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# The concentration gradient of boron along the growth direction in boron doped chemical vapor deposited diamond

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ABSTRACT

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#### 1. Introduction

Boron-doped diamond (BDD) film has unparalleled prospect in the applications of microelectrode used in vitro and in vivo. It shows excellent electrochemical properties such as low background current, low detection limit and wide electrochemical potential window, chemical inertness and excellent biocompatibility [1,2]. BDD films are required to possess relatively low resistivity in these applications since high resistivity can be detrimental for the device operation [3]. Therefore, the potential resistivity gradient across the film thickness for the current transport in the growth direction should be seriously concerned [4]. The resistivity of diamond film is strongly dependent upon the doping level [5]. The boron uptake during growth has been found to be dependent on the film structures, such as surface facet orientation [6], grain size, grain boundary [7] and defects [8] etc. It is wellknown that the film structures will evolve with the increase of the film thickness. That means the boron uptake would change in the growth direction, thus influencing the properties of diamond film. Therefore, the investigation for the change of boron concentration

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http://dx.doi.org/10.1016/j.matlet.2015.05.069 0167-577X/© 2015 Elsevier B.V. All rights reserved. in the growth direction becomes meaningful to the structural and chemical control of BDD films. The depth profiles of boron in diamond films with thickness less than 1  $\mu$ m have been analyzed previously [9], by employing destructive SIMS [10,11]. However, SIMS requires flat and relative large samples since the typical analytical volume is 20–30  $\mu$ m in diameter and  $\sim \mu$ m in depth [12], making it difficult to be applied in the boron determination of diamond film micro-device. And there are few papers reporting

The boron concentration in the growth direction of hot filament chemical vapor deposited boron doped

diamond film is studied. Raman spectroscopy showed that the asymmetry of 1332 cm<sup>-1</sup> peak was en-

hanced in the growth direction. The estimated boron content from the position of the Lorentzian con-

tribution to the 500 cm<sup>-1</sup> Raman feature and the electron probe microanalysis on the cross-section of

the diamond film reveal a monotonically increasing of boron concentration in the film growth direction.

In this work, BDD polycrystalline films with different thicknesses were deposited on tungsten wires. The characterizations of diamond films and boron concentration in the growth direction in cross-section have been carried out by Scanning electron microscopy, Raman spectroscopy and EPMA. We found that the boron concentration increases in the growth direction, which supplied a new view to understand the boron doping in BDD film.

the concentration profiles of boron in the thicker diamond films.

#### 2. Experimental details

Diamond films were grown using a hot-filament-assisted chemical vapor deposition reactor system. Prior to diamond film deposition, the tungsten wire substrates (diameter of 100  $\mu$ m, length of 2 cm) were electrochemically etched in aqueous solution of 1 M NaOH at +4 V (vs Ag/AgCl) for 5 min and then immersed into 30%





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HF solution for 5 min. After that, the wires were ultrasoniccleaned in acetone and deionized water for 10 min consecutively. Then tungsten wires were suspended vertically and ultrasonic pretreated in nano-diamond colloid for 30 min and in ethanol for 2 min successively. Finally, wires were mounted horizontally on a stainless steel stage in the chamber. The reaction gas was a mixture of 1.0 sccm CH<sub>4</sub>, 49.0 sccm H<sub>2</sub>, and 0.5 sccm B<sub>2</sub>H<sub>6</sub> as doping source. The total gas pressure was maintained at 3.5 kPa. The substrate temperature was maintained at around 700 °C. Two samples were prepared with deposition time of 40 min and 180 min, respectively.

The surface and cross-section morphology were analyzed by FEI Sirion200 field emission scanning electron microscopy (SEM). The diamond film quality and the boron concentration were investigated by a micro-Raman spectrometer (LabRAM ARAMIS), at an excitation wavelength of 532 nm (argon ion laser) with a power of 21 mW and a typical resolution of  $1-2 \text{ cm}^{-1}$ , which has a 2 µm-in-diameter circle spot. Electron probe micro-analyzer (EPMA, JXA-8230) was used to yield composition depth profiles by performing a point by point line-sweep along the cross-sectional surface.

#### 3. Results and discussions

Fig. 1 shows the SEM images of BDD films. The average thickness of film with 40-min is  $2.0 \ \mu\text{m}$  and 180-min is  $9.1 \ \mu\text{m}$ , respectively, shown in Fig. 1(a) and (b). A distinct columnar structure



Fig. 2. Raman spectra of the surface of diamond films with different deposition time.

is observed at the cross-section of the thicker diamond film in Fig. 1(b). The diamond film near substrate is nanocrystalline and gradually develops into microcrystalline with increasing thickness. A close packing and continuous diamond films are presented in Fig. 1(c) and (d). The faceted diamond grains mainly consist of (111) facets in both films and have size about 200–300 nm after



Fig. 1. SEM images of BDD films with different deposition times: (a,c) 40-min, (b,d) 180-min, (a,b) are the corss-section images and (c,d) are the surface images.

40-min deposition and  $\sim\!1\,\mu m$  after 180-min deposition. It indicates that the grain size increases with the prolonged deposition time.

