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Full Length Article

Microstructure of 800 keV Ar ion irradiated thin ZrC films

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ABSTRACT

Very thin ZrC films, grown on (100) Si substrates at a temperature of 500 °C by the pulsed laser deposition (PLD) technique, were irradiated by 800 keV Ar ions with fluences from 1×10^{14} cm^{-2} to 2×10^{15} cm^{-2}. Films structure was investigated using grazing incidence X-ray diffraction technique. High resolution transmission electron microscopy investigations were used to study the microstructural modifications induced by Ar ion irradiation. TEM results showed that ZrC films retained their nanocrystalline structure with average crystalline grain dimensions slightly increased, while the Si substrate was damaged for a fluence of 1×10^{14} cm^{-2} and then amorphized for higher irradiation fluences. The oxide surface layer thickness formed during atmosphere exposure of films slightly increased along with the increase of the irradiation fluence, while the amorphous interface between the deposited film and the crystalline Si substrate disappeared. No major defects, voids or precipitates were found in the irradiated nanocrystalline ZrC films.

1. Introduction

There has been lately a renewed interest in thin films of zirconium carbide due to their attractive properties: a very high melting point, a stable fcc-type structure that could accommodate without phase change large Zr to C variations from room temperature up to the melting point [1], high hardness (30–40 GPa) [2,3], good wear resistance [4], and good electrical and thermal conductivity [5,6]. More recently, because of its low cross section capture for neutrons and good retention properties of fission products, ZrC has been tested as a protective coating on nuclear fuel for the reactors that could operate at very high temperatures [7–9]. Thin ZrC films have been obtained using chemical vapor deposition [10], magnetron sputtering [4,11], ion beam sputtering [12] or pulsed laser deposition (PLD) techniques [3,13–15]. We have previously shown that PLD grown ZrC films are nanocrystalline and possess excellent mechanical properties [16].

Several studies regarding the effect of ion irradiation on the properties of single crystal or large grain ZrC have been recently published [17–19]. More recently, the effect of irradiation on nanocrystalline films has been investigated [20], since very thin films having small grain sizes, many grain boundaries, and possibly a high density of structural and stoichiometric defects, could exhibit new and interesting effects. These investigations could be very relevant for ZrC coatings applications, since such thin films used for fuel encapsulation are usually nanostructured. The effect of Ar ion irradiation on mechanical, electrical and visible to infrared optical properties of PLD grown ZrC films has been recently reported [21]. As opposed to single crystalline and large grain materials [22], the nanostructured films exhibited after irradiations with a fluence of 1×10^{14}–1×10^{15} cm^{-2} a strong decrease of hardness and Yong modulus values [22]. An increase of optical conductivity and grain size was also observed from IR optical reflectivity measurements. Further irradiation at a higher fluence of 2×10^{15} cm^{-2} resulted in small changes only. We used transmission electron microscopy (TEM) to investigate the microstructure of Ar ion irradiated ZrC thin films and understand the effect of irradiation on its structure and properties.

2. Experimental details

The PLD experimental set up used to deposit the films is a typical one apart from the very good residual vacuum in the low 10^{-8} mbar range that is achieved before the films growth [14,16]. A KrF excimer laser (λ = 248 nm, pulse duration τ = 25 ns, 6 J/cm^2 flu-

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ence, 40 Hz repetition rate) was used to ablate a polycrystalline ZrC target (from Neyco, France) under a CH_4 atmosphere of around 2×10^{-5} mbar. The films were collected on (100) Si substrates heated at 500 °C and then slowly cooled to room temperature under several mbar of CH_4.

After deposition, the films were irradiated under vacuum at room temperature by 800 keV Ar ions at a flux of 10^{11} cm^{-2} s^{-1}. Three distinct irradiations were performed with fluences of 1×10^{14}, 1×10^{15} and 2×10^{15} cm^{-2}, respectively. The structure of the films was investigated using grazing X-ray diffraction (GIXRD) with the aid of an Empyrean (Panalytical) instrument working with a Cu anode in a parallel beam geometry.

The microstructure of the films was investigated using a high resolution transmission electron microscope (HRTEM). The sample were firstly mechanically polished and then ion-beam milled at a voltage of 3 kV and a current of 5 mA up to perforation. After the formation of the hole, the ion-beam thinning was continued with a smaller voltage of 2 kV and a current of 4 mA for 30 min and finally with 0.5 kV and 3 mA for another 30 min, in order to remove debris or amorphous layer produced by high-voltage ion-beam milling. The bright-field TEM and HRTEM images were obtained using a Tecnai G^2 F30 S-TWIN and Titan Themis transmission electron microscopes.

The elemental composition and thickness of the films was determined using Rutherford Backscattering Spectrometry (RBS) analysis performed with ^{4}He ions at 2.6 MeV. The measurements were performed using a ^{4}He^{++} beam extracted from the Alphatross ion source of the 3 MV Tandetron accelerator of IHIN-HH. The alpha particles were detected with a passivated, ion implanted silicon detector placed at 165° with respect to the incident beam direction.

