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Studies on ZrO_2 Thick and Thin Films: Structural, Morphological, Optical and Microstructure Behaviour

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ABSTRACT

In present work we have synthesized ZrO_2 thick and thin film by different techniques. Prepared ZrO_2 thick and thin films were investigated by different analytical techniques such as XRD, FESEM, FETEM, and UV-Visible spectral studies. From these studies, it was observed that the size of the synthesized films is found within 25 nm and 7 nm crystallite sizes for thick and thin film respectively. Crystanality, grain size, band gap, activation energy and other for both films were discussed, interpreted and reported. Comparative studies in all aspects were presented in this work.

1. Introduction

ZrO_2 has potential as a thermal barrier coating in devices due to its low thermal conductivity [1]. Zirconium oxide possesses the amazing ability to conduct electricity through the migration of oxygen ions (O^{2-}) [2]. Therefore, in the present work it is used to fabricate thick film resistor. This property is seen at temperatures above 250 °C. ZrO_2 has been widely used for various applications such as semiconductor in dye- sensitized, solar cell, fuel cell, transparent optical device, optical coatings, solid electrolytes for gas sensors, for medication, and resistive gas sensors [3-7].

Sensors in the form of thick films are very attractive and have been widely used in gas sensing application. The main advantages of thick film sensors are simple construction, small size, good sensitivity, selectivity, quick response and fast recovery time, low operating temperature, high stability, good accuracy, easy processing, reproducibility, low Cost and low consumption. It is flexible and versatile technology wherein resistors and capacitors of various values, combinations can be fabricated with basic thick film functional materials with desired pattern on substrates [8].

The spray pyrolysis technique has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells. The properties of deposited thin films depend highly on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process parameters [9,10]. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystalline, etc. Processes involved in spray pyrolysis technique, such as atomization of the precursor solution, aerosol transport, and decomposition of the precursor are discussed in this review. Only rough models about the mechanism of film formation have been published so far. Many authors have suggested that a modified CVD process occurs close to the substrate. However, many observations contradict the involvement of CVD process during the spray pyrolysis process [11-16].

In the present investigations, ZrO_2 thick and thin films were prepared by different method. Structural properties, surface morphology, microstructure property, elemental composition and optical band gap energy were studied using X-ray diffraction, FE-SEM, TEM, EDAX and UV-spectroscopy respectively.

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2. Experimental Methods

2.1 Preparation of Thick Films

Zirconium dioxide was prepared by dissolving 25 g of Zirconyl (IV) chloride octohydrate ($ZrOCl_2.8H_2O$) [Sigma-Aldrich] in 200 mL deionized water. The solution was stirred at 98 °C for 2 h in which drop wise aqueous ammonia solution was added until a pH value of 9.3 achieved after with subsequent filtration and washing to obtain $Zr(OH)_4$. This compound was dried at 100 °C for 24 h, heated at 1 °C/min up to 600 °C and calcinated for 3 h to produce ZrO_2 and it was dried, grinded for formation of small grains and calcinated at 800 °C in muffle furnace for few hours.

$$Zr(OH)_4 \xrightarrow{600^{\circ}C} ZrO_2 + 2H_2O\uparrow \quad (1)$$

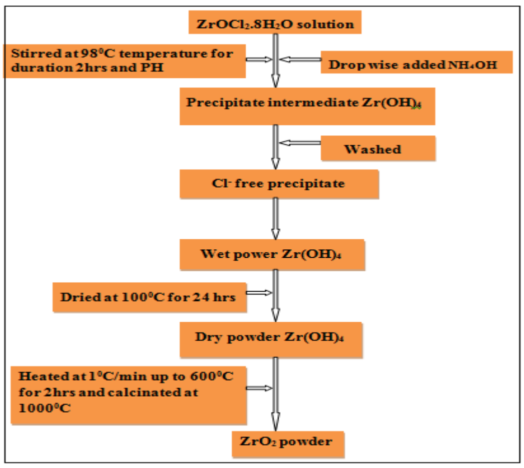

Fig. 1 Flowcharts represent schematic synthesis of ZrO_2 powder to prepare thick films

2.2 Preparation of ZrO_2 Thin Film Precursor

The precursor used in this study was zirconium oxychloide octohydrate ($ZrOCl_2.8H_2O$). It consists chloride ions and 8 water molecules, therefore most common solvents seemed to be water. 1.6102 g $ZrOCl_2.8H_2O$ was dissolved in 100 mL double distilled water to produce 0.05 M precursor spraying solution.

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2.3 Deposition of Nanostructured ZrO_2 Thin Films

As prepared precursor solution of $ZrOCl_2.8H_2O$ (0.05 M) was sprayed, through a glass nozzle of 0.1 mm bore diameter on hot glass substrate at temperature 350±5 °C at spray rate 5 mL/min for different spray time 30 min and these deposited samples for various deposition time is referred. The horizaonatal movement was kept uniform and compressor air pressure controlled between 3 to 8 kg/cm^2, this had been done to optimized viscosity and surface tension and momentum of the droplet. Also, substrate to nozzle distance played better role and kept as 28 cm.

