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The effect of substrate temperature and growth rate on the doping efficiency of single crystal boron doped diamond

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ABSTRACT

The substrate growth temperature dependence of the plasma gas-phase to solid-phase doping efficiency in single crystal, boron doped diamond (BDD) deposition is investigated. Single crystal diamond (SCD) is grown by microwave plasma assisted chemical vapor deposition (MPACVD) on high pressure, high temperature (HPHT) type Ib substrates. Samples are grown at substrate temperatures of 850–950 °C for each of five doping concentration levels, to determine the effect of the growth temperature on the doping efficiency and defect morphology. The substrate temperature during growth is shown to have a significant effect on the grown sample defect morphology, and a temperature dependence of the doping efficiency is also shown. The effect of the growth rate on the doping efficiency is discussed, and the ratio of the boron concentration in the gas phase to the flux of carbon incorporated into the solid diamond phase is shown to be a more predictive measure of the resulting boron concentration than the gas phase boron to carbon ratio that is more commonly reported.

1. Introduction

Diamond is an exceptional material, not only for its well-known mechanical properties, but also for electronic properties such as a wide bandgap, high breakdown voltage and high electron and hole mobilities. As an electronic material, diamond has the potential to revolutionize high-power, high-frequency devices, especially when operating in high temperature environments. The vertical architecture Schottky barrier diode is one such application where diamond would be particularly well suited [1]. The realization of vertical diode structures requires the ability to reliably produce free-standing (>300 μm) boron doped diamond substrates, with low resistivity via heavy doping (>10^{20} cm^{-3}).

One of the obstacles in achieving heavily boron-doped free standing single crystal diamond substrates is that of the doping efficiency. Several groups [1–3] have reported that a lower percentage of boron from the plasma feedgas is incorporated into the grown solid phase diamond as the boron to carbon ratio in the plasma feedgas increases. In our previous work [4] we saw higher doping efficiencies than what was predicted in the work of Achard et al. [1,2], and we suggested that it might be due to the higher substrate temperatures during growth that we used in our growth processes. To better understand the role of substrate temperature during growth, a series of experiments that varied the growth temperature and boron to carbon feedgas ratio have been performed.

2. Material and methods

Boron doped diamond was deposited on 3.6 mm × 3.6 mm type Ib HPHT diamond seeds with nominal thicknesses of 1.4 mm using a microwave plasma-assisted CVD reactor [5]. The growth surfaces were measured by XRD to be less than 1° off of the (100) crystallographic orientation. The reactor operates at 2.45 GHz with a molybdenum substrate holder that is water cooled. In all of the deposition experiments of this work, the reactor pressure of 240 Torr, the methane concentration of 3.75% in the plasma feedgas, and the total flow rate of 400 sccm were held constant. Diborane was used as the boron source in the feedgas. Using this growth regime, three growth temperatures were initially tried, and the resulting grown defect morphologies are shown in Fig. 1. The sample grown at 1050 °C showed a large number of pyramidal hillock type defects and polycrystalline regions. The formation of polycrystalline regions at higher deposition temperatures may be expected, and has been noted by other groups as well [6]. Soot deposition during boron doped diamond growth is known to increase with increasing microwave power levels [2], and so there were additional concerns that increasing the microwave power to achieve higher temperatures would produce more soot deposition at higher doping levels. As a result, 1050 °C was eliminated as a temperature from the experimental design. Samples were therefore grown at either 850 °C or 950 °C, as measured at least hourly during deposition by

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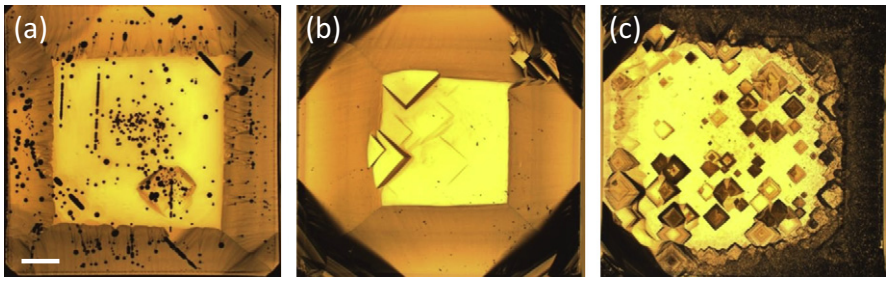

Fig. 1. Optical micrographs, taken in reflection mode, showing the defect morphologies of samples grown with [B]/[C] = 666 ppm in the plasma gas phase at three different substrate growth temperatures: (a) 850 °C, (b) 950 °C, (c) 1050 °C. The scale bar for all three images, in the lower left corner of (a), is 500 μm.

one-color optical pyrometer. During the temperature measurement, the handheld pyrometer is focused across many points on the sample surface, and a number of readings are taken. The highest repeatable measurement taken while in focus on the sample surface is used as the temperature result. Measurements taken this way show good stability and repeatability, and are not subject to the inconsistencies associated with a fixed pyrometer that can sometimes move or lose focus during a long deposition. It is expected that the effect of taking the measurement partly through the bottom edge of the plasma ball does not contribute significantly to the measured temperature, since measuring the temperature of the holder next to the sample through the plasma ball yields a temperature below the detection threshold. Only the temperature during growth and the diborane concentration were varied in the experimental design, and the other deposition variables were held constant in order to minimize the influence of other factors on the growth. The deposition conditions are given in Table 1.

