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The Influence of Annealing Temperature on the Structural and Optical Properties of ZrO₂ Thin Films and How Affects the Hydrophilicity

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Abstract: Zirconium oxide (ZrO₂) thin films were prepared by the sol-gel dip coating technique, in combination with annealing at different temperatures in air atmosphere, with the final goal of studying the water wettability of the surface. The annealing effects on the structural and optical properties of the ZrO₂ films were investigated to check the characteristics of the material. X-ray diffraction (XRD) patterns of ZrO₂ annealed at 450 °C and 550 °C show the formation of tetragonal phase, with layers constituted by nanoparticles with average particle size of 21 nm and 25 nm, respectively. Fourier-transform infrared spectroscopy (FT-IR) spectra revealed the presence of vibrational modes associated to ZrO₂. Photoluminescence (PL) and ultraviolet-visible spectroscopy (UV-Vis) spectroscopy was used for optical properties. All deposited ZrO₂ thin films presented a high optical transparency, with an average transmittance above 70% in the visible range (400–700 nm). The hydrophilic properties of ZrO₂ films were characterized by means of the measurements of the contact angle. When the sample was annealed at 550 °C, the hydrophilicity reached the best behavior, which was explained as an effect of the structural and morphological change of the films.

Keywords: ZrO₂ thin films; hydrophilicity; annealing temperature; sol-gel; ceramic thin films

1. Introduction

Zirconium oxide (ZrO₂) is a very useful semiconductor material with several application areas such as catalyst [1], sensor of chemical species [2], corrosion resistant coatings [3], and in solid oxide fuel cells as a solid electrolyte [4]. In general, three polymorphs are known for ZrO₂: monoclinic (<1170 °C), tetragonal (1170–2370 °C), and cubic (>2370 °C) [5]. ZrO₂ is a widely studied material, due to its special properties, such as a wide band gap (5.1–7.8 eV) [6], a dielectric constant (12–25) [7,8], good mechanical strength [9], high thermal expansion coefficient [10], and excellent hydrophilic properties [11].

For the ZrO₂ films synthesis, a large variety of preparation methods have been applied: chemical spray pyrolysis [12], hydrothermal synthesis [13], electrodeposition [14], chemical vapor deposition (CVD) [15], atomic layer deposition [16], and sol-gel [17], among others. However, the sol-gel technique has been extensively applied due to some advantages, such as low temperature of synthesis and processing, surface homogeneity, control over the stoichiometry of films, large area deposition, and economic benefits [18]. Nowadays, ZrO₂ hydrophilic films have attracted scientific and technological interest due to its applications in anti-fogging and self-cleaning surfaces [11,19] and superficial painting and protecting, etc. [20]. The hydrophilic properties of ZrO₂ are determined by the following parameters:

surface roughness characteristics [11], surface chemistry, free energy, and morphology [21]. The change of hydrophilic properties of ZrO_2 after thermal treatments has become the material important for a large variety of applications, like the surface wettability controllable-switching and self-cleaning of many kinds of surfaces. This phenomenon, considered as thermo-induced hydrophilicity, is observed in the change of the water contact angle with the annealing temperature. Ye et al. [22] reported that the phenomenon can be explained by taking into account three aspects: (1) the cleansing effect, (2) the phase transition of crystal, and (3) the porosity change. Shirtcliffe et al. [23] found that tetraethyl orthosilicate (TEOS) foams are hydrophilic when they are annealed at temperatures greater than 400 °C, due to their surface chemistry starting to change, which occurs when organic groups migrate away from the surface. Meng et al. [24] reported that the annealing temperature can convert the TiO_2 thin films into a material gifted with excellent hydrophilic surfaces. In fact, poor hydrophilicity is observed in amorphous TiO_2 films; however, when the rutile phase rises by the increase of the annealing temperature, the hydrophilicity enhances. In mixed phases of anatase and rutile, where the mass fraction of anatase phase is 13%, the hydrophilicity is optimal [24]. Simon et al. [25] reported the inclusion of Poly(methyl methacrylate) and Pluronic-F127 in ZrO_2 - TiO_2 layers to obtain superhydrophilic surfaces. These authors also reported a smooth spreading and channeling of the water by means of porous structure and high roughness, named the “wicking effect”. Here, the water is drawn from the pores by the water in contact with the surface material, and by capillary and suction, which slips smoothly on the channels of the rough surface. The vast majority of hydrophilic surfaces studied are dioxide titanium based.

