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Dear Reviewer and Editor,

We would like to thank each of you for your comments. The manuscript has been improved as requested by putting the references in the correct format and redoing Fig. 5a.

Best regards,

Tim Grotjohn

NDNC 2007

Abstract: 00207

Title: Boron doped diamond deposited by microwave plasma-assisted CVD at low and high pressures

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Primary Novelty Statement:

The uniform deposition of boron-doped polycrystalline diamond across 5 cm diameter substrates at pressure regimes from 35-120 Torr is reported. The electrical conductivity, crystal size and boron content are measured versus pressure and spatial position on the substrate.

Authorship Statement:

The submission of the manuscript has been approved by all co-author.

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Boron doped diamond deposited by microwave plasma-assisted CVD at low and high pressures

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ABSTRACT

Boron doped diamond is deposited over a range of pressures and chemistries including pressures from 35-120 Torr and gas chemistries including hydrogen-methane-diborane and argon-methane-hydrogen-diborane mixtures. The diamond deposition system is a 2.45 GHz microwave resonant cavity system. Diborane (B_2H_6) gas chemistry has been utilized with flow rates of 2.5-100 ppm. At low pressures of 35 Torr polycrystalline films are deposited using a feed gas mixture of hydrogen and 0.5% methane. At moderate pressures of 95 Torr, diamond films are grown using 60% Ar, 39% H_2 and 1% CH_4 . For the high pressure experiments of 120 Torr, polycrystalline films are deposited using 98% H_2 and 2% CH_4 . The deposition rate ranges from 0.3 to 1.6 $\mu\text{m/hr}$. This investigation describes the relationship of the diborane flow rate and pressure versus the resulting film morphology, electrical properties, and morphology of the deposited films. The deposition of boron-doped polycrystalline diamond is done on 5 cm diameter silicon and silicon dioxide coated substrates. The resistivity spatial variation across the wafer was $\pm 5\%$ indicating a good uniformity.

Keywords: diamond film, p-type doping, electrical conductivity

INTRODUCTION

Diamond has unique semiconductor properties like wide bandgap, high breakdown voltage, and high electron and hole mobilities, which makes it a suitable candidate for applications in high temperature electronics and MEMS-based devices. Because of the potential applications in high frequency, high power electronics, the growth and characterization of p-type semiconducting diamond is of considerable interest. It is also used as material for temperature and pressure sensors, and as an electrochemical electrode. Impurity doping of diamond can be achieved by introducing boron in the gas phase during the diamond deposition process. Boron doping affects the morphology, structure and electrical properties of the diamond films. It is known that high boron-doping levels can result in the formation of electronic defects in the coating [1, 2]. Consequently, highly controlled and efficient boron-doping is important.

This study investigates the variation in electrical conductivity and boron content of diamond films resulting from varying the boron concentration in the deposition plasma gas phase at different pressure regimes. The current work focuses on the deposition of polycrystalline boron-doped diamond from low and high pressure (35-120 Torr) with variation of the boron content in the feedgas. Specifically, the morphology, growth rates and electrical properties will be studied with varying boron contents in the film and at different deposition pressure regimes. The uniformity in the coating morphology and resistivity across 5 cm diameter substrates will be studied as well. This study particularly focuses obtaining high electrical conductivity in the diamond films for electrochemical electrode applications.

EXPERIMENTAL DETAILS

Diamond films are deposited using a microwave plasma enhanced chemical vapor deposition system. The diamond deposition system is a 2.45 GHz microwave resonant cavity system[3]. Boron doped polycrystalline diamond is deposited with various crystal sizes and electrical properties by adjustments in the feedgas and deposition pressure. The substrates used are 0.5 mm thick silicon (Si) and 1 μm silicon dioxide (SiO_2) on 0.5 mm Si substrates. They are pre-cleaned ultrasonically in acetone, ethanol, and deionized water for 2 minutes. Then they are ultrasonically seeded in a diamond slurry for 40 minutes. Next they are post-cleaned ultrasonically in acetone, ethanol, and deionized water for 2 minutes and dried in nitrogen. Diborane gas chemistry is utilized across the pressure range from 35-120 Torr with diborane flowrates of 2.5-100 ppm. The methane percentages are in the range of 0.5-2%. Substrate temperatures range from 700-925 $^{\circ}\text{C}$ and deposition times vary from 12-15 hrs. The experimental

parameters of each experiment are listed in Table 1. The samples are analyzed for grain size and thickness using a JOEL6400 SEM, diamond quality and boron content in the coating using a SPEX 1250M Raman spectrometer, and sheet resistivity using a Lucas Signatone four-point probe head and stand. Images of the samples are also taken using a Nikon Optical Microscope.

