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Very hard ZrC thin films grown by pulsed laser deposition

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Abstract

Thin ZrC films were grown on (1 0 0) Si substrates at temperatures from 30 to 500 °C by the pulsed laser deposition technique. Auger electron spectroscopy investigations found that films contained oxygen concentration below 2.0 at%, while X-ray photoelectron spectroscopy investigations showed that oxygen is bonded in an oxy-carbide type of compound. The films' mass densities, estimated from X-ray reflectivity curve simulations, and crystallinity improved with the increase of the substrate temperature. Williamson–Hall plots and residual-stress measurements using the modified $\sin^2 \psi$ method for grazing incidence X-ray diffraction showed that the deposited films are nanostructured, with crystallite sizes from 6 to 20 nm, under high micro-stress and compressive residual stress. Nanoindentation investigations found hardness values above 40 GPa for the ZrC films deposited at substrate temperatures higher than 300 °C. The high density of the deposited films and the nm-size crystallites are the key factors for achieving such high hardness values.

Keywords: ZrC; Hard coatings; Pulsed laser deposition; X-ray diffraction

1. Introduction

ZrC is a ceramic material that also possesses metallic characteristics, which explains its excellent properties: very high melting points,[1] high hardness, (30–35 GPa),[2,3] good wear resistance,[4] high thermochemical stability,[5] low electrical resistivity,[6] low work function,[7] high optical emissivity,[8] low neutron cross section capture,[9] and good biocompatibility.[10] The properties of ZrC have been used in many demanding applications, where the role of the microstructure and composition of the deposited films are critical and should be investigated to further improve them. ZrC thin films have been deposited using various techniques such as dc magnetron sputtering,[11] e-beam evaporation,[12] chemical vapor deposition,[13] and pulsed laser deposition (PLD).[14]

We have grown ZrC thin films using the PLD technique.[15–18] By increasing the laser fluence and repetition rate and improving the vacuum conditions, high quality ZrC films exhibiting hardness values above 35 GPa[18] have been deposited. The role of the growth temperature on the microstructure, strain, and hardness of the deposited ZrC films has been investigated and the results are presented below.

2. Experimental details

The experimental set up used to deposit ZrC films uses a KrF excimer laser ($\lambda = 248$ nm, pulse duration $\tau = 25$ ns, 8.0 J/cm^2 fluence, 40 Hz repetition rate). The ultimate pressures in the deposition chamber were in the low 10^{-6} Pa range to minimize oxygen incorporation. Films were deposited from a polycrystalline ZrC target (Plasmaterials, Inc.) on p^{++} (1 0 0)Si substrates (MEMC Electronic Materials, Inc.) at nominal substrate temperatures of 30, 300 and 500 °C under a high purity atmosphere of CH_4 (2×10^{-3} Pa). Previous results showed that a low CH_4 pressure during deposition and cooling down stages has beneficial effects on the structure and properties of deposited films.[15]

X-ray reflectivity (XRR) curves were acquired with a Panalytical X'Pert MRD instrument working with Cu $K\alpha$ radiation and set up in a parallel beam geometry by using an X-ray mirror and a (1/32)° slit on the incident-beam side and a thin-film collimator and 0.1 mm slit on the diffracted beam side. The deposited films' mass density, thickness, and surface roughness values were obtained from simulations of the XRR curves using

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a commercially available software (X'Pert Reflectivity from Panalytical) based on the Parratt formalism.[19] The same instrument was used to collect symmetrical and grazing incidence X-ray diffraction (GIXD) patterns. The stress of the deposited films was obtained by acquiring patterns at various ψ-tilting angles or acquiring offset scans and plotting the d-space values versus $\cos^2\alpha \sin^2\psi$, where $\alpha = \theta_B - \omega$.[20,21] The crystallite sizes were evaluated from Williamson–Hall plots.[22] Atomic force microscopy (AFM) images of the film surfaces and nanoindentation sites were also recorded.

The chemical composition of the deposited films was investigated by Auger electron spectroscopy (AES) in a Perkin-Elmer PHI 660 system (5 kV, 30° take-off angle) and by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5100 ESCA system using Mg $K\alpha$ radiation. AES and XPS survey or high-resolution spectra were collected after various time cycles of Ar ion sputtering (4 kV, 1–3 μA/cm^2; for XPS measurements the Ar ion beam was rastered over an area of 10 mm × 7 mm).

