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Reduction of dislocation densities in single crystal CVD diamond by using self-assembled metallic masks

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ABSTRACT

The development of diamond-based electronic devices designed to operate at high power is strongly hampered by the lack of low dislocation single crystal material. Dislocations in Chemically Vapor Deposited (CVD) diamond are indeed generally responsible for leakage current, seriously deteriorating the performance of the devices. They can be due to defects such as polishing damage or contamination found at the substrate's surface, or they can directly originate from existing bulk defects that extend into the homoepitaxial layer. Although significant improvements have been achieved by using adapted surface treatments, dislocations found in CVD diamond grown on standard quality single crystal substrates are still typically in the range 10^5–10^6 cm^{-2}. In this work, we report on a new growth strategy aiming at preventing threading dislocations from propagating into CVD diamond layers. It is based on the selective masking of existing defects revealed at the surface of the substrates by Pt nanoparticles. The interaction of dislocations with such embedded particles has been assessed and critical remarks are given as to the use of this technique in order to reduce dislocation densities in synthetic diamond.

1. Introduction

Diamond is a material with unique physical characteristics that could help push the boundaries of power electronic devices. Indeed, thanks to its high breakdown voltage (10 MV/cm), its high thermal conductivity (2200 $W \cdot m^{-1} \cdot K^{-1}$) and carrier mobilities (up to 4000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ measured for electrons [1]) diamond is the ultimate material for power electronics. In this context, a strong craze for the development of "all diamond" power devices is palpable. Despite difficulties with n-type doping both unipolar devices based on p-type doping with boron such as coplanar Schottky diodes [2,3], as well as bipolar devices have been developed [4,5]. Although blocking voltage capabilities of several kV have been achieved, increasing the operating current relies on vertical devices with larger electrode size [6,7]. Since the number of critical extended defects increases with the device size, they become a major issue plaguing the device reproducibility [8]. Threading dislocations (TD) can for example reduce the maximum breakdown field by causing current leakage [9]. They can also act as efficient recombination centers for electrons and holes inducing carrier mobilities decrease. In this context, there is a strong need for developing a technology allowing the growth of dislocation-free diamond layers by Plasma Assisted Chemical Vapor Deposition (PACVD).

In achieving this objective, the crystalline quality of the initial substrate, usually a High Pressure High Temperature (HPHT) crystal, is obviously of prime importance since extended defects tend to directly propagate from the seed into the epitaxial layer. But new dislocations are also generated from the interface due to surface defects (contaminations or polishing marks) or lattice mismatch [10] leading to densities of 10^5–10^7 cm^{-2} that are much higher than typical values for standard quality *Ib* HPHT material [11]. Treatments to remove surface defects such as plasma etching, or chemo-mechanical polishing are helpful in reducing the total amount of dislocations [12–16] but they cannot entirely suppress them. Using exceptional quality diamond substrates that were submitted to an optimal surface treatment can lead to dislocation densities as low as 400 cm^{-2} [17,18]. However the ability to obtain higher quality material than the initial standard substrate would be of great relevance to integrate diamond at a larger scale into highly efficient electronic devices.

Other semiconductor materials such as gallium nitride (GaN) or silicon carbide (SiC) have faced similar challenges. A powerful technique that has been developed for heteroepitaxially-grown GaN to reduce dislocation densities consist of masking a portion of the surface with a discontinuous layer of silicon nitride (SiN). This treatment is followed by epitaxial lateral overgrowth (ELOG) over the SiN mask, leaving threading dislocations either blocked by the mask or laterally bended over it [19]. A decrease from typically 10^9 to 10^7 dislocations per cm^2 has been achieved [20] which directly translated into more efficient optoelectronic devices such as lasers and diodes.

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Several attempts have been made to reduce dislocation densities using lateral overgrowth strategies in heteroepitaxially grown CVD diamond films [21,22]. Coalescence of diamond areas above micro-stripped patterns on a MgO/Ir template led to a significant enhancement of crystalline quality. By growing for an extensive period of time (thickness > 1 mm), dislocation densities were also found to be reduced down to about 10^7–10^8 cm^{-2} in heteroepitaxial films grown on $Si/ZrO_2/Ir$ which translated into improved electronic properties [23]. In a different approach, Bauer et al. have grown single crystal films through metallic masks made from iridium. The metal mesh was overgrown by diamond [24] but no effect on dislocation densities was reported. Other authors have also successfully embedded metallic platinum particles [25,26] or gold droplets in an attempt to reduce stress in (111)-grown diamond films [27].

In this work we report on a technique inspired from ELOG and adapted to the case of homoepitaxial CVD grown diamond. A selective masking of existing defects in the diamond substrate was achieved through the use of self-assembled platinum particles. This step was optimized in order to achieve a perfect match between the metallic mask and the dislocation network. CVD diamond overgrowth was then carried out to assess if their effect on dislocation propagation in the CVD layer. The results are discussed based on statistical and structural characterizations.

