Diamond & Related Materials 76 (2017) 38–43

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Plasma etching phenomena in heavily boron-doped diamond growth

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ABSTRACT

Heavily boron-doped diamond growth turned into etching when boron-to-carbon molar ratios in the feed gas exceeded 1% and the carbon fraction was below 0.7%, under the constant microwave power density and gas pressure. Doping efficiency, diamond surface morphology, and plasma optical emissions have been investigated. Bright BH ($A^1\Pi$–$X^1\Sigma$) emission, at *ca.* 433 nm, has been correlated with etching features observed on the diamond surface. The analysis of the boron concentration by cathodoluminescence has revealed no diamond film growth under the bright BH emission conditions. The study of plasma optical emissions put forward the contribution of boron species in the chemical etching process.

1. Introduction

Heavily boron-doped diamond (HBD) layers are expected to revolutionize power electronics [1–4], spintronic [5], and optical systems [6]. The keystones of such progresses are the metal-to-insulator transition at [B] ≈ 3×10^{20} cm^{-3} in diamond [7], and the superconductivity at higher boron concentrations, typically [B] > 5×10^{20} cm^{-3} [7–9]. However, the crystalline quality of HBD layers must be excellent to be embedded into electronic or optical devices, *e.g.* low dislocation density, no interstitial boron atoms, and no boron dimers. As example, dislocations inherited from HBD layers are often recognized as the source of leakage currents and low breakdown voltages in Schottky diodes [1,2]. Likewise, interstitial boron atoms and boron dimers are supposed to lower the superconducting transition temperature [9]. In a recent study, the presence of interstitial boron atoms or boron dimers in HBD layers has been most likely correlated to dislocation generation [10]. For instance, misfit dislocations are the consequence of the lattice mismatch between undoped and HBD layers, because the covalent radii of boron and carbon atoms are different in length, with respect, 88 and 77 picometers [11]. Therefore, boron doping induced an anisotropic lattice strain, which is accommodated by the tetragonal deformation of the diamond crystal lattice along the growth direction [9,11]. In theory, the strain is relaxed above critical thicknesses, which engender isomorph crystal lattice expansion, and misfit dislocations formation [12]. However, the presence of interstitial boron atoms and boron dimers triggered experimentally the relaxation of HBD layers those thicknesses were lower than predicted by theoretical models [12], thus multiplying dislocations [9,10,13]. Therefore, we could expect to reduce drastically the dislocation density in HBD layers by removing interstitial boron atoms and boron dimers.

We believe that interstitial boron atoms and boron dimers could be eliminated by performing microwave plasma-assisted CVD (MPCVD) diamond growth with a high microwave power density. Definitely, the increase of the microwave power density aimed to produce more atomic hydrogen in the plasma, which selectively etched away graphitic phases, and subsequently ensure the growth of diamond layers with a high crystalline quality [14–16]. However, HBD growths carried out under high microwave power density condition revealed a fall of boron doping efficiency, when boron-to-carbon molar ratios increased in the source gas [17,18]. Furthermore, Tokuda et al. [19] observed the roughening of HBD layers when boron-rich source gas mixtures were employed, and the authors suggested an unusual diamond growth mode. Diamond growth modes are determined by complex gas-surface exchanges and surface rearrangement reactions [20,21]. Since a decade, the gas phase chemistry and distribution of "active" species in the plasma have been studied as function of MPCVD conditions and sources gas mixtures in order to obtain reproducible diamond growth rate, doping profile, and the best crystalline quality [20–22]. Nevertheless, plasma diagnostics performed in MPCVD conditions suitable for boron-doped diamond growth concerned mid-range boron-to-carbon molar ratios in source gas, where no changes of growth mode were observed.

