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Optical and mechanical characterization of zirconia–carbon nanocomposite films

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Abstract

The focus of the present work is the study of carbon co-deposition effect on the optical and mechanical properties of zirconia films. Optical and dielectric constant, band gap and transition lifetime of such composite systems were determined, as well as their elasticity properties. The thin ZrO_{2-x}–C films were sputter-deposited on silicon and polycarbonate, from a pure ZrO_2 and graphite targets in a radio-frequency argon plasma.

Besides the zirconia phase and crystalline parameter changes induced by carbon addition, the electronic properties to the films were significantly modified: a drastical optical gap lowering was observed along an increased electronic dielectric constant and refractive index. The invariance of the film elasticity modulus and the similarity of the optical transition lifetime values with those of pure amorphous carbon films indicate an immiscibility of the ceramic and carbon components of the film structure.

Keywords: Tetragonal zirconia; Amorphous carbon; Optical properties; Nanocomposites; Elasticity

1. Introduction

In recent years, transparent conductive oxides have received considerable attention with the ever increasing demand for materials with low electrical resistance and high transparency in the UV–visible–near IR light wavelength. Thin films of refractive oxide materials are a family of such importance in thin film optical coating applications because of their structural, optical, electronic and optoelectronic characteristics. Besides, ambient substrate temperature deposition conditions are of great importance concerning the potential applications such as development of coatings on temperature sensitive substrates (organic for example). In order to anticipate the needs of future areas such as those of the flexible panel displays and photovoltaics, new materials are currently under development by many research groups, with the principal objective to increase the conductivity while still maintaining the optical transparency. So far, oxides like ZnO, CdO, SnO_2 are the most studied materials as transparent conductive oxides (TCO) candidates [1,2].

There are few studies instead concerning the potentiality of ZrO_2 as a TCO. Sc_2O_3-doping of tetragonal zirconia with high electrical conductivity obtention has been reported by Hirano et al., in this case doping acted through the increase of the ionic conductivity [3]. Doped zirconia with organic molecules has been considered by Zevin and Reisfeld as a suitable candidate for use as active waveguides and waveguides sensors in the optical and laser fields [4]. An early study of Qadri et al. considered co-deposited ZrO_2–ZnO as having potential for optoelectronic applications [5].

In a previous work of the authors, ZrO_2–C nanocomposite films have been found to undergo a phase modification of zirconia, from a monoclinic phase structure in pure zirconia films to a tetragonal one, together with changes in the residual strain and grain size of the zirconia phase, the latter being in the 40–50 nm range [6]. In this paper we present preliminary results of optical and mechanical measurements performed on this kind of films, which were characterized in view of applications as TCOs.

2. Experimental details

2.1. Film deposition

The zirconia–carbon films were sputter-deposited on polycarbonate (PC) and Si(100) substrates in a radio-frequency (r.f.) planar sputtering chamber, in 0.5 Pa argon atmosphere,

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from two separated targets of 78 cm^2 area: monoclinic zirconia and graphite. The samples were mounted on a rotating holder, without any external heating. Pure zirconia and pure amorphous carbon films were also deposited and served as reference. Two energetic conditions of the film deposition were applied for the growth of pure zirconia, by using two r.f. powers at the ZrO_2 target: 300 W and 200 W. The films deposited with such parameters will be referred to as Zr_{300} and Zr_{200} respectively with the subscript recalling the used r.f. power. The carbon content in the zirconia–carbon films was varied by tuning the r.f. power applied to the graphite target and to the zirconia target. A same amount of carbon of ~10 at.% in the Zr_{300} and Zr_{200} films could be obtained respectively with a power of 100 W and 250 W at the graphite cathode. In both cases, the power at ZrO_2 cathode was the same as for pure zirconia films growth. The carbon-containing Zr_{300} and Zr_{200} films will be named Zr_{300}:C and Zr_{200}:C respectively. Table 1 summarizes the conditions of the films growth and the film labelling.

2.2. Film characterization

The film thicknesses were measured with a stylus Dektak profilometer.

The film chemical composition was determined by X-ray photoelectron spectroscopy (XPS). The XP spectra were recorded in a Scienta ESCA 200 spectrometer, with monochromatized AlKα.

Optical transmittance (T) measurements were made with a Jasco V-550 spectrophotometer, provided with a Czerny–Turner single monochromator and a photomultiplier detector, in the 200–850 nm wavelength range at normal incidence, to determine the film absorption coefficient α, the Tauc gap [7] as well as the real and imaginary part of the refractive index (n,k). The latter were determined following the Swanepoel envelope method applied to the transmittance spectra [8]. For all the films, the latter presented interference fringes. An example from a Zr_{200} film is shown in Fig. 1(a).

