Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 03, pp.13922-13926, March, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

ZINC DOPED CERIUM OXIDE THIN FILMS PREPARED BY SPRAY PYROLYSIS METHOD

***Govindarajan, D. and Nithya C. K.**

Department of Physics, Annamalai University, Annamalai Nagar, Chidambaram-608 002, Tamil Nadu, India

ARTICLE INFO

Article History:
Received 15th December, 2014
Received in revised form
28th January, 2015
Accepted 28th February, 2015
Published online 31st March, 2015

Key words:

Thin films, CeO_2, Zn, XRD, UV-Vis, SEM.

ABSTRACT

Zinc doped Cerium Oxide thin films were prepared by spray pyrolysis technique. The CeO_2 and Zn doped CeO_2 thin films were deposited on the glass substrates (350°C) with two different Zn concentrations (4 and 8%). The prepared film has been characterized by X-ray Diffraction (XRD), Ultraviolet-Visible Spectroscopy (UV-Vis), and Scanning Electron Microscope (SEM). XRD analysis revealed that the films are well crystallized in nature having cubic fluorite structure with a grain orientation along (111) plane. CeO_2 thin films exhibits transparent in visible region and strong absorbance in the UV-Vis region. It was also observed that significant effect of Zn content on the transmittance and band gap energy of CeO_2 thin films. SEM micrograph shows that the particles are spherical in shape.

Copyright © 2015 Govindarajan and Nithya. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Cerium oxide (CeO_2) thin films continuous attracting attention for scientists because of its cerium valence related optical property and its chemical stability used for many applications such as solid oxide fuel cells (SOFCs) (Steele, 1993; McAleese *et al.,* 1996), miniature capacitors (Nakazawa *et al.,* 1995; Roh *et al.,* 1997) and counter electrode in smart window devices. CeO_2 has unstable fluorite structure where the Ce^{4+} has tendency to be transformed into Ce^{3+}. These unique property combined with high UV absorbing ability, high refractive index and high transparency in the visible light region have been used in specific applications, including polishing material for glass, polymer and wood, UV-blocker and filter and as an additive to glass to protect sensitive materials (Goharshadi *et al.,* 2011; Karakoti *et al.,* 2008). Thin films can be prepared via many methods such as RF magnetron sputtering (Ryasnyanskiy *et al.,* 2007), pulsed layer deposition (PLD) (Reintjes, 1984), vacuum evaporation (Ahalapitiya, 2003) and spray pyrolysis (Oleynik and Adam, 2003). The high quality thin films prepared in this work are using a cost effective spray deposition technique.

However, the effects of zinc doped CeO_2 thin films have been rarely reported. In the present work, structural and optical properties of undoped and Zn doped CeO_2 thin films have been reported.

***Corresponding author: Govindarajan, D.**
Department of Physics, Annamalai University, Annamalai Nagar, Chidambaram-608 002, Tamil Nadu, India.

MATERIALS AND METHODS

The spray pyrolysis experimental arrangement has been described elsewhere (Addou *et al.,* 1999). The thin films of CeO_2 and Zn doped CeO_2 were deposited on to glass substrates, heated at 350° C from an aqueous solution containing hepta hydrate cerium chloride and zinc chloride. The spraying flow rate was set to 2ml/min and nozzle to substrate distance was about 20 cm. Before spraying, the glass substrates are properly cleaned and annealed at 100°C for 30 minutes, in order to eliminate water molecules. X-ray diffraction (XRD) patterns of samples were recorded with a "Xpert PRO" X-ray diffractometer using Cukα radiation. The optical transmittance and absorption characteristics were measured with a LAMDA 25 PERKIN ELMER spectrophotometer in the wavelength range of 300 – 800 nm. The surface morphologies of CeO_2 thin films were examined by SEM (JEOL Model, JSM-5610LV). The Mitutoyosurftest SJ-301 is a stylus-type Instrument is used for measuring the thickness of the films.

