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Impact of Molarity on the Structural, Morphological and Optical Properties of CeO_2 Thin Films Prepared by Spray Pyrolysis Technique

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Abstract: CeO_2 thin films are deposited on glass substrate by spray pyrolysis technique (SPT) at 623 K using different molar concentration of cerium chloride precursor solution. The structural, morphological and optical properties of films were investigated by a set of characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM),UV-VIS-IR. The estimation of crystallite size is 80-120 nm, which is confirmed by Scherer formulae from XRD pattern. XRD analysis shows that the film has cubic fluorite phase with orientation along (111) for all molarity. The optical energy gap decreased with the increase of crystallite size (98-120 nm) due to the size effect.

Keywords: Molar concentration, CeO_2 films, morphology, structure, Optical properties, crystal size.

1 Introduction

Thin-film deposition using metals materials have received more attention by researchers owing their enhanced electrical, magnetic and optical properties, for desirable applications [1-3]. Among the materials, Ceria (CeO_2) is a well-known material and CeO_2 film has unique properties which is well suitable for various biological and engineering applications. It exhibits good transmission in the infrared and visible region with high refractive index and wide optical energy gap of 3.4-3.6 eV [4-6].

Due to strong adhesion to surface between CeO_2 film and substrate, spray pyrolysis (SP) technique is used to deposit CeO_2 films on glass substrate [5]. These thin film of CeO_2 deposited on glass substrate exhibits high stability against chemical erosion and mechanical abrasion [6,7]. The structure of CeO_2 film showed face centered cubic structure (FCC) phase and it appeared as each cerium site is surrounding by eight oxygen sites and each oxygen sites has tetrahedron cerium sites in FCC arrangement [8].

Many literatures are available which reported the electrical, optical properties and structure of CeO_2 films using various deposition techniques such as reactive DC magnetron sputtering, electron beam evaporation, spray pyrolysis, thermal evaporation, laser ablation deposition and pulsed- laser deposition [9,10]. Among the different methods, spray pyrolysis was mainly used because of low cost and its simplicity to produce large-area, well adherence films and easy doping with desirable composition [11,12].

Pure and doped CeO_2 thin film is suitable for various applications in optoelectronic devices which is attributed to the transparent oxide film, having absorption in the visible and near-IR region. CeO_2 films are widely used in the semiconductor, electrochromic device, gas sensor, counter electrodes, magnetic materials and solid oxide fuel cells (SOFC) [13-14]. It has many other potential applications as photocatalysis materials and in gas sensors for high oxygen storage capacity. Because of release oxygen easily and its ability to absorb, the CeO_2 thin films used as solid oxide fuel cells. Besides, at a lower temperature, it has higher ionic conductivity [15-17].

This paper reports the preparation of CeO_2 thin films on glass substrates using SPT. The effect of molarity concentration on the structural, morphological and optical properties are investigated in detail.

2 Materials and Methods

The thin film of cerium oxide (CeO_2) is prepared by SPT.

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Firstly, the hepta-hydrate cerium chloride ($CeCl_3 7H_2O$) aqueous solution is prepared with different molarity, from 0.01, 0.03,0.05,0.1 to 0.2 M, by dissolving it in double-distilled water. Before starting spraying the solution on the substrate, the substrate is cleaned properly and anneal at 373 K to remove water molecules. It consists of liquid precursor with atomization metal salts and nozzles for droplet transport on to a heated substrate. On the substrate surface, decomposition and solvent evaporation result in the formation of the thin film.

The preheated substrate is maintained at a temperature of 623 K. The compressed air is used as carrier gas for spraying. The distance between substrate and nozzle is about 30 cm. The $CeCl_3H_2O$ solution is sprayed at spray rates of 2ml/min on to the glass substrate. The SPT exhibits good adherence with the substrate surfaces for the CeO_2 films.

"The structure of CeO_2 films are examined with X-ray diffractometer (Bruker, Germany) using CuKα radiation (40kV and 30mA). The surface morphology of CeO_2 thin films is examined by scanning electron microscope (SEM, Hitachi Model, 700 AT)". The optical absorption and transmittance characteristics are determined with UV-Vis-IR spectrophotometer (V-1200, UV-1600PC) in the wavelength range of 300-900 nm.

3 Results and Discussion

3.1. X-Ray Diffraction

Figure 1 shows the XRD patterns of CeO_2 films with different molarity of solution prepared at 623 k deposited on the glass substrate. XRD patterns of CeO_2 films exhibits single phase with a cubic fluorite structure. The pattern of CeO_2 film agrees with the JCPDS data 34-0394. It is also clear from the XRD spectrum that the variation in the molarity of solution in the range of 0.01 to 0.05 M leads to the formation of well-crystallized CeO_2 which is strongly oriented along the (111) plane[1,16]**.** The diffractions peaks of all samples located at 28.2,32.6,46.8, 55.6, 58.8, 68.2 and 76.4 can be indexed to the (111),(200),(220),(311),(222),(400) and (331) plans of a cubic fluorite structure, respectively as shown in Table 1

