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Phase evolution in zirconia thin films prepared by pulsed laser deposition

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ABSTRACT

Zirconia thin films were deposited on silicon (1 0 0) and quartz substrates using pulsed laser deposition. Phase formation in zirconia films was monitored as a function of substrate temperature (473–973 K) and oxygen partial pressure (0.001–1 Pa). Volume fraction of tetragonal zirconia is determined from X-ray diffraction and Raman analysis. Tetragonal volume fraction of zirconia films varies from 10 to 76% for different substrate temperature and oxygen partial pressure. Zirconia films show a good transparency in the visible region, except for the films deposited at 473 K and at 0.002 Pa. The band gap values and refractive index of the films are discussed in relation with the microstructure and phase composition of the zirconia films as well as with 8 mol% yttria stabilised zirconia films.

1. Introduction

Zirconium oxide (ZrO_2) is a transition metal oxide which offers several interesting technological applications due to its properties like high melting point, high refractive index, good thermal, chemical and mechanical stabilities, wide band gap, high dielectric constant and electrical resistivity. It finds applications in optical coatings, protective coatings and insulating layers [1–3], catalyst for alcohol synthesis [4], in fuel cells [5] as well as in thermal barrier coatings [6]. Three different phases of zirconium oxide are reported in literature, namely, monoclinic zirconia (m-zirconia) in the temperature <1443 K, tetragonal (t-zirconia) in the range 1443–2643 K and cubic phase (c-zirconia) in the range 2643–2903 K [7]. Among the three phases, tetragonal and cubic phases are formed at very high temperatures. But these high temperature phases can be retained at room temperature by doping with some suitable oxides such as aluminium oxide [8], yttrium oxide [9], magnesium oxide [10], and calcium oxide [9,11]. However, it is interesting to note that un-doped zirconium oxide can also be retained in tetragonal phase at room temperature in thin film forms [12,13], as a result of small crystallite size [12–16] and compressive stress [17]. Garvie [18] prepared tetragonal zirconia in powder form at room temperature and correlated the stability of the tetragonal phase with mean crystallite size and surface energy. The critical size for tetragonal to monoclinic transition has been reported to be 30 nm [13,18]. The critical size for the stabilisation of zirconia in tetragonal phase has been found to vary according to the preparation method. The reported value of critical crystallite size for the stabilisation of high temperature zirconium oxide phase is 50–55 nm for the films deposited by metal oxide chemical vapour deposition (MOCVD) [12], 18 nm for films deposited by thermal spray method [15]. Influence of crystallite size is mainly based on the increase in surface energy of zirconia by decreasing the crystallite size [18,19]. To stabilise the tetragonal phase at lower temperature, the following condition should be satisfied [18,19]:

$$(G_t - G_m) + (S_t\gamma_t - S_m\gamma_m) \le 0 \qquad (1)$$

where G_t, G_m are the molar free energy, γ_t and γ_m are the molar surface energy and S_t, S_m are the surface area of t-zirconia and m-zirconia phases, respectively. When crystallite size decreases, molar surface area increases and beyond certain value of molar surface area, G_t becomes less than G_m and the whole term in the above equation becomes negative, resulting in the stabilisation of tetragonal phase [18]. Compressive stress in the film can also stabilise the tetragonal phase at lower temperature when the molar volume of t-zirconia is lower than that of the m-zirconia [17,20].

Various methods such as MOCVD [12,21], chemical vapour deposition (CVD) [22], ion assisted deposition (IAD) [23], ultrasonic nebulisation and pyrolysis technique [2], pulsed laser deposition (PLD) [24–26], sol–gel method [27], sputtering technique [13,28], thermal oxidation [29], plasma and ion beam deposition [30] and electron beam deposition [31] have been used to prepare zirconia

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thin films. Also, the structural [2,26,32–34], optical [2,26,34–40], electrical [2,36,41–45], wear [28], luminescence [46], bioactivity and cytocompatibility [35] properties of the thin films of zirconium oxide were reported.

In the present work, zirconia thin films were prepared on (1 0 0) oriented silicon (Si) and quartz substrates by the PLD technique at different substrate temperature and oxygen partial pressure. Substrate temperature was varied from 473 to 973 K and the oxygen partial pressure from 0.001 to 1 Pa. The effect of substrate temperature and oxygen partial pressure on the formation of m-zirconia and t-zirconia phases was also investigated by Raman spectroscopy. Several experiments as a function of temperature and oxygen partial pressure over a wide range were carried out to establish phase mapping of zirconia in the films prepared by PLD technique. Variation in the optical properties is also studied at two different oxygen partial pressures and substrate temperature of 773 K and is discussed in relation with the microstructure of the zirconia films.

