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Modeling of nitrogen/diborane/methane/hydrogen plasma for nanocrystalline diamond growth: Comparison with experimental data

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ABSTRACT

Gas phase thermodynamic equilibrium calculations involving $N_2/B_2H_6/CH_4/H_2$ mixtures were performed to investigate the chemical interactions leading to boron incorporation and microstructure variations in microwave plasma assisted chemical vapor deposition of diamond films. Molecular fractions of several BH_x ($x=1–3$) species were calculated to study the incorporation mechanism of boron atom into diamond structure. A strong influence of the BH in causing the boron incorporation level in diamond lattice is confirmed by the correlation of its modeled equilibrium composition in the gas phase with boron content as determined experimentally. Nitrogen addition leads to nanocrystallinity and a reduction in boron incorporation due to a decrease in BH as additional B/N/H radicals are formed in the gas phase. We also obtained a good degree of agreement between the theoretically predicted CH_3/CN gas phase ratio and the experimental surface roughness trends as measured for all samples.

1. Introduction

Superior properties, such as highest hardness and modulus of any materials, low friction and stiction make ultra-smooth nanocrystalline diamond film an excellent candidate for MEMS devices [1,2]. It was reported that in H_2/CH_4 plasmas used for growing diamond films, an increased level of nitrogen to the feedgas will lead to a loss of faceting and a reduction of diamond-phase purity [3–5]. On the other hand, boron doped diamond films have attracted interest because boron atoms can be successfully and reproducibly incorporated into the diamond lattice and form a p-type semiconductor with tunable electrical conductivity [2,6,7]. Simultaneous addition of boron and nitrogen into gas reaction chemistry has been carried out and it was reported that although boron can be easily incorporated into the diamond lattice, nitrogen, on the other hand, competes with boron atoms in the plasma and acts to prevent boron incorporation into the diamond structure [8]. By using gas mixture of $H_2/CH_4/N_2/B_2H_6$, nanocrystalline boron doped diamond films can be made with improved open air thermal stability [9].

Afzal et al. [4] correlated thermodynamic equilibrium calculations with the chemical vapor deposition (CVD) diamond films in terms of changes in morphology, growth rate, quality, and texture of the diamond as a function of input nitrogen concentration. Corvin et al. [5] reported that a strong correlation exists between the observed ratio of CH_3/CN and the experimental results for RMS surface roughness and nanocrystallinity over a similar range of N_2/CH_4 ratios. Modeling of boron, nitrogen, hydrogen, and chlorine interactions have drawn considerate attention in the past decades, largely due to the need of understanding the synthetic route of BN by CVD processes [10–13]. A rapid interconversion between the various BH_x species driven by the family of H-shifting reactions: $H+BH_x \Leftrightarrow H_2+BH_{X-1}$, $X=1–3$ was proposed and observed [10,11]. In this study, a CHEMKIN [14] thermodynamic equilibrium package was used to model gas phase compositions for microwave plasma assisted CVD boron doped diamond growth with various $N_2/B_2H_6/CH_4/H_2$ mixtures and compared them to experimental measurements of boron incorporation concentration, nanocrystallinity, and surface roughness for boron doped diamond films grown with these mixtures.

2. Experimental details

For the CVD deposition experiments, mirror polished 7 mm diameter 2 mm thick titanium alloy (Ti–6Al–4V) discs with rms roughness ~15 nm were used as substrates for diamond deposition.

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Table 1
Kinetic data for boron related reactions in the nitrogen/diborane/methane/hydrogen plasma

