



# Vertical-substrate epitaxial growth of single-crystal diamond by microwave plasma-assisted chemical vapor deposition

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## ABSTRACT

Epitaxial diamond growth by microwave plasma CVD in a CH<sub>4</sub>/H<sub>2</sub> mixture was performed on vertically standing single crystal diamond substrates with high aspect (height-to-width) ratio. This “vertical growth” mode allows simultaneous diamond deposition on two large (1 0 0) faces of the substrate, in contrast to only one working face upon conventional horizontal arrangement of the substrate plate. A high plasma density gradient in vertical direction, the characteristic feature of the geometry used (the substrate acts as an antenna), coupled to high substrate temperature gradient ( $\Delta T \approx 150$  °C in the particular experiment), are shown to have a strong impact on the epilayer structure, that was characterized with laser scanning microscopy, Raman and photoluminescence confocal spectroscopy mapping across  $\approx 3$  mm high specimen. The single crystal film transformation to polycrystalline, and further, to nanocrystalline layer, going from top to bottom of the substrate, is described. The vertical distributions of the growth rate, intensity of photoluminescence of NV and SiV color centers imbedded in the diamond film, are measured with high spatial resolution on growth surface and in cross-section, which are also related to the film structure variation. These findings are of importance for search of optimal growth regimes of 3D diamond mosaics and large single crystals by MPCVD.

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## 1. Introduction

Single crystal (SC) diamond produced by chemical vapor deposition (CVD) technique is of high current interest as a functional material with superb mechanical, thermal, optical and electronic properties for advanced applications, such as powerful microwave electronic devices [1], quantum optics devices based on color centers [2], radiation-hard detectors [3,4], Raman lasers [5], multi-spectral optical components [6], and X-ray optics [7]. Microwave plasma CVD (MPCVD) allows synthesis of purest and high quality SC diamond. The CVD SC layers are commonly synthesized by epitaxial growth on diamond seeds, which are flat diamond plates with thickness  $\sim 1$  mm or less, and lateral size of several millimeters [8–15]. Typically (1 0 0)-oriented large face is exposed to the

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plasma to support the epitaxy, while the opposite face is not involved in the growth process. It would be attractive to deposit CVD diamond on both large faces of the seed, thus to increase the mass increment, by almost doubling the deposition area. This approach is difficult as the seed with high aspect ratio (height-to-width) is expected to undergo a highly nonuniform heating by the plasma cloud of a complex shape. Chen et al. [16] analyzed the lateral side of normally (horizontally) positioned substrate (SC diamond plate) with thickness of about 1 mm, and found a strong variation of the grown film structure, from graphite to epitaxial diamond across the plate height. Recently, Tzeng et al. [17] used MPCVD method to grow nanosized diamond particles on the Si substrate plates rotated by 90° (standing vertically 8 mm in height) in conditions of high vertical temperature gradient ( $\sim 200$  °C). However, such “vertical growth” mode for epitaxial deposition of single crystalline diamond layers was not reported so far, to our knowledge.

Here we describe the epitaxial diamond growth in a microwave plasma on a vertically standing single crystal diamond substrates

with the height significantly larger than the thickness, and characterize the structure of the produced material using laser scanning microscopy, Raman and photoluminescence spectroscopy mapping. The approach assumes the diamond epitaxy on two large faces (instead of only one, as usual), thus it promises to increase the substrate area exposed to diamond deposition, and the CVD diamond mass increment. In addition, the experiment shed light on features of the diamond growth process in highly nonuniform plasma environment, the situation occurring upon synthesis of large diamond crystals.

## 2. Experimental

A type Ib HPHT SC diamond substrate with dimensions  $3.2 \times 3.2 \times 1.0 \text{ mm}^3$  (Sino-Crystal Co.) was used for the epitaxial diamond film growth. Two  $3.2 \times 3.2 \text{ mm}^2$  large faces were (1 0 0) planes, while other four small surfaces had (1 1 0) orientation, confirmed by X-ray diffraction (0 0 4) polar figures using a Philips X'pert MRD system. The off-angle of  $0.27^\circ$  for {0 0 1} plane, and XRD (0 0 4) peak width (FWHM) of 31 arcsec were determined from rocking curve measurements.

After ultrasonic cleaning, the substrate was arranged vertically on a Mo substrate holder, with one of the small surface attached to the Mo holder. The diamond deposition was carried out in a microwave plasma CVD (MPCVD) reactor Plassys SDDR 150 (2.45 GHz, 5 kW) [18]. Prior the growth process the substrate etch pretreatment was performed in the plasma, first in pure  $\text{H}_2$  (30 min) and then in  $\text{H}_2/\text{O}_2$  plasma (10 min) at  $900^\circ\text{C}$ , to remove the surface defects. Later on, the growth process was performed in  $\text{CH}_4\text{-H}_2$  gas mixture with hydrogen flow rate 192 sccm and 8 sccm of methane, under the pressure 150 mbar, microwave power 2.8 kW and substrate temperature  $820^\circ\text{C}$ . A photograph of the hot sample in course of the CVD process is shown in Fig. 1(a). Because of large height of the substrate the plasma cloud around it is quite nonuniform, with bright emission “cap” on the top of the substrate (Fig. 1a). As a result, one can expect a significant vertical temperature gradient, the top part close to plasma core getting a higher temperature, while the bottom contacted with the water-cooled substrate holder, should be at a lower temperature. The difference in the temperature could be observed as a variation of the sample color (Fig. 1a). The substrate temperature was measured with a two-color pyrometer (Williamson Pro 92-40-C), that looked on a spot of  $\approx 3 \text{ mm}$  in diameter on one of the vertical large faces, the spot being comparable with the face size. Thus the pyrometer readings referred to an average temperature of the plate. After 15 h growth the seed crystal has been wrapped up with the CVD diamond layer on all sides except the bottom part (Fig. 1b).

