Applied Surface Science 306 (2014) 33–36

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Wear tests of ZrC and ZrN thin films grown by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 14 November 2013
Accepted 7 December 2013
Available online 16 December 2013

Keywords:
ZrC
ZrN
Hard coatings
Pulsed laser deposition

ABSTRACT

Very thin ZrC and ZrN films (<500 nm) were grown on (1 0 0) Si substrates at 500 °C by the pulsed laser deposition (PLD) technique using a KrF excimer laser. X-ray reflectivity investigations showed that films exhibited mass densities similar to bulk values. X-ray diffraction investigations found that films were nanocristalline, exhibited a (1 1 1) texture and high micro-strain values. Auger electron spectroscopy investigations indicated that films contained in bulk a relatively low oxygen concentration, usually below 2.0%. Atomic force microscopy found that ZrN films deposited under 2×10^{-2} Pa of N_2 exhibited a very smooth surface, with an rms value of only 3 Å, while wear tests found a low wear rate of only 4.5×10^{-6} mm^3/N m.

1. Introduction

Transition metal carbides and nitrides such as ZrC and ZrN possess both ceramic and metallic characteristics, which explain their excellent properties: very high melting points [1], high hardness (30–35 GPa) [2–4], good wear resistance [5,6], high thermochemical stability [7], low electrical resistivity [8], and good biocompatibility [9].

Pulsed laser deposition (PLD) technique has been recently used to grow such films at moderate substrate temperatures, upto 500 °C, to investigate their structure, composition and properties [10–12]. The results obtained so far indicated that the deposition of high quality ZrC and ZrN films required very low residual vacuum, high purity gases, high laser fluences and high repetition rates. Under such conditions, high density and nanocrystalline films that exhibited high hardness values were deposited at temperatures from 300 to 500 °C [10–13]. Uniaxial reciprocating sliding tests were performed on such PLD grown films that exhibited very high hardness values and the results are presented below.

2. Experimental details

The PLD experimental setup used to deposit the ZrC and ZrN films has been extensively described previously [10–13] and is only briefly described here. It uses a KrF excimer laser (λ = 248 nm, pulse duration τ = 25 ns, 6–8 J/cm^2 fluence, 40 Hz repetition rate) to ablate ZrC or ZrN polycrystalline targets (from Neyco, France) in a stainless steel chamber. The ultimate pressure in the deposition chamber was in the low 10^{-6} Pa. Films were deposited on p^{++} (1 0 0) Si substrates (MEMC Electronic Materials, Inc.) at a nominal substrate temperature of 500 °C under residual vacuum or a high purity atmosphere of N_2. The deposition conditions are displayed in Table 1. After deposition, the crystalline structure of the films was investigated in an X'Pert MRD instrument by X-ray diffraction (symmetrical and grazing incidence), while their mass density, thickness and surface and interfacial roughness were obtained from simulations of acquired and X-ray reflectivity curves.

The crystallite size and micro-strain were evaluated from Williamson–Hall plots [14] of the diffraction line parameters from patterns acquired using the grazing incidence X-ray diffraction (GIXD) geometry. Atomic force microscopy (AFM) images of surface as well as 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 (10 kV, 30° take off angle). AES spectra were collected after various time cycles of Ar ion sputtering.

The mechanical properties of the thin films were investigated using a nanoindentation device (Triboindenter, Hysitron, Inc.) equipped with a cube-corner diamond tip. To minimize substrate contributions, the indentation experiments were performed in load control, with maximum loads ranging from 750 to 5 μN and the hardness and reduced modulus were determined from

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http://dx.doi.org/10.1016/j.apsusc.2013.12.048

Table 1
Deposition conditions, lattice parameter, density, surface roughness, and structural properties of the deposited films.

Sample	Atmosphere [Pa]	Number of pulses	Lattice parameter from (1 1 1) line [Å]		Micro-strain [%]	Grain size [Å]
			XRD	GIXD		
ZrN_4	2×10^{-2} N_2	20,000	4.681	4.649	0.67	75
ZrC_1	Vacuum	20,000	4.735	4.724	0.80	107

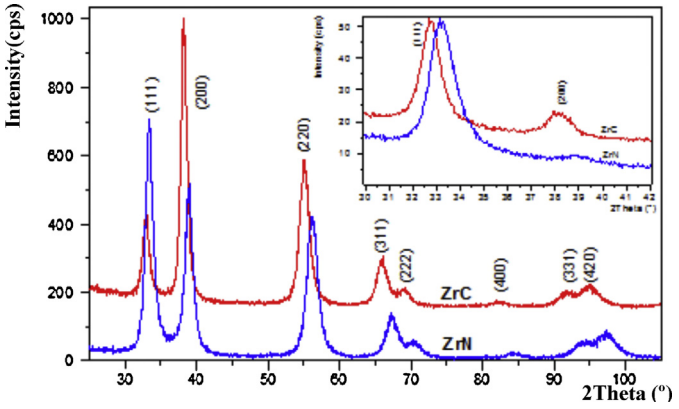

Fig. 1. GIXD and XRD (inset) patterns acquired from ZrC and ZrN films.

load-displacement contact depths between 20 and 30 nm, as described previously [12] following the model of Oliver and Pharr [15].