The optical gap value of the films, E_0, was derived from the Tauc plot $(\alpha E)^2$ versus the incident photon energy (E). E_0 is obtained by extrapolating $(\alpha E)^2$ to the zero value, following $(\alpha E)^2 = B\ (E - E_0)$, where B is a constant in the Tauc approximation of a parabolic behaviour of the bands near the edges and of a constant momentum transition [9]. An example is shown in Fig. 1(b). With the n and k values, the electron dielectric constant, ε, of the films was calculated.

Scratch tests were made on the films grown onto PC substrates, by means of a CSM instrument, using a spherical diamond indenter of 200 μm radius. The tests were exploited to determine the modulus of elasticity, Y, of the film material, through the dependence of the mean pressure below the indenter tip, more precisely through the halfwidth, A, of the track left after the scratch. E was derived from Hertz elastic theory which gives [10]:

$$A = \left(\frac{1}{2}\right)^{1/3} (W)^{1/3} \left(\frac{3R}{4}\right) \left(\frac{1-\nu^2}{Y}\right)^{1/3} \quad (1)$$

where W is the applied load, ν the Poisson ratio taken as 0.3 and R the diamond radius.

Application of this theory requires first to define the elasto-plastic regions of the film/substrate deformation. This can be done by following the variation of the track halfwidth, A, (measured by profilometry) as a function of the applied load. A

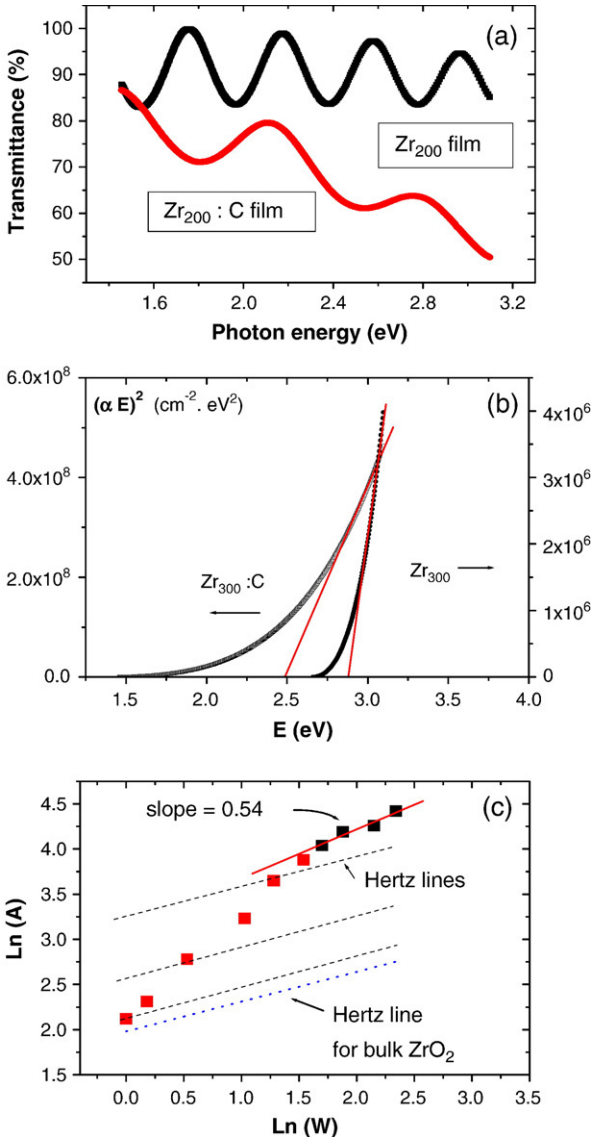

Fig. 1. (a) Transmittance spectra of the Zr_{200} and Zr_{200}:C films, 600 nm and 400 nm thick respectively. (b) Tauc plot from Zr_{300} and Zr_{300}:C films. (c) Ln(A) versus Ln(W) in Zr_{300} film. A is the scratch half-width (micron), and W the applied load (N).

Table 1
Film deposition parameters and labelling

Parameters	Film Zr_{300}	Film Zr_{200}	Film Zr_{300}:C	Film Zr_{200}:C
RF power				
Graphite target	–	–	100	250
Zirconia target	300 W	200	300	200