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# Effects of annealing temperature on the structural and photoluminescence properties of nanocrystalline ZrO<sub>2</sub> thin films prepared by sol–gel route

K. Joy\*, I. John Berlin, Prabitha B. Nair, J.S. Lakshmi, Georgi P. Daniel, P.V. Thomas

Thin film Lab, Post Graduate and Research Department of Physics, Mar Ivanios College, Thiruvananthapuram 695015, India

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# ABSTRACT

Highly transparent nanocrystalline zirconia thin films were prepared by the sol-gel dip coating technique. XRD pattern of  $ZrO_2$  thin film annealed at 400 °C shows the formation of tetragonal phase with a particle size of 13.6 nm. FT-IR spectra reveal the formation of Zr-O-Zr and the reduction of OH and other functional groups as the temperature increases. The transmittance spectra give an average transmittance greater than 80% in the film of thickness 262 nm. Photoluminescence (PL) spectra give intense band at 391 nm and a broad band centered at 300 nm. The increase of PL intensity with elevation of annealing temperature is related to reduction of OH groups, increase in the crystallinity and reduction in the non-radiative related defects. The luminescence dependence on defects in the film makes it suitable for luminescent oxygen-sensor development. The "Red shift" of excitation peak is related to an increase in the oxygen content of films with annealing temperature. The "Blue shift" of PL spectra originates from the change of stress of the film due to lattice distortion. The defect states in the nanocrystalline zirconia thin films play an important role in the energy transfer process.

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# 1. Introduction

Thin films of ZrO<sub>2</sub> have attracted special interest owing to their advantageous properties of being highly homogeneous, transparent and their applications in optical storage elements, scintillators and luminescent oxygen-sensors [1]. Of the many techniques used to prepare thin films, sol-gel fabrication has gained much interest because of its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, chemically homogenous films over large areas that can provide integration with other circuit elements. The sol-gel method can be successfully used for the preparation of pure oxide films applied in electronics and optics [2]. The synthesis of advanced ceramic materials as nanocrystals is one of the major fields in materials processing technology. Advantages of nanocrystalline films are superior phase homogeneity, sinterability and microstructure leading to unique mechanical, electrical, dielectric, magnetic, optical and catalytic properties [3,4].

Thermal annealing is a widely used method to improve crystal quality and to study structural defects in materials. Due to annealing, the structure and the stoichiometric ratio of the material will change. Such phenomena can have major effects on the optical properties, particularly the photoluminescence properties. Advanced materials for luminescent oxygen-sensors require modified surface with efficient oxygen exchange property and transparency high enough for luminescent light output.

Photoluminescence studies provide information about a material on electronic band transitions, structure, defects and chemical composition. The exciton luminescence and intrinsic defects related luminescence are known in a number of oxides. For ZrO<sub>2</sub>, the photoluminescence is of much interest for both theoretical and experimental investigations [5–7]. Some researchers observed a broad PL emission at 480 nm for bulk ZrO<sub>2</sub> [8,9], 385 nm for nanosized ZrO<sub>2</sub> [10] and 390 nm for ZrO<sub>2</sub> thin films [11], induced by UV irradiation.

However, not many studies have been done on the origin and the variation of PL properties of nanocrystalline ZrO<sub>2</sub> thin films with annealing temperature, especially on the UV-blue PL properties. If tough films are used, the abrupt interfaces that will appear in the multilayered devices will produce localized dielectric breakdown at weak spots, especially when the layers are very thin. When the films are not transparent, there is absorption and scattering of the emitted light [12]. Because of this, the devices do not have good resolution of PL peaks, contrast and efficiency. The sol-gel zirconia contains a large amount of OH groups. The existence of OH groups also results in shorter decay times and quenching of luminescence. Several reports are available on the optical properties of zirconia thin films [13–17], but in all these reports the transparency of the films is low, which restricts their use as good photoluminescent materials in optical applications.

<sup>\*</sup> Corresponding author. Tel.:+91 471 2531053; fax: +91 471 2530023. *E-mail address:* jolly2jolly@gmail.com (K. Joy).

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In this paper, we report the preparation of nanocrystalline transparent zirconia thin films by inorganic precursor route using zirconium oxychloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ). The sol was kept at an elevated temperature during deposition. An indigenously fabricated dip coating apparatus was used for coating. We investigated the structural and optical properties of the tetragonal thin films with special attention on its PL properties.