To investigate the mechanical properties of the thin films, a commercial nanoindentation device (Triboindenter, Hysitron, Inc.) equipped with a cube-corner diamond tip was set to run 100 indents per sample. The indentation experiments were performed in load control, with maximum loads ranging from 750 to 5 μN, decreasing by a constant increment of 7.53 μN, corresponding to maximum indentation depths of approximately 92.2 nm, 64.0 nm, and 65.9 nm, for ZC30, ZC300, and ZC500 samples, respectively. To minimize substrate contributions, the hardness and reduced modulus were determined from load–displacement contact depths between 20 and 30 nm, as described in Ref. 23 following the method of Oliver and Pharr.[24] For all samples evaluated, the load was increased to the maximum value over 1 s, held there for 1 s, and unloaded in 1 s. Due to preliminary AFM observations showing that indenter tips were being contaminated by the samples after several hundreds of indents, a tip-cleaning step was added between samples. This included indenting onto fused quartz four times at 1000 μN. The cube-corner tip was also recalibrated (49 indents, 500–3 μN, following Ref. 24) immediately before and after indents were performed on a set of samples. The second calibration was compared with the first, in order to verify that the superhard materials did not significantly alter the area function of the diamond tip.

3. Results and discussion

XRR curves acquired from films deposited at various substrate temperatures and their simulations are displayed in Fig. 1. One could observe that the values of the critical angle of the films, marked by lines in Fig. 1 and displayed in Table 1, are increasing with the increase of the substrate temperature. From simulations of the acquired XRR curves (with a model consisting of three layers: (1) the interfacial layer, accounting for the native oxide and any ions that were subplanted/mixed within this layer,[25–27] (2) the deposited ZrC layer, and (3) a surface contamination layer, accounting for the hydroxide/carbon-contaminated layer formed when samples were exposed to the ambient), we obtained values for the films' densities and surface roughness values, shown in Table 1, together with the deposition conditions

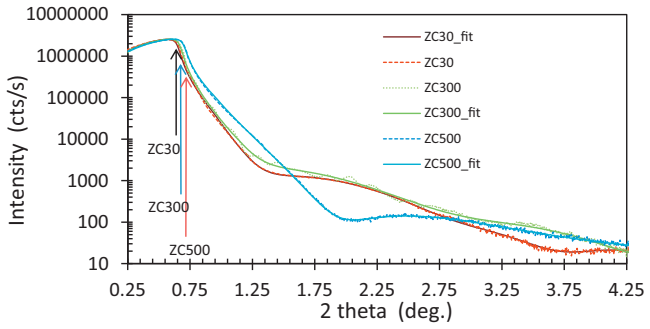

Fig. 1. XRR curves recorded from ZrC films deposited at 30, 300 and 500 °C.

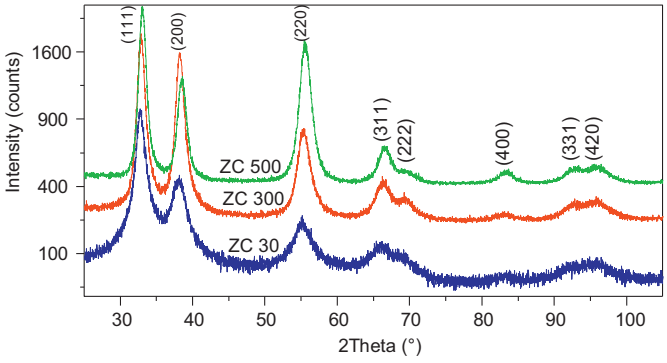

Fig. 2. GIXD patterns acquired from the deposited ZrC films.

used for these samples. The thickness of the top oxide layer was around 2.0–3.0 nm and its density ranged from 3.0 to 3.5 g/cm^3.

GIXD patterns acquired from the deposited films are displayed in Fig. 2. All peaks correspond to the rock-salt lattice of ZrC.[28] The crystallinity improves with the increase of the substrate temperature. Symmetrical XRD scans (not displayed) showed that films were (1 1 1) textured, a typical texture for rock-salt type structures, where (1 1 1) planes have the highest atomic density. Williamson–Hall plots ($B \times \cos\theta_B$ versus $\sin\theta_B$, where B is the full width at half maximum of the peaks, which was corrected for instrumental broadening, and θ_B is the Bragg angle), such as those shown in Fig. 3, were used to estimate the crystallite sizes and micro-strain values, which are displayed

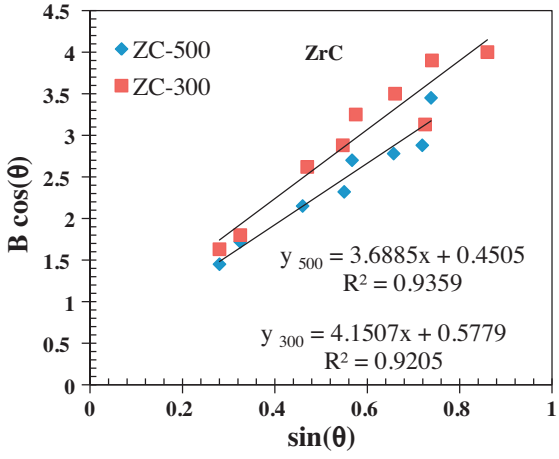

Fig. 3. Williamson–Hall plots for ZrC films deposited at 300 and 500 °C.