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Effect of substrate bias on the growth behavior of iridium on A-plane sapphire using radio frequency sputtering at low temperatures

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ABSTRACT

We present results on the investigation of the substrate bias effect on the growth behavior of iridium films deposited on A-plane sapphire by radio frequency (rf) sputtering at low substrate temperatures. Films deposited without substrate bias were compared to films deposited with simultaneous application of a second rf-plasma on the substrate. Resulting films were characterized by scanning electron microscopy, X-ray diffraction, and electron backscattering diffraction. We find that the application of an additional substrate bias has a strong effect on the growth behavior of Ir in such a way that preferential growth of iridium (001) on sapphire (11 − 20) at high deposition rates and at substrate temperatures as low as 350 °C becomes feasible.

1. Introduction

Second to osmium, iridium (Ir) is the densest metal with outstanding chemical and physical properties. It possesses a high melting point, low oxygen permeability, good chemical resistivity and very high oxidation resistance, which makes it a very attractive material for e.g. electrochemical electrode [1–4], as a suitable substrate for the growth of crystalline diamond films [5–10], or as protective coating of carbon materials [11,12]. As for many other noble metal catalysts, the electronic structure and catalytic activity of the iridium surface thereby strongly depend on its crystallographic orientation. However, it is often elaborate and expensive to manufacture single crystal surfaces with specified crystallographic orientations [13]. One approach to overcome this problem is the heteroepitaxial growth of thin metal films on dielectric substrates [14].

Various deposition techniques have been employed to prepare oriented iridium films on different substrates [15–19]. Excellent film qualities were achieved with electron-beam evaporation; however, very low evaporation rates (0.1–3 nm/min) [20] and high substrate temperatures (> 600 °C) necessary for oriented film growth limit potential substrates to high temperature resistant substrates, mostly binary oxides. Also, long process times might be an issue regarding commercialization of the process. On the other hand, radio frequency (rf) magnetron sputtering, compared to e-beam evaporation, provides additional freedom in the choice of deposition parameters and thus allows for an extended and more precise control of the evolving microstructure of deposited films [21–27]. Especially, additional substrate biasing provides control over the ion energy and the ratio of the accelerated-ion flux to the flux of deposited neutral particles on the substrate surface. It is demonstrated that these parameters significantly affect the growth behavior of thin-films [28] and may be utilized to lower the substrate temperature needed for oriented growth [21,29–32]. When compared to e-beam-evaporation, it is therefore expected that rf-sputtering with additional substrate bias allows for a greater variety of possible substrate materials, enhanced control of microstructure and intrinsic stresses in the deposited thin film and shorter process times.

In the above mentioned context, this work aims at the investigation of the effect of substrate bias on the morphology and crystallinity of iridium thin films grown at low substrate temperatures as well as the possibility to induce preferential orientation of the film in [001] direction at low substrate temperatures. In reference to the work of Tolstova et al. [21], we will show that the application of a substrate bias voltage leads to an oriented growth of Ir films on A-plane sapphire (11–20) at low temperatures. However, in contrast to their findings for the low-T heteroepitaxial growth of gold films on magnesium oxide, we applied a substrate bias only during the early stages (i.e. the nucleation stage) and not during the whole deposition process. After deposition of a thin ‘seeding layer’ (Ir deposited with substrate bias) further application of substrate bias is not necessarily required. On the contrary, we observe that continuous use of substrate bias leads to smaller and less well-oriented grains.

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2. Experimental details

The iridium layers were deposited by rf-sputtering using a custom-build S400-S3 sputter system (FHR, Dresden, Germany) fitted with an Ir target (99,9 at.%) supplied by EVOCHEM Advanced Materials GmbH, Offenbach, Germany. The A-plane sapphire (11–20) substrates were purchased from Situs Technicals, Wuppertal, Germany. Prior to the deposition process, the wafers were in-situ (1×10^{-7} mbar) annealed at 350 °C for 60 min, then Argon sputtered at 2×10^{-2} mbar by 350 V bias and 200 W for 8 min. The deposition rates were determined by measuring the layer thickness at a step edge resulting from a partial masking of the substrate. The substrate was mounted on a movable carrier which was heated from the backside with a ceramic radiant heater. The relationship between the temperature on the surface of the heater and the resulting substrate surface temperature was calibrated prior to the experiments with attached wire thermocouples (during the deposition, only the heater's surface temperature was measured). The distance between target and substrate was set to 110 mm. In order to investigate the influence of substrate bias on the growing microstructure of the film we deposited three iridium layers at 350 °C on A-plane sapphire (11–20). Sample 1 was deposited without substrate bias. Sample 2 was deposited with an additional bias applied to the substrate during the entire deposition process. For sample 3, the deposition process was divided into two subsequent steps. First, a thin (about 20 nm) iridium layer was deposited with additional substrate bias, henceforth referred to as seeding layer. After the seeding layer was completed, the substrate bias was turned off and iridium was deposited to a total layer thickness of approx. 300 nm. The thickness of sample 1, sample 2, and sample 3 was about 300 nm, 140 nm, and 300 nm, respectively. The deposition parameters with and without bias are listed in Table 1.