In this paper, we reported the effect of the annealing temperature on the structural and optical properties of the ZrO_2 films, with emphasis on the changes of the hydrophilic characteristics, synthesized by sol gel-dip coating method. The films were characterized by X-ray diffraction (XRD), photoluminescence (PL), Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle measuring.

2. Experimental Details

2.1. Preparation of Films

ZrO_2 films were deposited on glass substrates (Corning 2947, area $2.5 \times 7.5 \text{ cm}^2$) by the sol gel dip-coating method. The glass substrates were ultrasonically cleaned in a distilled and deionized aqueous solution for a couple of hours, and later they were immersed in an aqueous solution of chromic acid during 1 h, before finally being put in a nitric acid water-solution at 100 °C for 1 h. The glass substrates were immersed into the ZrO_2 growing solution at the dipping speed of 2 cm/s. The precursor solution was prepared using zirconium n-propoxide $\text{Zr}(\text{OCH}_3)_4$, and ethanol $\text{C}_2\text{H}_5\text{OH}$ as the solvent. First, a controlled amount of nitric acid was dissolved in 40 ml of ethanol by magnetic stirring for 15 min, then 9 ml of zirconium propoxide was added to the solution. The stirring was continued for 1 h to get a transparent yellowish solution. Last, the precursor solution was maintained at 7 °C for 24 h for aging. The removing rate of coated substrates was 2 cm/min. The ZrO_2 films were prepared with six coatings, each layer was kept dried at 250 °C for 5 min in an open atmosphere oven. The set of as-grown layers were dried at 250 °C for 30 min and annealed at 250, 350, 450, and 550 °C in air atmosphere after desired number of coating.

2.2. Characterization of Films

For phase analysis X-ray diffraction (XRD) (Rigaku, Tokyo, Japan) study of the thin films was carried out in a Philips X-ray diffractometer (PANalytical's X'pert PRO X-ray diffractometer), using $\text{Cu-K}\alpha$ radiation, with a wavelength of 0.15405 nm for the $20 \leq 2\theta \leq 80^\circ$ range. The voltage and current setting were 30 kV and 40 mA, respectively. The XRD data were registered with a step size of 0.02° (2θ) and 1 s per step. Photoluminescence (PL) signal was obtained at room temperature (RT) by optical excitation with a He-Cd laser, and luminescence was registered employing a Horiba/Spex 1404 0.85 m

Double Spectrometer. Perkin Elmer Spectrum GX spectrometer operating at 4 cm^{-1} resolution was used to obtain the Fourier transform infrared spectroscopy (FT-IR) (PerkinElmer Inc., Wellesley, MA, USA) spectra in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. The UV-visible transmittance spectrum (Thermo Fisher Scientific, Billerica, MA, USA) of thin films was recorded using Thermo Scientific™ Evolution 220 UV-Vis Spectrophotometer. Surface images of the films were achieved with a scanning electron microscope (SEM, Jeol JSM-6300) (SEMTECH Solutions, Inc., North Billerica, MA, USA). The roughness and surface topography of the ZrO_2 thin films were examined by AFM using a Park Scientific Inst. system. The hydrophilic properties of ZrO_2 thin films were evaluated by the contact angle measuring instrument (Dataphysics, model OCA 50) by depositing a $5\text{ }\mu\text{L}$ droplet of deionized water on the ZrO_2 thin films surface at RT.

