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Yttria-stabilized zirconia films grown by radiofrequency magnetron sputtering: Structure, properties and residual stresses

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Abstract

Thin (<10 μm) zirconium oxide films were deposited onto aluminum substrates by radiofrequency (RF) magnetron sputtering under different processing conditions. The structure, composition, residual stresses and mechanical properties were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and depth-sensing indentation. All the films evidenced a good adhesion to the substrate. The deposited material was always a mixture of tetragonal and monoclinic ZrO_2 phases in different amounts grown with a strong preferential crystallographic orientation along the axis perpendicular to the aluminum substrate. According to Raman spectroscopy characterizations, the monoclinic phase was shown to possess an inhomogeneous distribution along the film thickness. The films experienced compressive residual stresses of relatively high magnitude in the range 300–700 MPa with non-monotonous profiles along the film thickness. According to depth-sensing indentation techniques, the Young's modulus and the hardness of the films were also characterized and revealed in some cases a marked peak-load dependence.

Keywords: Nano-indentation; Scanning electron microscopy; Raman scattering spectroscopy; Sputtering; Zirconium oxide; Residual stress

1. Introduction

Zirconia films exhibit many remarkable properties, which confer on them a role of great interest both in theoretical studies and in practical applications. Their chemical stability, high dielectric constant, high melting point, high hardness, good thermal insulating characteristics offer the possibility of a wide diversification in practical applications such as thermal and chemical barriers, buffer layers for growing high temperature superconducting films and sensors in microelectronics. ZrO_2 films are also widely used as optical coatings due to their excellent properties such as high refractive index and broad region of low absorption in a wide spectral range. Many techniques, including sol–gel process [1,2], plasma-spray [3,4], electron beam evaporation [5,6] and sputtering [7,8] can be employed to deposit zirconia coatings. Among them, the sputtering method is a very attractive process for the production of coatings with high homogeneity, good uniformity and low deposition temperature.

It is well known that the microstructure and properties of the films are strongly influenced by the deposition conditions, so that finely tuning the process parameters is required in order to reach optimum performance. A common and crucial problem related to thin films is the adhesion to the substrate, which in turn affects the mechanical behavior. In particular, film–substrate interface adhesion may lead to significant residual strain as a result of the difference in thermal expansion coefficients between film and substrate. This already complex picture may be further complicated by the occurrence of tetragonal-to-monoclinic phase transformation of the zirconia material and by the rapid contraction of the

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coatings when they undergo rapid cooling from processing temperature to substrate temperature [4]. Generally, the parameters that influence the adhesion of the coating to the substrate are the same as those that influence the residual stress field in both coating and substrate. Among other parameters, the most important role is played by the nucleation and growth of film grains during deposition, and their interaction with the substrate. Both factors are responsible for the residual stress state of the film and consequently for the adhesion characteristics of the film to the substrate. It was previously reported that weak tensile stress of the coating induces extensive cracking [9] while a relationship exists between adhesion and the residual compressive stress in the film, this latter having a beneficial effect on coating adhesion, crack propagation, life time and fatigue lifetime [10].

Residual stresses in a coating are mainly due to the difference in thermal expansion coefficient between the film and the substrate; other sources of internal stress found in thin films are the presence of residual gas trapped into the film structure, phase transformation occurred during deposition, etc. [11]. Several techniques have been previously proposed to evaluate residual stresses as the Stoney method [12,13], X-ray diffraction [14,15] and bulge testing [16]. However, these methods only give an overall evaluation of the residual stress field, which is thus averaged over the entire thickness of the film. On the other hand, when the film thickness is high enough, by micro-focused Raman piezo-spectroscopy, it would be in principle possible to locally estimate the value of the stress field so that the stress field profile along the film thickness could be measured. This work focuses on the characterization of phase composition, structure, mechanical properties and residual stress profiles in ZrO_2 films deposited on aluminum by RF magnetron sputtering at ambient temperature under different processing conditions.

2. Experimental methods

ZrO_2 films were obtained by a magnetron sputtering instrument (Materials Research Corporation) equipped with a radiofrequency source at 13.56 MHz. Aluminum slabs $10 \times 10 \times 2$ mm were chosen as substrates. The surfaces were ground, mirror polished and ultrasonically cleaned in acetone for 30 min, prior to introducing in the sputtering chamber and pumping down to a base pressure of $(6–8) \times 10^{-5}$ Pa. High purity argon (99.999%) was then introduced into the chamber, bringing the pressure to the operating conditions. The target was sputter-cleaned for 20 min with Ar ions before starting deposition, with the substrate covered by a shield. Then, the shield was removed and ZrO_2 deposition carried out for 5 h at ambient temperature. ZrO_2 coatings were obtained using a fully dense, pure tetragonal ZrO_2 target, stabilized with 3% mol Y_2O_3 (3Y-TZP). The target, a dense ZrO_2 disk of 10 cm in diameter, was produced by cold isostatic pressing pure 3Y-TZP powder (Tosoh, Tokyo, Japan) and sintering at 1500 °C for 1 h. The distance between the target and the substrate was 80 mm in all the experiments. On the basis of preliminary tests, three different combinations of RF power and chamber pressure were chosen, as shown in Table 1. As a result of different processing conditions, three different films were investigated (henceforth, simply referred to as ZR1, ZR2 and ZR3; cf. Table 1). The film deposition was carried out at ambient temperature. As an indication of the substrate temperature, the temperature was recorded by a thermocouple embedded in the electrode on which the substrates were positioned was taken.

The films were examined by XRD analysis (Miniflex, Rigaku, CuKα radiation) to obtain the phase and structural composition. From diffraction peak width, the average crystallite size and the lattice microstrain were evaluated, according to the following equation [17,18]:

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + \frac{4\varepsilon\sin\theta}{\lambda}, \qquad (1)$$

where θ is the Bragg angle, β is the FWHM of the peak, after subtraction of the instrumental broadening, λ is the wavelength of the X-rays emitted by the Cu cathode, D is the crystallite size and ϵ is the lattice microstrain [19]. The crystallite size and lattice microstrain were evaluated by plotting $(\beta\cos\theta)/\lambda$ vs. $(\sin\theta)/\lambda$. The thickness and the microstructural features of the coatings were examined by SEM (Leica, Cambridge).

A quantitative estimation of both volume fraction of monoclinic phase and residual stress along the film thickness were obtained by Raman microprobe spectroscopy. Raman spectra were collected at room temperature with a triple monochromator spectrometer (T-64000, ISA Jovin-Ivon/Horiba Group, Tokyo, Japan) equipped with a charge-coupled detector (high resolution CCD camera). All measurements were carried out by using an Ar-ion laser, with excitation frequency of 488 nm and power of 200 mW. The waist of the incident laser beam on the focal plane was 1 μm in diameter. The spectra were recorded with steps of about 1 μm along the section of the zirconia films. The

Table 1
Operating conditions at which ZrO_2 films were obtained and their main properties

Sample	Power (W/cm^2)	Pressure (Pa)	Thickness (μm)	Deposition rate (nm/min)	Substrate temperature (°C)	Crystallite size (nm)	Lattice strain	Mean monoclinic volume fraction (%)
ZR1	2.5	1.2×10^{-1}	5.0	17	40	69.4	1.6×10^{-2}	15
ZR2	3.7	1.2×10^{-1}	6.1	20	60	54.6	1.4×10^{-2}	9
ZR3	3.7	6.0×10^{-2}	8.2	27	65	16.5	5.5×10^{-3}	21