To evaluate the temperature gradient a set of experiments for the vertical growth was performed using another MPCVD system ARDIS-100 [14], that has the process chamber equipped with several viewports convenient for optical emission measurements. A two-color pyrometer with spatial resolution of 0.8 mm (SensorTherm M322) was used to measure the sample temperature distribution in pure hydrogen and  $\text{CH}_4\text{-H}_2$  mixtures. The plasma cloud images were captured with a digital mirror camera (Canon EOS 650D) through a red (656 nm wavelength)  $\text{H}\alpha$ -filter, that passed only the  $\text{H}\alpha$  line emission in the plasma spectra [19]. As the  $\text{H}\alpha$  line is excited via electron collision, its intensity is proportional to the electron density, and, therefore, can be used for plasma mapping.

The surface morphology of the produced sample was examined with a laser scanning microscope (LSM) Olympus LS4000 and an optical profilometer NewView 5000 (ZYGO). The Raman and photoluminescence (PL) mapping were performed using a LabRam HR800 (Horiba Jobin-Yvon) spectrometer in a confocal configura-

tion with spectral resolution of  $2.0 \text{ cm}^{-1}$ , dispersion  $0.59 \text{ cm}^{-1}$  and spatial resolution of  $\sim 2 \mu\text{m}$ . The excitation laser beam ( $\lambda = 473 \text{ nm}$ ) was focused on the sample in a spot of  $2 \mu\text{m}$  in diameter, and the light from the sample has been collected in back-scattering geometry with microscope objective (Olympus, magnification  $50\times$ , numerical aperture  $\text{NA} = 0.55$ ). The Raman and PL mapping [18] of the large face were performed with a step of  $5 \mu\text{m}$  along the 3.35 mm long line going from the bottom to the top. The intensity of Raman peak ( $1332.5 \text{ cm}^{-1}$ ) and PL of neutral nitrogen-vacancy center  $\text{NV}^0$  (575 nm) and negatively charged  $\text{SiV}^-$  center (738 nm) were monitored by measuring the spectra in many locations. Then, the dependences of integral intensities within narrow spectral ranges of 504–506 nm for Raman, 567–583 nm for  $\text{NV}^0$  PL, and 730–746 nm ( $\text{SiV}^-$ ) on coordinate on the probed sample surface were obtained. In selected studies (without mapping) Raman spectra were taken with excitation wavelength  $\lambda_{\text{ex}} = 532 \text{ nm}$ .

## 3. Results

### 3.1. Growth surface morphology

The laser scanning microscope image of the large face, from the top to the bottom, of as-grown sample, reveals a gradually changing morphology, due to the temperature gradient, as shown in Fig. 2a. Several locations, of distinctly different morphologies, labeled A to H, were examined in detail with Raman spectroscopy, LSM and the optical profiler. The Raman spectra taken at  $\lambda_{\text{ex}} = 532 \text{ nm}$  in the eight characteristic locations are demonstrated in Fig. 2(b). The strong and narrow diamond Raman peaks at  $1332.5 \text{ cm}^{-1}$  present across the vertical face. The diamond quality in the most part of the sample, between zones A and E remains rather high, yet, when going downward, the diamond Raman peak width (full width at half magnitude – FWHM) monotonically increases from  $2.3 \text{ cm}^{-1}$  (zone A) to  $4.2 \text{ cm}^{-1}$  (zone E).

No non-diamond carbon or PL features can be seen for the top part of the sample (points A, B), indicating high quality of the material. In the middle part (points C, D, E) a broad peak around  $1420 \text{ cm}^{-1}$  appears, revealing the zero phonon line (ZPL) in PL of  $\text{NV}^0$  center (575 nm). The intensity of  $\text{NV}^0$  increases along with the drop of the location height (or decrease of the temperature). This temperature-dependent NV PL seem to be in agreement with the finding of Tallaire et al. [20] that the NV centers creation efficiency is inversely proportional and extremely sensitive to the diamond growth temperature upon MPCVD process. We note also, the increase of nitrogen incorporation efficiency in diamond (as measured with SIMS) at the lowering the temperature has been recently reported by Lobaev et al. [21]. In the bottom part, occupying about 1/6 of all area (locations F, G, H) only the peaks of disordered  $\text{sp}^2$  carbon with D-band at  $1350 \text{ cm}^{-1}$  and G-band at  $1550 \text{ cm}^{-1}$  are revealed, indicating that non-diamond phases and/or nanocrystalline diamond were produced under such growth conditions.

The LSM images of the specific surface regions B, D, E, F, G and H (Fig. 2), with markedly different structures, are shown at higher magnifications in Fig. 3. The top part, where the temperature was the highest, exhibited a step growth mode typical for epitaxial diamond growth, with the terrace width of around  $30 \mu\text{m}$  and step height of  $\sim 200\text{--}400 \text{ nm}$ . In the region between B and D, the typical step-flow features still present, with the distance between the growth steps reducing, while the temperature continues to decrease towards the bottom. In zone E, the terrace shape changes to a squama-like structure. Poly-nanocrystalline and non-diamond phases begin to form near the bottom part, as evidenced by the Raman spectra for zones F and G, and seen as dark regions in optical microscope images below the middle part of the sample.

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