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Structure and hardness of quaternary TiZrSiN thin films deposited by reactive magnetron co-sputtering

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ABSTRACT

The addition of Si into (Ti,Zr)N films is considered to be perspective for their hardness enhancement as well as improvement of oxidation and wear resistance. In the present work, the influence of the silicon content and deposition temperature (270 and 600 °C) on the structural and mechanical properties of magnetron sputtered TiZrSiN films is investigated. The elemental composition was determined by Rutherford backscattering and wavelength dispersive X-ray spectrometry methods, the structure and phase formation were analyzed by transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Depending on Si content, x, and deposition temperature, T_s, $(Ti,Zr)_{1-x}Si_xN_y$ films were formed in the following states: i) single-phase, cubic (Ti,Zr)N solid solution, ii) dual-phase nanocomposite consisting of nanograins of c-(Ti,Zr)N solid solution surrounded by an amorphous SiN_z phase, iii) amorphous phase. Higher deposition temperature (T_s = 600 °C) promotes the formation of nanocomposite structure and reduces the intrinsic compressive stress. The maximum hardness values (26–29 GPa) are observed when Si content is in the range $0.07 \le x \le 0.15$ for both deposition temperatures.

1. Introduction

Multicomponent alloying of transition metal (TM) nitride systems is attracting considerable interest to enhance the performance of hard and wear-resistant coatings [1–6]. The presence of alloying elements such as Cr and Al drastically improves the oxidation resistance, Zr and V contribute to a better wear resistance, whereas Si increases the hardness and thermal stability [7]. Depending on elemental composition, the hardness of multinary TM nitride coatings may span a broad range of values, but a hardening is usually achieved compared to parent binary systems, with a maximum hardness between 20 and 40 GPa [7–12]. In particular, (Ti,Zr)N coatings show an enhanced hardness compared to TiN and ZrN coatings deposited under the same conditions [7,13,14]. The increased hardness reported in (Ti,Zr)N coatings is due to a solid solution strengthening mechanism which provides an energy barrier to the movement of dislocations throughout the distorted lattice as larger Zr atoms substitute for Ti ones [13]. Recently, quaternary TiZrAlN coatings were found to exhibit distinct microstructures depending on their composition and deposition conditions and a significant hardness enhancement was reported for nanocomposite structures [15,16]. Therefore, when forming multicomponent TM nitride films the determination of correlation of their structural and phase state with the mechanical properties is essential.

Protective coatings based on ternary and quaternary nitride systems, such as Ti–Zr–N, Ti–Al–N, Ti–Si–N, Ti–Al–V–N, Ti–Al–Si–N and others, are perspective as wear-resistant coatings for metal-machining operations at elevated temperatures [7,8,17,18]. (Ti,Zr)N coatings exhibited better wear resistance as compared with TiC, TiN and (Ti,Al)N coatings [7]. The improved cutting performance of the (Ti,Zr)N coatings was attributed to the stabilization effect of zirconium in the fcc TiN lattice, and to the formation of very thin zirconium oxide layer on top of the coating that reduced diffusion wear.

It was reported that, besides higher values of hardness (>30 GPa), the oxidation resistance of TiSiN films at elevated temperatures was superior to that of TiN [9]. The formation of amorphous SiN_x interlayers at the TiN grain boundaries [9,11,12] is thought to suppress the oxidation process along these high diffusive paths, thus protecting the surrounded two-phase TiN/SiN_x structure. This is why the addition of Si into (Ti,Zr)N films is foreseen to be beneficial for their hardness, corrosion and radiation stability enhancement. Meanwhile, there are no data reported on the equilibrium phases in the Ti–Zr–Si–N system.

Here we attempt to synthesize TiZrSiN alloys in thin film form using magnetron sputter co-deposition from elemental targets under reactive

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atmosphere. The objective of the present study is to provide some information on the phase formation, crystal structure and mechanical properties (hardness) depending on film composition and substrate temperature.

2. Experimental details

TiZrSiN thin films were deposited on (001) Si wafer covered with native SiO_2 (~2 nm thick) layer using reactive unbalanced magnetron co-sputtering from elemental targets under Ar + N_2 plasma discharges [16]. Deposition was carried out at two different substrate temperatures T_s = 270 °C and 600 °C in a high vacuum chamber (base pressure ~10^{-5} Pa) designed by Alliance Concept and equipped with 7.5 cm diameter water-cooled planar magnetron sources. Ti (99.995% purity), Zr (99.2% purity) and Si (99.995% purity, *p*-type doped) 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 Si content, x, in the films was varied by changing the rf power supply of the Si target, P_{Si}, from 0 up to 250 W, while maintaining the dc power supply of Ti and Zr targets constant (see Tables 1 and 2). The Ti and Zr target powers were adjusted so as to obtain practically equal Ti and Zr concentration in the synthesized films that corresponds to the optimal Ti:Zr ratio of ternary TiZrN films which possess enhanced physical-mechanical properties [14,19,20]. A constant bias voltage of −60 V was applied to the substrate using an rf power supply. The Ar + N_2 working pressure was fixed at 0.20 Pa, corresponding to 10 sccm of Ar. N_2 flow was varied from 1.3 to 1.5 sccm (T_s = 270 °C) and from 1.1 to 1.9 sccm (T_s = 600 °C). This corresponds to N_2 partial pressure in the range of (2.3–2.7) × 10^{-3} Pa (T_s = 270 °C) and (8.3–16) × 10^{-3} Pa (T_s = 600 °C), as measured using MKS MicroVisionPlus mass spectrometer. The substrate stage was rotated at 15 rpm to ensure thickness and composition uniformity during all deposition. At T_s = 270 °C the film thickness was ~320 nm both for X-ray diffraction (XRD) analysis and hardness measurements. At T_s = 600 °C the film thickness was ~430 nm (for XRD analysis) and ~1 μm (for hardness measurements).