The surface of the samples was characterized by scanning electron microscopy (SEM, Zeiss Supra 40VP) using a surface-sensitive in-lens detector. To determine the crystallographic orientation, the electron microscope is equipped with an EDAX DigiView electron backscattering diffraction (EBSD) camera. The data acquisition and analysis was done using the TSL OIM Data Collection 5.31 and the TSL OIM Analysis 5.31 package, respectively. The EBSD patterns were recorded at 20 kV, with a working distance of 15 mm and sample tilt of 70° with respect to horizontal. Figs. 3 and 5 were recorded with a spatial resolution of 20 nm^2. Figs. 4 and 6 were recorded with a spatial resolution of 10 nm^2. For interpreting the growth behavior, the orientation map (inverse pole figure (IPF map) and the [001] pole figure were recorded for all five samples. The orientation map represents a 2 µm × 2 µm measurement area and the color code visualizes the lattice planes parallel to the sample surface. Areas with (001) orientation are shown in red, while areas with (111) and (101) orientation are shown in dark blue and green, respectively. Areas where no distinct orientation information could be obtained are colored in black. The EBSD [001] pole figure illustrates a stereographic projection of each {001} plane in respect to the sample normal of each pixel of the measured sample area and thus provides information about the in-plane and out-of-plane orientation of the measured sample surface. The X-ray diffraction (XRD) measurements were performed with a Bruker AXS D8 Advance equipped with an open 1/4-circleeulerian cradle. The primary X-rays were focused on the sample using a double pin-hole with a diameter of 0.8 mm. In the Θ-2Θ-mode the diffracted X-rays were detected using a Bruker AXS Lynxeye detector. The rocking curves were measured with a scintillation counter.

Table 1
Experimental conditions for Ir thin films deposited with bias assisted rf-sputtering.

Growth parameters	Seeding layer	Top layer
Base pressure (mbar)	$3,5 \times 10^{-7}$	
Sputtering gas	Argon, purity 6 N	
Deposition pressure (mbar)	$1,0 \times 10^{-2}$	
Deposition temperature (°C)	350	
Deposition rate (nm/min)	4–4.5	8–10
Substrate Power density (W cm^{-2})	0.056	0
Target Power density (W cm^{-2})	1.23	1.23

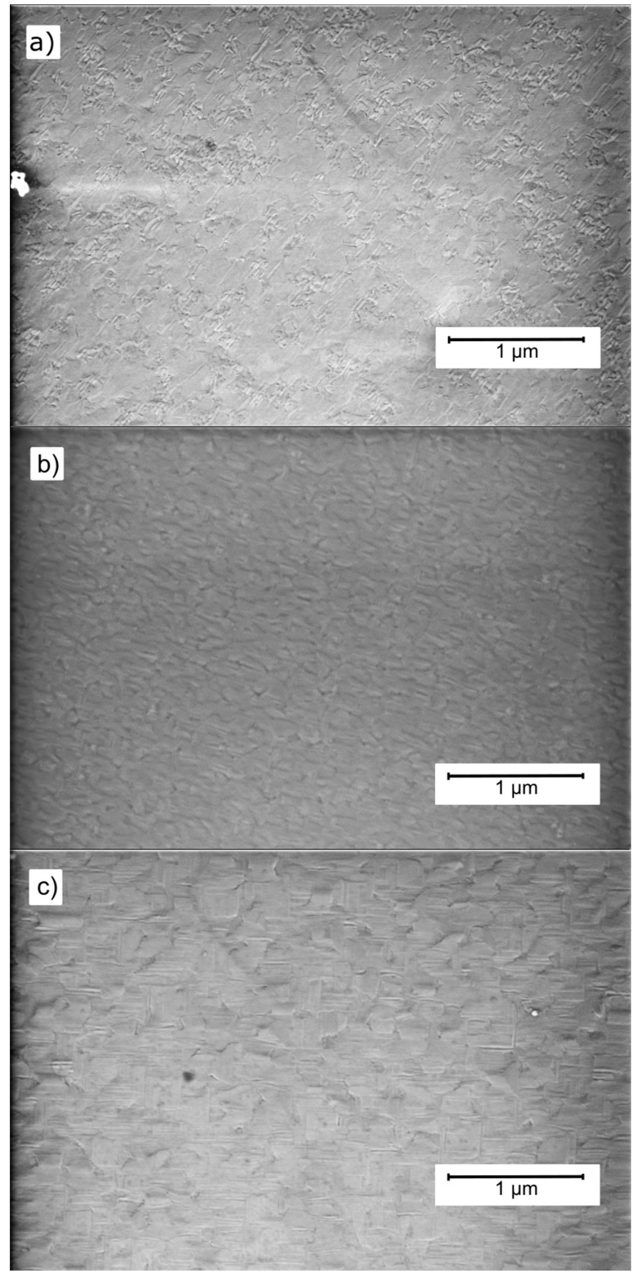

Fig. 1. Scanning electron microscopy (SEM, in-lens, 1 kV, working distance of 1.4, 1.5, and 1.6 mm) images of iridium deposited on A-plane sapphire using rf-sputtering at 350 °C. a) Deposited without substrate bias (Sample 1). b) Deposited with substrate bias voltage of 156 V (Sample 2). c) Deposited in a two-step process (Sample 3).

3. Results

Fig. 1a) shows the scanning electron microscopy (SEM) image of sample 1 (deposited without substrate bias). The surface features domains with two morphological characteristics. One set of domains appears to consist of small crystallites with a typical grain size < 100 nm, while the second set exhibits a low electron contrast which indicates a smooth or nano-crystalline texture. The borders between these two regions are serrated and do not exhibit a particular symmetry. Fig. 1b)