



Interface features of the HPHT Ib substrate and homoepitaxial CVD diamond layer

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ABSTRACT

This is a detailed study of the interface features of the HPHT Ib substrate and the homoepitaxial CVD diamond layer. Homoepitaxial diamond layers were prepared by a commercial type 30 kW dc arc plasma Jet CVD on (100) substrates with gas mixture of Ar/H₂/CH₄. The internal stress and the fluorescence properties of the cross-section of the single crystal diamond bulk were characterized with polarizer optical microscopy, micro-Raman spectroscopy, and photoluminescence, as well as DiamondView luminescence imaging. A higher stress region in the homoepitaxial diamond layer near the substrate with width about 15 μm was found exhibiting higher nitrogen content and presented different fluorescence properties. Studies on the surface morphology of the initial growth diamond indicated that the transformation of the surface morphology from growth hillocks to macrosteps, may play a crucial role in the interface feature.

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1. Introduction

Diamond is one of the most promising semiconductor materials owing to its excellent electrical, thermal, and mechanical properties. Although polycrystalline CVD diamond films, particularly high-oriented diamond films, have been pursued toward the applications on the active electronic devices and have shown drastic improvement in electrical characteristics, the randomly oriented grains and existence of a small amount of sp² carbon bonds on the grain boundaries of the polycrystalline CVD diamond have led to the degradation of electrical and optical properties compared with single crystal diamond, and subject to considerable limitations of the widespread use in many fields. Recent progress in the synthesis of high-quality homoepitaxial CVD diamond layers have opened interesting prospect for the development of diamond electronic devices, particularly in the field of high-power electronics, accompanied by considerable progresses in basic research [1–3]. Important developments have been made in understanding the mechanisms of CVD diamond growth [4,5], nitrogen doping, and its effect on diamond growth [6–9]. However, despite of the potential for gaining insight into the details of the growth mechanism, there are few studies of the interface features of homoepitaxial diamond film growth on HPHT Ib diamond seeds [10].

It is well known that HPHT synthetic type Ib (100) single crystal diamond plates are generally used as the seeds for homoepitaxial diamond films growth. As name indicated, HPHT diamonds are converted by high-purity graphite powder in an environment similar to its natural kind, at temperature of 1500–2000 °C, under pressure of 5–6 GPa with

the presence of catalysts such as Fe, Ni, and Co [11]. Some research conducted by the HPHT diamond manufacturers in the past years claimed that diamond free of impurities, inclusions, and cracks can be made due to many factors associated with its production processes [12,13]. Due to the rapid growth of HPHT synthetic type Ib single crystal diamond, which is done in a week or two rather than several billion years as natural diamond, significant amount of crystallographic defects inside the synthetic diamond crystal structure may be built up, such as the nitrogen impurity, the catalysts-induced inclusions, and the dislocations, etc. [14,15].

For homoepitaxial CVD diamond growth, the substrate, particularly the substrate surface, is an essential element for high-quality single crystal diamond growth [16]. The metal inclusions caused by catalysts are deleterious to the CVD diamond growth because they can promote the formation of sp² phases as well as the non-epitaxial growth [17]. The dislocations present on the substrate surface can propagate to the epitaxial layer during the growth, which becomes a much more problematic source of defects [18,19]. Different chemical treatments can efficiently eliminate these residual impurities at the surface. Although plasma pretreatments are effective for removing the dislocations induced by substrate polishing [20–23], they have no effect on the dislocations initially existing in the seed crystal and only the lattice mismatch atoms around the dislocations that reach the surface are removed, leading to etch pits on the substrate surface.