## 2. Experimental details

In the present study, inorganic precursor route was chosen for the fabrication of nanocrystalline transparent zirconia thin films. Zirconium oxychloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) (Zigma-Aldrich 99.5%) was used for the preparation of the precursor solution [18]. A homogeneous solution (2 wt%) of zirconium oxychloride octahydrate in 2-butanol and ethanol (in the ratio 1:1) was prepared, by mixing 1 mole of zirconium oxychloride octahydrate in 1/3 of the total volume of mixed 2-butanol and ethanol. The solution was stirred for 45 min using magnetic stirrer. The water for hydrolysis and nitric acid for oxidation were then added to the salt–alcohol solution. Subsequently, the rest of 2-butanol and ethanol mixed with the required amount of acetylacetone, were added under vigorous stirring in a controlled manner. The stirring was continued for another 90 min to get a clear transparent sol–solution.

The precursor solution thus prepared, was heated to 40 °C and deposited onto clean and chemically etched corning glass substrates, using the dip coating apparatus. The coating parameters were optimized as 10 cm/min lifting speed and 90° vertical lifting, depending on the viscosity and concentration of the precursor solution. The dip coated films were dried at room temperature and pre-fired at 150 °C for 1 h. This process of coating and drying was repeated 12 times, as 12 coatings were required to obtain useful data from X-ray diffraction characterization. The decomposition temperature of zirconium organometallic compounds is approximately 450 °C [19]. Four sets of temperatures 200, 300, 400 and 500 °C were selected for annealing the films. The samples were heated at the rate 4 °C/min and held at these temperatures for 1 h each, during the course of annealing. The films were then cooled to room temperature at the same rate. The structural and optical characteristics of these films were studied.

Crystalline phase of the Zirconia thin films was characterized by X-ray diffraction (XRD) using the X-ray diffractometer (Model—PW 1710 PHILIPS). The FT-IR spectra of the gel powder have been recorded in the 4000–400 cm<sup>-1</sup> range with the Perkin-Elmer 1600 Fourier Transform instrument using the KBr pellet technique. Optical transmittance was studied using a spectrophotometer (Model—JASCO-V550). PL spectra were recorded using a Perkin-Elmer Fluorescence Spectrometer (Model-LS55) with a 40 W Xenon Lamp as the excitation source and 2.5 nm excitation and emission slit width.

#### 3. Results and discussion

#### 3.1. X-ray diffraction studies

The X-ray diffraction spectra of sol-gel derived  $ZrO_2$  thin films (12 layer coatings) on corning glass substrates annealed at different temperatures 300, 400 and 500 °C are shown in Fig. 1. The spectra revealed that  $ZrO_2$  coatings remained in the amorphous state up to 300 °C. In our study it was observed that  $ZrO_2$  thin films annealed at the relative low temperature of 400 °C attained crystallinity, having tetragonal (T) phase of zirconia ( $2\theta$ =30.31°, 50.55° and 60.59°) with preferred orientations in T



Fig. 1. XRD pattern of nanocrystalline  $ZrO_2$  thin films (12 coatings) on corning glass annealed at 300, 400 and 500  $^\circ\!C.$ 



Fig. 2. FT-IR spectra of the gel heat- treated at different temperatures.

 $(1\ 1\ 1)$  plane. The intensity of the  $(1\ 1\ 1)$  peak was enhanced in the film annealed at 500 °C. The grain size of the nanocrystalline film was calculated from the FWHM of the diffraction peak  $(1\ 1\ 1)$  using the Scherrer equation [20]

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where *D* is the grain size, K=0.9 is a correction factor,  $\beta$  is the full width at half maximum (FWHM) of the most intense diffraction plane,  $\lambda$  is the wavelength of X-ray (CuK<sub> $\alpha$ </sub> radiation  $\lambda=1.5405$  Å) and  $\theta$  is the Bragg angle.

The grain size of the thin film increased from 13.6 nm at 400 °C to 15.5 nm at 500 °C. The (1 1 1) peak position also shifted from 30.31° to 30.49°. The calculated lattice constant(c) for the films annealed at 400 and 500 °C are equal to 0.510 and 0.509 nm, respectively. The changes in  $2\theta$  angles of (1 1 1) peak and lattice constants indicate a change in the stress [21] in zirconia thin film, with the increase in temperature.

