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Effect of the oxygen partial pressure on the toughness of tetragonal zirconia thin films for optical applications

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ABSTRACT

The zirconia thin films (80–120 nm thick) were deposited on (1 0 0) silicon substrate using metal organic chemical vapor deposition. The effect of oxygen partial pressure during the process and post annealing step on the structure, microstructure and mechanical properties were investigated. Under peculiar experimental conditions, nano-crystallized tetragonal thin films were obtained. The film structure was stable when annealed and some of the films exhibited large toughness values, up to 3.9 MPa $m^{1/2}$. This high toughness value is interesting to use this material as a protect layer for optical applications as this zirconia layer displays a minimum reflectance in the near infrared window. This minimum reflectance could be shifted depending on the thickness of the films.

1. Introduction

Zirconia has received much attraction due to its good mechanical, optical, thermal and electrical properties. Zirconia has interesting physical properties such as a relatively high dielectric constant (~37 for the dielectric static response of the cubic and tetragonal ZrO_2 phases calculated by Zhao et al.) [1]. It has a high melting point (~2680 °C) [2], high refractive index (~2.1 to 2.2), a wide energy band gap (~5.6 to 7.8 eV) [3] and high mechanical strength and toughness [4,5].

However, these properties depend on the zirconia structure as for example, the dielectric constant decreases to ~20 for the monoclinic phase [1]. The tetragonal phase exhibits also better mechanical properties (harder and tougher) than the monoclinic phase and thus is a potential candidate for optical application as a protective layer against mechanical aggressions. Whether it is bulk zirconia or thin film, the tetragonal phase is metastable at room temperature [6] and transforms into the more stable monoclinic phase. It is possible to stabilize this metastable tetragonal phase by the control of the crystallites size through temperature and/or the oxygen partial pressure adjustments during the process [7] and also residual stresses [8,9].

Zirconia thin films have already been prepared by different methods like molecular beam epitaxy [10], electron beam evaporation [11], pulsed laser deposition [6], magnetron sputtering deposition (PVD) [2] and finally pulsed liquid injection metal organic chemical vapour deposition (MOCVD) [3,12] that is versatile to a further scale-up of the process and involves simple experimental operation.

Thus, zirconia thin films have found important applications such as dielectric layers in electronic devices [13,14], as element in the fuel cells [15] or as an element in the matrix of composite ceramics resistant to high temperatures [16]. They are also investigated for optical applications including high reflectivity mirrors, filters and active optical devices [17].

Mirrors and antennas embedded in aircraft consist of a stack of layers deposited on a solid support. Some of these layers have active components (such as filters in frequency) and are tunable (electrically or optically). An upper layer protects the device from external aggression or stresses such as natural rainfall erosion and also ensures an efficient transmission of radiation (UV–visible, infrared according to scenario) [18]. It has been demonstrated that toughness parameter was directly related to the damage threshold in the experiments of rain erosion [19].

Targeted toughness values in mode I of about 2 MPa $m^{1/2}$ eliminate the majority of known ceramics. Materials such as diamond, sapphire (Al_2O_3), aluminum nitride (AlN) and aluminum oxynitride (AlON) have interesting properties with toughness in mode I respectively between 7 and 1.5 MPa $m^{1/2}$.

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Table 1
Deposition conditions of ZrO_2 thin films by MOCVD.

Substrate temperature (°C)	900
Total pressure (Pa)	100
Carrier gas (l min^{-1})	N_2 (0.5)
Reactive gas (l min^{-1})	O_2 (0–0.5)
Dilution gas (l min^{-1})	N_2 (0–0.5)
Total gas flow rate (l min^{-1})	1
Precursor	$Zr(thd)_4$
Solution concentration (mol l^{-1})	0.05
Injection frequency (Hz)	2
Evaporation temperature (°C)	250
Thickness (nm)	80–120

As it presents both good optical [17] and mechanical properties [20], tetragonal zirconia film could be attractive for mirrors and antennas applications. We have already demonstrated that it was possible to elaborate thin or thick tetragonal nanostructured zirconia films by MOCVD technique using appropriate experimental conditions [12]. Thus, the aim of this paper is to investigate nano-crystallized zirconia thin films for this optical application by varying the grain size, structure and oxygen partial pressure during elaboration and/or annealing of the various films.