3. Results and Discussion

3.1. X-ray Diffraction

The phase composition of the synthesized ZrO_2 thin films was characterized by XRD. Figure 1 exhibits the X-ray diffraction (XRD) patterns of ZrO_2 thin films deposited on Corning 2947 substrates at equal growth times, but at different annealing temperatures (T_a). The XRD patterns of the films sintered at $T_a = 250\text{ }^\circ\text{C}$, $350\text{ }^\circ\text{C}$, $450\text{ }^\circ\text{C}$, and $550\text{ }^\circ\text{C}$ are shown in Figure 1a–d. At the bottom of Figure 1e, the diffraction file of ZrO_2 (PDF #50-1089) is plotted. For the high T_a values, the samples present only the tetragonal crystalline phase of ZrO_2 [26]. The diffractograms of the film deposited at $T_a = 250\text{ }^\circ\text{C}$ and $350\text{ }^\circ\text{C}$ exhibit a signal associated with an amorphous material. The patterns of the films deposited at $450\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$ show both a peak with the higher intensity at 30.29° , corresponding to the (011) plane of the baddeleyite structure. These films grow with the (011) as preferred orientation. The presence of the reflection peaks at 35.28° , 50.42° , 50.75° , 60.26° , and 63.02° correspond to the (110), (112), (020), (121), and (202) planes of this same phase, respectively. The presence of some reflections from other phases are not observed. From the XRD patterns, it can be deduced that the as-deposited ZrO_2 thin films remain amorphous until $T_a < 350\text{ }^\circ\text{C}$. However, other authors have observed that by adding a low concentration of sulfur the crystallinity arises even at T_a as low as $200\text{ }^\circ\text{C}$, stabilizing predominantly the tetragonal phase [27]. Garvie found that the tetragonal phase stabilization in ZrO_2 can be attributed to crystal-size effects [28]. The increasing sharpness of the XRD peaks with increasing temperatures indicates the gradual ripening of the ZrO_2 phase, and gradual growth of tetragonal ZrO_2 crystallites. These results are in agreement with those of Cassir et al. [29], and Li and Su [30], who obtained non-crystallized deposits close to $250\text{ }^\circ\text{C}$ and $350\text{ }^\circ\text{C}$, as well as Lin et al. [31] and Lin et al. [32], who obtained crystallized deposits close to $450\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$. From the XRD patterns, the Full Width at Half Maximum (FWHM) of the diffraction reflection, $\lambda = 1.5406\text{ }\text{\AA}$ is the X-ray wavelength (for $\text{CuK}\alpha$ line), θ is the angle of reflection, and $K = 0.94$ is the shape factor was used to estimate the crystallite size (CS) using the Scherrer formula [33]. An XRD pattern of silicon wafer was used for instrumental error compensation and calibration of JADE 6.5® analysis software. For $T_a = 450\text{ }^\circ\text{C}$ the average crystallite size was around 21 nm , which slightly increases to 25 nm for $550\text{ }^\circ\text{C}$. Similar results have been reported in the literature: 17 nm , 20 nm , and 22 nm at $450\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$, respectively [34–36].

Figure 1. X-ray diffraction (XRD) patterns of Zirconium oxide (ZrO_2) thin films annealed at different temperatures (a) 250 °C, (b) 350 °C, (c) 450 °C, and (d) 550 °C. (e) At the bottom, the standard JCPDS card data for tetragonal ZrO_2 are provided as references (PDF #50-1089).

3.2. FT-IR Spectroscopy

For the vibrational properties study, FT-IR spectrometry was employed, FT-IR spectra of the as-prepared and annealed zirconia thin films measured along the 400–4000 cm^{-1} range are presented in Figure 2. The FT-IR spectra were employed to check the formation of nanocrystalline zirconia in the tetragonal phases. The most vibrational bands observed in the spectra corresponds to bonds existing in ZrO_2 . The metal and oxygen bonds (Zr-O) are situated between 400 and 820 cm^{-1} [37–39]. The weak bands at 1260 cm^{-1} can be associated to carboxylate (COO^-) groups [40]. Navio and coworkers reported that, for the ZrO_2 tetragonal phase stabilization, the oxygen ion vacancy density needed may be originated only if carbonaceous material is present in the oxide lattice. In this manner, the stabilization, to a high degree, of tetragonal ZrO_2 structure is induced by carbon impurities [41,42]. The signal centered at 1350 cm^{-1} can be ascribed to stretching modes of terminal groups Zr-O- [43]. As per Bermúdez et al., the peak in the vicinity of 1610 cm^{-1} and the peak within the region, 1150–1350 cm^{-1} are characteristic of tetragonal ZrO_2 [44]. Peaks of around 1610 cm^{-1} and 3600 cm^{-1} are attributed to the vibration modes of the –OH bond related hydroxyl groups [45,46], and the one at around 2200 cm^{-1} to CO_2 [47]. These vibrational modes, come of OH from ambient, and CO_2 from ambient and solution residual [48].

Figure 2. Fourier transform infrared (FT-IR) spectra of ZrO₂ samples after annealing at different temperatures.

