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Mosaicity, dislocations and strain in heteroepitaxial diamond grown on iridium

H. Bensalah [a], I. Stenger [a], G. Sakr [a], J. Barjon [a,*], R. Bachelet [b], A. Tallaire [c], J. Achard [c], N. Vaissiere [d], K.H. Lee [d], S. Saada [d], J.C. Arnault [d]

[a] Groupe d'Etude de la Matière Condensée (GEMaC), Université de Versailles St Quentin en Yvelines, CNRS, Université Paris Saclay, 45 Avenue des Etats-Unis, 78035 Versailles, France
[b] Université de Lyon, Ecole Centrale de Lyon, INL-UMR5270-CNRS, Ecully, France
[c] Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux (CNRS UPR 3407), Villetaneuse, France
[d] CEA, LIST, Diamond Sensors Laboratory, Gif sur Yvette, France

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ABSTRACT

The present study provides a multi-scale investigation of the crystalline quality and the structural defects present in heteroepitaxial diamond films grown on iridium/$SrTiO_3$ (001) substrates by microwave plasma assisted chemical vapor deposition. X-ray diffraction, Raman spectroscopy and low temperature cathodoluminescence are combined to accurately characterize the mosaicity, the density of dislocations and the residual strain within the films. X-ray diffraction and Raman results confirm a structural quality at the state-of-the-art according to the epitaxial relationship ⟨100⟩diamond(001) // ⟨100⟩iridium(001) // ⟨100⟩$SrTiO_3$ (001). In addition, Raman and cathodoluminescence observations on cross-sections reveal the presence of local strain.

1. Introduction

Promising advances have been recently reported for the growth of diamond single crystals on large areas [1]. Cloning and tiling of diamond single crystals allow enlarging lateral dimensions of homoepitaxial diamond films [2]. At the same time, heteroepitaxial diamond constitutes a credible alternative to homoepitaxy for the next generation of power electronic or radiation detection applications. Indeed, the upscaling perspectives for the growth process are particularly interesting for producing large diamond surfaces, compatible with microelectronic technologies [3]. Among the potential substrates, iridium is up to now the best candidate to heteroepitaxially grow high quality diamond by the Chemical Vapor Deposition (CVD) technique. This behavior is related to a specific reactivity of iridium surface towards active species during Bias Enhanced Nucleation (BEN) [4] compared to other substrates like silicon [5] or silicon carbide [6,7]. After BEN, surface investigations revealed diamond nucleation within specific areas called domains [8]. Contrary to other substrates, growth of diamond nuclei is prevented at this stage. Iridium epitaxial layers are currently deposited onto single crystal MgO, $SrTiO_3$ or up-scalable substrates like YSZ (Yttria-stabilized zirconia)-buffered on silicon (001) [9].

However, the crystalline quality of heteroepitaxial diamond grown on iridium is still limited by some important problems such as the residual mosaicity, the residual strain and the presence of a high density of dislocations. For a quantitative evaluation of dislocation density in heteroepitaxial diamond, C. Stehl et al. have used chemical etching and they obtained values in the range of 7×10^9–5×10^7 cm^{-2} for 10 and 1000 μm diamond thicknesses, respectively [10]. While using μ-Raman spectroscopy and X- ray diffraction, M. Fisher et al. have demonstrated that stress up to several GPa can be generated in diamond grown on iridium [11]. These problems can affect the electron-hole mobility-lifetime product and the charge collection efficiency of detectors [12]. In fact, a careful control of the growth conditions is required to decrease the density of defects and then improve the quality of diamond films.

The objective of the present work is to provide a better understanding of the specific defects like dislocations and strain in heteroepitaxial diamond films grown on iridium/$SrTiO_3$ (001). The analysis is carried out by combining different techniques including Raman, X- ray diffraction and cathodoluminescence (CL) at 10 K using a multi-scale approach. Cross-sections of samples were also prepared to follow the dislocation propagation along the growth axis.

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[*] Corresponding author.
E-mail address: julien.barjon@uvsq.fr (J. Barjon).

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2. Experimental details

Diamond thin films were heteroepitaxially grown on Ir/$SrTiO_3$ (001) substrates by microwave plasma assisted chemical vapor deposition (MPCVD). First, iridium layers (200 nm) were deposited by e-beam evaporation under secondary vacuum ($<10^{-6}$ mbar) on 5×5 mm^2 (001) $SrTiO_3$ single crystals purchased from CrysTec Inc. The sample temperature was measured by an infrared pyrometer with a precision of 0.3% on a SiO_2 wafer placed next to $SrTiO_3$ substrates. The iridium growth rate was 1.5 nm/min and the substrate temperature was 980 °C. The polar and azimuthal mosaicity of these layers were measured by X-ray diffraction and can be as low as 0.14° and 0.12°, respectively.

To induce diamond epitaxial nucleation on Ir, a Bias Enhanced Nucleation (BEN) procedure was applied. The experimental conditions are provided in Table 1. A negative bias voltage of -307 V was applied to the substrate. The BEN step was followed by a first growth step of 60 nm performed in the same MPCVD reactor [8]. A second growth step was necessary to achieve thick diamond films in the order of 300 μm thickness, by using the high growth rate (6 μm/h) conditions of homoepitaxial growth well-mastered at LSPM [23]. This was carried out in a bell-jar type reactor (Plassys BJS150). No nitrogen was intentionally added to the gas phase. Four samples were obtained by varying the second growth step duration: 0 (no second growth step), 18, 30 and 48 h. At the end, the diamond layer thicknesses are: 60 nm, 90 μm, 200 μm and 320 μm, respectively.