The elemental composition of the as-deposited TiZrSiN films was determined using Rutherford backscattering (RBS) or wavelength dispersive X-ray spectrometry (WDS). RBS was performed at the High Voltage Engineering tandetron accelerator system (Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University) using 2.0 MeV He^+ ions. The obtained spectra were fitted using SIMNRA software [21]. WDS was carried out using an Oxford Instruments spectrometer unit attached to a JEOL 7001F-TTLS scanning electron microscope. WDS scans were acquired sequentially on Ti, Zr, Si, N, O and C elements using a 10 kV high voltage, a probe current of 20 nA and a typical image magnification of 12,000×. The quantification was carried out using INCA Energy + software. The characteristic peaks and background intensities were registered at optimized wavelengths using appropriate analyser crystals and normalized to commercial standards. In particular, for the determination of the N content, a systematic correction procedure accounting for Ti *Ll* and N Kα lines overlap was implemented using a bulk TiAlC homemade standard sample.

Plan-view transmission electron microscopy (TEM) study was performed for selected samples, of two types. Thin (~60 nm) TiZrSiN film was deposited either directly onto a TEM copper grid, covered with an amorphous SiO_x-on-carbon membrane, or onto a crystalline rock-salt piece. The first type of the samples could be directly observed while for the second type it was necessary to dissolve the NaCl in distilled water in order to place the thin film on a Cu grid. A JEOL 3010 ARP microscope operating at 300 kV was used to observe the microstructure of the thin films either in the conventional bright field, selected area electron diffraction (SAED) or high resolution mode (point resolution of 0.185 nm). In the latter case, the obtained images are directly interpretable without further simulation.

XRD analysis was employed for structural identification using a D8 Bruker AXS X-ray diffractometer operating in Bragg–Brentano configuration and equippedwith $Cu_{K\alpha}$ wavelength (0.15418 nm) and an energy dispersive Si(Li) detector (Sol-X detector) defined with a 0.2 mm opening angle slit. The size of coherently diffracting domains for evaluation of the grain size (along the growth direction) was calculated from the broadening of the (200) diffraction peak of TM nitride solid solution using the Scherrer's equation, i.e. ignoring in a first approximation the contribution of microstrain. The mass density of the films was determined from X-ray reflectivity (XRR) measurements using a procedure described elsewhere [16].

X-ray photoelectron spectroscopy (XPS) data for TiZrSiN thin films were obtained using the upgraded vacuum generator ESCALAB MKII spectrometer fitted with XR3 twin anode. The non-monochromated MgK_α X-ray source was operated at $h\nu$ = 1253.6 eV with 300 W power (20 mA/15 kV), and the pressure in the analytic chamber was lower than 5 × 10^{-7} Pa during the spectral acquisition. Core level lines were acquired with the electron analyser pass energy of 20 eV for narrow scans and resolution of 0.05 eV. The binding energies employed for calibration were 83.96 eV for Au $4f_{7/2}$ and 932.6 eV for Cu $2p_{3/2}$. The spectra calibration, processing and fitting routines were done using Thermo Scientific Avantage software (5.918). All spectra were recorded at 90° take-off angle and referenced to the C (1 s) line of the adventitious carbon set at the binding energy of 284.6 eV. The "smart background" was used for background subtraction which iteratively adjusts the background. Standard Scofield factors were used for calculation of the elemental composition.

The intrinsic stress developing during growth was investigated using real-time in situ wafer curvature technique based on multiple beam optical stress sensor (MOSS). The set-up implemented in the deposition chamber has been described elsewhere and previously employed during reactive magnetron sputter-deposition of TiZrN and TiZrAlN films (see [16,22,23]). Measurements were performed on 175–200 μm thick Si substrates.

The hardness and elastic modulus of the films were studied by nanoindentation using a Nano Indenter-G200 system (Agilent Technologies, USA) equipped with a continuous stiffness measurement attachment

Table 1
Process parameters and elemental composition determined by RBS of as-deposited magnetron sputtered TiZrSiN films at fixed working pressure (0.20 Pa), substrate temperature T_s = 270 °C and bias voltage V_s = −60 V.

Si target RF power supply (W)	N_2 flow (sccm)	N_2 partial pressure (mPa)	Concentration, at.% (RBS method)				Si/(Ti + Zr + Si) concentration ratio, x	Grain size (nm)
			Ti	Zr	Si	N		
0	1.3	2.3	26.3	23.4	–	50.3	–	20.5
60	1.4	2.0	28.3	26.5	4.2	41.0	0.07	11.8
80	1.5	2.2	29.6	26.4	6.8	37.2	0.11	8.8
120	1.5	2.3	31.8	28.0	13.5	26.7	0.18	4.1
200	1.5	2.7	29.2	26.7	15.8	28.9	0.22	–

The DC power supply of Ti and Zr targets was fixed at 300 and 220 W, respectively. Grain size of c-(Ti,Zr,)N solid solution extracted from XRD line broadening of (200) peak is also presented.