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Influence of oxygen content on structure and properties of multi-element AlCrSiON oxynitride thin films

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ABSTRACT

Multi-element oxynitrides of type Al–Cr–Si–O–N were prepared using r.f. magnetron sputtering from $Al_{80}Cr_{2.5}Si_{17.5}$ (at.%) target composition and $O_2/(O_2+N_2)$ gas flow ratio between 0 and 100%. Two series of samples varying from pure nitrides to pure oxides and deposited at 400 °C and 650 °C were investigated by (WDS EPMA) + SIMS, XRD, SEM, and nanoindentation measurements. Chemical analysis revealed that the incorporation of oxygen into the films increases much faster than the fraction of oxygen in the gas flow so that the oxide phases can be formed from the gas ratio of about $O_2/(O_2+N_2)=20\%$. Addition of oxygen gradually alters the crystallinity of nitride phases due to the incorporation of interstitial atoms and the formation of metal vacancies, but nitride lattices seem to survive up to the overall oxygen incorporation of about 40% into the film. Up on supplying more oxygen flow, the amorphisation of films continues by absorbing more oxygen atoms up to the range of $O_2/(O_2+N_2)\approx 80\%$ to 90%. Beyond that limit, the formation of crystalline α-Al_2O_3 was observed, probably stimulated by the presence of α-Cr_2O_3 and SiO_2 in the films. Transition from nitride to oxide has strong consequences on film hardness, which changes from 30–33 GPa for nitrides to 12–13 GPa for amorphous layers, and increases again to 20–25 GPa for pure oxides.
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1. Introduction

Owing to a combined metallic–covalent–ionic character of bonding, oxynitride thin films offer a wide range of structural design concepts in optimizing material properties [1]. Among this particular family of ceramics, transition metal oxynitrides have attracted both technical and scientific interests, because of their remarkable mechanical, thermal, electrical and optical properties [2–5]. The oxygen content, film homogeneity, and crystallographic structure were reported to have a great influence on the final properties of the films.

Most of the works on oxynitride thin films were devoted to ternary compounds and their deposition drawbacks such as low deposition rate and arcing [6], sticking coefficient difference between oxygen and nitrogen [7], and higher reactivity of oxygen compared to nitrogen [8]. Recently, researchers have focused on developing quaternary or higher multi-element oxygen containing thin films to meet requirements for higher strength and wider functionality. Stüber et al. [3] studied the growth and microstructure formation of Cr–Al–N–O coatings deposited by reactive magnetron sputtering and non-reactive sputtering from segmented targets following a combinatorial material science approach. All coatings independent of their elemental composition showed nanocrystalline building blocks with high hardness and greater toughness. Hirai et al. [9] showed that the Cr–Al–N–O films do not oxidize below 900 °C and keep their B1(NaCl) structure up to 1100 °C.

The system Ti–Al–N–O has been considered by several authors [2,10,11]. Luthier and Lévy [10] reported the formation of nanocrystalline (Ti,Al)N uniformly dispersed in an amorphous Ti–Al–O matrix leading improved mechanical and optical properties. Tönshoff et al. [11] demonstrated a superior performance of oxygen-rich Ti–Al–N–O coated tools in dry drilling operations and showed that a small amount of oxides in the coatings can inhibit from further oxidation. Sjölèn et al. [2] described the formation of arc evaporated Ti–Al–N–O coatings versus O_2/N_2, and showed that the growth starts by the formation of dual layer architecture at the film–substrate interface, which transforms into the steady-state growth of nanocomposite architecture made of oxides and nitrides. In another approach and for attempting to extend the life time and performance of hard coatings, Zabinski et al. [12] proposed the oxide phase of oxynitrides as the solid lubricant in wear resistant matrix.