3. Results and Discussion

3.1 X-Ray Diffraction Study

Fig. 2 (a-b) shows XRD pattern of thick and thin films respectively. The hkl planes (200) and (222) corresponding to monoclinic phase of ZrO_2. The plane (111), (220), (311) and (400) corresponding to tetragonal phase of ZrO_2. All the peaks well matched with standard JCPDS data cards 17-0923, 36-020 and 34-1084.

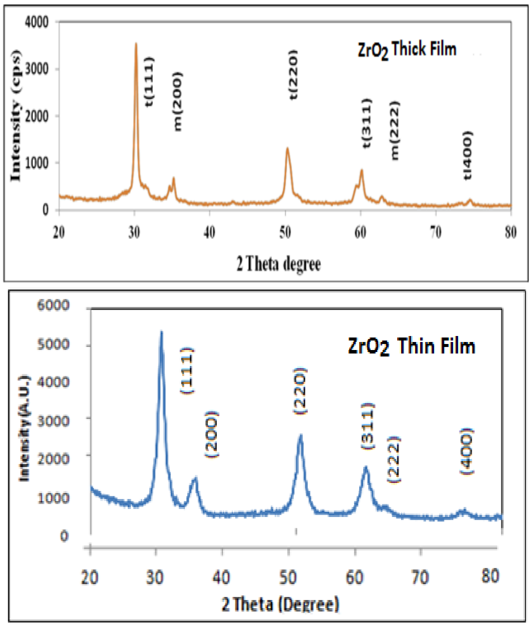

Fig. 2 XRD of ZrO_2 for (a) thick films and (b) thin films

The average crystallite size of ZrO_2 thick and thin film was determined using Debye- Scherrer's formula,

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

where, D = Average crystallite size, λ = X-ray wavelength (1·542 Å), β = FWHM of the peak in radians and θ= Diffraction peak position. It was found to be 25 nm and 7 nm crystallite sizes for thick and thin film respectively.

3.2 SEM Images of Surface Morphology

Fig. 3 (a and b) shows surface morphology of pure ZrO_2 thick and thin films. From the images, it is clear that the grains are bulk and nanocrystalline in nature and the grains are found to be spherical in nature and uniformly distributed.

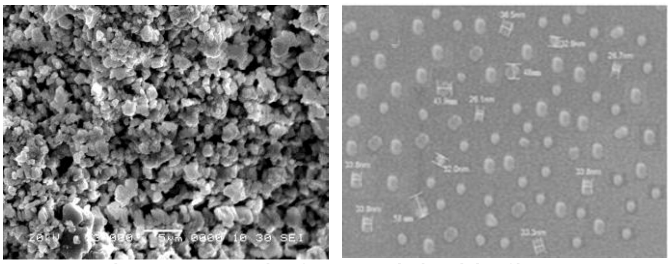

Fig. 3 SEM and FESEM micrographs of pure ZrO_2 thick and thin film

3.3 Elemental Analysis using EDAX

The quantitative elemental composition of Zr and O associated in thick and thin film sensor element was carried out and shown in Table 1. Atomic wt.% of cations (Zr) and anions (O) are 66.45 and 33.55 respectively. It is matched with theoretical expected wt.% percentage. A nanocrystalline ZrO_2 thin film is observed to be nearly stochiometric in nature.

Table 1 Elemental compositional analysis of ZrO_2 thick film and ZrO_2 thin film

Elemental	Fired ZrO_2 thick films		Annealed ZrO_2 thin films	
composition	mass %	at %	mass %	at %
Zr	74.33	66.45	71.00	33.04
O	25.7	33.55	29.00	66.96
ZrO_2	100	100	100	100

3.4 TEM analysis of Microstructural Property

3.4.1 Thick Film Analysis

Microstructural property studies were carried out using TEM as shown in Fig. 4 (a) values were observed using SAED pattern which is shown in Fig. 5.

