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Influence of Al content on the phase formation, growth stress and mechanical properties of TiZrAlN coatings

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ABSTRACT

Quaternary $(Ti,Zr)_{1-x}Al_xN$ transition metal nitride films, with Al content x ranging from 0 to 0.37, were reactively sputter-deposited from individual metallic targets under $Ar+N_2$ plasma discharges on Si substrates at $T_s=270$ °C. The influence of Al addition on the crystal structure, phase formation, growth morphology and intrinsic stress development, electrical and mechanical properties was systematically investigated. Three distinct compositional regions were evidenced: i) for $0\leq x\leq 0.07$, films develop a columnar structure consisting of cubic TiZr(Al)N grains with (111) and (200) preferred orientation, large compressive stresses up to ~−4 GPa and hardness increase from ~20 to ~24 GPa, ii) for $0.09\leq x\leq 0.16$, Al incorporation favors the growth of nanocomposite films consisting of (200)-oriented cubic TiZr(Al)N nanocrystals surrounded by a highly-disordered matrix, accompanied by a decrease of compressive stress, whereas a maximum hardness H~27 GPa and *H/E* ratio of 0.105 is reached at x~0.12 and x = 0.14, respectively, and iii) $x>0.16$, XRD amorphous films are formed, with reduced mechanical properties. The structure–stress-properties relationship is discussed based on evolutionary growth regimes induced by incorporating a high-mobility metal in a refractory compound lattice.

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1. Introduction

Multicomponent alloying of transition metal (TM) nitride systems is attracting considerable interest to improve further the performance of hard and wear resistant coatings [1–6]. In particular, alloying TiN, ZrN or CrN with AlN is known to increase oxidation resistance, while retaining high hardness. But these favorable properties depend on the crystal structure of as-grown TM–Al–N thin films [7–15] and subsequent phase transformations occurring under thermal work load conditions, e.g. during cutting or milling operations [9,10,15–20]. It is well known that metastable cubic (c) solid solution $Ti_{1-x}Al_xN$ films with NaCl structure can be synthesized by physical vapor deposition, such as cathodic arc evaporation [7,8] or magnetron sputtering [9–12], for AlN mole fractions up to 0.6–0.7, while higher Al contents $(x>0.7)$ favor the hexagonal ZnS-wurtzite (w) structure, resulting in lower mechanical properties. Ab initio calculations [21–23] confirmed that the maximum (metastable) solubility limit of AlN in c-Ti–Al–N is ~0.7, while the predicted existence field of the cubic phase in the isovalent $Zr_{1-x}Al_xN$ and $Hf_{1-x}Al_xN$ systems is comparatively reduced to $x\leq 0.5$ [23,24]. Strategies aiming at stabilizing the cubic structure of $Ti_{1-x}Al_xN$ films at higher Al content have been proposed [25,26], among which substitutional alloying with TM like Cr [1,2,21], Ta [5,27], Zr [21,28,29] or Hf [3,4] has received recent interest. In addition to improved thermal stability (age hardening), quaternary Ti–Al–TM–N films with TM = W or Mo are also predicted to exhibit toughness enhancement [6].

Ternary Ti–Zr–N thin films grown by vacuum arc [30,31] or magnetron sputtering [32] have shown to exhibit enhanced hardness compared to TiN, due to solid solution strengthening. But the oxidation behavior was not improved compared to TiN, since the ternary alloys were found to fully oxidize at temperatures between 500 and 600 °C [33]. Similarly to TiAlN, it is therefore expected that addition of Al into TiZrN would yield a higher oxidation resistance by promoting the growth of an outer, passive Al_2O_3 layer. In a recent study, Chen et al. [29] have shown that incorporation of Zr (up to $z=0.29$) in $Ti_{1-x-z}Al_xZr_zN$ (with $0.37\leq x\leq 0.55$) delays the formation of detrimental w-AlN phase upon annealing in vacuum and assists the formation of a dense oxide scale for $z=0.05$. However, a systematic investigation of phase formation upon alloying Al to Ti–Zr–N has not yet been reported.

