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Investigations on the oxidation of zirconium nitride films in air by nuclear reaction analysis and backscattering spectrometry

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Abstract

The thermal oxidation of dc magnetron sputter deposited thin ZrN films in air in the temperature range of 100–475 °C has been studied by depth profiling N using nuclear reaction analysis (NRA) involving $^{15}N(^{1}H,\alpha\gamma)^{12}C$ resonance reaction and O using 3.05 MeV $^{16}O(\alpha,\alpha)^{16}O$ resonant scattering. The structural and morphological changes accompanying the process have also been investigated. NRA/backscattering spectrometry measurements show that oxidation results in the formation of $ZrO_{1.8\pm0.1}$ at the surface. An interface consisting of Zr, O and N is also formed underneath the surface oxide. For an isothermal annealing, oxide layer as well as interface exhibits parabolic growth with the duration of annealing. The diffusion of oxygen through the already grown oxide layer ($D = 5.6 \times 10^{-14}$ cm^2 s^{-1} at 475 °C) forms the rate-controlling step of oxidation. The diffusion may be facilitated by the high concentration of oxygen vacancies in the oxide layer. Glancing incidence X-ray diffraction (GIXRD) measurements indicate that zirconia films formed are phase-singular (monoclinic) and are textured in (2 0 0) and (3 1 1) orientations. Examination by scanning electron microscopy (SEM) reveals the formation of blisters on sample surfaces on prolonged oxidation. The blistering can be attributed to intrinsic growth stress arising due to the larger molar volume of zirconium oxide in comparison to zirconium nitride, a fact demonstrated by the depth profile measurements as well.

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1. Introduction

Thin films of transition metal nitrides such as TiN and ZrN find applications in tribology, microelectronics (as diffusion barriers) and decorative coatings due to their high hardness, chemical inertness, excellent wear resistance and prominent coloration in the visible wavelength region. In these applications thermal stability of the coatings is an important consideration, particularly in conditions wherein the coatings are exposed to oxidative environments at high temperatures. The growth of oxide layer brings about significant modifications in the tribological, electrical and chemical properties of the coatings and thereby limits their applicability. These nitrides are thermodynamically stable but are susceptible to oxidation, which can be inferred from the heats of formation of TiN (−80 kcal mol^{-1}) and TiO_2 (−219 kcal mol^{-1}), and ZrN (−87.3 kcal mol^{-1}) and ZrO_2 (−261.5 kcal mol^{-1}). In view of its importance, the oxidation behavior of nitride coatings has been a subject of several studies [1–3]. The oxidative environment in these studies is usually dry oxygen or air in the temperature range of 300–1200 °C. The growth kinetics of oxide layer has been the main objective of the most of the investigations while some have focused on the microstructural changes accompanying the process [1,4–7]. The diffusion of oxygen through the already grown oxide layer is considered to be the rate-limiting factor in the oxidation, which manifests itself in the form of colour changes and formation of blisters over the film surfaces.

In the present paper the oxidation behavior of ~4500 Å ZrN/Si films in air at temperatures ≤500 °C is reported. The study assumes significance on two accounts namely (a) ZrN films are grown by reactive dc magnetron sputtering and (b) high resolution depth profile measurements of N as well as O have been performed to obtain a better insight into the progress of oxidation from surface to the interior of the film. Previous reports deal with the oxidation of ZrN films grown by rf

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sputtering [4], unbalanced magnetron sputtering [7], ion beam sputter deposition [8] or vacuum arc evaporation [9]. Coatings deposited by reactive dc magnetron sputtering have so far not been investigated in this regard. Films prepared by physical vapour deposition (PVD) techniques are, in general, non-stoichiometric, and may contain lattice point defects and impurities, which can affect their oxidation behavior [3]. As discussed in the succeeding sections, the films used in the present study are stoichiometric and devoid of such metallic impurities as Zr or Hf and non-metallic impurities as C or O. Secondly, in previous studies the progress of oxidation has been monitored by Rutherford backscattering spectrometry (RBS) by taking the changes in the features of only Zr signal into consideration [1,4,8]. No separate measurements on O and or N are reported. Oxidation initiates at the surface and proceeds into the interior of the film, presumably, with the ingress of oxygen and outgress of nitrogen. It is therefore desirable to measure, in addition to Zr, N as well as O at any given depth below the surface for a comprehensive understanding of the processes. From this standpoint of view high resolution depth profile measurements of N and O were performed which were accomplished by $^{15}N(^{1}H,\alpha\gamma)^{12}C$ nuclear resonance reaction analysis (NRA) and 3.05 MeV $^{16}O(\alpha,\alpha)^{16}O$ resonant backscattering spectrometry, respectively.