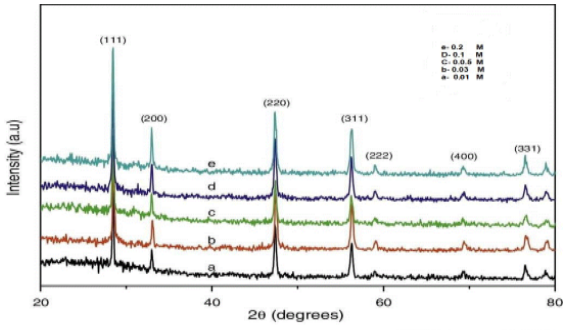

Fig. 1. XRD patterns of CeO_2 films prepared with different molar concentration

Table 1. XRD analyses parameters for CeO2 film

hkl planes	111	200	220	311	222	400	331
2Θ(deg.)	28.2	32.6	46.8	55.6	58.8	68.2	76.4

Scherer's formula used to calculate crystallite size from XRD data is given as,

$$D = \frac{K\lambda}{\beta COS\theta} \text{.....(1)[18]}$$

"where λ is the wavelength of the X-ray, D, β represent the crystallite size, and full-width half maximum of diffraction peak, respectively".

Some parameters like microstrain (ε) , lattice constant and density of dislocation(δ) of the films are calculated with different molarity and are listed in Table 2. The following equations were used to calculate dislocation density (δ) and micro-strain (ε) respectively

The change in the molar concentration results in getting different size of CeO_2 crystallites size. The size of all crystallites is in the nanometer range.

$$\delta = \frac{1}{D2} \text{ .....(2)} \quad [18]$$

$$\varepsilon = \frac{\beta COS\theta}{4} \text{.....(3)} \quad [18]$$

From Table 1, the dislocation density and lattice parameter is increased with a decreasing in the crystallite size. One of the general experimental facts is that the lattice parameters show expansion with reduction in particle size for nanoparticles of oxides while the nanoparticles of metal exhibit a lattice contraction. This lattice expansion with concentration variation is attributed to the strain of lattice, which is induced by the increase of Ce^{3+} ions because of the formation of oxygen vacancies [19].

Table.2 Density of dislocation, micro-strain and lattice parameters of the thin films with different molar concentrations

Mole concentration	Thickness t	D nm	Dislocation density($x10^{14}$)	Micro-strain ($x10^{-4}$)	Lattice Constant ((Å)
0.01	83	108	0.71	0.056	5.399
0.03	103	98	0.85	0.37	5.435
0.05	132	71	1.56	0.81	5.439
0.1	178	89	1.43	0.053	5.441
0.2	201	92	0.84	0.048	5.449

3.2 Scanning Electron Macroscopy

Fig. 2 shows the SEM image of CeO_2 thin films at 623 K. It reveals that the film prepared with 0.01 and 0.03 M concentrations show spherical shaped particles with some voids. The film formed exhibits uniformity, smoothness, crack-free and high adhesion to the glass substrate. The smooth uniform surface of film depends on the molar concentration as the lower concentration produced rough surface up to 0.05 M and when the molarity is increased,

smoothness of thin-film increased and also some cracks have appeared on the surface. The formation of microcracks is observed in the 0.1 and 0.2 M concentration, which is primarily due to the thermal stress[20].

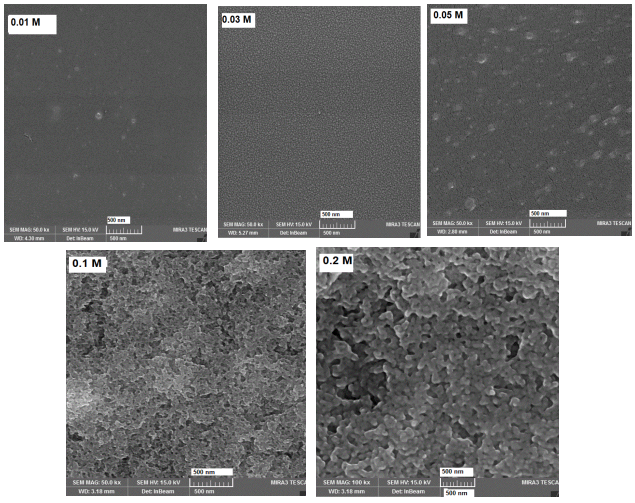

Fig.2 SEM images for CeO_2 thin films with different molar concentration

3.3. Transmittance spectrum near infrared

Figure 3 shows transmittance spectra of CeO_2 films with thickness of 98, 110, 112, 114 and 120 nm, depending on the molarity of solution. The prepared films are mainly transparent in the visible which near infrared regions indicate that the films are uniform and have well adherence to the glass substrates. It is observed that the transmission decreases with increasing in molar concentration"[21].

The molarity effects on transmittance is reflected as, on increasing the molar concentration in turn reduces transmittance which is attributed due to the bonding between oxygen and cesium ion as covalent bonds [19]. Furthermore, the incident light transmittance is decreased at shorter wavelengths. So the outer orbits electrons were transferred to the higher energy levels to occupy vacant position of energy bands.

