GPa, and a H concentration of 26.2 at.%. As $F_{B_2H_6}/F_{C_2H_2}$ is increased, a monotonic decrease in the compressive stress, from -6.8 to -2.7 GPa, is observed and is correlated with the concurrent increase in B and H contents. The hardness, however, exhibits no change for $F_{B_2H_6}/F_{C_2H_2}$ ratios up to 0.4, after which it drops to about 20 GPa as $F_{B_2H_6}/F_{C_2H_2}$ is increased to 1.67. It was observed that the increase of H concentration in DLC films coincided with an increasing H concentration in the PIIP deposition atmosphere. However, according to the analyses from Schenk *et al* [8], the incorporation of B

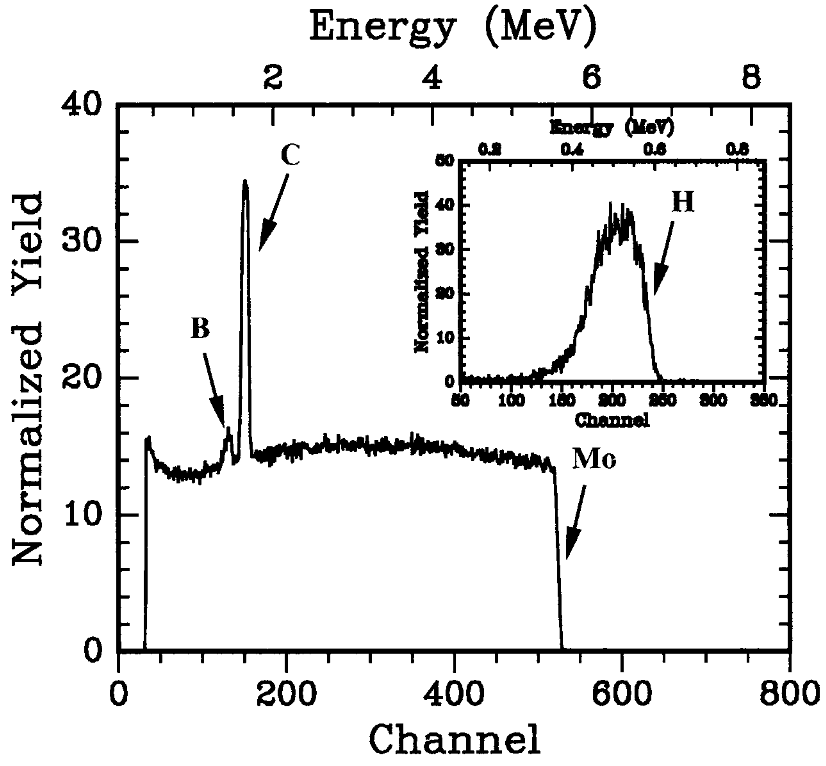

Figure 1. An IRBS spectrum of the 9.6 at.% B-doped DLC film on Mo sheet. The inset is an ERD spectrum obtained from the film for hydrogen content measurement. The beam-incidence angles were 60° and 75° for RBS and ERD measurements, respectively.

promotes H to form sp^3 CH$_n$ ($n = 1$) bonding sites in DLC films, which promotes the formation of a strongly bonded three-dimensional atomic network in an amorphous DLC matrix [4]. This is consistent with figure 2 which shows DLC films having up to 9.6 at.% B and high H content still exhibiting high hardness in the range 22.8–28.7 GPa. Also, B doping results in lower compressive stresses that are reduced by at least 35% as compared with those in undoped DLC films. However, it should be noted that the increase of the $F_{B_2H_6}/F_{C_2H_2}$ ratios to 1.2 or higher results in excessively high H concentrations of 37.5–40.7 at.%, much higher than those in the undoped DLC films. The increase of H concentration above 37.5 at.% possibly overwhelms the effects of B dopant on the formation and properties of DLC films, as high H concentration enhances the forming of a polymeric sp^3 CH$_n$ ($n \geqslant 1$) structure, which changes the bonding constraints of sp^3 bonded carbon by binding more H atoms, and thus relaxes the stress and reduces the hardness of DLC films [4], as the data show in figure 2(a).

