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Epitaxial growth of mosaic diamond: Mapping of stress and defects in crystal junction with a confocal Raman spectroscopy

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ABSTRACT

We studied defects and stress distributions in mosaic epitaxial diamond film using a confocal Raman spectroscopy, with a special attention to the junction area between the crystals. The mosaics was grown by microwave plasma CVD on closely arranged (100)-oriented HPHT type Ib substrates. The width of stress affected and defect enriched region around the junction show a tendency of extending with the film thickness, from ≈40 μm on the film-substrate interface to ≈250 μm in the layer 500 μm above the substrate, as found from the mosaics analysis in cross-section. The stress field around the junction demonstrates a complex pattern, with mixed domains of tensile and compressive stress, with maximum value of $\sigma \approx 0.6$ GPa. A similar non-uniform pattern was observed for defect distribution as well. No sign of amorphous sp^2 carbon in the junction zone was revealed.

1. Introduction

Diamond, with its remarkable electronic and photonic properties, is the highly demanded material for high frequency-high power electronics, laser optics and radiation imaging detectors [1–3]. To compete with well-developed wide band-gap semiconductors such as SiC or GaN, diamond should be exploited in form of wafers with diameter larger than 1 in. at least. Polycrystalline diamond wafers produced by chemical vapor deposition (CVD) technique are now available in dimensions in excess of 4 in. [4]. However, due to grain boundaries, defects and stress, the performance of polycrystalline CVD diamond (PCD), is commonly inferior compared to that for single crystal (SC) diamond, with rear exclusions, like the microwave transistors (MESFET) with very high characteristics formed on hydrogenated PCD surface [5]. The CVD SCs are epitaxially grown on SC diamond substrates, produced by high temperature – high pressure (HPHT) technique, or CVD method, or, more rear, by cutting the natural stones. However, all these substrate sources suffer from a small size, typically of a few millimeters only. Since the availability of large area SC diamond seeds is limited and their cost is high, a technique to grow quasi-SC structures with increased size, so called "mosaics", has been developed as an alternative [6–13]. The approach involves arrangement in close proximity of a number of precisely cut, polished and crystallographically oriented seed crystals of single-crystalline diamond substrates. A homoepitaxial diamond layer is then grown over the substrates and bridges the gap between them, forming one continuous single-crystalline diamond layer. A further improvement in diamond mosaic technique has been made by Yamada et al. [14–19] who introduced identical *clone* seed substrates to minimize their differences in off-angle, purity, dimensions and structure. In this way they synthesized a mosaic diamond wafer with dimensions 40×60 mm^2, which consisted of 24 SC diamond plates, by using microwave plasma CVD (MPCVD) [14].

It was found, however, that the structure of the material grown in junctions is rather defected [8,10,13]. The high internal stress originated on the junctions can build up to the values capable to cause the crystal cracking [7,18,19]. Therefore, the study of defects and stress distribution within the crystal junctions and in the vicinity is important to obtain reliable growth of large-area SC dia-

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mond mosaics. In view of a small width of the junctions (typically the gap between the tiled crystals is a few to several tenses of micrometer), a local analysis of the structure, like microRaman spectroscopy, should be preferably exploited. The confocal Raman spectroscopy allows the stress mapping with spatial resolution of the order of 1 μm as was reported for polycrystalline diamond films [20] and single crystal CVD diamond [21]. Yamada et al. [19] probed the crystal quality of the boundaries for mosaics prepared by MPCVD and found the diamond Raman peak width Δν in the junction to show no big difference for thin (100 μm) and thick (~1 mm) epitaxial diamond layers. On the other hand, the Raman peak width in the junction was broadened compared to that for interior region far from the junction, thereby confirming an inferior quality of diamond in the junction zone. Muchnikov et al. [13] reported on Raman mapping across the junctions on polished mosaics surface, and demonstrated, that the defected and stress zones can extended far, up to 300–350 μm, from the junction line. Since the mapping was performed in previous studies from the growth side only, the issue on defected zone localization at different thickness of the growing layer remains unexplored. The information on evolution of the film structure in the junction would be useful for better understanding of the mosaics growth process.

In the present work we used a high resolution Raman mapping of stress and defect abundance (via Raman peak broadening measurement) in cross-section of a simple mosaic crystal in order to monitor, how the junction region evolves with the growth process. We found a monotonic increase of the width of defected and strained zone around the junction with the film thickness, and a complex pattern of stress distribution, with the stress building up to 0.6 GPa within this zone. The results are further complemented with SEM and XRD characterization of the CVD diamond mosaics.