2. Experimental details

Commercially available High Pressure High Temperature (HPHT) *Ib* diamond crystals from Sumitomo were used: all the crystals had their two sides polished and dimensions of 3×3 mm^2. In order to efficiently remove the surface damaged layer (due to polishing) a plasma treatment was performed in a microwave bell-jar CVD reactor with a H_2/O_2 (98:2) gas mixture at 830 °C during 90 min. The working pressure was 200 mbar and the injected microwave power was 3 kW. This step also ensured that the substrate is covered with etch-pits (EP) in the shape of inverted pyramids due to preferential etching at defects outcropping at the surface, essentially dislocations [28]. This is illustrated in Fig. 1a and b. The lateral sides of the etch-pits are oriented along <110> directions while their depth and shape might change slightly depending on the defect involved and the etching duration [29].

Platinum deposition was then performed in a homemade MOCVD reactor equipped with a liquid injection system (Kemstream, Vapbox 500). In this kind of system, vaporization of the liquid precursor is achieved under conditions of pressure and temperature allowing a sufficient precursor vapor pressure for the deposition (while remaining within its stability range). The platinum precursor used is Dimethyl(norbornadienyl)platinum (nbd-Pt-Me_2) [30–32]. Its vaporization was carried out at a pressure of 10^{-3} mbar for a temperature of 80 °C and with a small amount of added oxygen (a few sccm) in order to assist decomposition. This precursor was chosen due to its high volatility and its stability at temperatures up to 300 °C. MOCVD is also particularly adapted to the deposition of uniform and conformal layers even on rough surfaces such as the etched diamond substrate. The liquid precursor is injected in the reactor chamber with a pulse frequency of 3 Hz. The layer thickness is adjusted by setting the number of pulses. 10 to 50 nm thin-layers were deposited.

Platinum film dewetting was then performed in a microwave bell-jar CVD reactor under pure H_2 plasma and with a sample temperature around 800 °C, a microwave power of 3 kW and a pressure around 200 mbar. The treatment duration was adjusted from 5 min to 1 h so as to get an almost perfect match between Pt nanoparticles and EP.

To embed the particles, diamond growth was finally performed in the same CVD reactor and under the same power/pressure conditions with a H_2/CH_4 (95:5) mixture at 850 °C. Growing the diamond layer directly after the H_2 plasma thermal annealing allows avoiding plasma interruption which is well known to favor defect formation [33]. The growth was sustained to get roughly an 80 μm thick film. It was followed by a short etching treatment under H_2/O_2 (98:2) which aims at revealing dislocations appearing at the surface of the CVD layer. The full procedure used in this work is schematically illustrated in Fig. 2.

Images of the samples were taken by Scanning Electron Microscopy (SEM) in a ZEISS Supra after coating the surface with a thin sputtered amorphous carbon layer in order to make it conductive. This layer can then be removed by a short plasma etching treatment under pure H_2 so that it will not affect further growth when needed.

A laser optical microscope (Keyence VK 9700) was used to acquire surface morphology images from which EP density could be measured. TEM lamellae with thicknesses of about 200 nm have been machined on a FEI Helios 600i SEM-FIB, using Ga ions with intensities ranging from 21 to 0.08 nA (Fig. 8). TEM observations and measurements were performed both on a JEOL 2010 and Philips CM20FEG. Cathodoluminescence (CL) imaging was performed in a Horiba Jobin Yvon system using a 10 kV electron beam produced in a JEOL7001F scanning electron microscope equipped with a field-emission-gun. The diamond film was coated with a semi-transparent gold layer in order to conduct away electrical charges and cooled down to 10 K thanks to a liquid helium cold stage. The luminescence was collected by a parabolic mirror and focused on a monochromator equipped with a 600 grooves/mm diffraction grating. Monochromatic CL images were taken by filtering the near-band-edge diamond emission (excitonic recombinations at 235 nm) through the monochromator equipped with a UV photomultiplier detector synchronized with the beam scanning.

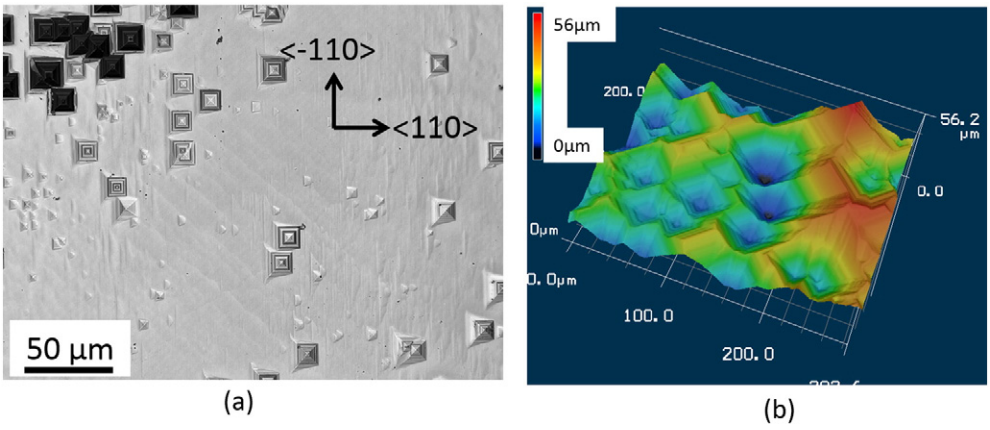

Fig. 1. Laser microscope image of the surface of a H_2/O_2 plasma etched diamond. (a) Top view after a short etching, (b) 3D view after a longer etching (4 h) leading to deep pyramidal etch-pits. Those features are related to preferential etching at dislocations. The vertical dimensions are indicated next to the color scale.