2. Experimental

2.1. Deposition of ZrN films

ZrN films were deposited by reactive dc magnetron sputtering on Si (1 1 1). Prior to the coating process the substrates were ultrasonically cleaned successively in trichloroethylene, acetone, methanol and propanol, and subsequently dried under flowing hot air. A Zr disk (99.9%), 4 in. in diameter, was used as the target. Before deposition, the chamber was evacuated to 2×10^{-5} Torr to avoid contamination during deposition process. The Zr target was pre-sputtered to remove native oxide with a shutter shielding the substrates. Subsequently high purity working gas (Ar) and reactive gas (N_2) were introduced into the chamber, using separate mass flow controllers to regulate their flow rate and deposition was carried out. The deposition parameters are as follows: target to substrate distance: 5 cm, substrate bias: −100 V, current: 0.5 A, substrate temperature: 300 °C, N_2 flow rate: 5.0 sccm, Ar flow rate: 20 sccm, and deposition time: 15 min. In one of the interesting instances of deposition of zirconium nitride films by dc magnetron sputtering, Del Re et al. prepared films containing three phases of zirconium nitride (ZrN, Zr_3N_4, ZrN_2) in which they could detect different metastable compounds [10].

2.2. Isothermal annealing

To investigate their oxidation behavior, the films were exposed to static air in the temperature range of 100–500 °C for different durations in an open-ended quartz tube furnace. The films were placed on a clean Pt foil during annealing. To avoid thermal shock, the films were introduced into the furnace at room temperature and the annealing temperature was attained at a constant heating rate of 5 °C/min. After soaking at a temperature for a specified period, the films were cooled with the same rate until a temperature of 40 °C was attained.

2.3. Phase analysis and morphological examination

To identify the crystalline phases present in the virgin as well as isothermally processed films X-ray diffraction experiments were performed using a STOE X-ray diffractometer (Cu Kα radiation) in glancing incidence configuration (GIXRD). The patterns of the films were recorded under identical conditions. The peak positions and the full width at half maximum intensity (FWHM) corresponding to different planes were obtained by fitting the recorded peaks with Voigt function. The average crystallite dimension, L, was calculated by the Scherrer formula, $L = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of Cu Kα radiation, θ the Bragg angle and β is the FWHM after correction for instrumental broadening. The morphology of the specimens was examined by a scanning electron microscope (SEM, Philips XL30).

2.4. Ion beam analysis

Ion beam analysis (RBS, NRA and $^{16}O(\alpha,\alpha)^{16}O$ resonant scattering) of the films was carried out by a 3 MV Tandetron at the Surface and Profile Measurement Laboratory of the centre. The depth profiling of nitrogen by $^{15}N(^{1}H,\alpha\gamma)^{12}C$ nuclear reaction was accomplished by bombarding the specimens with a well-collimated proton beam ($\Phi = 1$ mm, current = 250 nA) beyond the resonance energy of 429 keV in 1–2 keV steps [11]. The 4.4 MeV γ-rays, characteristics of this reaction, were detected by a 7.6 cm × 14.2 cm bismuth germenate (BGO) detector placed at a distance of 5 cm behind the targets at 0° angle relative to the incident beam. The integral counts between 3 and 4.7 MeV energy window of the mutlichannel analyzer served as the nitrogen signal. A well characterized 5200 Å silicon nitride film on GaAs of composition $N_{\mathrm{Si}} = 0.34$, $N_{\mathrm{N}} = 0.46$ and $N_{\mathrm{H}} = 0.2$ served as a standard for N quantification. Ziegler–Biersack [12] stopping cross-sections were used in the calculation of atomic composition and thickness of the films.

RBS measurements were carried out using 2.4–3.5 MeV α-particles. For depth profiling oxygen by $^{16}O(\alpha,\alpha)^{16}O$ resonant scattering, incident α-beam energies were >3.05 MeV. In all backscattering spectrometry (BS) experiments the α-beam was collimated to 1 mm and was incident normally on the films. The backscattered particles were detected by a silicon surface barrier detector subtending a solid angle of 1.2 msr, set at a laboratory angle of 170°. The experimental backscattered spectra were simulated by SIMNRA [13] to obtain the atomic composition and thickness of the films. Ziegler–Biersack stopping cross sections were used in the simulation.

3. Results and discussion

Fig. 1 shows the GIXRD patterns of a virgin zirconium nitride film and films annealed isothermally in air at 475 °C for

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