In order to grow HBD layers with a high crystalline quality, we surveyed a wide range of boron-to-carbon molar ratios in source gas, and we investigated the effects of source gas composition on diamond growth mode, and active species in the plasma discharge. At first, we

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http://dx.doi.org/10.1016/j.diamond.2017.04.007
Received 16 February 2017; Received in revised form 24 March 2017; Accepted 7 April 2017
Available online 08 April 2017

focused on the evolution of surface morphology and doping efficiency. Then, we performed a systematic diagnostic of plasma discharges by mean of optical emission spectroscopy (OES). Finally, we determined critical MPCVD conditions for growing HBD layers.

2. Experimental details

In this study, we employed three fine polished Ib-type (100)-oriented $3 \times 3\,mm^2$ diamond substrates, called hereafter substrate #1, #2, and #3. Each substrate has been cleaned in a typical boiling acids mixture [14], and rinsed with deionized water, prior to be transferred in the MPCVD chamber. Our experiments have been carried out under mostly constant MPCVD conditions: i) chamber pressure: $p = 80$ Torr, ii) incident microwave power regulated by an auto-matching tuner: $P = 1$ kW, and iii) total gas flow rate: $F_{total} = 250$ sccm. We used as source gases 9 N's purified H_2, 6 N's purified CH_4, and “diluted” TMB (1060 ppm in H_2), where TMB is the abbreviation of trimethylborane, $B(CH_3)_3$. The vacuum base pressure of the MPCVD chamber before experiments was $2–5 \times 10^{-6}$ Pa. The temperature of diamond substrates has been measured by a disappearing filament pyrometer from the top window of the MPCVD chamber. A miniature spectrometer (USB2000 + UV–VIS – Ocean Optics) has been connected to the side viewport of the MPCVD chamber located at 12 cm from the diamond substrates *via* an optical fiber. Sample holder temperature, beam voltage, and probe current used in cathodoluminescence experiments were 80 K, 15 kV, and 150 nA respectively.

3. Growth mode

We started by looking at the impact of the atomic fraction of boron in feed gas on the diamond surface morphology and doping efficiency. We defined the atomic fractions of boron and carbon in feed gas as $x_B = F_{TMB}/F_{total}$ and $x_C = (F_{CH4} + 3 \times F_{TMB})/F_{total}$, where F_{TMB} and F_{CH4} corresponded to the flow rate of “pure” TMB and methane, respectively. The desired molar ratio of boron-to-carbon in feed gas (x_B/x_C) has been obtained by adjusting F_{TMB} and F_{CH4}. In order to simplify this study, x_C has been kept constant 0.5%.

3.1. Surface morphology

Substrate #1 has been exposed sequentially to four kind of plasma discharges named P-1, P-2, P-3, and P-4, where x_B/x_C were 300 ppm, 5000 ppm, 20,000 ppm, and 6000 ppm, respectively (Fig. 1). Each MPCVD process was 10 hour-long. Once the plasma discharge stopped, the surface of substrate #1 has been analyzed *ex-situ* by Nomarski interference contrast (NIC) optical microscope, and 3D laser microscope (LM). In order to highlight the sequential modification of its surface morphology, we drew a schematic cross-section of substrate #1 after each MPCVD process, summarized in Fig. 1.

The growth of new diamond layers on substrate #1 after P-1 and P-2 has been suggested by the emergence of pyramidal hillocks (PHs), and a prismatic texturing of its borders, probably triggered by the micro-faceting caused by laser cut and fine polishing. PHs are usually appearing on diamond surfaces, as it is considered to accompany dislocations [16]. The RMS roughness of the PHs-free portions of surface after P-1 and P-2 was *ca.* 3 nm.