RESULTS AND DISCUSSIONS

In the initial set of experiments, the chamber pressure is maintained at 35 Torr, microwave power is 1.6 kW, gases used in the plasma are 99.5% H₂, 0.5% CH₄, and 2.5-100 ppm B₂H₆. The deposition times varies from 12-15 hrs. The plan-view SEM images in Fig. 1 show that the grain size of the B-doped diamond films decreases with increasing boron content in the diamond films. Grain size was measured using the SEM images. An image area of 2 μm x 2 μm is chosen and several lines are drawn across the length of the image at different places. Then the number of grains is counted along a 2 μm length for example and the grain size along that length was determined by the method of intercepts. The average grain size was determined by making several such measurements across the width of the image. With B₂H₆ concentrations varying from 2.5 ppm to 100 ppm in the plasma, the average grain size decreased from 0.87 μm to 0.59 μm as seen in Figs 1a-1e. The thickness of the coatings is measured using cross-sectional SEM images. The growth rates are determined from these values knowing the deposition time. The growth rates for diamond deposition decrease from 0.42 μm/hr to 0.3 μm/hr as B₂H₆ increases from 2.5 ppm to 100 ppm. These values are listed in Table 1.

In the second set of experiments, the deposition conditions are a pressure of 95 Torr, microwave power of 1.4 kW, plasma gas composition of 60% Ar, 39% H₂, 1% CH₄, and 2.5-20 ppm B₂H₆. In Figs 2a-2c, plan-view SEM images of the B-doped diamond coatings on Si with B₂H₆ varying from 2.5-20 ppm can be seen. The average grain size varied from 3.71 μm to 1.28 μm. The thickness of the coatings were in the range of 17-20 μm for deposition times of 13-15 hrs. The growth rate was ~1.3 μm/hr and did not change much with varying the boron content in the feedgas.

In the third set of experiments, the deposition conditions are a pressure of 120 Torr, microwave power of 4 kW, plasma gas composition of hydrogen with 2% CH₄, and 2.5-25 ppm diborane. Fig. 3 shows optical images of the deposited films. The average grain size varied from 12 to 7.5 μm and the growth rate from 1.7 to 1.6 μm/hr as the diborane flow rate increased from 2.5 to 25 ppm.

In the 35 Torr, 95 Torr and 120 Torr pressure regimes, the grain size decreases with increasing boron. This may be due to the formation of defects from excess boron that leads to renucleation during the film growth. The effect of pressure on boron-doping efficiency is important in order to obtain good quality, large grain size and highly conducting coatings. Raman spectroscopy is a useful tool to evaluate quality of the coatings in terms of the sp^3 and sp^2 contents. In addition, boron content in the diamond can be determined. Figs. 4a shows the Raman spectra for films grown at 35 Torr and doped with 2.5 -100 ppm of B_2H_6 . Fig. 4b shows the films grown at 95 Torr and doped with 2.5-20 ppm of B_2H_6 . Finally, Fig. 4c shows the Raman spectrum for the film grown at 120 Torr and doped with 25 ppm of B_2H_6 .

In general, polycrystalline B-doped diamond films show a Raman spectrum where the 1332 cm^{-1} diamond vibrational mode peak intensity decreases and then shifts down in its wave number with increasing boron in the coatings. Two new bands also appear at 500 cm^{-1} and $1200\text{-}1220\text{ cm}^{-1}$ at high boron levels [4-6]. The 1200 cm^{-1} peak has a small shift, whereas the 500 cm^{-1} has a large shift with increasing boron concentrations in the films. The high boron content ($>10^{20}$ atoms/ cm^3) increases the probability of creating a structural defect when boron atoms enter a substitution site of diamond [7]. Formation of boron clusters due to interstitial incorporation of boron is another factor that can disrupt the diamond lattice during growth [6]. Also, intraband optical transitions occur due to the interference of the phonon and the impurity band induced electronic states [9]. A peak fitting program is used to fit the Raman spectra with Lorentzian and Gaussian peaks corresponding to the vibrational modes present in the diamond coating as shown in Fig. 5a. It is seen that the center of the Lorentzian component of the 500 cm^{-1} peak (C_{500}) downshifts significantly as a function of the boron content. A numerical value for the boron content in the diamond coating can be obtained using the equation [10]

$$B = 8.44 \cdot 10^{-30} \cdot \exp(-0.048 \cdot C_{500}\text{ cm}^{-1}) \quad (\text{cm}^{-3}) \quad (1)$$