Fig. 2 shows the Raman spectra of these two diamond films with different thickness. It is observed that the peak intensity of zone-center optical phonon Raman line at 1332 cm<sup>-1</sup> becomes weaker and its asymmetry increases as the deposition time increases. The increasing asymmetry of peak 1332 cm<sup>-1</sup> means the higher boron concentration in diamond film [9]. The broad band  $500 \text{ cm}^{-1}$  and  $1200 \text{ cm}^{-1}$  related to boron doping appear significantly [13]. Compared with the thinner sample, the 500  $\text{cm}^{-1}$ band from thicker sample slightly shifts towards lower wavenumber and its intensity increases. Study reveals that the higher the B concentration is, the lower the wavenumber of the maximum of  $500 \text{ cm}^{-1}$  band would be [13]. The  $1200 \text{ cm}^{-1}$  band position seems identical. Combined with the fact that the Raman detect zone is only  $\sim 2 \,\mu m$  in depth, we thus speculate the boron concentration increases with growing thickness of diamond film. To further validate our speculation, the cross-section analysis by Raman and EPMA on the thicker sample has been carried out.

Fig. 3 shows the Raman spectra obtained from the cross-section of the thicker sample. Four points have been successively tested from nucleation surface (point 1) to growth surface (point 4) along the growth direction. It is observed that the  $1332 \text{ cm}^{-1}$  peak progressively broadens and shifts toward lower wavenumber as it is far away from the nucleation surface. Its asymmetry appears and enhances gradually, indicating the boron concentration increases along the growth direction. The broad band at 1500 cm<sup>-1</sup> assigned

to sp<sup>2</sup> carbon which mainly exists in grain boundaries becomes weaker. It is reasonable to consider that, due to the columnar growth which is shown in Fig. 1(b), the crystal size is small and high density grain boundaries exist in initial growth stage. The crystal size increases in the growth direction, resulting in the decrease of density of grain boundaries. So the content of sp<sup>2</sup> carbon decreased. The broad band center at 500 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> appear apparently starting from the 2<sup>nd</sup> test point. Bernard et al. [9] found an empiric fit as a sum of a Gaussian and a Lorentzian component can be satisfied to fit the broad band 500 cm<sup>-1</sup>. There is a simple and accurate relationship between the wavenumber in cm<sup>-1</sup> of the Lorentzian component of the 500 cm<sup>-1</sup> broad band and the boron concentration [B]  $\times$  cm<sup>-3</sup>.

### $[B] \times cm^{-3} = 8.44 \times 10^{30} \exp((-0.048W)(cm^{-1}))$

*W* is the wavenumber of Lorentzian component of the 500 cm<sup>-1</sup> broad peak. After a polynomial curve background was subtracted [10], point 2, 3 and 4 have been fitted. The wavenumber of Lorentzian component in these 3 fitted spectrums are approximately 487.1 cm<sup>-1</sup>, 480.7 cm<sup>-1</sup>, 475.4 cm<sup>-1</sup> respectively, showing a systematically decreasing trend in Fig. 3 (b1, b<sub>2</sub>, b<sub>3</sub>). The boron doping levels [B] were calculated to be 5.92, 8.05, 10.38  $\times 10^{20}$  cm<sup>-3</sup>, which have been plotted in Fig. 3(c). Obviously, there is a monotonically increasing of boron concentration in the growth direction.

Fig. 4(a) and (b) shows the profiles of carbon and boron, respectively, from the EMPA line analysis in the thicker diamond



**Fig. 3.** (a) Raman spectra of the cross-section of diamond film (start from nucleation surface and along the growth direction to growth surface, from point 1 to point 4) for 180 min deposition time and measured with a 2  $\mu$ m interval. (b) The fit of 500 cm<sup>-1</sup> peak of (b<sub>1</sub>) point 2, (b<sub>2</sub>) point 3, (b<sub>3</sub>) point 4. (c) The calculated boron concentration of different points.



Fig. 4. EPMA line analysis of the cross-section of diamond film with 180-min deposition time.

film. The carbon content is the lowest in the substrate and presents mainly in diamond film. Boron exists only in diamond film and its content exhibits a virtually monotonic increase in the growth direction across the film, which is consistent with the Raman results.

The above analysis indicated that the boron doping is inhomogeneous in the growth direction. The main change of polycrystalline diamond film in the growth direction is the growth of typical columnar structure which has been illustrated in Fig. 1(b). The grain size increases in the growth direction, resulting in less boundaries. The test spot sizes are fixed for both Raman and EPMA measurements. Hence more boundaries are covered on nucleation surface than on growth surface. Considering the depletion of grain boundaries is evidenced in CVD diamond films [14], it is properly speculated that the virtually monotonic increase of boron in the growth direction in BDD films is resulted from the structural change, namely, less boundaries, in the growth direction of the films.

#### 4. Conclusions

The boron concentration in the growth direction was investigated

in the BDD polycrystalline film deposited on tungsten wires. The gradually increasing asymmetry of 1332 cm<sup>-1</sup> peak in Raman obtained from cross-section of the BDD reveals that the boron concentration is increase in the growth direction. The fitting of 500 cm<sup>-1</sup> peaks and the line analysis of EPMA further manifests that the increasing of boron concentration is virtually monotonic. The increasing concentration was ascribed to the columnar structure evolution of diamond film during CVD process.

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