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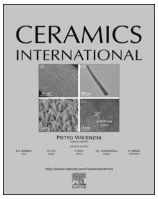

Effect of withdrawal rate on the evolution of optical properties of dip-coated yttria-doped zirconia thin films

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ABSTRACT

In this work, the Swanepoel method is described and applied for determining various optical parameters and thicknesses of dip–coated yttria–doped zirconia thin films. Using this method the influence of the withdrawal rate on optical parameters was studied. The characterization of the deposited thin films was carried out by optical microscopy and FT–IR spectrophotometry. As expected, coating thickness was closely related to the withdrawal rate and consequently influenced optical parameters such as refractive index, extinction coefficient, and absorption coefficient. Regarding the average refractive index of the prepared thin films, n is in the 2.0 – 2.2 range, the higher refractive index average value being obtained with films deposited at 25 mm min^{-1} (n = 2.19). The value of the optical band gap was also studied, this increased with withdrawal rate and was quite similar to values reported by other investigators at 50, 25 and 10 mm min^{-1}. Thus, this study proposes analysing the influence of the withdrawal rate for the manufacture of different types of thin films with previously specified optical parameters.

1. Introduction

It is well known that crystalline ceramics present an excellent combination of mechanical, thermal and chemical properties that make them highly useful for the protection of metal and glassy substrates against numerous problems, such as corrosion, erosion and high temperatures [1].

Zirconium oxide (zirconia, ZrO_2) thin films have a wide range of applications in engineering of optical materials such as reflective mirrors, interference filters, and electro-optical devices [2–5], mainly due to their unique properties such as high refractive index (2.0 – 2.2), low optical loss, large optical band gap (3.8 – 3.2 eV), and transparency [6,7]. Attending to their physical properties such as high optical dielectric constant (~25) and thermal stability can also make them suitable candidates for replacing SiO_2 films in semiconductor technology [8]. Zirconia exhibits three polymorphic phases as a function of the temperature, namely, monoclinic, tetragonal and cubic. Large volume changes occurring during phase transition into the low temperature monoclinic phase lead to undesired crack formation and the material falls into pieces [9]. Its tetragonal phase exhibits optimal mechanical properties, so in order to avoid undesirable phase transitions zirconia requires stabilization [10]. The high temperature zirconia phases (tetragonal and cubic phases) can be stabilised at room temperature by adding suitable oversized cations, stabilising the tetragonal or the cubic phase depending on the concentration of the stabiliser. Y_2O_3, containing Y^{3+} cations, is one of the most frequently used materials as a stabiliser, with the tetragonal phase being stabilised by Y_2O_3 concentrations from 2 to 8 mol%. The cubic phase is stabilised at a concentration higher than 8 mol% [11]. In addition to the stabilization, Y_2O_3 improves the thermal stability and anti-aging performance of the materials. This fact together with the abundance of yttrium resources lead to consider the Y_2O_3 an attractive dopant [12]. The stabilization mechanism of ZrO_2 by Y_2O_3 has been widely studied by Fabris et al. [13].

Although there is a wide range of possibilities for preparing oxide thin films (sputtering, physical vapour deposition, chemical vapour deposition, etc.) [14], the sol-gel method is one of the most used solution-deposition methods [15]. The basis of this technique is to coat a substrate with a precursor solution containing the requisite stabiliser in the required proportion, allowing solvent evaporation and/or chemical reactions to transform it to a gel layer. The organic components of the gel are subsequently eliminated by heat treatments, to obtain the desired crystalline thin film [16]. The sol–gel method has numerous advantages [17–19], such as the excellent adhesion and purity of the coatings obtained, low processing temperature and cost, and simplicity [20]. Moreover, incorporation of the dopant is easy by this technique [16]. Additionally, thin films may be successfully

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obtained by numerous techniques (spin–coating, electrodeposition, dip–coating, etc.) [21–23]. Among them, the immersion method, known as "dip–coating", has many advantages such as the possibility of coating large surfaces, the simplicity of the equipment, and low cost [24]. For these reasons, dip coating was selected as the coating method in the present work.

There are various methods for the assessment of the optical properties of thin films, such as Kramers-Kronig analysis, the classical oscillator fit procedure, and the Swanepoel method [25–28]. Among them, the Swanepoel method was widely used in several studies [29–32] because it enables determination of numerous optical parameters of thin films, such as refractive index, absorption coefficient and optical band gap from only the transmittance spectrum [33]. Moreover, it enables the determination of the thin film thickness [34].

In the present paper, we show the optical properties of the growth of 3 mol% yttria–doped zirconia (3YSZ) crystalline thin films made by the sol–gel method and deposited on glassy substrates through the dip-coating technique at various withdrawal rates. The optical properties were obtained using the Swanepoel method.

