Diamond & Related Materials 83 (2018) 162–169

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Reduction of dislocation densities in single crystal CVD diamond by confinement in the lateral sector

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ARTICLE INFO

Keywords:
Single crystal diamond
Threading dislocation
Pyramidal shape substrate
Plasma assisted CVD
Extended defect
Confinement
Growth sector boundary

ABSTRACT

The use of diamond as a semiconductor material in power electronics applications is held back by the presence of vertical threading dislocations that are believed to deteriorate device performance. Reducing their occurrence in single crystal diamond is therefore crucial. Recently we found that thick CVD diamond grown on the inclined plane of a pyramidal-shape substrate can lead to dislocation bending from a [001] to a [110] direction (Tallaire et al., 2013a [1]). In this work we further explore this strategy for the growth of thick crystals with low dislocation density. It is shown that the boundary angle between inclined lateral and top faces plays a critical role in preserving bent dislocations during the entire growth run. Indeed under well-chosen growth conditions, a boundary angle of at least 45° ensures that dislocations never intercept the top face and are confined in a lateral sector. We eventually show clear evidence of dislocation density reduction in the crystal using this approach.

1. Introduction

Diamond exhibits properties that meet many technological challenges and current energy requirements. It is a material with unique physical characteristics that could help push forward the boundaries of not only power electronic devices [2] but also spintronic and quantum information processing devices based on the properties of luminescent centers [3] or high-energy particle detectors [4].

During the last two decades, important progresses have been made in the synthesis of high quality and high purity thick single crystal diamonds using both High Pressure High Temperature (HPHT) [5] and Plasma Assisted Chemical Vapor Deposition (PACVD) techniques [6]. These efforts were mostly driven by highly promising applications in electronic devices such as Schottky diodes and transistors [2], optics for X-ray [7], Raman lasers [8], high-energy particle detectors [4] as well as magnetic sensors [9]. Despite significant achievements, device performance remains far below the theoretical capacities of the material, in particular because of a high density of extended defects such as threading dislocations (TD). For power devices, these lead to an increase in leakage current [10,11] as soon as electrodes' diameter exceeds a few hundreds of micrometers and to a reduction in the maximum breakdown field [12]. Furthermore, the stress field that surrounds dislocations affects light propagation and generates optical birefringence [13], and unwanted background luminescence [14], thus plaguing the use of diamond for optical windows [7] or Raman lasers [8].

Many studies have been carried out recently in order to observe the type and the propagation direction of dislocations in diamond by cathodoluminescence (CL) or X-ray topography (XRT) but also to quantify dislocation densities through selective etching [13,15]. TDs either directly originate from dislocations or stacking faults already present in the substrates [16] or they are generated at the substrate/layer interface due to the presence of contaminants, surface polishing damage [17,18], or even a strong lattice mismatch [19].

Several techniques have been developed in an attempt to reduce dislocation density such as in-situ chemical etching treatments using H_2/O_2 plasma [20], ex-situ physical etching with an inductively coupled plasma source (ICP) or chemical mechanical polishing (CMP) [21] of the substrate prior to growth. These methods limit or even annihilate the formation of new dislocations at the re-growth interface by eliminating mechanical polishing damage at the surface. Nevertheless, dislocations originating from bulk defects in the substrate cannot be easily eliminated and inevitably propagate in the growth direction [22], leading to CVD single crystal diamond with a relatively high dislocation density typically in the 10^5–10^7 cm^{-2} range [23].

By carefully controlling the growth temperature of their HPHT process, Sumiya et al. [24] have shown that large defect free areas can be grown for type *IIa* material. Mokuno et al. [25] have shown that

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https://doi.org/10.1016/j.diamond.2018.02.010
Received 22 December 2017; Received in revised form 8 February 2018; Accepted 12 February 2018
Available online 13 February 2018

starting from this dislocation-free type *IIa* HPHT substrate a thick CVD film with a dislocation density as low as few hundreds per cm^2 can be obtained. However, the cost of these substrates (up to several tens of thousands of euros), in addition to their availability, does not allow an easy industrial scaling up. Hence there is a strong need for developing new strategies and technologies based on standard "low-cost" HPHT substrates that typically contain dislocation densities in the 10^4–$10^6\,cm^{-2}$ range. One possible approach consist in deviating dislocations away from the growth direction which can be done by using a crystal with a large offset angle (> 10°) [22,26]. This has for example been explored in the Aspect Ratio Trapping (ART) strategy for different heterosystems such as Ge/Si or GaAs/Si, where growth occurs laterally from the sides of deep patterned substrates, leading to a confinement of dislocations in lateral sectors. Consequently, a reduction of dislocation densities was obtained. Only few attempts were made to adapt these strategies to diamond and they were mainly restricted to the specific heteroepitaxial growth system of diamond on iridium in which dislocation densities can be up to 10^9–$10^{10}\,cm^{-2}$ [27,28].

In a previous study, we have shown that the use of pyramidal-shape substrates with angle above 20° improve the morphology of intrinsic thick monocrystalline diamond films [1]. Dislocation bending was observed but TD density remained high. In this paper, we report more specifically the effect of varying growth conditions on the dislocation propagation from pyramidal-shape substrates with a 20° angle. We then propose a strategy using these engineered-shape substrates to achieve a confinement of dislocations in lateral sectors during thick homoepitaxial growth.