3.3. UV-Vis

A wide distribution of light wavelength absorption is an important property should possess every good photocatalyzer [49]. The optical transmittance (T_o) spectra of the ZrO₂ thin film deposited at 250 °C, 350 °C, 450 °C, and 550 °C are shown in Figure 3a. The thin films exhibit continuous transmittance across the UV-vis spectrum, with decreasing transmittance near the UV region. The ZrO₂ films of this work showed a high transparency, with an average optical transmittance >70% in the 400–700 nm range, that enables them for transparent electronic applications, moreover, the absence of interference fringes indicates the films are thin, and the lack of multiple reflections at the air/film and film/substrate interfaces, facilitates a maximum transmittance of light through the films volume [50]. In addition, the presence of no fringes assures thickness uniformity. A shift of the transmittance curves toward the region of lower wavelength values is observed, which suggested a decrease of the thin films thickness, which supports the profilometer results on the increase of annealing temperature; moreover, different research groups have reported similar observations on other ZrO₂ films [51–54]. This variation (wavelength shift) of the optical properties plays also as a basic requirement for a material that modifies its photocatalytic behavior. The direct optical bandgap was calculated using the Tauc's method, $(\alpha h\nu)^2$ data was plotted versus the photon energy ($h\nu$), the extrapolation of the linear section of the curve to $(\alpha h\nu)^2 = 0$, that is the energy axis, as observed in Figure 3b–e, provides the E_g value. Here, α is the optical absorbance coefficient ($\alpha = [\text{Log}(100/T_o)] / [\tau \text{Log}e]$). The all E_g values have been determined to be, 4.0 ± 0.1 , that is, E_g has, within the error bar, practically the same value for all T_a s. It is well known that a population of localized states intervenes as an important factor to alter sensitively the states into the band gap. This density is generally attributed to the presence of impurities, defects, and disorder into the material lattice, which, in turn, leads to the decreasing E_g . Nevertheless, the crystalline quality is, in general, improved with T_a s, thus, it can enlarge the E_g value [55]. In our case, both effects can be compensated. The high T_a values help to reduce the density of defects and disorders in the material, so the density of the local states also decreases. The transmission peaks in the low wavelength region can arise (see Figure 3a), due to the valence band to conduction band transition [56]. However, these peaks in the transmission spectra are located at lower energy, as compared with the optical band gap 5.00 eV reported for bulk ZrO₂ [57]. The result indicates that a considerable contribution from states exists, so that affects the transmission in that region. A large amount of surface defects can appear on the zirconia nanocrystals, due to their high surface/volume ratio [58,59]. It is worth noting that the

E_g values obtained in our study are comparable with most of the ones reported in samples prepared by others processes [60–62], and have even more similarity with those reported for ZrO_2 thin films prepared by Carević et al. (4.10 eV) [63] and Vaizogullar (4.11 eV) [64].

Figure 3. (a) Transmittance spectrum of ZrO_2 thin films at different annealing temperature. (b–e) Band gap was determined by optical method using $(\alpha h\nu)^2$ versus $h\nu$ plots.

3.4. Photoluminescence Spectroscopy

The photoluminescence (PL) technique is one of the most used optical methods for the semiconductor analysis. It has a powerful and sensitive ability to find presence of impurities, exciton fine structure, and defects, which commonly affect the material quality. High purity ZrO_2 shows, in general, several broad emission-bands, which depend on the preparation techniques and excitation energy [65]. ZrO_2 thin films of 250 °C and 350 °C mainly present two emission signals: one centered at 423 nm (2.93 eV) and the other at 532 nm (2.33 eV). For the 450 °C and 550 °C samples, three emission bands are present: one centered at 414 nm (3 eV), 434 nm (2.86 eV), and 532 nm (2.33 eV). The observed photoluminescence in ZrO_2 films is probably due to non-stoichiometric material because an oxygen

deficiency, originated by oxygen vacancies, formed when ZrO_2 is synthesized [66]. Most peaks present in the PL spectra are transitions involving defects, which are after modified due to different T_{as} . therefore, an evident variation of the PL bands intensity for the different films is expected. A representative fluorescence spectrum excited with a wavelength of 325 nm and measured at RT, shown in Figure 4, exhibits four emission PL bands. The PL peak at 414 nm has been associated to Zr^{4+} vacancies, which is one of most intense peaks considered to be originated from emissions of free-exciton recombination at near band edge (NBE) [67]. Liang et al. [68] have reported that large amounts of surface defects should exist on the as-synthesized ZrO_2 crystallites, because of the relatively high surface area. In the case of the emission at around 423 nm, it has been assigned to electron transitions from F-centers excited states to the ground state [69]. This emission can be compared with the 425 nm (2.92 eV) PL emission band in $\text{Zr}_{1-x}\text{Mn}_x\text{O}_2$ prepared by chemical synthesis and associated to oxygen vacancies, as reported previously by Pattanaik et al. [70]. Selvam et al. reported that oxygen-vacancies present in the lattice of ZrO_2 nanocrystals are responsible for that PL emission [46]. The blue band at 434 nm is originated by singly ionized two-oxygen-vacancy $(\text{F}-\text{F})^+$ defects [71]. The peak at 532 nm could be ascribed to the emission from NBE transitions [65]. In the case of the complete emission band, transitions from all the mid-gap trap states are involved, such as surface defects and oxygen vacancies (O_v), grain boundaries [72].