On the contrary, we noticed a dull and damaged diamond surface after P-3, where $x_B/x_C = 20{,}000$ppm. The NIC microscopy indicated the disappearance of PHs and the presence of cavities. The 3D LM has confirmed that the surface of substrate #1 was covered by etch pits (EPs), although relatively flat EPs-free portions of surface were conserved. The overlap of NIC micrographs revealed a strong correlation between the location of EPs and PHs (white arrows in Fig. 1). We also presumed that EPs followed same crystalline defects at the origin of PHs, as reported in the literature [16]. Such inhomogeneous surface morphology suggested a chemical etching enhanced at the defective points of the crystal, rather than a physical attack that would uniformly roughened the whole surface, *e.g.* by ions bombardment. After P-4, multitudes of freshly new grown PHs were found in place of former EPs (Fig. 1). Hence, the reduction of x_B/x_C in P-4 had engendered a newly grown diamond layer that partially filled out EPs, and flattened the entire surface.

3.2. Boron doping efficiency

We observed a complete modification of the surface morphology on substrate #1 at high x_B/x_C. To foolproof this study, cathodoluminescence (CL) analyses have been performed to evaluate the boron concentration in diamond layers. We presuppose that the layer deposited on substrate #1 after P-2 had a constant boron doping over the thickness of 10 µm. CL data have been measured at different points over the surface of substrate #1 after P-2, and such typical CL spectrum is displayed in Fig. 2. It showed a dominant transversal optic bound exciton (BE_{TO}) at *ca.* 238 nm, and a tiny transversal optic free exciton (FE_{TO}) at *ca.* 235 nm, characteristic of a boron-doped diamond layer [23]. According to the procedure described in Ref. [23], we estimated the boron concentration in the diamond layer around $2 \times 10^{19}\,cm^{-3}$ from the intensity ratio of BE_{TO}-to-FE_{TO} ($I_{BE/FE}$) at 80 K.

Afterward, we analyzed the CL from substrate #1 after P-3 (not shown). However, the values of $I_{BE/FE}$ measured after P-3 and after P-2 were very similar. As detailed previously (Fig. 1), x_B/x_C has been quadrupled between P-2 and P-3, so the boron concentration in the layer deposited in P-3 must be larger than in P-2, which logically contributed to a bigger $I_{BE/FE}$ after P-3. Nevertheless, a constant $I_{BE/FE}$ could be explained by the fall of boron doping efficiency or the decrease of growth rate. Those effects have been reported when large x_B/x_C were employed in MPCVD to grow HBD layers [17–19].

We decided to reproduce the experiment on substrate #2, in order

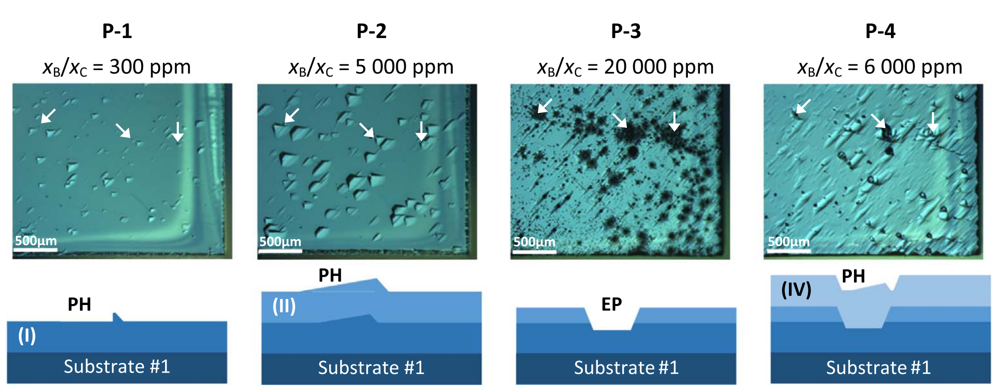

Fig. 1. Boron-to-carbon molar ratios in feed gas (x_B/x_C), NIC micrographs of substrate #1, and schematic cross-sections related to MPCVD experiments P-1, P-2, P-3, and P-4. MPCVD conditions: $x_C = 0.5\%$, $F_{total} = 250$ sccm, $p = 80$ Torr, $P = 1$ kW, $t = 10$ h. PH: pyramidal hillock, EP: etch pit.