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Study of the structure of titanium thin films deposited with a vacuum arc as a function of the thickness

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ABSTRACT

Polycrystalline titanium thin films have been widely employed as interlayer between the substrate and different coatings in order to improve adhesion strength, corrosion resistance and wear performance, as well as to promote the growth of crystalline phases of the coating. The thickness of the Ti layer can be relevant on the behavior of the coatings, however very few studies have been carried out. In this work, the crystal structure of polycrystalline titanium films deposited with a vacuum arc discharge on monocrystalline silicon wafers (100) was studied and a dependence on the film thickness was found. The presence of the fcc phase of titanium was observed for the thinnest films with a critical thickness estimated in 300 nm, a much larger value than those reported for other deposition processes. For larger thicknesses, the films grew as α-titanium with a preferred orientation in the [100] direction. The obtained results agreed with a growth model based on the matching between the film and the substrate lattice. The characteristics of the films deposited in two steps, which had not been previously investigated, reinforced the suggested model.

1. Introduction

Polycrystalline titanium thin films have been widely employed as interlayer between the substrate and different coatings, on metallic, semiconductor or ceramic substrates and for metallic, metallic compounds or carbon coatings. The Ti interlayer has been included in order to improve adhesion strength, corrosion resistance and wear performance, as well as to promote the growth of crystalline phases of the coating [1–3]. In some works the influence of the Ti interlayer thickness on the properties of multilayer systems has been analyzed, the thickness of the Ti layer being relevant on the behavior of the coatings. However, very few studies about the dependence of the characteristics of Ti films on the thickness have been carried out.

At ambient condition, Ti is in the hexagonal-close-packed (hcp) crystal structure, which is referred to as α phase. This structure transforms to a body-centered-cubic (bcc) structure, called β phase, when the temperature is higher than 1155 K. At room temperature, the α phase transforms to the hexagonal ω phase (three atoms per unit cell) when the pressure is increased between 2 and 9 GPa. Other two high pressure phases, γ-Ti (distorted hcp) and δ-Ti (distorted bcc), have been found. At room temperature, the phase transition from ω-Ti to γ-Ti occurs at 116 GPa, and into δ phase at 140 GPa [4].

The face centered cubic (fcc) Ti phase has been only found in thin films and in high energy milled powder. Wawner Jr. and Lawless were the first to report the fcc Ti phase in Ti films epitaxially grown on NaCl single crystals [5]. Afterwards, some investigations about epitaxial growth of Ti thin films on metallic substrates and on semiconductors have been published (e.g. Al [6,7] and SiC [8]). In all cases, at the onset of the growth the Ti atomic structure presented the fcc phase, which seemed to perfectly match the substrate lattice in the directions parallel to the surface plane. At a critical thickness the hcp phase appeared, this being the predominant phase for thicker films. The reported critical thickness values varied from 1 to 20 nm for epitaxial growth. Beyond this thickness, axial alignment with the substrate was only partially preserved, and off-normal alignment was lost. The disorder in the film at coverage larger than the critical thickness was associated with the formation of misfit dislocations or the relaxation to the hcp phase of Ti [6]. More recently, a study of the dependence of the crystalline structure on the thickness in polycrystalline Ti films deposited on Si substrates by DC magnetron sputtering has been presented [9]. The authors analyzed the structure, textures and stresses of Ti films with thickness in the range of 140–720 nm. In that work, from the deconvolution of Ti X ray diffraction peaks the fcc and hcp phases were detected in the thinnest films, while for films with a thickness larger than 500 nm only the hcp phase was identified. They suggested that fcc Ti is locally stable in highly stressed hcp Ti matrix at relatively low thin film thicknesses.

In view of the lack of information about the crystal structure of polycrystalline Ti films deposited with vacuum arcs on monocrystalline

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silicon wafers (100) as a function of the film thickness, a systematic study on this subject was carried out. The structure, the morphology and the residual stresses of the films were studied. Characteristics of films deposited in one and two steps were compared.

2. Experimental details

The system employed to produce the cathodic arc discharge had a high power DC source (model ARCC 18KW 150 A, ALTATEC) connected to a titanium cathode and to a grounded annular copper anode. In Fig. 1 a schematic view of the complete device is shown. The cathode was a cylinder of 55 mm in diameter and 40 mm thick, the anode had an internal diameter of 80 mm and was electrically insulated from the cathode and the vacuum chamber. The vacuum chamber consisted of a stainless steel cylinder (50 cm long, 10 cm internal diameter). The vacuum system was made up of a diffusion pump assisted by a rotary vane pump that reached a base pressure lower than 10^{-6} Pa. The anode and the cathode had water cooling. In order to initiate the discharge, an auxiliary electrode (trigger) in contact with the cathode was used. The discharges were run at a current of 110 A and discharge voltage was 25 V. The pressure during the discharges remained lower than 10^{-6} Pa.

The employed substrates were monocrystalline silicon wafers (100) doped with boron with a surface area of 20×20 mm^2 and 375 μm thick. Samples were located facing the cathode on a grounded holder at a distance of 300 mm. The samples were exposed to the discharge for times ranging from 30 to 180 s, in one or two steps. For samples grown on two steps, there was an average waiting time of 15 min between steps while maintaining the chamber pressure below 10^{-6} Pa.

The thickness of the films was determined by cleaving the samples and studying the profile by scanning electron microscopy (SEM), using a microscope Philips 515 with an Oxford Instruments INCA Energy 250 with a Si(Li) detector (10 mm^2 in area) for electron dispersive spectroscopy (EDS).