	Reactions	A	N	E_u (J/mol)	Reference
1	$H+H+H_2=H_2+H_2$	1×10^{17}	−0.6	0	10,11
2	$BH+H\Leftrightarrow B+H_2$	1.1×10^{6}	2.3	7022	10,11
3	$H+BH_2\Leftrightarrow H_2+BH$	5×10^{5}	2.3	13,440	10,11
4	$H+BH_3\Leftrightarrow H_2+BH_2$	1.7×10^{5}	2.8	24,066	10,11
5	$B_2H_6+H_2\Leftrightarrow BH_3+BH_3+H_2$	2.4×10^{13}	0	163,800	10,11
6	$H+B_2H_6\Leftrightarrow H_2+B_2H_5$	1.7×10^{5}	2.8	24,070	10,11
7	$BH_3+C_2H_4=$product	6.0×10^{12}	0.0	0.0	10,11
8	$BH_2+CH_4\Leftrightarrow BH_3+CH_3$	6.0×10^{13}	0.0	0.0	10,11
9	$BH_3+C_2H_2\Leftrightarrow$products	6.0×10^{12}	0.0	0.0	10,11
10	$H+BH_2=H_2BH$	1.00×10^{13}	0.0	0.0	11
11	$C+BH=CH+B$	7.56×10^{6}	0.66	11,723.0	9
12	$C+BH_2=CH+BH$	5.98×10^{6}	0	98,111	9
13	$BH_3+BH_3NH_3\Leftrightarrow H_2+BH_3+BH_2NH_2$	2.5×10^{10}	0.78	96,230	9
14	$BH_3NH_3=H_2+BH_2NH_2$	1.35×10^{12}	0.78	96,230	9
15	$NH_3+BH_3NH_3=H_2+NH_3+BH_2NH_2$	9.5×10^{2}	2.89	16,230	9
16	$CH_4+BH=$product	2.0×10^{2}	0	0.0	9
17	$C_3H_8+BH=$products	7.8×10^{6}	0	39,740	9
18	$H+B_2H_5=BH_3+BH_3$	5×10^{12}	0	0.0	16
19	$B_2H_5=BH_3+BH_2$	3.0×10^{11}	0	35,000.0	16
20	$BH_2+BH_2=B_2H_4$	2.0×10^{5}	0	0.0	16
21	$B_2H_6=B_2H_5+H$	2.0×10^{1}	0	0.0	16
22	$B_2H_4=BH_2+BH_2$	2.0×10^{1}	0	0.0	16
23	$H+B_2H_5=BH_3+BH_3$	5.0×10^{12}	0	0.0	16
24	$BH_3+B_2H_6=B_3H_7+H_2$	2.5×10^{11}	0	31,500.0	16
25	$B_5H_{11}=B_5H_9+H_2$	1.0×10^{12}	0	126,000.0	16
26	$B_3H_7+BH_3=B_4H_{10}$	1.0×10^{13}	0	14,700	16
27	$H+B_2H_5=BH_2+BH_2+H_2$	1.0×10^{13}	0	0.0	16
28	$H+B_2H_5=B_2H_4+H_2$	5.0×10^{12}	0	0.0	16
29	$B_2H_5+B_2H_6=B_4H_{10}+H$	8.0×10^{11}	0	35,700	16
30	$H+B_2H_6=H_2+B_2H_5$	1.0×10^{13}	0	420,000	16
31	$BH_2+B_2H_6=B_3H_7+H$	1.0×10^{13}	0	117,600	16
32	$BH_2+BH_2+M=B_2H_4+M$	2.0×10^{13}	0	0.0	16
33	$B_2H_4+B_2H_6=B_4H_{10}$	1.0×10^{9}	0	0.0	16

The rate constant $k = AT^n e^{-E/RT}$, $R=8.36\times10^{-3}$kJ/mol deg.

Prior to deposition, samples were seeded by ultrasonic agitation in a diamond powder (1–2 μm)/water solution for 40 minutes. Two series of deposition runs were performed. For sample series I, the flow rates of H_2, CH_4, and N_2 were fixed at 500, 88, and 8.8 sccm, respectively. Diborane was added at different flow rates to produce seven smooth, uniform films having faint blue color (due to boron incorporation). The flow rates of diborane ranged from 0.05 to 0.35 sccm with increments of 0.05 sccm. As a control, one nanocrystalline film was produced without diborane addition to the feedgas. For sample series II, H_2, CH_4, and diborane flow rates were fixed at 500 sccm, 88 sccm, and 0.2 sccm, respectively, but different nitrogen concentrations were added to produce eight films using N_2/CH_4 ratios of 0, 0.02, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.57. For each experiment in both series, the operating pressure was 35 Torr, the forward microwave power was 850 ± 15 W, the average substrate temperature was 810 °C ± 20 °C, and the deposition time was 2 hours. The thickness of each film was measured by *in situ* optical interferometry and an average film thickness of 2.75 ± 0.21 μm was determined. Glancing angle X-ray diffraction (XRD) with an incidence angle of 5° was used to measure the variation in the lattice parameter of diamond with incorporated boron in the diamond lattice. Boron concentration was then estimated by using the measured lattice parameter for doped films in a Brunet's model [5], which illustrates the relationship between incorporated boron concentration and the lattice constant for the CVD boron doped polycrystalline diamond films. Film rms roughness values were obtained from the surface profilometry studies.