Figure 4. Photoluminescence (PL) spectra of ZrO_2 thin films measured at different annealing temperature.

3.5. Scanning Electron Microscope

The micrographs were recorded using an accelerating voltage of 1.0 kV with a $\times 50,000$ magnification. The micrographs of ZrO_2 thin films were recorded in samples with the different T_{a} values studied. Figure 5a shows a sample which mostly presents a flat surface, is highly homogeneous, and has no cracks, and also looks somewhat spongy, with some surface imperfections like dark spots, which probably are a product of polycondensation (sol/gel) and/or densification cases. In Figure 5b, the film looks something dense without any cracks, scales, or pores. In addition, some bulges and pits irregularly distributed on the surface were observed [73]. It is believed that this fact is related to the crystallization of the thin film and with the formation of ZrO_2 . For the samples annealing at 450 °C and

550 °C (Figure 5c,d), it can be observed that both thin films are polycrystalline. Figure 5c shows that the thin film has a high homogeneity on the surface, with some nanocrystals with the size dispersed in the 30–60 nm interval. In addition, these nanocrystals are distributed non-uniformly and discontinuously on the surface of the ZrO₂ sample, as shown in Figure 5d. The size of nanocrystals can increase up to ~100–150 nm, because they gradually agglomerate, giving place to a particle whose size augments as the annealing temperature increases. The shapes and sizes of these nanocrystal are found to depend on the annealing temperature. It can be observed that these shapes gradually transform from nanocrystal shapeless at 450 °C, until exhibiting tetragonal morphology at 550 °C [74].

Figure 5. Scanning electron microscopy (SEM) images of ZrO₂ thin films at different temperatures of annealing: (a) 250 °C (b) 350 °C, (c) 450 °C, and (d) 550 °C. In the images, the white bars at the bottom indicate 100 nm.

3.6. Atomic Force Microscopy

In order to further investigate the effect of the annealing temperature on the surface appearance of the ZrO₂ thin films, a quantitative method for examining the morphology and structure is obtained, studying the roughness of AFM surface measurements. Figure 6a,c,e,g shows three-dimensional AFM images where the surface morphology can be appreciated. Figure 6b,d,f,h shows the roughness taken over 2 μm $\times$ 2 μm area of the surface coatings. The thin film roughness after the treatment at different T_{as} , determined by the AFM analysis, can be seen in Figure 6i. Figure 6i shows the thickness versus T_{a} plot. The mean roughness (MR), and root mean square roughness (RMSR), which represent the arithmetic average of the deviations from the median plane, are displayed in the upper inset. Area measure of the surface imperfections. Our results show a small increase in roughness after thermal annealing. As shown in Figure 6a, the surface roughness of the as-grown ZrO₂ thin film is 0.312 nm, the increase in roughness after thermal annealing can be explained by the grain growth, the sintering process and some structure densification of the films [75,76].

Figure 6. Cont.

Figure 6. Three-dimensional atomic force microscopy (AFM) images of ZrO_2 thin films of annealed at different temperatures: (a) 250 °C, (c) 350 °C, (e) 450 °C, and (g) 550 °C. Roughness was taken over areas of $2 \mu\text{m} \times 2 \mu\text{m}$ of the coatings at (b) 250 °C, (d) 350 °C, (f) 450 °C, and (h) 550 °C. (i) Thickness versus annealing temperatures (T_a), the upper inset shows the mean roughness (MR) and the root mean square roughness (RMSR) vs. T_a . Lower inset shows MR and RMSR in percent values vs. T_a .