In the present work, we use in situ stress measurements, X-ray diffraction (XRD) and X-ray reflectommetry (XRR), transmission electron microscopy (TEM), electrical resistivity and nanoindentation measurements to study the influence of Al incorporation on the structure, phase

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formation, stress development, electrical and mechanical properties of magnetron sputtered $(Ti,Zr)_{1-x}Al_xN$ films with x ranging from 0 to 0.37.

2. Experimental details

2.1. Thin film growth and real-time stress evolution

$(Ti,Zr)_{1-x}Al_xN$ thin films were deposited on (001) Si wafer covered with native (~2 nm) oxide using reactive unbalanced magnetron co-sputtering under $Ar+N_2$ plasma discharges. Deposition was carried out at the substrate temperature $T_s=270$ °C in a high vacuum chamber (base pressure ~10^{-5} Pa) equipped with 7.5 cm diameter water-cooled planar magnetron sources. Metallic Ti (99.995% purity), Zr (99.2% purity) and Al (99.999% purity) targets, placed in a confocal configuration at a distance of 18 cm from the substrate holder, were used for co-sputtering. Prior to deposition, all targets were sputter-cleaned for 3 min in pure Ar plasma discharge, while the substrate was shielded by a shutter. The atomic fraction of Al relative to metallic elements, x, in the films was varied from 0 to 0.37 by tuning the rf power supply of the Al target from 0 to 200 W, while maintaining the dc power supply of Ti and Zr targets constant at 300 and 220 W, respectively. The Ti and Zr target powers were chosen so as to obtain a Ti:Zr concentration ratio in the synthesized coating of about 1:1. A constant bias voltage of −56 V was applied to the substrate using a rf power supply. The working pressure was fixed at 0.20 Pa (10 sccm of Ar flow), while the N_2 partial pressure was systematically adjusted using MKS MicroVisionPlus mass spectrometer to be in a range of $1.8–2.5\times10^{-3}$ Pa, corresponding to optimized conditions to synthesize stoichiometric TiZrN films in metallic target mode [32]. The substrate stage was rotated at 15 rpm to ensure thickness and composition uniformity during all deposition. Details on the deposition process parameters are reported in Table 1. The film thickness h_f was varied between ~50 to ~350 nm by adjusting the deposition time. The growth rate (R) was determined from accurate determination of film thickness using X-ray Reflectivity (XRR) measurements (see Section 2.2) on a ~50 nm thick film series (total deposition time of 150 s).

A multi-beam optical stress sensor (MOSS) developed by kSA was implemented into the deposition chamber, so that in situ stress measurements could be carried out, enabling one to obtain real time information on the stress evolution during growth [34]. The MOSS relies on the monitoring of the spacings between an array (3×3 in our geometry) of laser beams reflected off the sample surface and recorded on a CCD camera. The change in curvature, $\Delta\kappa$, is deduced from the mean value of the differential spot spacing, $\delta D/D_0$, using the following expression, valid for small angle approximation, $\Delta\kappa=\frac{\delta D}{D_0}\frac{\cos\alpha}{2L}$, where α is the incident angle of the laser beam measured with respect to the sample normal and L the optical path length from the substrate to the CCD camera. The geometrical factor $\cos\alpha/2L$ was calibrated using a set of flat and reference mirrors with known radius of curvature. The change in curvature is related to the average biaxial film stress, σ_{avg}, according to the Stoney equation $\sigma_{avg}\ h_f=\frac{1}{6}\Delta\kappa\ M_s h_s^2$, where h_f is the film thickness, h_s the substrate thickness and M_s the biaxial elastic modulus of the substrate ($M_s=180.5$ GPa for Si (001)). By convention, a negative value of σ_{avg} corresponds to a compressive stress. The acquisition time, in static mode (no rotation of the substrate holder), was 0.8 s, corresponding to an average of 4 data points. With our own experimental set-up, a typical curvature resolution of 0.2 km^{-1} is attained, giving a stress sensitivity of 0.29 N/m for a Si substrate with $h_s=200$ µm.

