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Epitaxy of iridium on $SrTiO_3$/Si (001): A promising scalable substrate for diamond heteroepitaxy

Kee Han Lee [a,*], Samuel Saada [a], Jean-Charles Arnault [a], Rahma Moalla [b], Guillaume Saint-Girons [b], Romain Bachelet [b], Hakima Bensalah [c], Ingrid Stenger [c], Julien Barjon [c], Alexandre Tallaire [d], Jocelyn Achard [d]

[a] CEA, LIST, Diamond Sensors Laboratory, F-91191 Gif-sur-Yvette, France
[b] Institut des Nanotechnologies de Lyon (INL — CNRS, UMR 5270), École Centrale de Lyon, 36 av. Guy Collongue, 69134 Ecully cedex, France
[c] GEMAC, Université Versailles St. Quentin, France
[d] LSPM, Université Paris 13, Sorbonne Paris Cité, CNRS, 93430 Villetaneuse, France

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ABSTRACT

Iridium epitaxy on $SrTiO_3$/Si (001) was investigated using field emission scanning electron microscopy (FE-SEM), spectroscopic ellipsometry, X-ray diffraction (XRD) and atomic force microscopy (AFM). Thermal stability of $SrTiO_3$ buffer layers (12–40 nm thick) was first investigated by annealing at different temperatures (620 °C–920 °C) under vacuum to optimize iridium epitaxy conditions. The surface morphology was monitored by FE-SEM and optical constants by spectroscopic ellipsometry. Iridium films were then deposited and their morphology and crystalline quality were evaluated by FE-SEM and XRD. It was found that iridium epitaxy is optimized at 660 °C on $SrTiO_3$ films thicker than ~30 nm. The polar and azimuthal mosaicities of the iridium films on $SrTiO_3$/Si (001) were 0.3° and 0.1°, respectively. These epitaxial iridium films were further used for diamond heteroepitaxy. The bias enhanced nucleation (BEN) treatment resulted in highly homogeneous and dense diamond domains. Heteroepitaxial diamond films were further grown by microwave plasma enhanced chemical vapor deposition (MPCVD) on 7 × 7 mm^2 Ir/$SrTiO_3$/Si (001) substrates and characterized by XRD.

1. Introduction

The unique properties of monocrystalline diamond, like its wide band gap, high mobility for both charge carriers (electron and hole) and high breakdown voltage [1] support its technological development for power electronic devices [2]. However, the size of the monocrystalline CVD diamond is limited by the small dimensions (few mm^2) of commercially available HPHT diamond substrates. As far as today, heteroepitaxy is the most promising method for diamond surface upscaling [3]. Different substrates (or template layers) are used for diamond heteroepitaxy like silicon, silicon carbide and iridium. Iridium is, by far, the best candidate resulting in highest epitaxial rate (>90%) [4]. This is explained by its specific reactivity towards CVD plasma compared to silicon and silicon carbide [5,6]. Since iridium monocrystals are not available, thin epitaxial layers need to be deposited on other bulk substrates such as MgO [7] or $SrTiO_3$ [8]. However scaling up with these material systems is not straightforward. Silicon substrates would be preferable, because of a better up-scaling potential, low cost, compatibility with existing silicon-based technologies and more favorable thermal expansion mismatch with respect to bulk oxide substrates. YSZ (Yttria-stabilized zirconia)-buffered silicon (001) substrates [9] have been used for iridium epitaxy but they encounter a relatively high lattice mismatch (over 5%).

$SrTiO_3$-buffered Si (001) thus appears as a good system due to a smaller lattice mismatch with iridium (1.7%) (Fig. 1) compared to its alternatives (9.8% for MgO and 5.3% for YSZ). High-quality epitaxial $SrTiO_3$ thin films can be obtained on Si (001) by molecular beam epitaxy (MBE) [10–12]. Schreck et al. reported the use of Ir/$SrTiO_3$/Si (001) substrates for diamond heteroepitaxy [13]. Nevertheless, this group shifted to Ir/YSZ/Si (001) substrates. In this study, $SrTiO_3$-buffered Si (001) substrates were used for iridium deposition. We relied on our previous studies on bulk $SrTiO_3$ (001) substrates [14–17] and defined appropriate conditions for iridium deposition on $SrTiO_3$/Si substrates. Multiple parameters were considered for optimizing iridium deposition on $SrTiO_3$/Si such as deposition temperature and the effect of thickness of the $SrTiO_3$ layer. Several iridium films deposited with near-optimal conditions were used for bias enhanced nucleation (BEN) [18] to study the effect of the quality of iridium films on diamond nucleation. Large high-quality homogeneous heteroepitaxial diamond films were obtained on optimized Ir/$SrTiO_3$/Si (001) multilayered substrates.

* Corresponding author.

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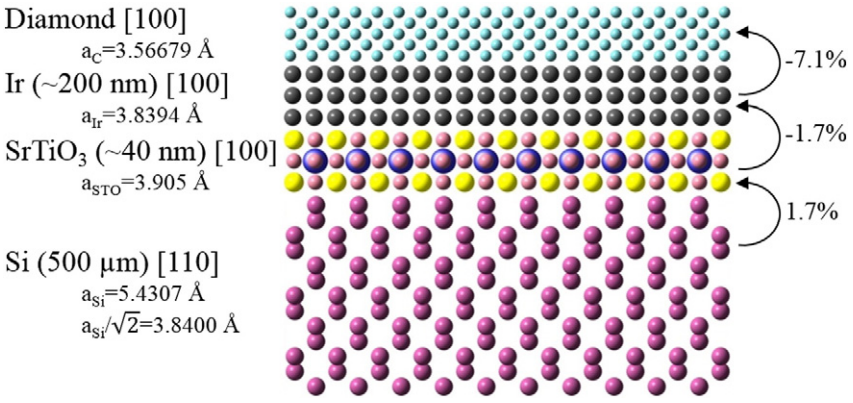

Fig. 1. Scheme of the Ir/$SrTiO_3$/Si multilayer substrate for diamond heteroepitaxy.