It is known that the onset of metallic conductivity in diamond happens when there is $> 10^{20}\text{ cm}^{-3}$ of boron in the lattice [7]. In Fig. 5b it is seen that this can be achieved with 25 ppm of B_2H_6 in the feed gas at a chamber pressure of 35 Torr. Whereas, at 95 Torr in the chamber with the argon/hydrogen/methane gas mixture the transition takes place with only 2.5 ppm of B_2H_6 . At 35 Torr, the boron content in the films is in the range of $10^{20}\text{-}10^{21}\text{ cm}^{-3}$ only at the high concentration of 50-100 ppm B_2H_6 in the plasma. Whereas, at 95 Torr those levels of doping can be achieved at 2.5-20 ppm of B_2H_6 in the plasma. At 120 Torr with hydrogen/methane chemistry the boron concentration is 10^{21} cm^{-3} for a diborane flow rate of 25 ppm.

Fig. 6 shows the electrical conductivity. The conductivity values at the various boron doping levels are in the range of $0.03\text{-}11\text{ (ohm-cm)}^{-1}$ at 35 Torr with B_2H_6 values of 2.5 to 25 ppm and $68\text{-}330\text{ (ohm-cm)}^{-1}$ at 95 Torr with B_2H_6 concentrations of 2.5 ppm to 20 ppm in the feed gas. At 95 Torr and 20 ppm B_2H_6 the conductivity is 330 (ohm-cm)^{-1} , which can only be achieved with 100 ppm of B_2H_6 at 35 Torr. The conductivity at 120 Torr varied from 3.2 to 96 (ohm-cm)^{-1} with a 2.5-25 ppm B_2H_6 variation in the feed gas. At the center of the substrate sample deposited with 25 ppm B_2H_6 , the conductivity was 96 (ohm-cm)^{-1} and at the edge it was $101.5\text{ (ohm-cm)}^{-1}$. The spatial variation of the electrical conductivity across the 5 cm diameter of the substrate was $\pm 5\%$.

CONCLUSIONS

Boron-doped diamond was deposited on Si and SiO_2 substrates at 35 Torr and 120 Torr in a H_2/CH_4 plasma and at 95 Torr in a $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma. The diborane doping levels in the plasma gas flow were in the range of 2.5-100 ppm. With these conditions, the deposition plasma coated uniformly across 5 cm diameter substrates. The grain size and growth rate of the coatings decreased with increasing B_2H_6 levels in the gas phase. The minimum amount of diborane needed to obtain high (metallic-like) conductivity at 35 Torr in a H_2/CH_4 plasma was 25 ppm and at 95 Torr in a $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma was 2.5 ppm. The $\text{Ar}/\text{H}_2/\text{CH}_4$ gas chemistry at 95 Torr produced higher conductivity polycrystalline diamond with a smaller grain size than the H_2/CH_4 at 120 Torr.

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Table and Figure Captions

Table 1. Experimental details in the pressure range of 35-120 Torr.

Fig. 1. SEM plan-view images of boron-doped diamond films at 35 Torr with B₂H₆ concentrations of (a) 2.5 ppm, (b) 7.5 ppm, (c) 25 ppm, (d) 50 ppm, and (e) 100 ppm.

Fig. 2. SEM plan-view images of boron-doped diamond films at 95 Torr with B₂H₆ concentrations of (a) 2.5 ppm, (b) 10 ppm, and (c) 20 ppm.

Fig. 3. (a) Optical microscopy images of B-doped diamond films grown at 120 Torr, 4 kW, 2% CH₄, 98% H₂, 6 hrs and (a) 2.5 ppm B₂H₆, (b) 25 ppm B₂H₆.

Fig. 4. Raman spectra of B-doped diamond coatings (a) 35 Torr with 2.5-100 ppm B₂H₆ (2.5 ppm curve reduced by factor of 3); (b) at 95 Torr with 2.5-20 ppm B₂H₆; and (c) 120 Torr with 25 ppm B₂H₆.

Fig. 5. (a) Fitting plot for the Raman spectra of a 20 ppm (95 Torr) B₂H₆ diamond film and (b) film boron content versus B₂H₆ content in the plasma feedgas at 35 Torr, 95 Torr and 120 Torr.

Fig. 6. Variation of electrical conductivity of B-doped diamond films at 35 Torr, 95 Torr and 120 Torr versus B₂H₆ concentrations in the plasma feedgas.