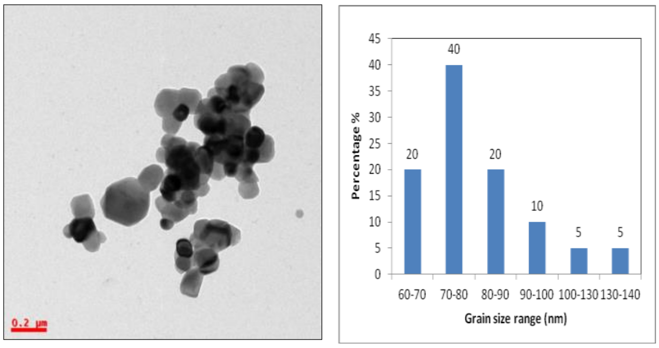

Fig. 4 TEM image of disspersed ZrO thick film sample and grain size histogram

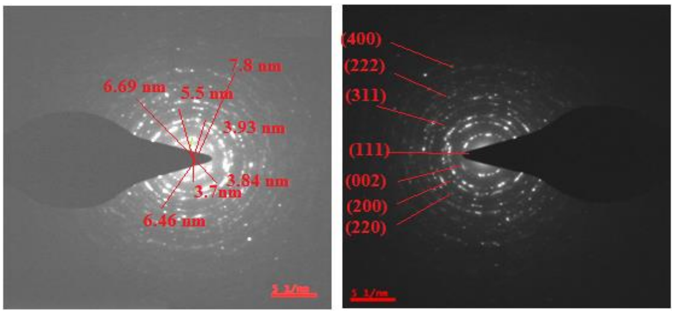

Fig. 5 SAED pattern for ZrO_2 thick film sample

It was observed that d values calculated from XRD and TEM were well matched with d values of standard reported JCPDS data cards 17-0923, 036-0420, 81-1550 and 37-1484.

3.4.2 Thin Film Analysis

Fig. 6 (a) and (b) are the TEM images of the ZrO_2 thin film sample and Fig. 6(c) is the HRTEM image of the same sample. Fig. 6(d) is the SAED image of the thin film sample. TEM images confirms the nanocrystalline nature of the films. The average particle size calculated from TEM image is found to be 34 nm. Also, d spacing values estimated using XRD and TEM analysis and they are well match with standard data card.

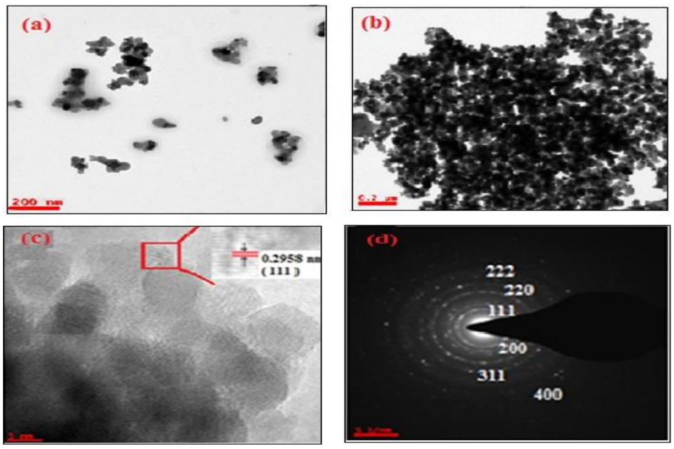

Fig. 6 (a-b) TEM images, (c) HRTEM image and (d) SAED pattern thin film sample

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3.5 Optical Properties

The variation of absorption with wavelength (nm) is shown in Figs. 7 (a) and (b). The absorbance of the film decreases gradually with increase in wavelength.

The optical band gap E_g is calculated using the formula,

$$E_g(eV) = h\upsilon = hc = \frac{hc}{\lambda} = \frac{1240}{\lambda(nm)} \qquad (2)$$

where h is planks constant, ν is frequency, c is speed of light, and λ is the wavelength in nm at interpolation of the linear portion of the curve, which determines the band gap in eV.

The observed band gaps are 4.67 and 4.8 eV for thick and thin film respectively. It is found that increase in band gap may be due to decrease in grain size [17-23].

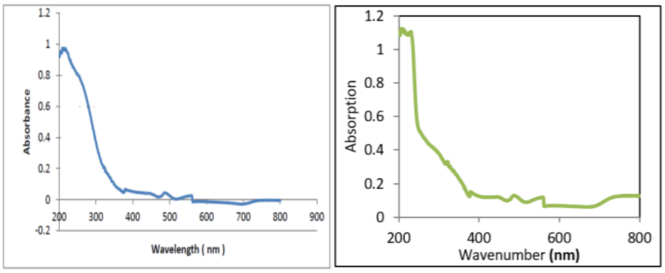

Fig. 7 (a-b) Absorption spectra of ZrO_2 thick and thin films

3.6 Comparative Reports from the Studied Analytical Techniques

Table 2 concludes that thin films are suitable for different application since it provides significant properties of thin films.

Table 2 Comparative study of structural, morphological and optical band gap energy of ZrO_2 thick and thin film

Analytical technique	Properties	Thick film	Thin film
XRD	Average crystallite size	25 nm	5.8 nm
SEM/FESEM	Average Grain size	71 nm	37 nm
TEM	Average Particle size	70-140 nm	33 nm
UV-spectroscopy	Band gap	4.67 eV	4.8 eV
Nature of film	Structure	Polycrystalline(Bulk)	Nanocrystalline

4. Conclusion

The ZrO_2 powder can be prepared using $ZrOCl_2.8H_2O$ as starting material. Thick films of ZrO_2 were prepared using screen printing techniques and thin films by spray pyrolysis techniques. XRD confirmed the identity of ZrO_2 powder and thick films. Surface morphology studies from SEM and TEM analysis confirmed that grains are observed to be mixed shape of spherical and tetragonal nature. From the EDAX spectra it is confirmed that initially ZrO_2 powder was nonstoichiometric and after firing it was found to be stoichiometric in nature. Optical band gap of films fired at different temperature was found as 4.67 and 4.8 eV.

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