### 3.2. FT-IR spectroscopy

Fig. 2 shows the FT-IR spectra of the gel, heat treated at different temperatures. The FT-IR spectrum, of the gel heat treated at 200 °C, showed an absorption band at 465 cm<sup>-1</sup>. This band was shifted to 484 cm<sup>-1</sup> on heating the gel at 500 °C. The peaks 465 and 484 cm<sup>-1</sup> are attributed to Zr–O stretching in

tetragonal ZrO<sub>2</sub> [22,23]. This shift in the absorption band at 465 cm<sup>-1</sup> to a higher frequency, with increase in annealing temperature, is attributed to an increase of the Zr–O bond strength. This can also be correlated to the crystallization with increase in temperature as is evident in the XRD spectra. The bands observed at about 1450–1578 cm<sup>-1</sup> are characteristic of Zr–O–C species. The bands at 3200–3600 cm<sup>-1</sup> are characteristic of OH groups. Absorption due to C–H vibrations was also observed at around 2335 and 1381 cm<sup>-1</sup> and that of C–C vibrations at 1635 cm<sup>-1</sup>. The –CH<sub>2</sub> distribution peak is shown at 1029 cm<sup>-1</sup>. With thermal treatment, the absorption due to Zr–O–C and OH groups decreased and eventually disappeared while that of Zr–O–Zr increased with the temperature [24].

#### 3.3. Optical studies

Fig. 3 shows the spectral transmittance of nanocrystalline  $ZrO_2$  thin films (12 coatings) on corning glass, annealed at different temperatures. The optical constants of zirconia thin films are highly influenced by the structure[25], composition and method of fabrication. Roughly, the spectrum can be divided into two regions: a transparent oscillating region and a zone of strong absorption, where the transmittance decreases drastically. If thickness is not uniform or is slightly tapered, all the interference effects will be smoothed out in the transmission curve. The presence of these oscillations in the Fig. 3 is indicative of the homogeneity and uniform thickness of the films [26,27].

The film thickness, porosity and refractive index of nanocrystalline transparent  $ZrO_2$  thin films, at different annealing temperatures, have been determined (Table 1) from the transmittance spectra following Swanepoel's envelope method [17,26]. An average transmittance greater than 80% was observed for all the annealed samples in the visible region. The high average value of transmittance in the visible region is indicative of homogeneity and chemical



**Fig. 3.** Transmission spectrum of nanocrystalline  $ZrO_2$  thin films on corning glass (12 coatings) annealed at (a) 200 °C (b) 300 °C (c) 400 °C and (d) 500 °C.

#### Table 1

Thickness, refractive index, porosity and average transmittance ( $\lambda = 550 \text{ nm}$ ) of the nanocrystalline ZrO<sub>2</sub> thin films (12 coatings) annealed at different temperatures.

Annealing Temperature T <sub>a</sub> (°C)	Thickness (nm)	Refractive index <i>n</i>	Porosity	Transmit- tance T (%)
200	514	2.01	0.208	88
300	505	2.02	0.197	83
400	338	2.15	0.056	83
500	262	2.18	0.022	82

purity. It was also seen that the interference fringes shifted towards the lower wavelength (blue shift) region with the increase in annealing temperature, which is compatible with a lower optical thickness, increase in oxidation and change in packing density (Table 1) [28]. Broadening of peak fringes was also caused by the decrease in thickness with temperature. As temperature was increased, the refractive index of the films increased, getting closer to the value (2.2) reported for pure ZrO<sub>2</sub> [29]. This behavior is compatible with the phase transformation (Fig. 1), which accounts for the decrease in transparency due to the presence of tetragonal ZrO<sub>2</sub> in the film [30]. The decrease of transmittance and the increase of refractive index can be ascribed to the decrease in porosity. Film thickness decreased with temperature vielding the desired zirconium oxide, deposited on the substrate. Optimum processing temperature, which resulted in high quality zirconia films, is 500 °C in terms of minimum film thickness, minimum transparency, minimum porosity and the desired phase formation (Table 1).

# 3.3.1. Photoluminescence

Fig. 4 shows the excitation and PL spectra, obtained for nanocrystalline transparent ZrO<sub>2</sub> thin films on corning glass with different numbers of coatings, annealed at 500 °C. The PL spectra of the films exhibit an intense peak at 391 nm and a broad band at 300 nm. Monitoring of the 391 nm emission band revealed that excitation at 243 nm produced a large intensity. It is well established that defects and vacancies in semiconductors and insulators can lead to the formation of localized states near the conduction band edge. The perturbations due to defects and impurities are characterized by discrete energy levels that lie within the band gap. When the concentrations of such (structural or composition) defects become sufficiently large, they may either segregate to form cavities or distribute in the atom network. Intrinsic (delocalized) states may then be affected by the resulting distortion of the lattice. The principal intrinsic defect in nanocrystalline zirconia is anion vacancies. UV irradiation of this dielectric insulator gives rise to broad absorption in the 240-900 nm spectral region. This has been assigned to the formation of electrons (F and F<sup>+</sup> centers) [31]. Two different mechanisms have been proposed to explain ZrO<sub>2</sub> luminescence [32,33], an impurity luminescence center model and a structure defect model—electron trapping by the anion vacancies  $(F^+ singly)$ ionized oxygen vacancies). The sol-gel process leads to the existence of large amounts of surface defects (oxygen-vacancy) in ZrO<sub>2</sub> nano thin films due to their large surface area [34]. Currently, the structure defect model mechanism is generally accepted.