2.2. Microstructural characterization and electrical resistivity

X-ray diffraction (XRD) was employed for structural identification using a D8 Bruker AXS X-ray diffractometer operating in Bragg–Brentano configuration and equipped with $CuK_{\alpha1}$ wavelength (0.15418 nm) and an energy dispersive Si(Li) detector (Sol-X detector) defined with a 0.2 mm opening angle slit. Appearance of new phases was analyzed by deconvolution procedure of diffraction lines using Lorentz's function. The grain size was evaluated according to the broadening of the (200) diffraction line using the Scherrer's equation, i.e. ignoring in a first approximation the contribution of microstrain. Integrated intensities, I_{hkl}, of the (111) and (200) peaks of $(Ti,Zr)_{1-x}Al_xN$ films were normalized with respect to the corresponding integrated intensities of the Al-free film (x=0), after background subtraction. The (200) texture coefficient, T_{200}, was calculated according to $T_{200}=\frac{I^*_{200}}{I^*_{200}+I^*_{111}}$ where I^*_{hkl} refer to normalized intensity.

The atomic fraction of metallic elements (Ti, Zr and Al) in films deposited on glassy carbon substrates was determined by energy dispersive X-ray spectroscopy (EDX) with a global accuracy of ±2%, using an Oxford Instruments AZTek EDX unit attached to a JEOL 7001F-TTLS scanning electron microscope (SEM) operated at 20 kV. The nitrogen concentration was quantified by the method of Rutherford backscattering (RBS) using He^+ ions with the energy of 1.6 MeV at the High Voltage Engineering tandetron system accelerator. The obtained spectra were fitted using SIMNRA software. The mass density, ρ, film thickness and surface and interface roughness were quantitatively determined from XRR measurements performed on a Seifert XRD 3000 apparatus using a channel-cut Ge (220) monochromator to select the $CuK_{\alpha1}$ line (0.15406 nm) exclusively, with a low divergence. An optical model based on Parratt's formalism [35] and assuming a three-layer stacking (topmost surface layer, film layer and film/substrate interface layer) was used for the refinement procedure. The relative error in the determination of film thickness and mass density from XRR is estimated to be ±1% and ±3%, respectively. Studies of the film's surface topography were performed in a Multimode Digital Instrument atomic force microscope (AFM) working in tapping mode, while fracture

Table 1
Process parameters and elemental composition determined by EDX and RBS of as-deposited magnetron sputtered TiZrAlN coatings at fixed working pressure (0.20 Pa), substrate temperature $T_s=270$ °C and bias voltage $V_s=-56$ V. The dc power supply of Ti and Zr targets was fixed at 300 and 220 W, respectively.

Al target RF power supply (W)	Al target discharge voltage (V)	N_2 flow (sccm)	p_{N2} (mPa)	Growth rate, R (Å/s)	[Ti]/([Ti]+[Zr]) (EDX)	[Al]/([Al]+[Ti]+[Zr]) (EDX)	N concentration, at.% (RBS)
0	0	1.3	1.8	3.1	0.50	0	50
20	130	1.3	1.9	3.1	0.50	0.03	54
30	155	1.3	1.9	3.1	0.50	0.05	/
40	185	1.4	1.8	/	0.50	0.07	/
50	205	1.4	2.2	3.2	0.50	0.09	/
60	230	1.5	2.0	3.2	0.50	0.12	/
70	250	1.5	2.3	/	0.50	0.14	42
80	274	1.5	1.9	/	0.50	0.16	/
100	310	1.5	2.0	/	0.50	0.21	/
120	350	1.6	2.2	3.6	0.50	0.25	33
200	480	1.6	2.4	3.9	0.49	0.37	28

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