Thin nanocrystalline zirconia films prepared by pulsed laser deposition

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Abstract. In the present work, thin zirconia films were prepared by pulsed laser deposition at different substrate temperatures and oxygen partial pressures. The substrate temperature was varied from 400 °C to 600 °C, and the oxygen pressure, from 0.01 to 0.05 mbar. The effect was investigated of the substrate temperature and oxygen pressure on the formation of m-zirconia and t-zirconia phases. The formation of a cubic phase of ZrO2 by using targets doped with 3 and 8 mol % content Y2O3 was also investigated. The variation in the optical properties was studied and discussed in relation with the zirconia films' microstructure.

1. Introduction
Zirconium oxide (ZrO2) is a transition metal oxide offering several interesting technological applications due to its properties, such as a high melting point, a high refractive index, good thermal, chemical and mechanical stabilities, a wide band gap, and high dielectric constant and electrical resistivity. These include optical coatings, protective coatings and insulating layers, catalyst for alcohol synthesis, fuel cells, thermal barrier coatings and application in the field of biomedicine [1-4]. ZrO2 has three well-defined polymorphs depending on the temperature conditions of preparation: monoclinic, tetragonal and cubic [5]. The phase transformations cause extensive cracking in the sintered ZrO2 material; if this aspect is not controlled or suppressed, it would preclude the use of ZrO2 in the field of advanced ceramics. On the one hand, the stability of zirconia could be appropriately controlled through carefully tailoring its chemical composition and grain size [5]. On the other hand, the high temperature phases can be retained at room temperature by doping with some suitable oxides, such as aluminium oxide, yttrium oxide, magnesium oxide, and calcium oxide [5].

ZrO2 thin films have been prepared by several methods, such as chemical vapor deposition [6], electron beam evaporation [7], sputtering [8], pulsed laser deposition (PLD) [9-12], etc. Among these methods, the PLD stands out as a simple technique enabling one to prepare high-quality thin films.
from a wide variety of materials and compounds. Mishra et al. [9] reported fabrication of zirconia thin films by PLD. The authors focused their attention on the phase evolution of zirconia produced in a wide range of substrate temperatures and oxygen pressures. Balakrishnan and co-workers [10] investigated the influence of the oxygen partial pressure on the microstructure, morphology, and optical properties of pulsed-laser-deposited ZrO$_2$ films. However, the process parameters for stable zirconia films deposition were not defined there.

In this work, thin ZrO$_2$ films were deposited by PLD using pure and Y$_2$O$_3$ doped zirconia targets. The influence was investigated of the substrate temperature and oxygen partial pressure on the structure, composition, morphology and optical properties of the films. The optimal process parameters for deposition of monophase zirconia films were determined.

2. Experimental
Thin ZrO$_2$ films were produced by PLD in a standard on-axis configuration. The third harmonic of a Nd:YAG laser ($\lambda = 355$ nm, pulse duration $\tau = 18$ ns, and repetition rate of 10 Hz) with a laser fluence of 3 J cm$^{-2}$ was used for ablation of a ceramic ZrO$_2$ target. The target was prepared by using commercially available zirconia powder (99.99 \% purity) compressed at a pressure of 10 MPa using a uniaxial press and sintered at 1200 °C for 4 h. Both (100)-oriented Si and quartz substrates were used for thin-film depositions. The target-substrate distance was kept at 4.5 cm. The experiments were carried out at different substrate temperatures in the range of 400 - 600 °C. All experiments were performed in an oxygen atmosphere with the pressure being varied from 0.01 to 0.05 mbar. The duration of samples depositions was fixed at 60 or 90 min. A set of experiments were made by using Y$_2$O$_3$-doped ZrO$_2$ targets, namely, 3 and 8 mol\% yttria stabilised zirconia (YSZ). The YSZ films were produced under conditions of growth optimized for deposition of pure ZrO$_2$ films.