It is believed that step-flow growth was helpful to the growth of high-quality (100) CVD diamond with fewer lattice defects and could increase its growth rate. Several methods have been adopted to achieve step-flow growth, such as high growth temperature [9,24], low methane concentration [24], nitrogen doping [7,9]. However, at the beginning, the growth units may give priority to incorporate into the lattice

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at the etch pits without additional energy input for the creation of an atomic step on the flat surface. This may lead to different growth mechanism of homoepitaxial layer near the substrate and at the top surface as it revealed. In this paper, we reported our work on the studies of the transformation of CVD homoepitaxial diamond growth mechanism near the substrate and the interface features of the HPHT Ib substrate and homoepitaxial layer.

2. Experimental

The single crystal diamond bulk, which is studied in the present work, was synthesized by a commercial type 30-kW dc arc plasma jet CVD operated at gas recycling mode that had been reported in our early papers [25–27]. Carefully polished commercial $3.5 \times 3.5 \times 1 \text{ mm}^3$ HPHT synthetic type Ib (100) single crystal diamond plate with surface roughness $R_a < 10 \text{ nm}$ was used as the substrate. Before deposition, the substrate was boiled in an acid mixture ($\text{HNO}_3:\text{H}_2\text{SO}_4 = 2:10$) to eliminate catalysts-induced inclusions at its surface, then cleaned ultrasonically with deionized water and acetone, finally etched 15 min by a H_2/Ar plasma for surface modification pretreatment to remove (reduce) the surface damage induced by mechanical polishing. After the plasma treatment, the substrate surface was severely roughened and the surface roughness R_a up to 23.61 nm was measured. The substrate was brazed using a Fe–Ni base welder alloy in a rectangular hole on the $\Phi 65 \text{ mm}$ diameter molybdenum holder to ensure the uniform temperature. The substrate temperature was maintained at $1000 \pm 10 \text{ }^\circ\text{C}$ and monitored by IR pyrometer. The feed gas was Ar, H_2 , and CH_4 with the flow rates of 2.8 slm, 8 slm, and 65 sccm, respectively. No additional N_2 was introduced as an independent feed gas into the chamber to enhance the growth in our experiment. The chamber pressure was kept at the range of 4.0–4.5 kPa. The surface morphology of the diamond plate was characterized by optical microscope after H_2/Ar plasma pretreatment and 30, 60, and 90 min deposition. After 30 h growth, the single crystal diamond bulk was cut into a slice by a Nd: YAG laser, and then mechanically polished. A cross-section parallel to the growth direction was obtained as shown in Fig. 1.

The polished parallel-sided sample allowed the recording of crossed polarizer optical micrographs (PLM) to show birefringence resulting from the stress in the sample. It also allowed UV-excited luminescence images to be recorded for the substrate, the homoepitaxial layer and their interface. Such image was recorded by a DiamondView™ luminescence imaging system (DiamondView) provided by the Diamond

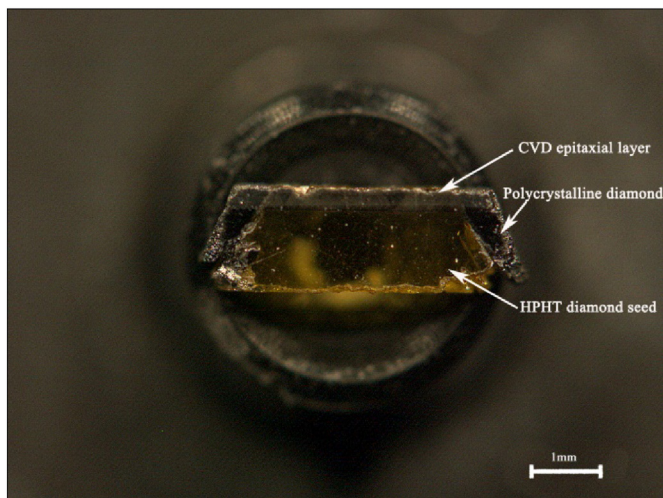


Fig. 1. Optical microscope image of the cross-section of the single crystal diamond, wherein the translucent section (upper) is the CVD epitaxial layer, the yellow part is the HPHT diamond seed, and the dark part around the seed is the polycrystalline diamond layer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Trading Company (DTC). In this instrument, sample was excited at wavelengths shorter than 230 nm by a filtered xenon arc lamp source. Photoluminescence (PL) and Raman spectra were measured at 77 K by using a Horiba JY HR800 micro-Raman spectrometer fitted with laser wavelengths of 488 nm and 514 nm, respectively. Beam diameter about $2 \mu\text{m}$ was adopted for the measurement.