2. Experimental procedure

2.1. Substrates and characterization of the substrates

Patterned FTO (TEC15) glass pieces (Pilkington TEC) with a size of 30 × 20 × 3 mm, supplied by Xop Glass, were used as substrates in this work. The used glass substrates were coated with an adhesive film of Fluorine doped Tin Oxide (FTO). According to the company, these FTO-glass pieces have a visible transmission above 82% and their resistance is in the range of 12–14 Ω/sq. Fluorine doped tin oxide has been recognized as a very promising material because it is relatively stable under atmospheric conditions, chemically inert, mechanically hard, high-temperature resistant, and shows a high tolerance to physical abrasion [35]. Furthermore, this material is cheaper compared to indium tin oxide, which is one of its competitors in the market [36] and it enhances the adherence of the thin film – substrate system [37,38]. FTO glass has been used and studied by various authors, such as Chiappim et al. [37] and Q. Xiao-Dong et al. [39].

The FTO-glass test pieces were previously cleaned by immersion in an ultrasonic bath with distilled water. Then, before coating, the bare substrates were optically characterized by spectrophotometry using a Helios α spectrophotometer (Thermo Spectronic, UK) at room temperature.

2.2. Sol-gel solution preparation

The 3 mol% yttria–doped zirconia sol-gel solution was prepared in accordance with a previously reported procedure [10] by mixing two prepared solutions. The first solution was prepared by mixing and stirring zirconium (IV) n-propoxide (ZNP) with propanol (PrOH) and adding H_2O and HNO_3 in a molar ratio 1/15/6/1. The second solution was prepared by mixing Yttrium acetate (AcY) with 2-Propanol (2-PrOH), H_2O, and HNO_3 in a molar ratio 1/15/6/1. The mixture was mechanically stirred for 30 min. The mixture was finalised by adding distilled H_2O under continuous stirring conditions, maintaining these conditions for further 1 h.

2.3. Preparation of the films

The deposition of the yttria–doped zirconia films on the glass substrates was carried out in air by using the dip-coating technique. This technique is carried out through the immersion of substrates in a vessel containing the previously prepared coating solution. Therefore, a thin film adheres to the FTO-glass surface when it is vertically extracted at a given withdrawal rate [40]. In the present work, the deposition was performed at various withdrawal rates: 135 mm min^{-1}, 50 mm min^{-1}, 25 mm min^{-1}, and 10 mm min^{-1} (Table 1). During each test, the withdrawal rate was maintained constant throughout the entire test period. With the aim of evaluating the influence of withdrawal rate on the thin film optical properties and thickness, the samples were sintered at the same temperature. The sintering temperature was set at 500 °C on the basis of previous work [41,42]. The sintering process was carried out in a Nabertherm® oven for 2 h by applying heating and cooling rates of 3 °C min^{-1}. Thanks to this slow heating/cooling ramp, crack formation is inhibited by allowing the stress arising from the crystallization and thermal expansion to relax without causing fissures [43]. Furthermore, the coated samples were previously dried in the oven at 100 °C for 60 min applying the same heating/cooling rate. This previous phase of drying minimizes the content of organic residues in the coating, which reduces the stress in the film [44].

Table 1
Nomenclature used for each sample depending on the withdrawal rate.

Thin Film Sample	Withdrawal Rate (mm min^{-1})
S10	10
S25	25
S50	50
S135	135

2.4. Characterization of the films

The structural quality and the appearance of fissures and cracks in the films was checked by optical microscopy using a Nikon® Epiphot 300 reflected-light optical microscope.

The transmittance spectra of the films were acquired via conventional spectrophotometry using a Helios α spectrophotometer (Thermo Spectronic, UK) at room temperature. The experimental data were collected in the ultraviolet-visible and near-infrared ranges (λ = 300–1000 nm) with 1 nm of step width. In the measurement, air was used as a reference. From the transmittance spectra and using the Swanepoel method [26], the refractive index (n(λ)), thickness (t), absorption index (α(λ)), and extinction coefficient (k(λ)) of the films were calculated. Subsequently, the optical band gap (E_g) was calculated from α(λ) values. These parameters are considered to be fundamental for the optical characterization of thin films [45], since n(λ) and k(λ) are fundamental in the simulation of the spectroscopic characteristics of optical layers [46], α(λ) has a strong impact over the thermal efficiency of coated elements [47], and E_g is one of the most important physical parameters of crystalline, amorphous and glassy materials [48]. The accuracy of the Swanepoel method for measuring these parameters is better than 1% and, consequently, this method is clearly and excellent option in this study.

According to Parralejo et al. [49], the existence of a minimum film thickness is required to ensure the presence of interference effects in the spectrum, and this is why a single layer was deposited on the FTO-glass substrate, to generate a transmission spectrum with successive maxima and minima.

3. Results and discussion

3.1. Characterization of the substrates

The FTO glass pieces were optically characterized by spectrophotometry to obtain their transmittance spectra. Fig. 1 shows the spectrum of the FTO-glass substrate in comparison to the spectrum of glassy substrate (without adhesive film). The glassy substrate transmitted all the light reaching it, while the FTO film prevented some transmission. The visible transmission of the FTO glass reached 86.6%, which is in agreement with the information provided by the company (visible transmission above 82%).