P (Torr)	W_f (kW)	H ₂ (sccm)	Ar (sccm)	CH ₄ (sccm)	B ₂ H ₆ (ppm)	B/C (ppm)	T _s (°C)	Growth Rate (μm/hr)	Grain size (μm)
35	1.6	194	0	1 (0.5%)	2.5	1000	696	0.42	0.86
35	1.6	184	0	1 (0.5%)	7.5	3000	734	0.34	0.72
35	1.6	149	0	1 (0.5%)	25	10000	716	0.41	0.82
35	1.6	99	0	1 (0.5%)	50	20000	725	0.37	0.67
35	1.6	0	0	1 (0.5%)	100	40000	741	0.3	0.59
95	1.4	73	120	2 (1%)	2.5	500	852	1.31	3.71
95	1.4	68	120	2 (1%)	10	2000	860	1.32	1.28
95	1.4	58	120	2 (1%)	20	4000	862	1.32	1.73
120	4	191	0	4 (2%)	2.5	250	924	1.7	12
120	4	146	0	4 (2%)	25	2500	870	1.58	7.5

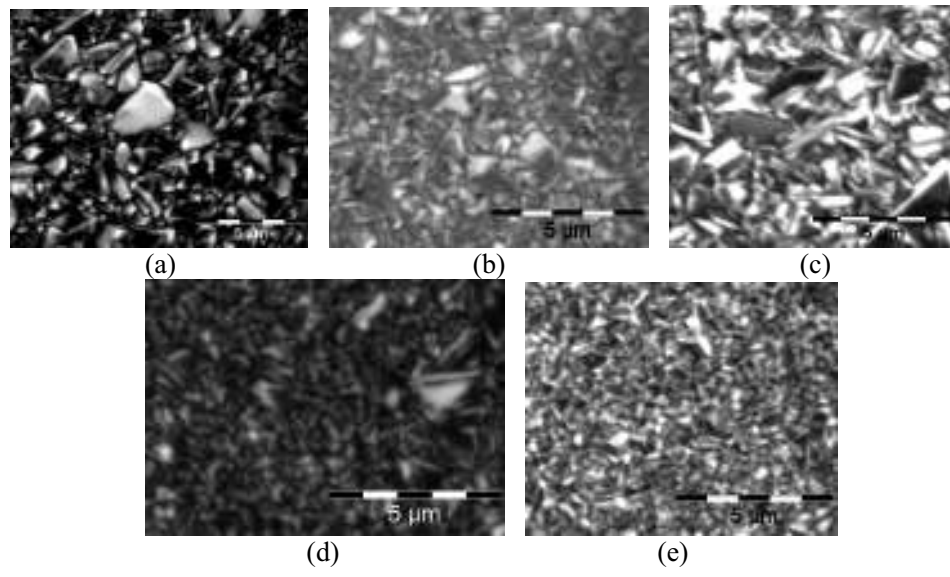


Fig. 1.

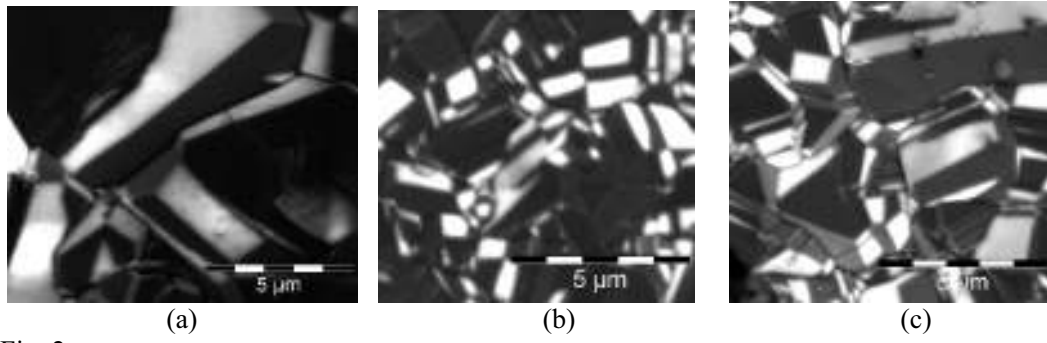


Fig. 2.

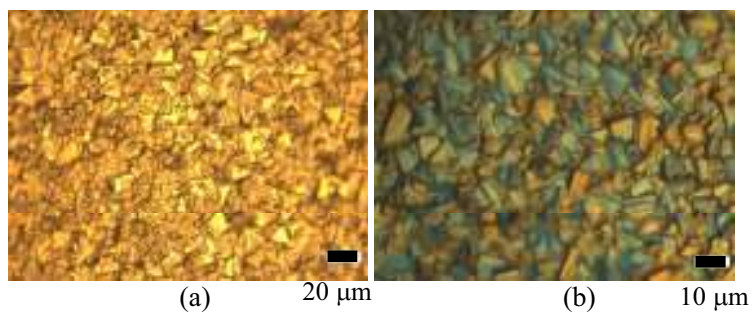


Fig. 3.

