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Characteristics of ZrC/ZrN and ZrC/TiN multilayers grown by pulsed laser deposition

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ABSTRACT

ZrC/ZrN and ZrC/TiN multilayers were grown on (1 0 0) Si substrates at 300 °C by the pulsed laser deposition (PLD) technique using a KrF excimer laser. X-ray diffraction investigations showed that films were crystalline, the strain and grain size depending on the nature and pressure of the gas used during deposition. The elemental composition, analyzed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), showed that films contained a low level of oxygen contamination. Simulations of the X-ray reflectivity (XRR) curves acquired from films indicated a smooth surface morphology, with roughness below 1 nm (rms) and densities very close to bulk values.

Nanoindentation results showed that the ZrC/ZrN and ZrC/TiN multilayer samples exhibited hardness values between 30 and 33 GPa, slightly higher than the values of 28–30 GPa measured for pure ZrC, TiN and ZrN films.

1. Introduction

The excellent mechanical properties and thermochemical stability of refractory metal carbides and nitrides recommend them for important applications as hard and protective coatings [1–3]. It is generally rather difficult to deposit high quality ZrC films because of their high melting temperature, low sputtering rate, and high reactivity with oxygen or water vapors [4]. Driven by stringent requirements of special applications, such as coatings for field emission tips, nuclear fuel or outer space thermal radiators [5–7], significant progress has been made in the last decade and good quality ZrC films were obtained by using either physical vapor deposition (PVD) or chemical vapor deposition (CVD) based techniques [8–12]. As one of the most versatile research technique, pulsed laser deposition (PLD) allows for relatively low to moderate deposition temperatures of refractory carbides and nitrides without sacrificing their crystalline quality [13–15]. Some of the best mechanical properties of ZrC yet reported were measured on films deposited using the PLD technique [16,17]. Furthermore, it has been showed that by using a higher repetition rate laser for ablation, the substrate temperature could be reduced to only 300 °C while the growth rate is increased and the crystalline quality maintained [18].

The deposition of multilayers with different crystalline lattices that could block at their interfaces the propagation of dislocations from one material to another was shown to be a way of increasing the hardness of such thin film structure [19–22]. Since it is known that generally carbides are more brittle than nitrides and that the refractory metal nitrides exhibit very similar properties to carbides, being also used as hard and protective coatings [1,3,16,23–25], we have investigated ways to further improve the quality of films by depositing multilayers of ZrC and a refractory metal nitride such as ZrN or TiN [26] and present new results here.

2. Experiment

The depositions were performed in a PLD system using a KrF excimer laser (λ = 248 nm, pulse duration τ = 25 ns, 8.0 J/cm^2 fluence, 40 Hz repetition rate) that has been already described in detail elsewhere [18,26]. The films were deposited for tens of minutes from polycrystalline ZrC, ZrN, and TiN targets (Plasmaterials, Inc.) on p^{++} (1 0 0) Si substrates (MEMC Electronic Materials, Inc.) that were cleaned in acetone, then ethanol, rinsed in deionized water, and finally blown dry with high purity nitrogen before being loaded into the deposition chamber. The nominal substrate temperature was set at 300 °C. Depositions were performed under a high purity atmosphere of CH_4 or Ar (2×10^{-3} to 10^{-2} Pa). After

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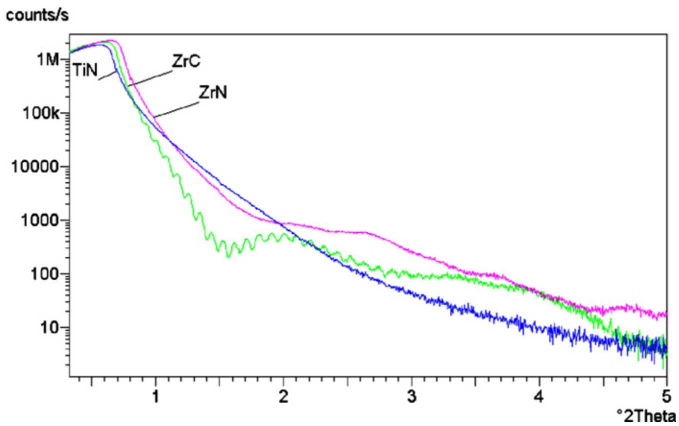

Fig. 1. XRR curves recorded from pure ZrC, TiN, and ZrN deposited films.

deposition, the films were slowly cooled to room temperature under the same atmosphere as that using the deposition, but at a much higher pressure of around 10^4 Pa.