RESULTS AND DISCUSSION

Structural characterization

Fig.1 shows the XRD patterns of undoped and Zn doped CeO_2 thin films consist of (111), (200), (220) and (311) diffraction peaks corresponding to 2θ = 28.6°, 33°, 46.9° and 56° respectively. No other peaks belonging to other phases are detected by XRD. This indicates the phase purity of the films and also confirms that the doping of Zn does not affect the cubic fluorite structure CeO_2. It is clear that the peaks of the Zn doped CeO_2 films were broadening and shifted toward higher angles as compared with pure CeO_2 films. The broadening of the peaks indicates that CeO_2 and Zn doped CeO_2 films consist of nanometric size particle.

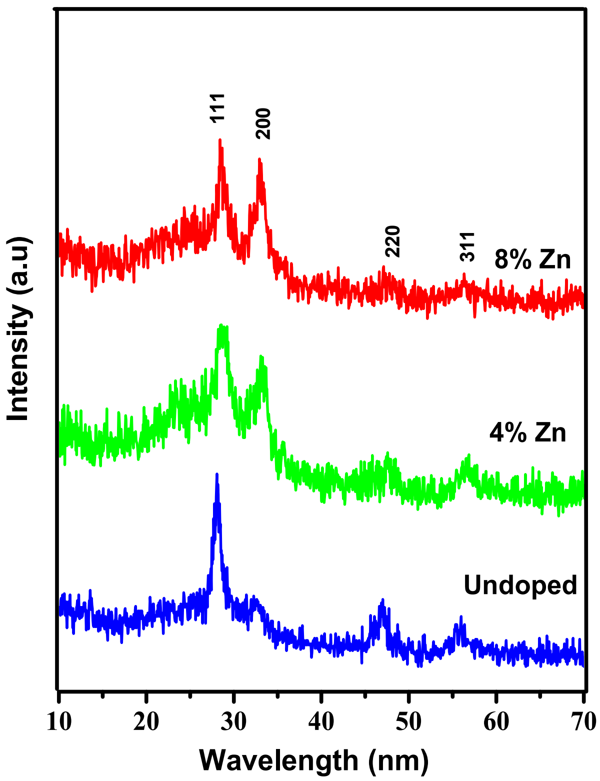

Fig. 1. XRD patterns for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

Optical properties

Fig.2 (a) and (b) shows the transmittance and absorbance spectra of undoped and Zn doped CeO_2 thin films measured in the wavelength range of 300 to 800 nm. The optical transmittance of the film changed from 65% to 78% (at 600 nm) with the increase of Zn doping percentage. The higher transmittance observed in the films (8% Zn) is attributed to less light scattering of photons and structural homogeneity (Bougrine *et al.,* 2005). The extinction coefficient (k) can be obtained from the relationship (Elkorashy, 1989)

$$k = \frac{\propto \lambda}{4\pi}$$

The variation of extinction coefficient with wavelength is shown in Fig.2 (d). Extinction coefficient is high in the wavelength range of 300–400 nm and low in the range of 400–800 nm. The rise and fall in the extinction coefficient is directly related to absorption of light (Prathap *et al.,* 2007). The refractive index n of the film is determined using the relationship (Giulio *et al.,*1987).

$$N = \frac{1 + R^{1/2}}{1 - R^{1/2}}$$

Where R is the normal reflectance. Fig.2 (e) shows the variation of refractive index of CeO_2 films with different wavelengths. It was observed that the refractive index increases in the UV region then decreases gradually from 2.27 to 1.69 in the high transmission range. The optical band gap of Zn doped CeO_2 thin film is estimated from Tauc relationship (Bardeen *et al.,* 1956) and the optical parameters of the Zn doped CeO_2 are presented in the Table 2.