Fig. 4. Excitation (left) and PL (right) spectra of nanocrystalline  $ZrO_2$  thin films on corning glass annealed at 500  $^\circ\text{C}.$ 

The broad emission band at 300 nm can be ascribed to the radiative decay of self- trapped excitons, which is created by optical excitation across the gap inducing an electron-hole pair. Analogous nature has been proposed for a broad emission observed from single crystals of zirconia [35]. The 391 nm zirconia emission peak can be due to the capture of electrons by oxygen vacancies from the conduction band [31]. In zirconia thin film prepared by sol-gel method, the groups coordinated on the surfaces of the films such as Zr(OH) could form electronic states different from those of bulk component. They may form dangling Zr bond during the condensation and dehvdration process. Because of these surface states, dangling bonds and other factors (such as the influence of  $O_2$  in the atmosphere), there are many  $Zr^{4+}$  defect sites. The existence of such defect  $Zr^{4+}$  sites (more likely at irregular near-face sites) may photogenerate Zr<sup>3+</sup> centers by electron capture. The excitation band corresponds to the spectral range of the extrinsic absorption of ZrO<sub>2</sub> caused by preexisting defects [36]. The energy gap of tetragonal ZrO<sub>2</sub> phase is greater than 5 eV [37]. The excitation band at 243 nm (5.1 eV) corresponds to energy near the energy gap of ZrO<sub>2</sub> tetragonal



**Fig. 5.** (a) Excitation spectra of nanocrystalline  $ZrO_2$  thin films (12 coatings) on corning glass annealed at different temperatures. Inset shows the red shift of the excitation peaks. (b) PL spectra of nanocrystalline  $ZrO_2$  thin films (12 coatings) on corning glass annealed at different temperatures. Inset shows blue shift of the emission peaks.

phase. It was seen that PL intensity increased as the number of coatings increased. Further a nine-fold increase in the intensity of the PL was affected by the increase of thickness of the film from  $\sim$ 35 to 262 nm (1 coating to 12 coatings). This increase in the emission intensity is due to the increase in surface density of the photoexcited electrons and holes, which governs the behavior of the charge carriers in the intrinsic defect states.

Fig. 5a and b shows the PL spectra of nanocrystalline ZrO<sub>2</sub> thin films (12 coatings) on corning glass annealed at different temperatures. It was seen that with the increase of temperature, the luminescent peak intensity increases. The variation in the PL intensity with temperature is effected by the crystallinity of the films [22] and the quenching mechanism by OH groups [38]. This clearly indicates the reduction of OH groups and increase in Zr–O–Zr, by increasing the treatment temperature, as is evident in the FT-IR spectrum (Fig. 2). In addition at low temperature the oxygen sub-lattice may contain many defects, both inside the film and at the surface [39]. Such defects would be expected to produce various non-radiative centers and hence reduce light emission. After annealing at high temperature, these non-radiative related defects could be reduced and re-structured with a consequent increase in PL.

It can also be seen that the position of excitation peak exhibits a red shift and the emission peak exhibits a blue shift from 397 to 391 nm, with increase in annealing temperature. A red shift in the excitation peak of zirconia thin films, is observed when increasing the annealing temperature [40,41]. This latter shift might be due to an increase in the oxygen content of the films. Hence, the increased oxygen content implies a lower number of such oxygen vacancies. Less number of oxygen vacancies implies a decrease in the band gap energy [31]. The blue shift of the emission peak for the samples treated at lower temperature, is much larger. The blue shift from 397 to 391 nm is believed to originate from the change of stress in the thin film due to lattice distortions [39].

## 4. Conclusion

Homogeneous nanocrystalline  $ZrO_2$  thin films have been fabricated from  $ZrOCl_2 \cdot 8H_2O$  on corning glass substrates by sol-gel dip coating method by keeping the sol at an elevated temperature. The films were crystallized in a pure tetragonal structure at a low annealing temperature 400 °C. An average transmittance greater than 80% was obtained for the film of thickness 262 nm, annealed at 500 °C. The increase of PL intensity with increase in annealing temperature is related to their crystallinity, reduction of OH groups and decrease in the non-radiative related defects. The red shift in the excitation peak is due to the reduction in oxygen vacancies. The blue shift in the PL peak is because of the change of stress in the thin film. Thus the modified sol-gel method allows one to fabricate highly transparent nanocrystalline zirconia thin films with a refractive index 2.18 and intense PL emission in the range 350–440 nm.

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