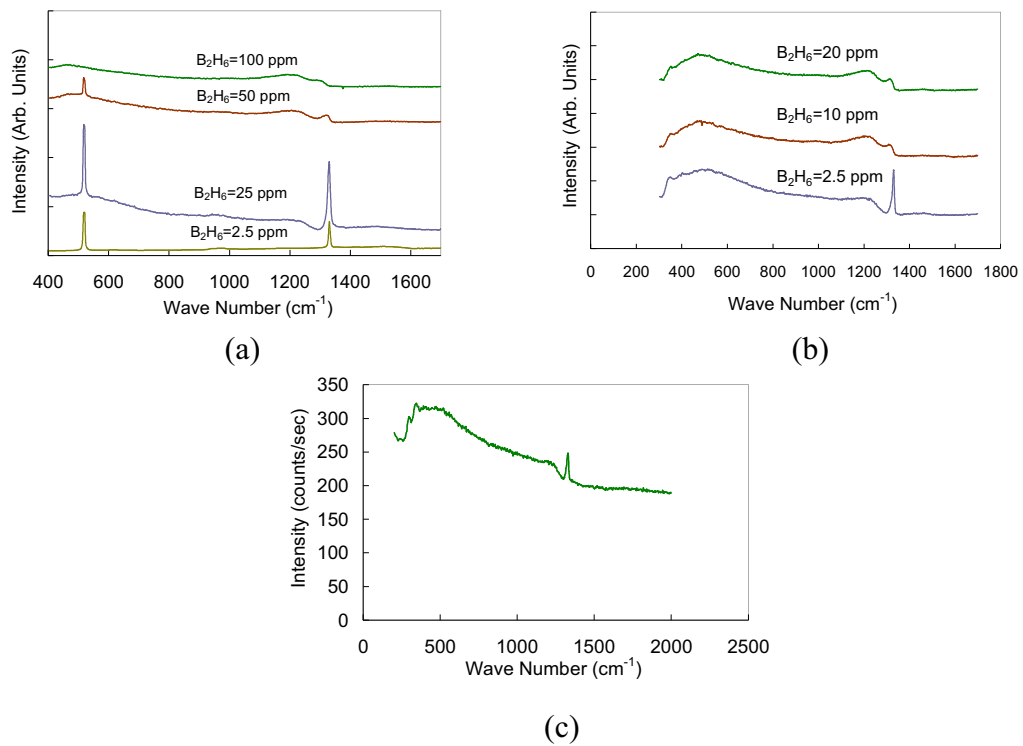
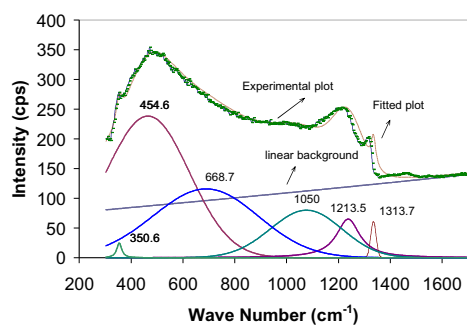
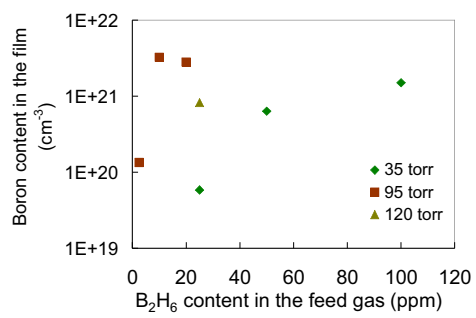


Fig. 4.



(a)



(b)

Fig. 5.

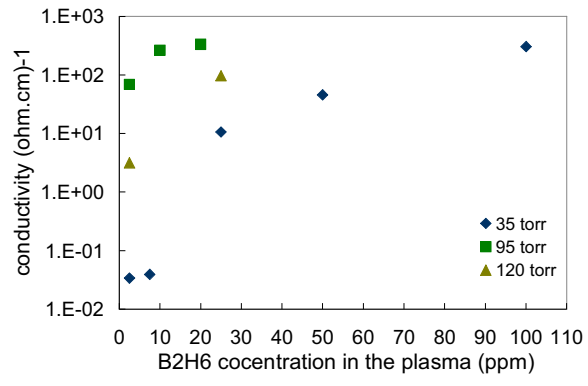


Fig. 6.