3. Results

The deposited PLD films usually exhibit an elliptical dome-shaped thickness profile. Examples of thickness and composition variations in PLD grown ZrC films, measured by RBS in several points along the larger elliptical axis of the deposited film are shown in Fig. 1. To increase the accuracy of the RBS measurements, this particular investigated film was thicker than those used for irradiation. The films used for irradiation were around 150–200 nm thick in order to place the end of range damage and implanted Ar ions deep into the Si substrate [17].

One could note that the film has a uniform thickness (<5%) area of around 1 cm^2. Besides Zr and C, the target was contaminated by Fe and Hf (around 0.005%). Also, the C/Zr values are lower in the central part, around 0.80–0.85, where the film was directly bombarded by energetic species than towards the periphery, where the ratio is around 0.90. According to these RBS results, the PLD grown films tend to be slightly Zr rich, similar to reports about ZrC films deposited using other techniques. All of the investigations reported here were performed as much as possible in this uniform central area.

Typical GIXRD patterns acquired from a ZrC film before and after Ar ion irradiation at a fluence of 2×10^{15} cm^{-2}, the highest used in this study, are shown in Fig. 2. By carefully inspecting the GIXRD results presented in Fig. 2, one could note that (i) the film retained its nanocrystalline structure, (ii) the XRD peaks shifted towards lower 2theta values after irradiation, indicative of a larger lattice parameter (see the inset in Fig. 2) and (iii) there were changes in grains orientations, illustrated by changes of the (1 1 1) and (2 0 0) peaks intensities. From a Williamson-Hall analysis of the GIXRD patterns like those displayed in Fig. 2, a growth of the average grain size from around 10 nm for the as-deposited films to 15–20 nm after irradiation was obtained, while the micro-stress values did not changed appreciably. From the shift of the diffraction peaks, as shown in the insert of Fig. 2, a swelling of around 1–2% was estimated, similar to changes in density calculated from X-ray reflectivity curves simulations previously reported [21].

TEM images as those displayed in Fig. 3 confirmed that the as-grown ZrC films were nanocrystalline and exhibited a slight (1 1 1) columnar texture, as previously shown by symmetrical XRD results [16,21]. One could observe in Fig. 3 several columnar grains, which almost extended through the whole film thickness. However, there were also grains with random orientations that were observed in TEM images. The selected area electron diffraction patterns, as the one shown in Fig. 3, confirmed that the films possessed an FCC type structure and were nanostructured. High resolution TEM images of the interface region between the deposited ZrC film and the Si substrate showed the presence of an amorphous region of around 1 nm in thickness, probably due to the native SiO_2 layer and several monolayers of ZrC that were not crystalline.

Fig. 4 shows a high resolution TEM image of the surface region. The presence of an amorphous layer at the top of the deposited film, around 4 nm thick, is clearly visible, which corresponds to a hydroxide layer that formed during film exposure to the atmosphere. The thickness of this hydroxide layer is similar to that previously estimated from XPS and XRR investigations [16,21]. Beneath this hydroxide layer, the ZrC film is well crystallized and compact, without any voids.

The interface region between the deposited ZrC film and Si after irradiation with a fluence of 1×10^{14} cm^{-2} is different from that observed for as-deposited films. The amorphous region located at

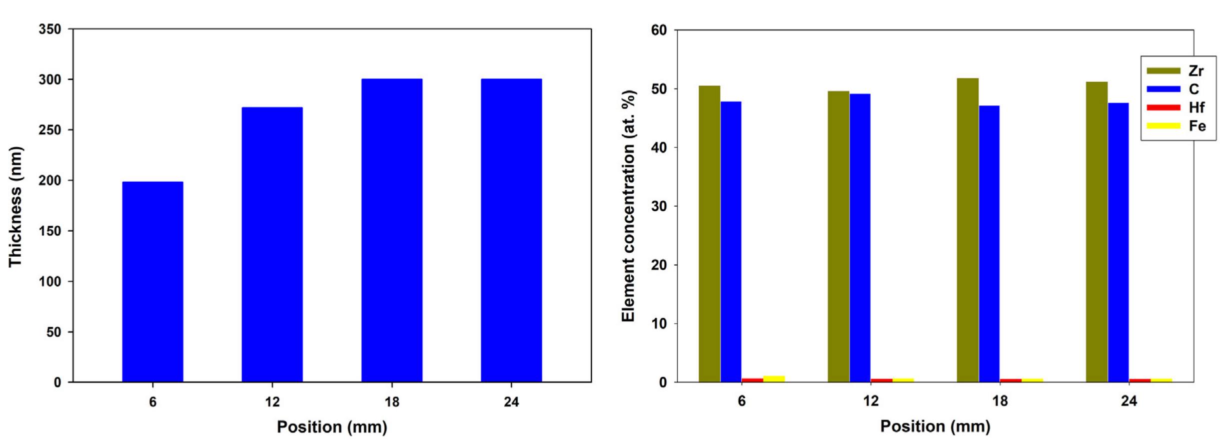

Fig. 1. Thickness and corresponding composition of a ZrC film measured by RBS in several locations 6 mm apart along the film greater elliptical axis.