The phase identification and phase evolution of the as-deposited films were studied by a Philips PW 1050 X-ray diffractometer (XRD) using CuK$_\alpha$ (0.15406 nm) radiation. Using the standard software of the XRD apparatus, the crystallites size, volume fraction and strain of both the monoclinic and tetragonal phases were calculated. The surface morphology of the films was examined by AC mode atomic force microscopy (AFM) (MFP-3D$^\text{TM}$, Oxford Instruments). The chemical composition and the oxidation state of the elements on the film surface were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on an AXIS Supra electron-spectrometer (Kratos Analytical Ltd.) using monochromatic AlK$_\alpha$ radiation with a photon energy of 1486.6 eV and a charge neutralization system. The binding energies (BE) were determined with an accuracy of ± 0.1 eV. The thickness of the films was measured using a Talystep profilometer. The optical properties of the films were determined by measuring the normal-incidence transmittance ($T$) of the films over the wavelength range 200 - 1200 nm using an Ocean Optics spectrophotometer.

3. Results and discussion

3.1. ZrO$_2$ films
The chemical composition of the ZrO$_2$ surface was investigated by XPS. The XPS spectra of ZrO$_2$ films deposited at a substrate temperature of 600 °C and under different oxygen pressures are presented in figure 1(a) and (b). Figure 1(a) shows the doublet peaks centered at 182.1 and 184.5 eV, corresponding to Zr3d$_{5/2}$ and Zr3d$_{3/2}$, respectively. The binding energies of Zr3d$_{5/2}$ in ZrO$_2$ (oxidation state Zr$^{4+}$) were reported to be in the range 182.2-182.6 eV [13,14]. At a substrate temperature of 600 °C, the increase of the oxygen pressure during deposition did not change the position of the Zr3d peaks (figure 1(a)). In the O1s region (figure 1(b)), the low binding energy component was attributed to oxygen in zirconium oxide (Zr$^{4+}$). The values reported for the binding energy of this component are in the range 529.5-530.2 eV [13,14]. The high binding energy component reported in the range of 531.0-532.1 eV probably corresponds to oxygen in the form of a hydroxide or other adsorbed species [13,14]. As it was expected, the high binding energy component increased with the increase of the oxygen pressure during deposition (figure 1(b)). Similar behaviour was observed with the samples.
produced at 400 °C and 500 °C. At a fixed oxygen pressure, no significant changes in the chemical states of the films were observed as the substrate temperature was increased from 400 °C to 600 °C. All deposited films could be classified as stoichiometric ZrO$_2$. However, at the highest oxygen pressure used in this work, the estimated oxidation state of the films was in the range 2.10-2.29.

Figure 1. XPS spectra of thin ZrO$_2$ films deposited at 600 °C substrate temperature and (a) 0.01, (b) 0.03, and 0.05 mbar oxygen pressure.

The crystalline structure of the zirconia thin films deposited at different substrate temperatures and oxygen pressures was investigated by XRD. The XRD patterns were indexed using the Reference Code 98-009-4931 and 98-008-6692. All the films were polycrystalline in nature having both monoclinic and tetragonal phases. In general, the XRD study indicated that the tetragonal phase content increased with the increase of the substrate temperature at a fixed oxygen pressure. The XRD patterns of the ZrO$_2$ films deposited at an oxygen pressure of 0.05 mbar and different substrate temperatures are presented in figure 2. As it is seen, the intensity of the peaks corresponding to t-zirconia increased with the increase in the substrate temperature, which indicated that the formation of a tetragonal phase is favoured at higher substrate temperatures [9,11]. The XRD patterns of ZrO$_2$ films deposited at a substrate temperature of 600 °C and different oxygen pressures are presented in figure 3. The XRD results indicated a decrease in the intensity of the peak of m-zirconia with the increase in the oxygen pressure. At the oxygen pressure of 0.05 mbar, all the peaks corresponding to m-zirconia disappeared pointing to the fact that the higher oxygen partial pressure favours the formation of t-zirconia [9,11]. The volume fraction of the phases and the crystallites size were calculated from the intensity of the (11-1) and (011) reflections corresponding to the m- and t-zirconia phases, respectively. The volume fraction of the tetragonal phase increased with the increase in the substrate temperature and the oxygen pressure. The crystallites size for both m- and t-phases of zirconia was evaluated as being in the range of 10-20 nm. In summary, the results of the XRD analysis showed that a higher substrate temperature and oxygen partial pressure favour the formation of the tetragonal phase, which is in agreement with results reported previously [9].