The films were characterized by X-ray reflectivity (XRR) in order to estimate their density. The measurements were performed in the D10A-XRD2 beamline of the National Synchrotron Light Source (LNLS), Campinas, Brazil, using an X-ray energy of 8 keV (λ = 0.1549 nm). The opening of the slit that defined the vertical size of the incident X-ray beam was 100 μm, located at 40 cm from the sample. A Mythen linear detector was placed at 100 cm from the sample with a 100 μm width slit. For films with thicknesses lower than 200 nm, a θ–2θ scan was performed varying the angle of incidence with respect to the surface from 0.1° to 2°. For films with thicknesses above 200 nm no oscillations were noticeable in the XRR pattern, so a diffuse scattering measurement (rocking scan) was employed.

The crystalline structure was analyzed by X ray diffraction (XRD) in Bragg–Brentano geometry. The diffractograms were measured using a Panalytical diffractometer Empyrean model with a CuKα source with a PixCel 3D detector. For this source the X ray intensity is 90% attenuated in a length of 1.1 μm of titanium. The angle 2θ was varied between 30° and 135°, avoiding the peak corresponding to silicon in $2\theta = 60°$ so as not to saturate the detector. The presence of macrostrains in the films

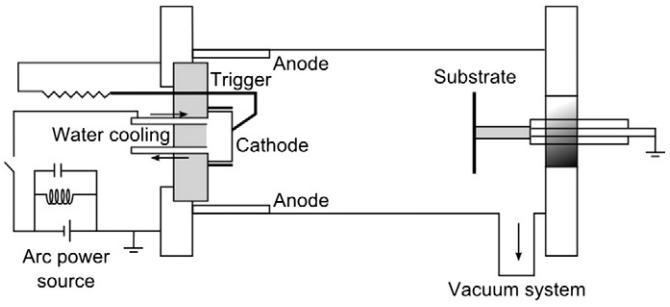

Fig. 1. Schematic view of the cathodic arc discharge system employed to grow the films.

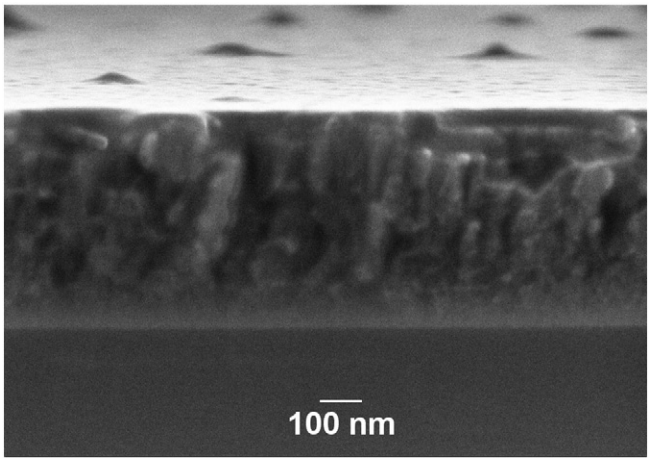

Fig. 2. Typical SEM image of a film depth profile.

was studied by the $\sin^2\psi$ method using a Panalytical X'Pert PRO diffractometer with a CuKα source.

3. Results

Fig. 2 corresponds to a typical image of the depth profile obtained by SEM for a film grown in a single discharge. The films displayed a compact columnar structure, with a column width of ~100 nm. The thickness of all the films was measured from images similar to that of Fig. 2, the growth rate resulting in (3.8 ± 0.3) nm/s. EDS compositional analysis indicated a minimum contamination of oxygen and carbon, and a titanium content higher than 80%.

The mass density of the films was estimated from the critical angle observed in XRR measurements. The critical angle was determined by fitting the interference maxima and minima by the modified Bragg equation when the θ–2θ scan was employed [10]; and from the position of the Yoneda peaks when the rocking scan was used [11]. In all cases the critical angle was estimated with an uncertainty of ~5%, the mass density of all the films was found to be in the range (4.3 ± 0.2) 10^3 kg/m^3.

The crystalline structure of the films was studied by XRD, the deposition time and the thickness for the presented samples are shown in Table 1. Fig. 3a shows the diffractograms of films with different thicknesses grown in a single discharge, and Fig. 3b presents a detail of the main peaks for 2θ between 33° and 45°. The diffractogram registered for the silicon substrate and the tabulated peak positions corresponding to α-titanium are also included in Fig. 3.

For films (i) and (ii), no peaks corresponding to α-titanium were noted. Only one peak was observed at $2\theta = (37.05 \pm 0.03)°$ which cannot be attributed to the substrate or any other titanium compound (such as oxides or nitrates). The interplanar spacing associated with this peak was (2.424 ± 0.007) Å. Film (ii) also exhibited one additional peak at $2\theta = (78.75 \pm 0.03)°$. The corresponding interplanar spacing was (1.214 ± 0.007) Å, half the spacing associated with the previously mentioned peak. This indicated that both peaks correspond to the same crystallographic direction. This diffractogram was consistent with the reported fcc-titanium structure [9], therefore the peak

Table 1
Features of the films studied by SEM and XRD.

Sample label	Number of discharges	Total deposition time [s]	Thickness [nm]
(i)	1	30	115
(ii)	1	60	220
(iii)	1	120	430
(iv)	1	150	515
(v)	2	60 (2 × 30)	240
(vi)	2	180 (2 × 90)	750