



Optical study of defects in thick undoped CVD synthetic diamond layers[☆]



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ABSTRACT

The growth of thick single crystal synthetic diamonds by plasma-assisted chemical vapour deposition (PACVD) that are colourless and with a low impurity content is an important challenge to achieve gem-quality material. To this aim, advanced optical imaging and spectroscopy techniques are useful tools to optimize the growth process as well as to identify CVD-made diamond gems. In this paper, two thick synthetic diamond crystals with unique structural and spectroscopic properties were grown by PACVD without intentional addition of nitrogen and without any post-treatment to enhance their colour. While the first one, sample A, was 760 μm thick and exhibited a grey to greyish brownish colour quite unusual for undoped material, the second one, sample B, was exceptionally thick (3300 μm) and colourless. It was laser-cut and polished to obtain a high gem-quality round brilliant of 0.44 carat with G colour and VVS2 clarity grade. The amount, distribution and nature of defects in these synthetic crystals is discussed using a broad range of optical characterisation techniques towards growth optimization and getting a better understanding of the material properties (and their possible integration to the gem market).

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1. Introduction

Thick single crystal diamond films with a low defect density and controlled purity are highly required. Diamond has a huge potential for the fabrication of electronic devices, in particular for power applications where very large currents and high voltages are involved [1]. The last years significant developments have been achieved in 4 key areas (size, purity, surface finish and crystal perfection) unleashing a huge engineering potential in technological and industrial applications of single crystal (SC) CVD diamond [2–7]. Obtaining such freestanding diamond thin films by PACVD requires that the growth conditions are precisely controlled and tuned in order to achieve films with the desired properties.

Thick crystals would also be useful for gemmology or for optical and electronics applications. The interest for CVD synthetic diamond in the global gem diamond industry was witnessed by several recent reports in the diamond industry press, gemmological literature and the report of a small number of start-up companies that want to commercialize the production of CVD for gemstones [8–10]. In the mid 2000s millimetre-size gem-quality diamond crystals were demonstrated [11,12]. The growth of high-purity CVD diamond single crystal plates (with a nitrogen content typically below 10 ppb) with thicknesses of up to 2 mm was demonstrated at LSPM-CNRS [13]. Only very recently, high purity CVD diamond plates (with an area of a few mm^2) have

become commercially available [3], enhancing the potential for a wide range of high technology applications. For example having millimetre-sized (at least $3 \times 3 \times 3 \text{ mm}^3$) diamond crystal gives the opportunity to process the crystal in order to get large faces with the desired orientation such 113 or 111 that can later be used as a substrate. Moreover changing the growth direction is also known to affect dislocation propagation direction and could potentially help in getting low dislocation material. Dislocation-free non-birefringent material is highly desired for X-ray or laser windows and for Raman laser applications [4,14,15].

Nevertheless, the growth of very thick diamond crystals (>1 mm) without any intentional addition of impurities and that are completely colourless with a low defect content is a very important challenge. DTC scientists have previously reported the growth of gem-quality high-purity CVD diamonds (for purely research purposes) in reference [11]. The largest high-purity CVD that they report is 0.82 carat, after being faceted into a round brilliant. Y. Mokuno et al. reported on thin high-purity CVD films with thicknesses < 1 mm [16]. Additionally, Element Six sells high-purity “electronic grade” CVD diamonds to the technology industry, although they are ~0.5 mm thick.

Adding N_2 strongly helps increasing growth rates [17,18] and improving the crystal morphology by limiting twinning at the surface [19,20]. Considering these advantages, most studies reporting the synthesis of millimetre-thick crystals were usually performed with intentional nitrogen doping (up to several hundreds of ppm of N_2 [19,21]). However, this is at the expense of crystal purity as the nitrogen gets incorporated during growth leading to the creation of point defects and states in the band gap, deteriorating electronic properties and possibly hampering the final colour. The control of nitrogen-related

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defects and other impurities in high purity diamond is at the centre of attention due to the spin coherence properties that could open the door to room temperature quantum applications [22,23].

In this study, 2 thick single crystal synthetic diamond layers with unique structural and spectroscopic properties were grown without intentional addition of nitrogen or other impurities. The first one (sample A) was grown for high technology purposes, while the second one (sample B) was explicitly grown for research purposes in order to produce a faceted diamond.

Luminescence spectroscopy and imaging are important techniques for characterising optical defects in diamond [24]. As such, the origin and nature of the defects formed during epitaxial growth can be investigated. Combining advanced spectroscopy and imaging techniques in an innovative manner makes it possible to acquire in-depth structural and chemical information evidencing the growth history of diamonds. This is crucial in the optimization of thick CVD diamond growth, particularly with respect to dislocations and impurities.

2. Experimental details

2.1. CVD growth

The two synthetic diamond samples investigated in this paper were grown at LSPM-CNRS using the PACVD method. The samples were synthesised in a home-made microwave plasma reactor operating at 2.45 GHz. HPHT type Ib (100)-oriented synthetic diamonds were used as substrates. For sample A, CVD diamond growth was carried out on $3 \times 3 \text{ mm}^2$ substrate under standard growth conditions as described in reference [25]. These typically involve a relatively high power density (2.9–3.1 kW; 195–210 mbar) and a methane concentration of 4% in H_2 , without intentional addition of N_2 . The purity of H_2 was 9 N, while that of CH_4 was 6 N. Sample temperature was maintained around 850 °C during growth that lasted for around 110 h, leading to a film thickness of 760 μm (i.e. a resulting growth rate of 7 $\mu\text{m}/\text{h}$). The HPHT-grown substrate was subsequently removed by laser cutting and polishing leading to a freestanding CVD plate 620 μm -thick with lateral dimensions of 4.60 by 4.60 mm^2 .