2. Experimental details

Standard type *Ib* HPHT cubic-shape diamond substrates ($3 \times 3 \times 1.5\,mm^3$) having both their lateral and top faces oriented along the [100] directions were used. The substrates were polished by *Almax EasyLab* company into a pyramid having its lateral sides inclined by an off-angle of 20° with respect to the [001] directions as illustrated in Fig. 1a. The top square of the pyramid had an area of approximately $200 \times 200\,\mu m^2$ (Fig. 1b). After polishing, the pyramidal-shape diamond substrates were acid cleaned and submitted to an H_2/O_2 (98/2) plasma etching treatment in order to remove any defects and graphite residues [20]. This includes a micro-wave plasma power/pressure (3000 W/200 mbar), a temperature of 850 °C for 2 h. The angle and dimensions of the pyramid were measured using confocal laser microscopy (CLM) (*Keyence VK9700*).

Diamond growth was carried out using a high plasma density in a *Plassys BJS150* CVD reactor under optimized growth conditions [29]. This typically includes a high micro-wave plasma power/pressure (3400 W/240 mbar), a temperature of around 850 °C. High purity H_2 (9 N) and methane (6 N) at a ratio of 95/5 were used. The growth was sometimes interrupted and resumed in order to observe the evolution of crystal shape and dislocation propagation. The crystals were characterized by UV photoluminescence (PL) imaging using a *Diamond View*™ equipment. To reveal the distribution of dislocations, the samples were etched inside the CVD reactor using H_2/O_2 plasma (98/2) at a pressure of 200 mbar, a power of 3 kW and a temperature of about 850 °C for 5 min. Dislocations reaching the surface are thus evidenced by square etch-pits [30].

The extended defects propagating in the CVD grown diamond films were characterized by synchrotron radiation XRT in the Laue geometry at the BL9A beamline in Kyushu Synchrotron Light Research Center (Saga Light Source), with X-ray photon energy ranging from 4.5 to 25 keV. The images were taken using monochromatic X-rays incident beam, obtained by installing a monochromator consisting of two dislocation-free Si (111) channel-cut crystals with a parallel configuration at the first goniometer. We obtained projection images by placing the specimen on the stage attached to the second goniometer. For the CL experiments, two different set-ups were used. First a 20 keV, 10 nA electron beam from a JEOL 7001F SEM was used to excite CL while light was collected by a parabolic mirror and sent to a Horiba TRIAX 550 spectrometer. The spectral and imaging analysis were performed with a UV-enhanced silicon CCD camera, or a Hamamatsu (R943-02) photomultiplier tube. The second set-up used a similar configuration but was attached to a ZEISS EVO-MA15 microscope and the CL was excited using a 10 keV, 20 nA beam. For the measurements, sample temperature was kept to around 110 K.

3. Impact of pyramidal shape on dislocation propagation direction

After a 500 µm growth during 37 h, the lateral faces of the pyramid have disappeared to the favor of the top (001) surface. The final shape of the CVD crystal is not different to what would have been obtained with a cubic shape substrate, as can be seen on the optical images presented in Fig. 1c.

In order to observe dislocation propagation, a 1 mm-thick slice in cross-section was laser cut along the [100] direction (Fig. 2a) and the lateral faces of the slice were then polished. The result is presented in Fig. 2b.

Synchrotron radiation XRT of the slice is shown in Fig. 3a. On this picture, the initial angle of 20° at the level of the substrate can be observed, and most of the dislocations seem to originate from the initial substrate. Moreover, this picture confirms that the use of an engineered pyramidal-shape substrate has successfully changed the propagation direction of dislocations from typically [001] to a direction close to [110], since an angle of 45° with respect to the upper face can be measured next to the substrate/layer interface [22]. Unfortunately, observation near the surface of the film also shows that almost all dislocations end up perpendicular to the surface. This suggests that dislocations do not remain inclined throughout the entire growth and that eventually the beneficial effect of the substrate misorientation is lost.

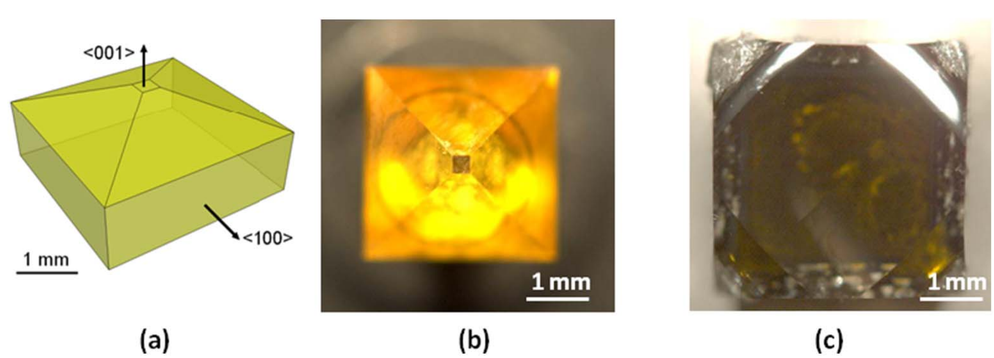

Fig. 1. (a) Schematic side view of the pyramidal-shaped substrate prior to growth, (b) optical top view image of the pyramidal-shaped substrate prior to growth and (c) optical top view image of the pyramidal-shaped substrate after growth of a CVD film with a thickness of 500 µm.