The influence of bombarding energy on the composition, hardness, and stress of B-doped DLC was examined by varying the applied dc-pulsed-bias voltage. The bias voltage was varied from −70 to −800 V while keeping other processing conditions constant (i.e. $F_{B_2H_6}/F_{C_2H_2} = 1$ and $F_{B_2H_6} + F_{C_2H_2} = 8$ sccm). Figure 3 shows that increasing the bias voltages from −70 to −350 V substantially reduces the H concentration, from 44.2 at.% to ~30 at.%, and increases the B content, from 7.7 at.% to ~10 at.%. The resultant DLC films exhibit high hardness (above 23 GPa) and reduced stress (−3.5 to −3.7 GPa). The maximum values were obtained for the DLC films prepared at a bias of −250 V. However, it is also found that further increasing

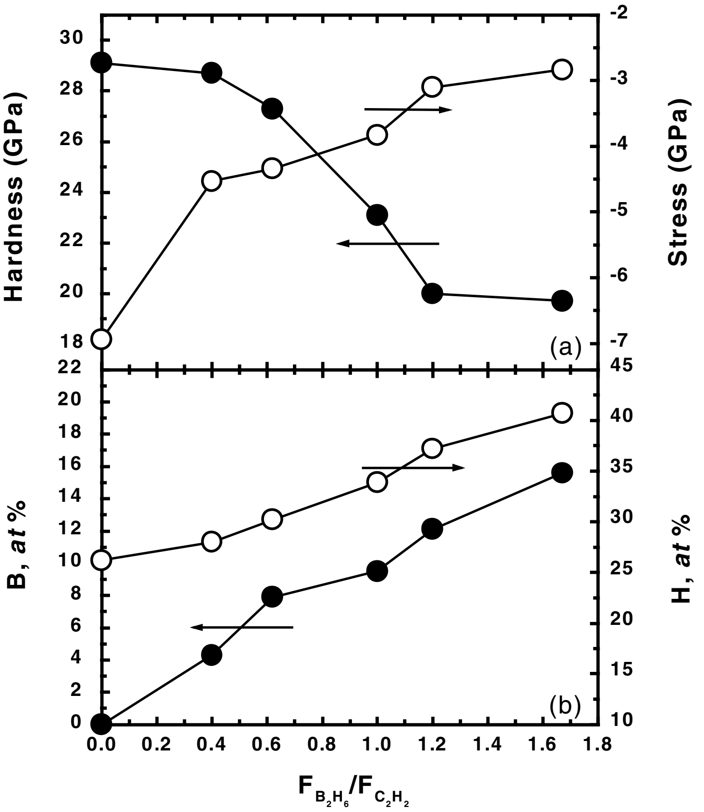

Figure 2. (a) Hardness, stress, and (b) B-dopant and hydrogen content in the B-doped DLC films. The films were prepared at various $F_{B_2H_6}/F_{C_2H_2}$ ratios and at constant conditions of a bias of −150 V and a gas flow of $F_{B_2H_6}$ + $F_{C_2H_2}$ = 6 sccm in the PIIP depositions.

the bias voltages (up to −800 V) does not obviously affect the B and H contents, but does induce lower hardness (below 17.6 GPa) and lower stress (−2.1 GPa).

It has been estimated that a carbon-ion energy of ~100 eV, induced by a bias of −150 V in Ar + C_2H_2 PIIP deposition [10], was optimal for producing maximal values in properties such as density, sp^3 fraction, stress, and hardness [3, 15]. Keeping a constant Ar flow of 12 sccm in all deposition tests, the bombarding ion flux (J_i) during PIIP DLC synthesis consists mainly of Ar ions. Changing the deposition gas flow from $F_{C_2H_2}$ = 4 sccm in DLC formation without B doping to $F_{B_2H_6}$ + $F_{C_2H_2}$ = 8 sccm with B doping increases the number of deposited atoms and the H concentration in plasma, both of which concurrently reduce the arrival ratio of bombarding Ar^+ ions (J_i) relative to the number of deposited atoms (J_a). A reduction of J_i/J_a will cause a reduction in the average energy (E_{ave}) per deposited atom, according to the following relationship [16]:

$$E_{ave} = E_{ion}(J_i/J_a). \tag{1}$$

In (1), E_{ion} is the average ion energy. It is clear that compensating for the reduction of E_{ave} by the reduction of J_i/J_a requires an increase in the negative bias voltage. For low J_i/J_a, the optimal energy condition for ion bombardment is shifted to higher negative bias voltages, up to −250 V, as shown in figure 3. The increased negative bias voltage promotes the incorporation of B and reduces the H content, which enhances the formation of DLC films with ~10 at.% B,