To increase fundamental understanding of the formation of oxynitrides and explore their structure–property relations, we have used $Al_{1-(x+y)}Cr_xSi_y$ ($x\leq 0.40$ and $y\leq 0.18$) targets to deposit multi-element thin films varying from pure nitrides to pure oxides by changing the O_2/N_2 ratio of the reactive gas flow in the sputtering chamber. The selection of target material was based on the structural and functional properties of nitride films of these types, as well as the role of Si on the formation of nanocomposite building blocks that have been well documented [13,14]. The addition of oxygen in these systems opens

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new option in microstructural design and property combination, but also challenges thin film processing and characterisation. Although the ability of such nitride based and oxide based films to wear protection is commonly known, that of coatings with intermediate O/N ratios, which are highly dielectric and thermal barrier is less reported. In this paper which is our first article in these materials, the results of 2 series of samples prepared from $Al_{80}Cr_{2.5}Si_{17.5}$ target are reported. The relationships between the gas composition and the film chemical composition, as well as the evolution of film microstructure and hardness resulted from gradual substitution of nitrogen atoms by oxygen atoms are discussed.

2. Experimental

Oxynitride films were deposited on Si(100) wafers covered with 100 nm amorphous SiO_2 layer to avoid possible diffusion of Si into the films. Depositions were carried out in an (N_2+O_2)/Ar atmosphere using a r.f. magnetron sputtering system powered at 150 W. The base pressure in the deposition chamber was less than 3×10^{-4} Pa and rose to around 2×10^{-1} Pa during deposition up on the introduction of working gases and partial closing of the turbopump outlet valve. Two series of oxynitride films were prepared at 400 °C and 650 °C by changing the $O_2/(N_2+O_2)$ ratio between 0 and 1 of the gas flow. A dc-bias of −50 V was applied to the substrate for all samples. A deposition time of 2 to 5 h was necessary to obtain a film thickness of about 1–1.5 µm, as measured by Tencor alpha-step 500 profilometer. Under these conditions, the mean deposition rate was about 12 nm/min for nitrides and about 3 nm/min for oxides. Deposition rate of oxynitrides was variable between the two limits depending on the oxygen content of the reactive gas. An example of such variations is displayed in Fig. 2 for the films deposited at 650 °C under (N_2+O_2)/Ar = 30%. In general, during a deposition experiment, deposition rate of oxynitrides is not constant, but gradually decreases with sputtering time and falls well below 1 nm/min at the end of experiment. The values of Fig. 2 correspond to the mean deposition rates averaged over the whole deposition time of each experiment. The crystal structures of the films were studied by X-ray diffraction (XRD) using a Rigaku diffractometer operating at 40 kV and 30 mA with mono-chromatized CuK_a radiation. The XRD reflections were collected in both Bragg–Brentano (θ–2θ) and grazing incidence ($\alpha=4°$) geometries for accurate analysis of samples, but here only grazing incidence spectrograms are reported. The chemical composition of the films was quantitatively analysed by combining EPMA (Electron Probe Micro Analysis) and SIMS depth profiling (Secondary Ion Mass Spectroscopy). SIMS is very convenient for in-depth profiling of elemental distribution and has a very high detection power even for light elements, but requires a correct set of relative sensitivity factors which can be supplied by EPMA.

The EPMA instrument was an automated CAMECA SX-100 using WDS (wavelength dispersive spectrometry) analysis, fitted with five simultaneously recording crystal spectrometers, covering different energy ranges. The electron beam was accelerated with 10–15 keV, and the source was a conventional W filament. The standards for calibration were pure bulk metallic elements, but for O and N, an oxide and a nitride material like CrN were used. SIMS analyses were carried out by using a CAMECA 4550, quadrupole, with the primary ion beam of 133Cs LMI (liquid metal ion) gun. The molecular secondary ions CsM^+ (Cs = Caesium, and M = element of interest isotope like Cr, Al, C…) were analysed based on the relative sensitivity factors from standards similar to the compositions to be examined, in order to eliminate matrix effects common to this technique. Depth profiles were recorded until the substrate was reached, and the averages taken from the film bulk were used as the measured compositional values. The detailed procedures for determination of chemical composition of nitrides and oxynitrides by a combination of WDS EPMA and SIMS were described elsewhere [15,16]. Films hardness and Young's modulus were determined using a nanoindenter XP (Nano Instrument Inc.) operating under continuous stiffness measurement method to provide hardness and modulus versus displacement into sample. The values corresponding to the penetration depth of 100 to 200 nm were taken and averaged over nine indentations to minimise the influence of surface roughness and substrate compliance. Cross-sectional morphology of samples was observed in a high resolution scanning electron microscope FEI/Philips XLF30-SFEG.