2. Experimental procedure

A zirconia target (25 mm diameter and 3 mm thickness) was prepared by using commercially available zirconia powder (99.99% purity) at a pressure of 10 MPa using a uniaxial press and was sintered at 1673 K for 6 h. Zirconia thin films were ablated using this target by the PLD technique at different substrate temperature and oxygen partial pressure. Excimer laser (Lambda Physik, Compex-205) with laser energy of 200 mJ/pulse and repetition rate of 10 Hz was used as an energy source. Substrate temperature was varied from 473 to 973 K and oxygen partial pressure was varied from 0.002 to 2 Pa. Both Si (1 0 0) and quartz substrates were ultrasonically cleaned with soap solution, water and methyl alcohol and then mounted onto the substrate holder using silver paste. The chamber was evacuated to a base pressure of 0.002 Pa using a turbo molecular pump and a rotary pump. The target was rotated with a speed of 10 rpm to avoid grooving of the target. A limited number of thin films of 8 mol% yttria stabilised zirconia (YSZ) were prepared from a sintered YSZ target on Si(1 0 0) and quartz substrates under similar deposition conditions for a comparative study. The thickness of the films was measured using a Dektak profilometer (DEKTAK 6M-stylus profiler). Phase identification and phase evolution of the deposited films were studied in an INEL XRG-3000 X-ray diffractometer (XRD) attached with a curved position sensitive detector using $\mathrm{CuK}_{\alpha1}$ (0.15406 nm) radiation. The crystallite size (D) was calculated for (2 0 0) and (0 0 2) reflections of m-zirconia and t-zirconia, respectively, using the following Scherrer formula with an accuracy of ±3 nm:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where λ is the wavelength of X-rays used, θ is the angle of diffraction and β is the full width at half maximum (FWHM) after subtracting instrumental broadening and $\beta = \sqrt{(B^2 - b^2)}$, where B is the FWHM of the peak and b is the instrumental broadening obtained from the standard Si powder received from National Physical Laboratory, New Delhi. From the XRD analysis of the films, the crystallite size, volume fraction and strain of both monoclinic and tetragonal phases were calculated. Volume fraction of tetragonal phase was qualitatively calculated using the prominent peak intensities of monoclinic ($I_{\mathrm{m}(2\,0\,0)}$) and tetragonal ($I_{\mathrm{t}(0\,0\,2)}$) phases by using Eq. (2).

$$V_t = \frac{I_{t(002)}}{I_{m(200)} + I_{t(002)}} \tag{3}$$

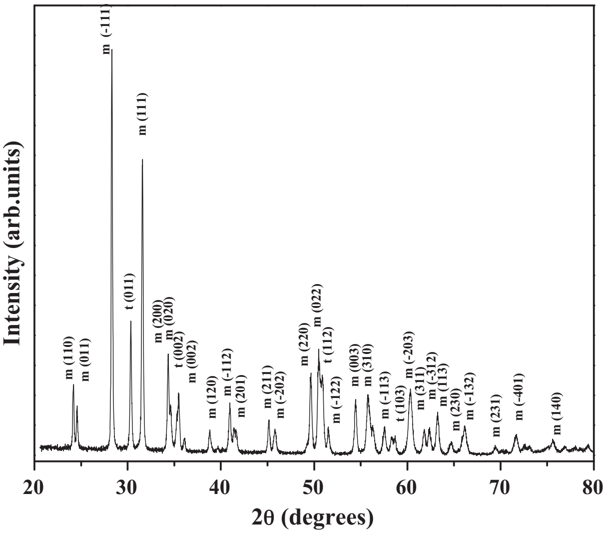

Fig. 1. XRD pattern of a zirconia target used in the PLD experiments.

The preferred orientation is, however, not taken into consideration in the above equation. The strain in the films was calculated using the following equation for the monoclinic and tetragonal phases:

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{4}$$

where ε is the strain in the film, β is the FWHM of (2 0 0) and (0 0 2) reflections of monoclinic and tetragonal peak of zirconium oxide, respectively and θ is the angle of diffraction.

Raman spectroscopy was performed using a spectrometer (HR 800, Jobin Yvon) equipped with 1800 grooves/mm holographic grating. The samples were placed under an Olympus BXFM-ILHS optical microscope mounted at the entrance of the Raman spectrograph. Argon ion laser of wavelength 488 nm was used as an excitation source. The laser spot size of 3 mm diameter was focused tightly on the sample surface using a diffraction limited (numerical aperture = 0.25 at 10×) long distance objective. The laser power at the sample was ~15 mW. The slit width of the monochromator was 400 μm. The back scattered Raman spectra were recorded using super cooled (~110 °C) charge-coupled device (CCD) detector.

Three sets of zirconia films were prepared on quartz substrates for optical property measurements. Two sets were prepared for different substrate temperatures (473–973 K) at oxygen partial pressure of 1 Pa and 0.002 Pa. The third set of samples were prepared at 773 K and different oxygen partial pressures (2–0.002 Pa). Optical properties of the films, such as transmittance, absorbance, band gap and refractive index were measured using an ultraviolet–visible (UV–vis) spectrometer (Jasco V-650, spectrophotometer) in transmission mode and band gap values were determined from Tauc plot [47] with an accuracy of ±0.1 eV.

3. Results and discussion

3.1. X-ray analysis

The XRD pattern of the sintered zirconia pellet indicates that the pellet contains a mixture of both tetragonal and monoclinic phases of zirconia and absence of any impurity phase in the target (Fig. 1). The XRD plot shows reflections at angles (2θ) 28.175°, 34.16°, 35.309°, 45.20°, 49.75°, 55.20°, 58.9°, 60.20° and 29.98°, 34.81°, 35.25°, and 50.37° corresponding to m-zirconia and t-zirconia phases, respectively. The XRD patterns were indexed using the JCPDS File no. 37-1484 and 50-1089 for m-zirconia and t-zirconia phases, respectively.