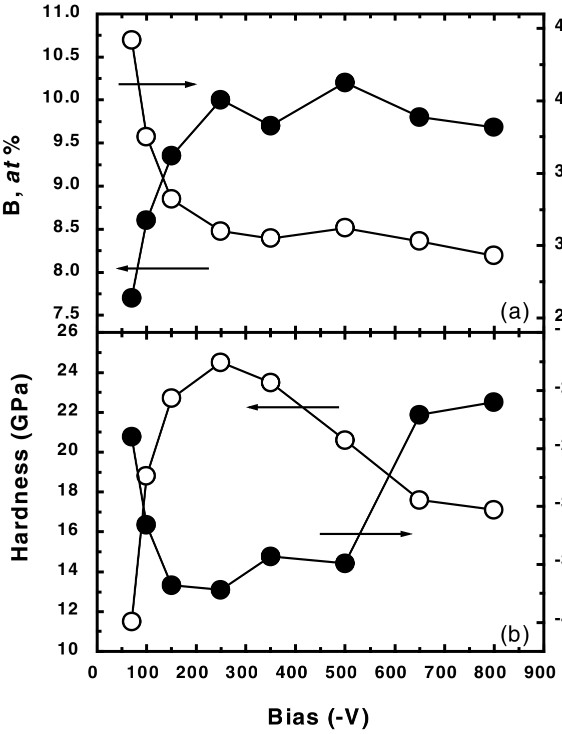

Figure 3. (a) B-dopant and hydrogen content and (b) hardness and stress of the B-doped DLC films prepared at different negative bias voltages. A gas flow of $F_{B_2H_6} + F_{C_2H_2} = 8$ sccm and a gas flow ratio of $F_{B_2H_6}/F_{C_2H_2} = 1$ were maintained during the film depositions.

a high hardness of 24.6 GPa, and a reduced stress of −3.7 GPa. However, further increase in the negative bias voltage (above −500 V) leads to an excessive value of E_{ave} that promotes the formation of sp^2 clusters and more defects in the film [15]. The resulting DLC film has lower hardness and stress (see figure 3).

The change of sp^3 (fourfold-coordinated) carbon bonding in the B-doped DLC films was characterized by Raman spectroscopy. The Raman spectra were collected by means of irradiation with a 514.3 nm laser (5 mW) beam focused on the film surface. The spectral resolution was 1 cm^{-1}. Figure 4(a) shows a series of Raman spectra of DLC films deposited by PIIP with different B-dopant concentrations. Using a Gaussian line simulation, the Raman spectrum can be decomposed into a G band at ~1550 cm^{-1} and a D band at ~1345 cm^{-1}, where the fitted solid line agrees well with the experimental data. Figure 4(b) indicates that the increase of the amount of B dopant induces the shift of the G peak to lower Raman frequency, from 1547.5 to 1522.5 cm^{-1}, and a simultaneous increase of the G-band FWHM (full width at half-maximum) for doping in the range of 4 to 10 at.% B. According to previous analyses of DLC Raman spectra [17], these trends suggest that an increase in the B-dopant concentration from 0 to 10 at.% induces an increase in the sp^3 carbon-bond content in the DLC films. However, the Raman spectrum of 12–16 at.% B-doped DLC films shows a reduction of the G-peak width, as compared with other spectra. This is an indication of the formation of the DLC films with lower hardness [17].