2. Experimental

ZrO_2 thin films were prepared in a cold-wall vertical MOCVD apparatus on Si(1 0 0) wafers. Prior to the deposition, the substrates ($10 \times 10\,mm^2$) were degreased in trichloroethylene, acetone and isopropanol, then rinsed in distilled water and dried with an N_2 flow. After this cleaning procedure, they were rapidly put into the CVD reactor under vacuum. The precursor was introduced in the reaction chamber by a direct liquid injection system. A solution containing the zirconium source ($Zr(thd)_4$ thd = 2,2,6,6-tetramethyl 3,5-heptanedionate) was pushed from a bubbler (at room temperature) to a vaporizer, where flash evaporation of the micro-droplets occur, the resulting vapor being transported toward the heated samples by a carrier N_2 (0.5 l min^{-1}) and reactive O_2 gas flow varying from 0 to 0.5 l min^{-1}. An additional dilution N_2 gas flow (varying at the same time from 0.5 to 0 l min^{-1}) was also introduced in the reactive chamber when reactive O_2 gas flow was lowered in order to counterbalance this gas loss and to maintain constant the total pressure level in the chamber. The samples were called OX50, OX20, OX10, OX7, OX5 and OX0 for respectively decreasing oxygen content in the gas phase. The deposition conditions are summarized in Table 1. Zirconium β-diketonate (provided by Epichem) was dissolved in cyclohexane with a concentration of 0.05 mol l^{-1} and was injected with a 2 Hz frequency into the evaporator (250 °C). The substrate temperature was set at 900 °C, and the total pressure was held at 100 Pa. Some samples were annealed just after the deposition process in the above-described reactor at 900 °C for 1 h under two different annealing atmospheres either $N_2 + O_2$ (so-called R–O_2) or N_2 (so-called R–N_2). This deposition and annealing temperature in the whole process was self-consistent with industrial applications on ceramic substrate such as embedded mirrors for example. In that case, the films were dense and homogeneous that was expressively necessary to develop this mechanical approach. At lower temperatures, the film quality was poor and disabling.

Experimental conditions were chosen so that the films were 80–120 nm thick.

The microstructure of ZrO_2 films was studied using a LEO 1521 SEM-FEG instrument.

Crystalline structures were evaluated by Grazing incidence (2°) X-ray diffraction that was performed on a Philips X'pert pro MRD diffractometer with Cu K_α radiation (λ = 0.15406 nm). The patterns were obtained by step scanning from 27° to 37° in 2θ with an increment of 0.025° and a counting time of 200 s per step. In this peculiar 2θ range, several tetragonal (t) and monoclinic (m) peaks were encountered. They were identified according to JCPDS files no. 37-1484 and 17-923 for monoclinic and tetragonal phases respectively. The crystallite size L_{cryst} (nm) can be determined by using Scherrer's formula [3] applied on the (t) zirconia $(1\,1\,1)_t$ reflection:

$$L_{cryst} = \frac{0.9\lambda}{\beta\ \cos(\theta)} \quad (1)$$

where λ is the X-ray wavelength, θ (rad) the diffraction angle and β (rad) the well-known full width of the peak at half maximum (FWHM).

The ratio of tetragonal phase in the films was calculated by applying the Garvie ad Nicholson empirical expression [21]:

$$\%(t) = \frac{I(1\,1\,1)_t}{I(1\,1\,1)_t + I(1\,1\,1)_m + I(1\,1\,1)_m} \quad (2)$$

Stress level in the zirconia films were estimated using the shift of the $(1\,1\,1)_t$ zirconia reflection and the $\sin^2\Psi$ method [22]. Up to fifteen diffraction patterns were collected at various Ψ ranging from −60° to +60° to calculate residual stress on the tetragonal phase.

Vickers micro-indentation tests (Shimadzu) were performed on each deposited film and on a reference silicon substrate at 245.2 mN load. A set of ten prints were completed and were observed by SEM in order to measure the print diagonals, to observe possible damage surrounding the prints, as micro-cracks, buckling or even spalling for instance and also to measure the length of the cracks surrounding the prints. Of course, due to the small thickness of the films, micro-indentation was not used to estimate the hardness of the films, but only to determine the hardness of the substrate (Si) and to study the damage differences according to the various films and substrate. The Vickers hardness (Hv) of the substrate and the "pseudo" hardness of the film/substrate system were also determined for the aim of the mechanical approach.

Berkovitch nano-indentation tests (Nanotest 550, Micro-Materials Ltd.) were used to evaluate the hardness (H) of the substrate and the Young's modulus (E) of the films. As the films were very thin, the nano-indentation tests with a penetration depth of 50 nm (i.e. for a load of about 2 mN depending on the hardness) was only used to determine the hardness of the substrate and the Young's modulus of each films and substrate by using the approach proposed by Oliver and Pharr [23]. For such an experiment, ten measurements at 50 nm were made. It means ten load cycles with imposed penetration depth, the unloading part of the curves showing only the film elastic relaxation. Young's modulus was always estimated using 80% of the unloading part of the curve.

UV–Visible spectroscopy was performed on a Cary 5000 UV–Vis–NIR spectrophotometer. The wavelength was scanned from 200 to 3000 nm and a silicon slide was adopted as a reference. The spectral reflectance on single face polished samples was measured and thickness and refractive index of the ZrO_2 samples were deduced by using the well-known TFCalc thin film design software (Software Spectra). The error in the measurement of the thickness is less than 2%.

3. Results and discussion

3.1. On the microstructure and structure

Whatever the oxygen deposition conditions, the microstructure of the oxide layers presented in Figs. 1a or 2a is homogeneous with crystallite sizes varying slightly from one sample to another while keeping in the uncertainties range. For a given sample, the thickness is homogeneous on the whole surface of the sample except for the borders of the samples. The porosity of the films seems