3.7. Measurement of the Contact Angles

The contact angles (CAs) of the water drop can be observed in snapshot images showing the on the samples, annealed with different T_a , are shown in Figure 7a–d. The contact (or wetting) angle is a measurement of the surface-surface wettability of a solid by a liquid. $CA > 90^\circ$ (high contact angle) is interpreted as unfavorable wetting, in this way, the fluid minimizes contact with the surface and forms a compact liquid droplet. Surfaces with $CA > 90^\circ$ are classified as hydrophobic, which show low wettability, adhesion, and surface free energy. When $CA < 90^\circ$, the surface is considered as hydrophilic. The Young-Laplace equation explains the drop-surface profile [77]. A simpler Young-Laplace approach is to consider that the drop profile is a spherical section. Under this assumption, we will applied the well-known A/2 method suggested to measure the drop CA. Here, three to five points on the surface drop are chosen to quickly obtain the sphere parameters. In this way, the corresponding static CA (θ) is calculated by obtaining several data of the diameter D and the height A of a drop [78]:

$$\frac{\theta}{2} = \frac{180}{\pi} \tan^{-1}\left(\frac{2A}{D}\right) \quad (1)$$

Figure 7. (a–e) Contact Angle of ZrO₂ thin films at different annealing temperatures (Ta).

Provided the drop volume is considered as a very small one, the gravity effect may not be taken into account as compared with the liquid surface tension, and the spherical assumption is enough valid with little random error [79]. The water drops volume for this work was set to be ~5 μ L. As shown in Figure 7a–d, the hydrophilicity of film for Ta = 550 °C is better than for 250 °C, 350 °C, and 450 °C. According to theory, CA is drastically influenced by the surface tension [80]. Figure 7e shows that the CA versus Ta plot for the four thin films studied describes a high linear inverse relation. This fact can be, in part, attributed to the surface roughness, added to defects formed on the surface (oxygen vacancies) [81]. The modification of the surface by thermal treatments influences the wettability of the samples, as shown in Figure 7.

The effect of annealing on most oxides is to provoke oxygen vacancies (O_v), whose density increases in a larger degree at the surface when Ta increases, where ZrO₂ is one of them [82]. The O_v influences, besides the roughness factor, the wettability properties of solid surfaces [81]. Some existent theories on the hydrophilicity contain an admissible explanation on the wettability of a liquid on a hydrophylic surface, which, for this work, should be considered in relation to the polar character of the H₂O molecule, because here, the effect of the surface charged defects (vacancies, impurities, etc) on the dipolar charge O^{2-} - $2H^+$ intervenes, that is, the dipolar charge of H₂O molecule is affected by the lack of electrical neutrality of surface. In Figure 8, a schematic image [83] of the ZrO₂ (011) tetragonal surface (the films present high preferred orientation along the (011) direction) with H₂O molecules, is represented in the case of (a) the hydrophobic character with no O_v on the surface, and (b) with O_v generated by the annealing.

Figure 8. Schematic diagram of the tetragonal (111) surface of ZrO_2 for hydrophobic (a) and hydrophilic (b) properties of the material. Dot lines represent the two dipoles obtained from the two H^+ with O^{2+} in the H_2O molecule.

4. Conclusions

The structural, morphological, and optical properties of ZrO_2 thin films, prepared by means of the sol-gel method using a simple precursor, were discussed in this work. The influence of annealing on the optical and structural properties of tetragonal ZrO_2 and, mainly, on the water wettability of the films. As the prepared samples are amorphous, they stay like this up to $T_a \approx 350^\circ\text{C}$. For $T_a = 450$ and 550°C , the ZrO_2 becomes crystalline. The crystallite size of the ZrO_2 thin films, increased as T_a increases, indicates improved crystallinity. Band gap energies of all the synthesized samples were estimated using the Tauc formulas. It was shown that ZrO_2 thin films in this work have a narrower band-gap than the bulk of those reported. The E_g of the samples lies between 3.929–4.037 eV. PL of the thermal annealed ZrO_2 films was studied for the different T_a values, lower PL intensity suggested more numbers of surface defects and oxygen vacancies. These results corroborated SEM analysis that evidenced homogeneous surface of the film, with an absence of cracks and good adhesion to the substrate. The surface morphologies of the ZrO_2 thin films showed that the mean and Rms roughness of the thin films increases with the increase of the annealing temperature. Measurements of the contact angles suggested that the decrease in contact angles with temperature is more sensitive to the change in water surface tension. The increase of the crystallite size, the augmentation of oxygen vacancies, and the roughness can influence the transformation of ZrO_2 from a low-hydrophilic to a high-hydrophilic material.

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