It was reported earlier that high compressive stress, hardness, and density are associated with a high fraction of sp^3 C–C bonds in DLC films [15,18]. The doping of B into the DLC films

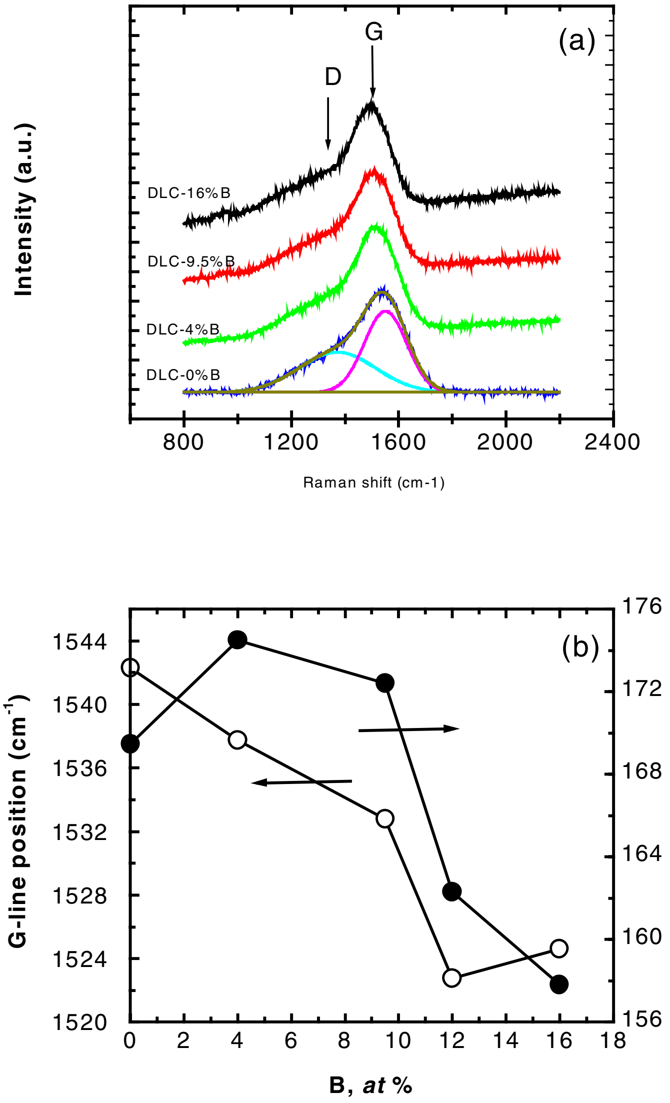

Figure 4. (a) Raman spectra and (b) the G-peak positions and the FWHMs of the DLC films prepared by PIIP with different B dopants. The films were synthesized with the same conditions as for figure 2.

by using B_2H_6 obviously raises the H concentration. The increased H content is correlated with the increase of the amount of sp^3 C–H hybridization, which increases the sp^3 cross-linking region in the DLC films and correspondingly causes a reduction in the residual stress [4, 7] (see figures 2 and 3). However, since the B–C bond is stronger than the C–C bond and the C–H bond stronger than the B–H bond, the doped B tends to bond with carbon rather than hydrogen in DLC films, to form the sp^3 carbon neighbours, and thus suppresses the formation of aromatic sp^2 bonds [7]. Higher hardness values above 23 GPa support the concept that the incorporation of B dopants in DLC films, up to 10 at.%, induces an increase in the sp^3 carbon bonding, which is confirmed by the Raman spectra analyses. The optimal balance between the B-dopant and H concentrations makes it possible for B doping to promote the formation of sp^3 bonds, enhance the hardness, and reduce the stress in DLC films.

In summary, the functional hardness and residual stress of the B-doped DLC films are highly dependent upon the B-dopant content, the hydrogen content, and the ion impingement parameters in PIIP depositions. Doping with B contents up to 10 at.% is confirmed to favour the formation of DLC films with increased sp^3 carbon-bonding fraction, higher hardness, and reduced stress. The B-doped DLC films exhibit a maximum hardness of 28.7 GPa along with a compressive stress that is reduced by 35% relative to that for DLC films without doping. Increasing the negative bias voltage up to -250 V results in a reduced hydrogen concentration and the formation of 10 at.% B-doped DLC films with a higher hardness of $\sim$24.6 GPa. The improved sp^3 bonding structure and the enhanced properties can be reached through the incorporation of 4–10 at.% B in the PIIP DLC films.

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