3. Results and discussion

Birefringence induced by internal stress in the single crystal diamond was measured by polarized light microscopy, taken with transmitted light. Fig. 2 shows the PLM image of the cross-section of the single crystal diamond. It shows that there is a high-contrast stripe presented in the CVD diamond layer near the HPHT diamond seed (Fig. 2 (a)), which indicates that different stress states exhibited in the epitaxial layer. The width of the high-contrast stripe is estimated to be about $15 \mu\text{m}$ from an enlarged view (Fig. 2 (b)) of the area marked with red block in Fig. 2 (a). The dark area marked with A, B, and C corresponds to the region containing non-epitaxial growth diamond grains.

Raman spectra from the area marked with the red block are shown in Fig. 3(a), where the numbers 1–7 corresponds to the locations crossing the interface between the HPHT seed crystal and the epitaxial layer as indicated in Fig. 2(b). The measurement locations with a pitch of $4 \mu\text{m}$ were parallel to the growth direction.

Fig. 3(b) shows the profile of the Raman shift of the diamond peaks measured across the interface, which were obtained by the standard Lorentzian fitting. Compared to the Raman peak position of stress-free diamond (near 1332 cm^{-1}), the Raman peak of HPHT substrate and the homoepitaxial layer shifted to higher wave number, which indicated compressive stress in diamond [28,29], while the peak position varies into lower value from the HPHT substrate to the homoepitaxial layer. It can be seen that there is a high-stress region in the epitaxial layer adjacent to the interface. The width of the higher stress region is $15 \mu\text{m}$ approximately.

It is worth mentioned that the stress estimated from the Raman peak shift is the general stress (the overall stress) including the thermal stress induced by the mismatch of the thermal expansion coefficient between the Mo holder and the Fe–Ni brazing alloy, and between the Fe–Ni and the diamond (HPHT seed with the CVD layer on it), and the intrinsic stress induced by the crystal defects (impurities, vacancies, interstitials, dislocations, grain boundaries, and so on) generated during the growth process. Generally speaking, it is hard to distinguish (to separate) the thermal stress and the intrinsic stress just by Raman or by X-Ray techniques. However, in the present investigation, technical cautions were made to partially release the thermal stress by a very slow post deposition cooling process. Since the deposition temperature was rather high (higher than $900 \text{ }^\circ\text{C}$), and the plasticity of the Fe–Ni alloy is very good, therefore, a large part of the thermal stress was released during the slow cooling process. Besides, thermal stress should be usually more or less evenly distributed over the whole sample area (except near the singularities (e.g. sharp corner and edges)), Therefore, the stressed area localized at the interface of the HPHT seed and the CVD layer should be induced by the intrinsic stress mainly.

Early works concluded that nitrogen is mainly incorporated into CVD diamond films in the substitutional sites as it is incorporated into the HPHT diamond [30]. The substitutional nitrogen and carbon will form C–N bond which is much longer than the C–C bond and so produce compressive stress to the carbon lattice around [31]. Lattice matching between the HPHT substrate and homoepitaxial CVD layer may cause the distortion in the HPHT substrate extends to the homoepitaxial layer. However, the stress-affected zone of point defects can only reach a few atomic layers, much narrower than the width of the high-contrast zone as indicated in the PLM image in Fig. 2(b) and the profile of the Raman shift (Fig. 3(b)).

The DTC DiamondView instrument is generally used for the evaluation of the types of diamond and for the identification of the synthetic

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