2. Materials and methods

2.1. $SrTiO_3$/Si wafer preparation

Epitaxial $SrTiO_3$ thin films were deposited by MBE on 500 μm thick (001) oriented silicon wafers [10,12]. Knudsen effusion cells were used for Sr and Ti evaporation. Before introduction in the reaction chamber, the Si substrates were cleaned by exposition to UV-O_3 ambient and in a buffered oxide etching (BOE) solution to remove the native SiO_2 surface layer. A controlled and clean SiO_2 thin layer was then formed at the bare Si surface by exposing again the surface to UV-O_3. The clean SiO_2 layer was then removed from the Si surface in the growth chamber by using the Sr-catalyzed desorption procedure consisting of annealing under ultra-high vacuum (UHV) at ~770 °C, leading to a self-limited coverage of 1/3 monolayer (ML) of Sr on the Si surface [19]. A completion to ½ ML of Sr at 500 °C was then performed. After this treatment, the substrate temperature was ramped down to 360 °C, and the samples were exposed to an O_2 partial pressure of 6.7×10^{-8} mbar for ~1 min. 10 ML of $SrTiO_3$ were then deposited (co-deposition of Sr and Ti) at this temperature and O_2 partial pressure, leading to the formation of partially amorphous $SrTiO_3$ layers. The samples were then crystallized by annealing at 420 °C during ~20 min under UHV, and the rest of the $SrTiO_3$ layer was grown at temperatures between 360 °C and 420 °C under an oxygen partial pressure of 1.3×10^{-7} mbar at a growth rate of ~1.5 ML/min [10]. By adjusting the deposition time, different thicknesses (12–40 nm) of $SrTiO_3$ films were achieved. The $SrTiO_3$ thicknesses were measured by X-ray reflectometry (XRR) and a spectroscopic ellipsometer. Their crystalline quality and morphology were monitored using *in situ* reflection high-energy electron diffraction (RHEED), XRD and FE-SEM. The $SrTiO_3$/Si wafer was cut into 5×5 mm^2 and 7×7 mm^2 samples by laser cutting and cleaving.

2.2. Iridium deposition on $SrTiO_3$/Si

Iridium was deposited with an e-beam evaporator at high temperature under secondary vacuum ($<10^{-6}$ mbar). Iridium rod with a purity of 99.9% was mounted in the e-beam evaporator [14]. Heating and cooling rate of ~25 °C/min was applied. Before each iridium deposition, the sample was heated at 400 °C during 4 h for degassing. The sample temperature was measured by an infrared pyrometer (1.45–1.8 μm) with 0.57 for emissivity. The deposition rate was calculated by weighting the sample before and after deposition with a high precision microbalance (Mettler Toledo MX5). 100 to 200 nm thick iridium films were deposited on $SrTiO_3$/Si at a growth rate of ~1 nm/min.

2.3. Bias enhanced nucleation (BEN) and growth of diamond films

BEN process was carried out for epitaxial diamond nucleation on the epitaxial iridium films deposited on $SrTiO_3$/Si substrates. The BEN process and the growth of diamond films were conducted in a MPCVD reactor. Further details of the different steps of BEN process were given in our previous study [14]. The BEN process and growth parameters used in this study are listed in Table 1. The temperature of the sample was measured using an infrared pyrometer (1.45–1.8 μm) with 0.19 for emissivity. For the nucleation process, microwave power of 450 W was used for 5×5 mm^2 Ir/$SrTiO_3$/Si substrates and 500 W for 7×7 mm^2 substrates. As for the growth step, 400 W was used for 5×5 mm^2 and 500 W for 7×7 mm^2. The microwave power was adjusted in order to maintain the plasma density constant between two different types of substrate holders (5×5 mm^2 and 7×7 mm^2).

2.4. Structural characterizations

Complementary techniques were used to characterize the samples at each step of the process, from $SrTiO_3$/Si (001) substrates to the diamond films, such as FE-SEM and AFM for tracking surface morphology and roughness, XRD for crystalline qualities and mosaicities of the films and *in situ* laser interferometry for the thicknesses of diamond films during growth [14]. The fraction of the surface covered by the domains generated after BEN (designated as the coverage ratio in the following) of the sample was calculated by averaging the coverage ratio of 200 FE-SEM images of the sample using ImageJ software. Horiba Scientific UVISEL spectroscopic ellipsometer (190–2100 nm) with an angle of incidence of 45° was also used for measuring the $SrTiO_3$ film thickness

Table 1
Nucleation and growth parameters of the 5×5 mm^2 sample. Values in brackets correspond to the conditions for the 7×7 mm^2 sample.

	Nucleation process			Growth
	H_2 cleaning	H_2/CH_4 stabilization	BEN	
CH_4 (%)	0	4	4	0.6
Pressure (mbar)	20	20	20	20
MW power (W)	450 (500)	450 (500)	450 (500)	400 (500)
Bias voltage (V)	0	0	−290	0
Substrate temperature (°C)	~680 ± 50	~700 ± 50	~740 ± 50	~700 ± 50
Duration (min)	10	10	40	120 and 540