2. Experimental

Two HPHT Ib diamond plates with 3 × 3 × 1.0 mm^3 dimensions (Sino-Crystal Co.), with {0 0 1} top and bottom faces, and the side surfaces perpendicular to ⟨1 1 0⟩ direction, were used as the substrates. The face orientation and (1 0 0) off-angle for the top large planes of the substrates were measured by X-ray diffraction (XRD) with Philips X'pert MRD system (Cu anode, resolution 0.004, scanning step 0.0004°, Ge(2 2 0) four crystal monochromator). The off-angles of 1.1° and 2.4° have been determined for the substrates, denoted hereafter as A and B, respectively. The difference in the substrate thickness was less than 20 μm. All six faces were polished to the roughness R_a of ≈2 nm, as measured with an atomic force microscope (Bruker Dimension Icon). The epitaxial diamond growth was performed in a 2.45 GHz, 5 kW microwave plasma CVD (MPCVD) reactor PLASSYS SSDR 150 using H_2-CH_4 gas mixture. After ultrasonic cleaning, two substrates were placed on a Mo substrate holder, with the sidewalls in close proximity to each other (with the gap between the substrates of about 90 μm), and with larger 3 × 3 mm^2 face up. The off-angle directions formed the angles of 42° and 37° with respect to junction line for substrates A and B, respectively, as shown by arrows on sketch of the aligned substrates in Fig. 1a.

Prior to epitaxial diamond growth, the substrate pretreatment was performed in pure H_2 and then in H_2/O_2 plasma at 900 °C, for 30 and 15 min, respectively, to etch surface defects. The diamond growth was achieved with the gas pressure of 280 mbar, gas flow rate 190 sccm hydrogen and 10 sccm methane (CH_4 concentration 5%), microwave power of 4.0 kW and substrate temperature 920 °C. The substrate temperature was measured with a two-color pyrometer (Willamson Pro 92-40-C).

The surface morphology of the produced mosaics was examined with a laser scanning microscope (LSM) Olympus LS4000, and a scanning electron microscope (SEM) Hitachi SU8000. Raman spectroscopy was performed using a LabRam HR800 (Horiba Jobin-Yvon) spectrometer in a confocal configuration with spectral resolution of 2.0 cm^{-1}, dispersion 0.59 cm^{-1} and spatial resolution of ~1 μm. The excitation laser beam (λ = 473 nm) was focused on the sample top surface or on polished cross-section, and the light from the sample was collected in back-scattering geometry with microscope objective (Olympus, magnification 100×, numerical aperture NA = 0.90). The unpolarized laser source has been employed, the laser power of 100 mW and power density being kept constant in all measurements. The diamond Raman peak position was measured with accuracy of ±0.3 cm^{-1} and the peak width with accuracy of ±0.5 cm^{-1}. In selected locations the Raman spectra with better spectral resolution were taken at 633 nm excitation wavelength using a Raman spectrometer LabRAM HR Evolution (Horiba Jobin-Yvon) with spectral resolution 1.5 cm^{-1} and dispersion 0.27 cm^{-1}. The accuracy in the Raman peak position and the peak width (FWHM) in this case were ±0.1 cm^{-1} and ±0.2 cm^{-1}, respectively, using a peak shape fitting procedure. Rocking curves for CVD layers was measured with the Philips X'pert MRD system. To analyze the structure of the junction extending from the HPHT substrate to the film top, the cross-section of the mosaics has been prepared by a laser cutting perpendicularly to the junction line, followed by a mechanical polishing to the roughness below 6 nm, as measured with an optical profilometer with the vertical resolution of ≈1 nm (NewView 5000, ZYGO).

3. Results

The mosaic sample after CVD diamond has been deposited for 40 h to get 610 μm thick CVD layer with growth rate of 15 μm/h, is shown in Fig. 1b. A dark strip appeared in the middle of the sample is the junction between the two crystals, denoted hereafter as A and B. The junction is parallel to ⟨1 1 0⟩ direction. The jointed crystals are surrounded by a belt of polycrystalline diamond film with width of about 1 mm, while the interior of the epitaxial CVD layer was free from inclusions of non-epitaxial (polycrystalline) diamond. The top view of the area in the vicinity of the junction is shown in more detail on the image taken with the laser scanning microscope Fig. 1c, it reveals the junction with typical width of 20 μm or less. A step growth mode on surfaces of both crystals is evident, the step flow direction forming an angle of ≈30° with the junction line.

A LSM image at higher magnification of a part of the interface with very narrow junction in form of a dip is displayed in Fig. 2. The steps from two sides meet at the junction, forming a shallow groove. However, in other parts of the junction, a deeper gap, of few micrometers, between two crystals could be found, as evidenced by the SEM image in Fig. 3. The junction is formed by two inclined planes forming a groove typically of 5–10 μm wide and ≈3–5 μm deep, as seen on this particular area, however, the groove dimensions can vary to some extent along the junction.

The structural quality of interior regions of the crystals was assessed from X-ray diffraction (rocking curves) for (0 0 4) reflection measured for the CVD diamond growth side. The rocking curves measured in central part (≈2.5 mm in diameter) of the crystals *A* and *B* (the junction zone was outside the X-ray beam), are shown in Fig. 4. The reflection for crystal A is positioned at ω = 59.92°, very close to the angle for unbent (1 0 0) face (ω = 59.7), and has the width (FWHM) Δω = 0.012°. The crystal *B* showed the wider peak with Δω = 0.021° shifted to ω = 56.93° as the result of a larger off-angle for the substrate *B*. The off-angles 0.2° and 3.2° determined from the rocking curves for crystals A