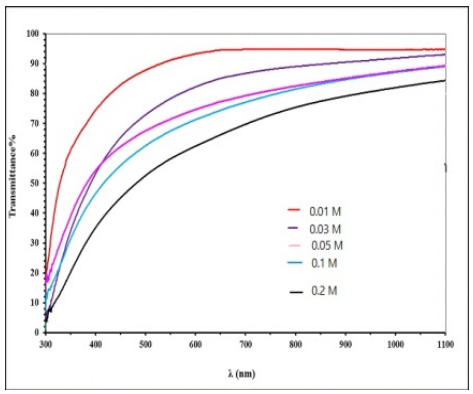

Fig. 3 Transmittance spectrum of CeO2 thin films with different concentration

3.4 absorption coefficient

The absorbance coefficient spectra of cerium oxide thin films prepared with various molarity are shown in figure 4. The spectra of absorption coefficient decreased with increasing wavelength and it exhibits high absorption coefficient value in UV region and constant in the visible region and near infrared regions. When the molar concentration increased, the absorbance spectra increasing up to 0.1 M, and then decreases because of the increase in pore size [21].

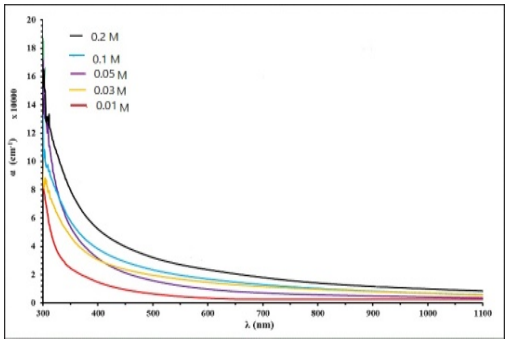

Fig. 4 Absorption coefficient f CeO_2 thin film with different molar concentration

3.5. Extinction Coefficient

The extinction coefficient (k) of the CeO_2 films is calculated using the relation $k = \alpha\lambda/4\pi$ where λ is the wavelength and α is the absorption coefficient. The results are shown in figure 5. The observed value of k is high for the wavelength range from 325 nm to 400 nm and is low in the higher range of wavelength from 450 nm to 1100 nm

The refractive index of the films with 0.01 M to 0.2 M found to be 1.193, 1.23, 1.29, 1.42 and 1.56, respectively. It is found that refractive index of the films decreases with an increase in the wavelength. The increase in refractive index for 0.05 M films suggests that the films are more absorbing than other mole concentration of the films. It may be attributed to the smaller crystal size at 0.05 M, which allows for closer packing, which is in good agreement with SEM observations [22].

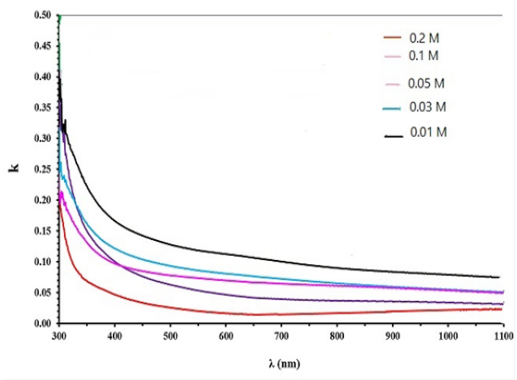

Fig. 5 Extinction coefficient vs wavelength for CeO2 thin films with different concentration

3.6. Optical Energy Gap

The incident photon energy (hν) depicted with $(\alpha h\nu)^2$ as shows in Figure 6. It is observed that the optical energy gap decreased with the increase of crystallite size (98-120 nm) due to the size effect, the concentration of Ce^{3+} ions and oxygen vacancies [18].

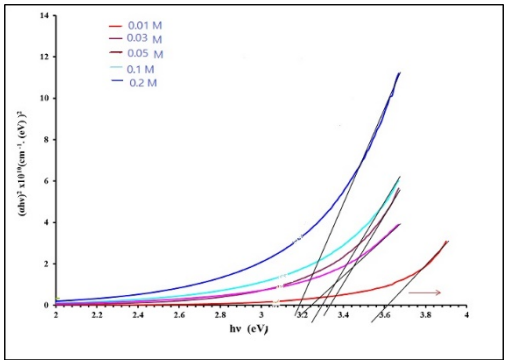

Fig. 6 Variation in $(\alpha h\nu)^2$ vs hν for CeO_2 with different molar concentration

4 Conclusion

The CeO_2 films were deposited on glass substrates with various molar concentration 0.01-0.2 M. The films deposited by spray pyrolysis technique is done by $CeCl_3 7H_2O$ as precursor. The XRD studies revealed the formation of polycrystalline ceria of cubic fluorite structure with the crystallite orientation preferred along (111) plane direction. The morphological analysis revealed that the particles are distributed uniformly on the surface and are confirmed through SEM. The UV-Visible spectra reveal that the films are transparent (70%) in the visible region and the bandgap is found to be in the range of 3.4 eV to 3.65 eV. Due to its nano-crystalline nature, the deposited CeO_2 thin films can be used for various applications.

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