Different techniques have been carried out to analyze the structural and physical properties of heteroepitaxial diamond samples. Conventional X-ray diffraction (XRD) gives a characterization of structural properties averaged over the crystal volume. On the contrary, Raman or CL are using focused beam and are then sensitive to a typical μm depth region. In order to understand the evolution of the heteroepitaxial diamond properties along the growth axis, heteroepitaxial diamond were characterized on the final growth surface but also on their cross-sections. For preparing cross-sections, the samples were cut by a Nd:YAG laser along the vertical (100) plane and then the edge was polished using argon ion beam in the Cross-Polisher JEOL IB- 09010CP at a voltage 4 kV during 10 h.

Confocal Raman spectroscopy and mapping of the 1332 cm^{-1} diamond line position and full-width-at-half maximum (FWHM) were performed on the samples. The data were recorded in a backscattering geometry using a Horiba Jobin Yvon confocal micro-Raman HR800. Excitation was performed with the 514 nm line of Ar^+ laser, focused onto the sample with an ×100 objective. A 632 nm He-Ne laser was also used in the same conditions to compare our data to the literature. By using an 1800 grooves/mm grating and a confocal hole of 50 μm, the spectral resolution was 0.9 cm^{-1} in the range of the diamond peak, while the interpixel distance equals to 0.48 cm^{-1}. The Raman mappings were recorded every 1 μm step thanks to a motor-driven XY table. Each spectrum was automatically fitted using a Lorentzian function in order to extract position and FWHM of the Raman line, further color-plotted in two-dimension graphs.

The structural properties of diamond films were investigated by X-ray diffraction. A Rigaku SmartLab diffractometer equipped with a high brilliance rotating anode and an in-plane arm (allowing grazing incidence XRD) was used. Conventional θ/2θ scan and ω-scan (rocking curve) were done on the symmetric reflection (004) to analyze the out-of-plane lattice parameter and the polar mosaicity (out-of-plane), respectively. The azimuthal mosaicity (in-plane) is evaluated by recording azimuthal scans (ϕ-scans) on asymmetric reflections. Reciprocal space maps have been further recorded around the symmetric (004) and asymmetric ($-1-13$) nodes to characterize the mosaicity and the possible residual strain. The azimuthal mosaicity and the microstrain level at the diamond surface has been also probed by surface diffraction in grazing incidence (GIXRD) conditions on (220) reflection (with fixed incidence of 0.35° and lateral soller slits of 0.114°).

CL spectra were collected using an optical detection system from Horiba Jobin Yvon SA, installed on a JEOL7001F field-emission scanning electron microscope (SEM). The samples were mounted on a GATAN cryostat SEM-stage, which was cooled at 10 K with liquid helium. The specimens were coated with a semitransparent gold layer of 5 nm in order to evacuate away electrical charges. The penetration depth of electrons in diamond is 0.9 μm depth with the 10 keV electrons used here. The CL emission was collected by a parabolic mirror and focused with mirror optics on the entrance slit of a 55 cm focal length monochromator. This achromatic all-mirror optics bench, combined with a suitable choice of ultraviolet (UV) detectors and gratings, provides an excellent sensitivity down to 200 nm. A silicon charge-coupled-display camera was used to record spectra. Monochromatic CL images were taken by filtering the excitonic signal through the monochromator equipped with a photomultiplier detector synchronized with the beam scanning.

Table 1
Experimental conditions of BEN and CVD growth steps applied to Ir/$SrTiO_3$ (001) substrates.

	Nucleation process			Growth1	Growth2
	H_2 cleaning	H_2/CH_4 stabilization	BEN		
CH_4 (%)	0	4	4	0.6	5
Pressure (mbar)	20	20	20	20	200
MW Power (W)	400	400	400	400	3000
Bias voltage (V)	0	0	-307	0	0
Substrate temperature (°C)	600 ± 50	650 ± 50	700 ± 50	600 ± 50	880 ± 30
Duration (min)	10	10	40–45	30	0, 18, 30 and 48 h

3. Results and discussion

3.1. Raman spectroscopy as a function of the film thickness

An optical image of the 320 μm thick heteroepitaxial diamond crystal is presented in Fig. 1. The diamond film is still standing on the 5×5 mm^2 Ir/$SrTiO_3$ (001) substrate, which indicates that the residual strain of diamond film is low enough to avoid its spontaneous

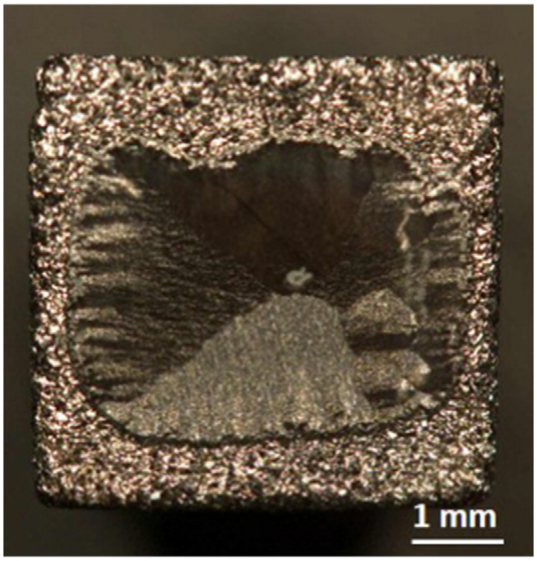

Fig. 1. Optical image of a 320 μm thick heteroepitaxial diamond film grown on Ir/$SrTiO_3$ (001) substrate.