The diamond substrates were acid cleaned prior to being loaded into the reactor, which is pumped down to a base pressure of <0.1 mTorr. Substrates are hydrogen plasma etched for approximately 20 min during the reactor ramp up procedure, during which the reactor pressure is brought up from the point at which the plasma is started at 5 Torr, to the growth pressure of 240 Torr. Deposition times are counted from the point when the reactor reaches 240 Torr and the methane flow is started. Depositions were run for 8 h, except for the two highest doping concentration runs, which had to be stopped early due to soot deposition on the reactor quartz dome after 6 h (SND33) and 7.5 h (SND34). Soot deposition places an upper limit on the possible duration of any heavily boron doped growth run [2], however it is possible to achieve thick films of over 300 μm by doing either lower boron concentration runs or multiple subsequent deposition runs on the same substrate. In this work only single deposition experiments were performed.

Microwave power was varied between 1.5 kW and 2.2 kW to maintain a constant substrate temperature, as given in Table 1. The microwave power was adjusted as needed during the runs, and most samples required greater applied microwave power at the beginning of deposition runs to maintain the set point temperature than near the end of the deposition. The microwave power is therefore given as a range in Table 1. The as-received type Ib HPHT substrates can vary in thickness by 100 μm or more, and since the same sample holder set was used for all the depositions, the thinner substrates were used for the 850 °C experiments, and thicker substrates were used for the 950 °C experiments. This was done to minimize the difference in the applied microwave power needed to maintain the required substrate temperatures, and therefore as similar a plasma chemistry as possible was maintained for the depositions from run to run. It should be noted however, that varying the applied microwave power from as low as 1.5 kW to as high as 2.2 kW may have an effect on the microwave power density, and therefore the plasma chemistry. The samples grown at 950 °C did require slightly higher applied microwave power, averaging 1.74–1.96 kW, while the samples grown at 850 °C averaged 1.58–1.9 kW. These two ranges have significant overlap, and the microwave power used for individual samples is quite similar. As a result, we attribute the differences noted in this work in samples from the two temperature set-point groups to be due to the growth temperature, rather than primarily due to a change in plasma chemistry.

Table 1
Experimental deposition conditions.

Sample	Growth temperature [°C]	Microwave power during growth [kW]	B/C gas phase [ppm]	Center growth rate [μm/h]	Corner growth rate [μm/h]	Grown thickness at center [μm]
SND24	850	1.6–1.8	666	2.1	5.5	16.6
SND22	950	1.7–1.9	666	2.0	10.6	16.2
SND25	850	1.6–1.9	933	5.0	10.1	39.7
SND26	950	1.8–2.2	933	1.2	8.4	9.3
SND27	850	1.6–1.9	1333	2.2	5.1	17.7
SND28	950	1.7–1.9	1333	1.1	4.4	9.0
SND30	850	1.5–1.8	2000	3.1	6.2	24.4
SND29	950	1.5–1.7	2000	2.1	9.1	16.5
SND33	850	1.6–2.1	3333	2.8	8.5	16.7
SND34	950	2.0–2.1	3333	1.5	8.6	11.4

Sample thickness is measured using a Solartron Metrology Linear Encoder (Model DR600) at several locations in the sample center, which is the region exposed for Fourier Transformed Infrared (FTIR) transmission spectroscopy characterization. The thickness at the corners is measured at several spots at each corner and given as an average over all four corners. Growth rates of 1–5 μm/h at the center and 4–11 μm/h at the corners were obtained, as given in Table 1.

The analysis of the FTIR transmission spectrum focused on the absorption feature at 1290 cm^{-1}, which is in the one phonon absorption range. Above boron concentrations of approximately 10^{18} cm^{-3}, the signal to noise ratio of the contribution due to the boron in the grown film becomes strong enough that an analysis of the 1290 cm^{-1} feature can be performed with an appropriate calibration to determine the boron content of highly doped samples. The FTIR transmission spectrum was measured using a circular aperture with a 1.5 mm radius. For each sample, spectra are first taken for the growth substrate prior to deposition, and then for the grown diamond film on the substrate after deposition. The absorption coefficient α was determined using Eq. (1), where T_{doped} is the transmission spectrum of the sample after growth, $T_{baseline}$ is the transmission spectrum of that sample's undoped HPHT seed prior to deposition, and t is the film thickness, measured in cm. The assumption implicit in this method of calculating the absorption coefficient is that any change in the transmission spectrum is due to the grown diamond film, and therefore any new absorption takes place within the grown thickness.

$$\alpha = -\frac{\ln\left(\frac{T_{doped}}{T_{baseline}}\right)}{t} \quad (1)$$