The films mass density, thickness, and surface roughness were investigated by X-ray reflectometry (XRR, Panalytical X'Pert MRD) using Cu K_α radiation. The same instrument was used for structural characterization in symmetric and grazing incidence X-ray diffraction (XRD and GIXD) using a parallel beam configuration. The grain size was evaluated following the Scherrer equation [27] and, where possible, by the model of Williamson and Hall [28]. The chemical composition of the 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 (300 W, Mg K_α). To obtain elemental depth profiles, measurements 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 a larger area of 10×7 mm^2). Cross section samples were prepared on a focused ion beam (Strata DB 235) for transmission electron microscopy (TEM) analysis on a JEOL 2010F instrument. The mechanical properties of the films were measured with a nanoindentation device (Hysitron inc.) equipped with a cube-corner diamond tip and set to run 100 indents per sample. The nanoindentation experiments were performed in displacement control with a contact depth of up to 30 nm. Hardness and reduced modulus were determined from the load-displacement data following the model of Oliver and Pharr [29], after excluding the results obtained for penetration depths smaller than 5 nm [30].

3. Results and discussion

XRR curves recorded from deposited pure ZrC, TiN and ZrN films are presented in Fig. 1. One could note different values for the critical angle of each material, a consequence of different density values. From simulations of the acquired curves using the Panalytical WinGixa™ software, which is based on Parrat's formalism [31], we obtained values for the films density and surface roughness that are shown in Table 1, together with the deposition conditions and hardness values. The Kiessig fringes [32] were only present in the XRR curve of ZrC sample, which was much thinner than the other

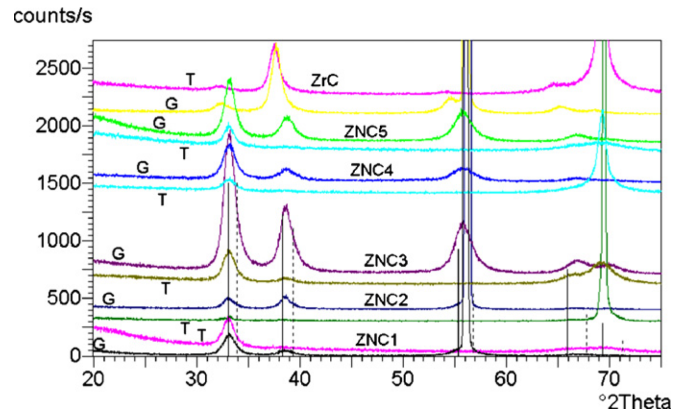

Fig. 2. XRD patterns (G, grazing incidence; T, symmetrical geometry) collected from ZrC/ZrN multilayers; the vertical bars are the reference diffraction peak positions of reference ZrC (full line, Card 35-0784) and ZrN (dotted line, Card 35-0753) powders [33].

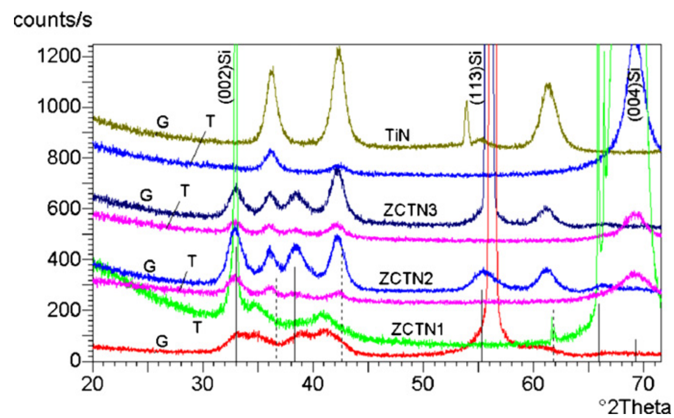

Fig. 3. XRD patterns (G, grazing incidence; T, symmetrical geometry) collected from the ZrC/TiN multilayers; the vertical bars are the reference diffraction peak positions of ZrC (full line) and TiN (dotted line, Card 32-1489) powders [33].

two films. According to the simulations results, the films oxidized when exposed to the ambient, the oxide layers being estimated to be around 2–3 nm thick. The XRR curves acquired from multilayers showed evidence of interference peaks due to the presence of many interfaces, but we could not fit them satisfactorily with a model, most likely due to variations of thickness from layer to layer. However, the critical angle values of the top ZrC layer were consistent with densities very similar to those estimated for pure ZrC films.

XRD and GIXD investigations showed that the deposited films were crystalline, as one can see in Figs. 2 and 3, where diffraction patterns from several representative samples acquired in symmetrical and grazing incidence geometry are displayed. The deposition conditions employed for each multilayer structure are displayed in Table 2. To facilitate a comparison, we also introduced in Table 2 and Figs. 2 and 3 some results from our previous study [26]. Since the lattice parameter of ZrC and ZrN are very similar, the recorded Bragg diffraction lines from ZrC/ZrN multilayers appeared as a convolution of the two lines, without being resolved. Analyzing the

Table 1
Deposition parameters and mechanical properties of grown pure films.

Sample	Deposition atmosphere (Pa)	Density (g/cm^3)	Roughness (nm)	Hardness (GPa)	Reduced Modulus (GPa)
ZrC	2×10^{-3} CH_4	6.45	0.5	30.1	226.0–228.3
ZrN	2×10^{-3} CH_4	7.09	0.6	28.5	214.5
TiN	2×10^{-3} CH_4	5.21	0.5	29.9	242.3