3. Results

3.1. Chemical composition by SIMS and EPMA

Fig. 1 shows typical examples of the WDS EPMA + SIMS profile of elemental distribution (at.%) for 4 different samples deposited at $O_2/(O_2+N_2)$ = 0%, 5%, 10%, and 56%, respectively. The vertical axis of the plots is in logarithmic scale to expand low content elements for better visualisation. Depth profiles of Fig. 1a correspond to a nitride film deposited at 650 °C under atmosphere N_2/Ar = 30% without introduction of oxygen in the gas flow. The oxygen content of the nitride film does not exceed 1% while the carbon content is estimated to be less than 2%. The values are reasonable for conventional sputtering, and remain within the range of experimental discrepancies due to the impurities in the gas flow, diffusion of atmospheric oxygen, pollution of pumping, analytical errors and instrument margins. According to the plot, the content of nitrogen remains practically constant through the film thickness at about 48.5%, where the relative concentrations of metallic elements Al:Cr:Si = 40.5:1.2:7.3 are comparable to their composition in the target material.

Addition of 2.1% oxygen into the reactive gas significantly modifies the composition of thin film (depth profiles not shown here). The average concentration of oxygen in the film was found to increase to 10.6%, decreasing thus the nitrogen content to 37.2%. Further increase of the oxygen ratio in the gas flow up to 5%, results in an oxynitride film with 41.5% oxygen and 5.7% nitrogen (Fig. 1b). When the oxygen ratio in the reactive gas reaches 10%, the oxynitride film exhibits 60.3% oxygen and only 2.8% nitrogen (Fig. 1c). Similarly, when the oxygen content of the gas flow increased to 56%, the oxygen content of the film augmented to 62% while the nitrogen content lowered to 0.8% (Fig. 1d). Another point revealed by this analysis is the relative concentration of metallic elements Al:Cr:Si = 40.5:1.2:8.9 in the films which shows only a slight difference with the nitride film mentioned above. The Cr/Al and Si/Al ratios are higher by 1% and 2%, respectively, in oxides than in nitrides. That means the substitution of nitrogen atoms by oxygen atoms does not change much the relative concentration of metallic elements in the films with respect to the target composition.

The results of SIMS profiling are reported in Fig. 2 which shows the variation of the overall oxygen concentration in the films versus the oxygen content in the reactive gas flow for 3 series of oxynitrides deposited at: 400 °C with (O_2+N_2)/Ar = 30%, 650 °C with (O_2+N_2)/Ar = 30%, and 650 °C with (O_2+N_2)/Ar = 50%. In all samples the ratio of oxygen to nitrogen sharply grows with the fraction of oxygen to nitrogen in the reactive gas, and reaches a plateau at around 15–20%. Beyond this limit the small amount of nitrogen in the film decreases slowly to give rise to pure oxides at higher oxygen ratio. In oxide films the concentration of oxygen was found to be slightly higher than the stoichiometric values. Even if the number of analysed samples in Fig. 2 is not exhaustive, the comparison of measurements for the films deposited at (N_2+O_2)/Ar = 30% shows that the oxygen content of samples prepared at 650 °C is higher than those at 400 °C. Similarly, raising (N_2+O_2)/Ar from 30% to 50% results in slight increase of oxygen concentration in the films at 650 °C. These suggest that the incorporation of oxygen atoms into the films becomes more effective with enhancing deposition temperature or increasing the reactive gas ratio in the sputtering process. Comparable

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