A linear reciprocating tribometer was used for friction and wear experiments [16]. Bearing grade Si_3N_4 balls of 1.59 mm radius were used as a pin material. A normal force of 1 N + −50 mN and sliding speed of 1 mm/s were used. Sliding was unidirectional, and the wear track length was progressively reduced from 10 mm in 1 mm steps. The result was a single wear track where 1 mm lengths of the track exhibited 10, 100, 200, and 500 cycles. The wear volume as a function of sliding cycles at these intervals was measured at the end of the test inside the 1 mm lengths using a scanning white light interferometer (SWLI; Veeco Wyko NT1100).

3. Results and discussion

Grazing incidence and symmetrical diffraction patterns acquired from the deposited films are displayed in Fig. 1. From the patterns acquired in the symmetrical geometry (see inset in Fig. 1), one could note that the films exhibited a strong (1 1 1) texture, more so for the ZrN film. The patterns acquired in the grazing incidence geometry displayed all the peaks corresponding to the rock-salt lattice of ZrC and ZrN [17,18]. Results of Williamson–Hall plots ($B \times \cos\theta_B$ versus $\sin\theta_B$, where B is the full width at half maximum of the GIXD peaks, which was corrected for instrumental broadening, and θ_B is the Bragg angle) for the crystallite sizes and micro-strain values are also displayed in Table 1. The observed micro-strain was caused by defects induced by energetic ions and atoms from the plasma that bombarded the growing film during deposition [19,20]. Since the higher N_2 pressure used during deposition also reduces the energy of the incoming species, a lower micro-strain value was found for the ZrN film. Differences in the lattice parameters, calculated from the (1 1 1) diffraction line positions acquired in the two geometries and shown in Table 1, were caused by a high compressive stress also induced by the high energy incoming species.

The films mass density, thickness, and surface roughness displayed in Table 2 were obtained from simulations of the XRR curves using a model consisting of three layers: interfacial layer, accounting for the silicon native oxide and any ions that were subplanted/mixed within this layer [19,20], the deposited layer and a surface contamination layer accounting for the formation of a hydroxide/carbon layer when films were exposed to the ambient. The thickness of the top contamination layer was around 20–25 Å and its density was around 3–5 g/cm^3, indicative of an oxyhydride layer.

One could note that the deposited films mass densities were very similar to bulk values and the surface of the films was very smooth, especially for the ZrN film. The very low rms roughness values were confirmed by AFM images acquired for the films and shown in Fig. 2. The ZrN exhibited a very smooth surface, with an rms values of the roughness of only 3 Å, half the value obtained for the ZrC film.

AES survey spectra, as those shown in Fig. 3, recorded after removal of more than 10 nm of surface material by Ar ion sputtering, indicated low oxygen concentrations within the deposited films. The Zr to N or Zr to C ratios were higher than 1, indicating either a strong preferential sputtering of the light atoms (C, O, N) or a substoichiometric compound. The ZrN film also contained C atoms. High resolution XPS investigations showed that the binding energy of C atoms, when present in bulk, was around 282.5 eV, corresponding to C bonded in a metallic carbide type of compound [13,21].

The results of nanoindentation measurement, hardness and Young modulus, are also displayed in Table 2. AFM investigations of the nanoindentation sites showed no measurable pile-up or distortions of the symmetrical shape, factors that could affect the accuracy of the measurements. The physics of nanoindentation measurements in films thinner than 1 mm is still a matter of debate [22]. However, the reported values could be taken as an indication of the hardness of these very thin films.

Films initially exhibited low friction coefficients, as shown in Fig. 4, where the measured friction coefficient is plotted versus

Table 2
Thickness, density and roughness values of the deposited layers estimated from simulations of acquired XRR curves.

Sample	Structure	Thickness [Å]	Density [g/cm^3]	Roughness [Å]		E [GPa]	H [GPa]
				XRR	AFM		
ZrN_4	Contamination layer	25	5.1	5	3	252	34.3
	Deposited layer	456	7.1	6			
	Interfacial layer	21	3.6	3			
ZrC_1	Contamination layer	19	2.8	14	6	248	39.5
	Deposited layer	388	6.7	5			
	Interfacial layer	21	2.4	3			