The surface morphology and roughness of the zirconia films were determined by AFM measurements. The AFM images of the ZrO$_2$ films produced at different deposition times are presented in figure 4. In both figures (a and b), one can see that the structure of the films is nanocrystalline. The films have well-defined grains with a narrow distribution and a surface roughness.
in the range of 1-3 nm. However, the increase of the deposition time led to the fabrication of films with a higher peak-to-value ratio (figure 4(a) and (b)).

Figure 2. XRD patterns of ZrO$_2$ films deposited at substrate temperature of (a) 400, (b) 500, and (c) 600 °C and 0.05 mbar oxygen pressure.

Figure 3. XRD patterns of ZrO$_2$ films deposited at substrate temperature of 600 °C and (a) 0.01, (b) 0.03, and (c) 0.05 mbar oxygen pressure.

Figure 4. AFM images of thin zirconia films produced at (a) 60 and (b) 90 min deposition time.

As it was mentioned in the Introduction part, the application of zirconia films strongly depends on the possibility to suppress the phase transformation during the fabrication procedure. The results reported above gave us a reason to define the optimal process parameters (substrate temperature of 600 °C and oxygen pressure of 0.05 mbar) for obtaining monophase nanocrystalline zirconia films with a slightly over-stoichiometric composition.

However, the thicknesses of the films, as measured by the profilometer, were found, as it was expected, to decrease with the increasing oxygen pressure [10]. At a pressure of 0.05 mbar, the deposition rate was estimated to be 0.006 nm/s. The increase of the deposition time led to a change in the crystalline structure of the samples and until the appearance of m-zirconia. This means that the optimal process parameters were determined for defined film thickness.

In order to overcome the phase transformation in zirconia, a set of experiments were performed by using 3 and 8 mol% Y$_2$O$_3$ doped zirconia targets.
3.2. YSZ films

The use of doped zirconia targets changed the crystalline structure of the films (not shown). A 3 mol % content of $\text{Y}_2\text{O}_3$ in the target led to the deposition of tetragonal zirconia, which corresponds well to the previous reports [5]. Increasing the doping content to 8 mol % $\text{Y}_2\text{O}_3$ in the target resulted in the fabrication of a cubic phase of zirconia [5,15]. It should be mentioned that doping with $\text{Y}_2\text{O}_3$ (for the concentrations used in this work) did not change the estimated value of the crystallites size.

A doping content of 3 mol % $\text{Y}_2\text{O}_3$ did not change significantly the surface morphology and film roughness (not shown). However, at the same film roughness, the films with 8 mol % YSZ had a higher peak-to-trough ratio (45 nm). Isolated droplets on the surface were also observed.

The influence of the dopants concentration was also revealed in the optical properties of the zirconia films. The optical transmission spectra of pure and yttrium stabilized zirconia films are presented in figure 5. All the films are transparent in a wide range of wavelengths. No significant difference was observed in the transmission spectra taken from pure and 3 mol% yttrium stabilized ZrO$_2$. The result is in agreement with the structural and morphology analysis discussed above. When the surface morphology was similar, a small volume fraction of m-zirconia did not change significantly the optical properties of the films. A major increase of the optical transmission was observed in the 8 mol% yttrium stabilized ZrO$_2$ films, its value reaching 94-97% in the visible range; we related this to the presence of cubic zirconia.

4. Conclusions

Thin nanocrystalline zirconia films were prepared by PLD. It was confirmed that the phase formation in zirconia is a complex process that strongly depends on the method of deposition, the process conditions, such as substrate temperature and oxygen pressure, and the thickness of the films. The optimal process parameters for preparing t-phase nanocrystalline zirconia films with a slightly over-stoichiometric composition were determined, namely, a substrate temperature of 600 °C and an oxygen pressure of 0.05 mbar. The cubic phase of zirconia films was prepared under the same process parameters by using a 8 mol% YSZ target.

Acknowledgments

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