The second sample in this study, referred to as sample B, was grown in 5 successive runs under similar conditions on a $3.5 \times 3.5 \text{ mm}^2$ HPHT substrate. In contrast to sample A, a higher power density was used (3–3.8 kW; 200–270 mbar) and a methane concentration of 5–6%. Power and pressure were adjusted to compensate for any temperature drift that might occur due to soot formation on the substrate holder and due to the increased dimensions of the sample that continuously penetrates into the hot plasma core. This allowed maintaining a substrate temperature around 850–900 °C. No intentional N_2 was added. Growth runs lasted respectively: 16 h, 77 h, 92 h, 41 h and 23 h. Interruptions were necessary for cleaning the chamber and remove soot after which the sample was reloaded into the chamber. Before growth was initiated, the sample surface was cleaned using pure H_2 plasma for a few minutes. After a total of 249 h of growth, polycrystalline defects formed at the rims of the crystal were so large that they started to encroach on the top surface which imposed the growth to be aborted. Further pursuing growth would have required re-polishing or laser-processing the sample which has never been performed here. In the end a 3.3 mm-thick film was obtained corresponding to an average growth rate of about 13 $\mu\text{m}/\text{h}$, which is higher than sample A due to the higher power density and methane content used. This represents a relatively high rate for a non-intentionally doped diamond crystal that is made possible by the design of the growth chamber allowing the use of this set of growth conditions. Although growth rates of a few tens of $\mu\text{m}/\text{h}$ have already been reported, they were usually obtained with the addition of hundreds of ppm of N_2 [26,27]. The lateral dimensions of the crystal were up to 12 mm corresponding to a gross weight of 6.86 carat (1 carat = 0.2 g). After processing by Diamcad, a faceted CVD synthetic gem stone of 0.44 carat was produced. The

polished stone had a diameter of 4.98 mm and a height of 2.95 mm. The entire process from as-grown to polished outcome is reported and studied by advanced optical characterisations.

2.2. Characterisation methods

The samples were examined by optical microscopy combined with luminescence spectroscopy and imaging techniques. Optical micrographs were recorded using the D-Scope stereo-microscope and a Leica DL LM microscope equipped with a Leica DFC digital camera. This setup allowed to evaluate the anomalous birefringence using crossed-polarized filtered (CPF) images and the acquisition of differential interference contrast (DIC) images. Differential Interference Contrast Microscopy (DICM) was used in order to enhance the topographic contrast.

Optical absorption spectra in the ultraviolet–visible–near infrared (UV–Vis–NIR) range were recorded at room temperature. For sample A, absorption spectra were collected at room temperature in transmission using a fibre-optic with a core diameter of 100 μm and a Ocean Optics Maya 2000 Pro spectrometer equipped with a Hamamatsu S10420 back-thinned FFT-CCD detector. Optical absorption spectra of the polished outcome of sample B were collected at liquid nitrogen temperature in a diffuse transreflectance setup using a Princeton Instruments Acton UV–Vis–NIR spectrometer.

For both samples Fourier Transform Infrared (FTIR) absorption spectra were recorded with up to 1024 scans and with resolutions of 4 and 1 cm^{-1} in the mid-IR (4000–500 cm^{-1}) range at room temperature on a Thermo Nicolet Nexus™ FTIR spectrometer equipped with a DTGS detector. For sample A, localised FTIR spectra were collected with a Continuum™ microscope using a $50 \times 50 \mu\text{m}$ aperture and a liquid nitrogen-cooled MCT detector. As for sample B, a diffuse reflectance accessory was used for the acquisition of FTIR spectra in the polished outcome.

The ultra-short-wave UV illumination of the DiamondView™ (DV) [28] generates luminescence surface patterns visualising growth and deformation structures. Raman and photoluminescence (PL) spectroscopy measurements were performed both at room and liquid nitrogen temperatures using a Renishaw InVia Raman microscope. Raman and PL spectra were collected using different lasers operating at the following excitation wavelengths: 325 nm (HeCd laser), 514.5 nm (tunable Ar ion laser) and 633 nm (He–Ne laser). In order to acquire in-depth information, extended depth profiles were recorded using the Raman spectroscope in the high-confocal mode using a Leica Fluotar L 50 \times objective. A 2D increment of 5 μm depth \times 50 μm across on the automated xyz stage was applied in combination with a slit width of 20 μm and a CCD area of 8 pixels (image height) \times 576 pixels (spectrometer range).

3. Results & discussion

3.1. Sample A

After growth sample A showed a fairly smooth morphology without any non-epitaxial defects formation or step bunching as illustrated in the topography enhanced DICM image in Fig. 1. Interestingly, after laser cutting and polishing, the freestanding CVD film displayed a grey to greyish brownish coloured region directly above the substrate growth area which is fairly rare for material grown under high-purity conditions. The distinct observation of this coloured zone above the HPHT substrate's area is illustrated in the optical micrographs under D65 daylight illumination and with colour saturation enhancement in Fig. 2(a) and (b) respectively. Outside the HPHT substrate's region a near-colourless edge zone was observed. Note that the colour distribution above the HPHT substrate is not uniform.

Obtaining colourless crystals is essential for the synthesis of thick gem-quality diamonds. The origin of the grey to greyish brownish

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