3. Modeling details

In the gas phase modeling, EQUIL module of the CHEMKIN [14] chemical kinetics software from Reaction Design was employed to calculate the equilibrium molecular fractions of selected gas phase species based on specific initial conditions. Reactions and temperature dependent rate constants for all C, H and N containing species involved in these calculations were obtained from Konnov's reaction database [15], which contains more than 1200 reactions associated with about 130 C/H/N related species. The boron related species reactions and their temperature dependent rate constants used in the present work were mainly obtained from open literature [10,11,16,17]. It is important to note that the literature regarding B/C or B/N coupling reactions in the gas phase is comparatively sparse [10]. Nonetheless, we have performed some preliminary model calculations appropriate to the near substrate surface region in the present reactor. Table 1 shows boron related reactions employed in this study. A gas phase temperature of 1400 K was chosen for our analysis since it represents a reasonable temperature near substrate surface for the microwave plasma assisted chemical vapor deposition conditions used in our experiments, although our conclusions are not very sensitive to this choice. We executed two equilibrium analyses by applying the experimental conditions of sample series I and sample series II.

4. Results and discussion

In our previous publications [8,9], we have shown that with small amount of diborane feedgas additions, a large fraction of boron atoms in gas phase can be incorporated into the diamond lattice. This allows consideration of the boron related species that may be responsible for the doping mechanism. The first group of gas phase species that immediately came to consideration were BH_X (X = 1–3). B_2H_6 is the dimmer state of BH_3 with a dimerization energy of −313.785 kJ/mol [18]. Thermal decomposition of B_2H_6 into BH_3 and the rapid interconversion between BH_X (X = 1–3) driven by the family of H-shifting reactions are likely to produce copious amounts of BH_X species at our deposition conditions. Analogues to CH_X (X = 1–3) insertion to diamond surface, BH_X can be attached to a vacant site by means of a B–H bond with further attachment of carbon radicals to form a boron containing diamond film. Fig. 1 shows the experimental data for boron concentration in the diamond films as determined for sample series I (as a function of B_2H_6 flow rate) and series II (as a function of N_2/CH_4 flow rate ratio). In the first series, the incorporated boron in the

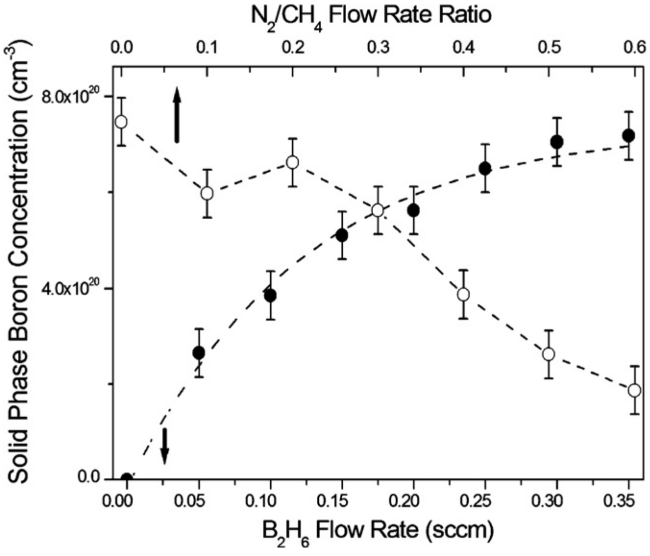

Fig. 1. Boron concentration as determined experimentally in the solid phase (diamond films) as functions of B_2H_6 flow rate (–●–) and N_2/CH_4 flow rate ratio (–○–). For series I, CH_4 fraction was fixed at 15% (in a balance of hydrogen) and N_2/CH_4 ratio was fixed at 0.1. Operating pressure was 35 Torr, and the gas phase equilibrium temperature was 1400 K. For series II, CH_4 fraction was fixed at 15% (in a balance of hydrogen) and B_2H_6 flow rate was fixed at 0.2 sccm. Operating pressure was 35 Torr, and the gas phase equilibrium temperature was 1400 K.