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Table 1. The Structural parameters of Undoped and Zn doped CeO_2 thin films prepared at 350°C

Mole concentration (M)	Thickness (t)	D (nm)	N ($x10^{15}$)	Dislocation density δ ($x10^{14}$ lines/m^2)	Microstrain ε ($x10^{-4}$)	Lattice constant (Å)	Volume of unit cell $(Å)^3$
0.03	112	75	265	1.77	0.764	5.440	160.98
4% Zn	113	73	290	1.87	0.764	5.221	142.31
8% Zn	152	70	443	2.04	0.771	5.210	141.42

Table 2. Optical parameters for Undoped and Zn doped CeO_2 thin films prepared at 350°C

	Transmittance (at 600 nm)	Refractive Index (n) (at 600 nm)	Band gap (eV)
Undoped	78%	1.40	3.30
4% Zn	71%	1.72	3.20
8% Zn	65%	1.82	3.25

The calculated parameters from XRD data are given in Table 1. It was found that by Zn doping into CeO_2 films, that the crystallite size and lattice parameters decreased. This is because the ionic radii of Ce^{3+} (0.103 Å) and Ce^{4+} (0.092 Å) are larger than that of Zn^{2+} (0.074 Å), it opens up the possibilities of easy substitution of Zn^{2+} in the CeO lattice. The microstrain (Hankare *et al.,* 2009) increased with Zn, which may be due to the presence of defects and vacancies in the Zn – Ce – O lattice (Rong and Watkins, 1987).

Where E_g is the optical band gap and A is a constant. Fig.2 (f) shows that the graph between $(\alpha h\nu)^2$ and the photon energy (hν) and indicates that the electronic transitions are direct in nature across the band gap of the films. The extrapolation of the linear part of the curves onto the energy axis allows to determine the optical band gap and its values varies in the range of 3.20 to 3.35 eV.

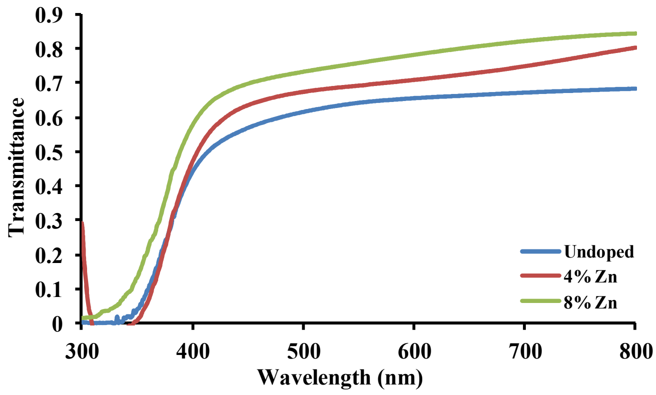

Fig. 2 (a). Transmittance vs Wavelength for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

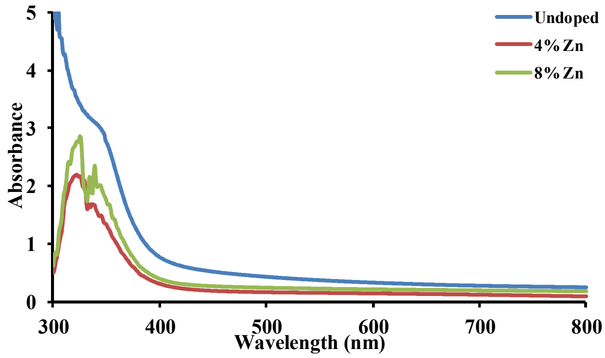

Fig. 2 (b). Absorbance vs Wavelength for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

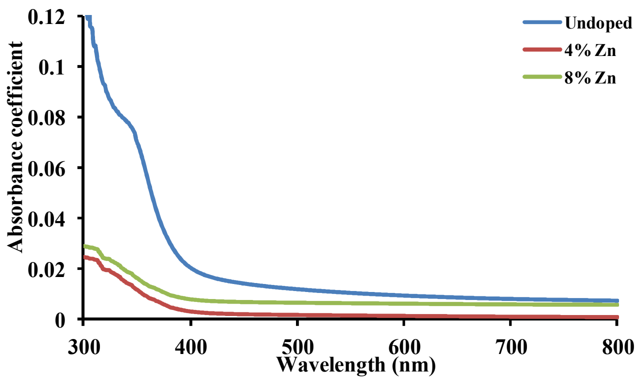

Fig. 2 (c). Absorbance coefficient vs Wavelength for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

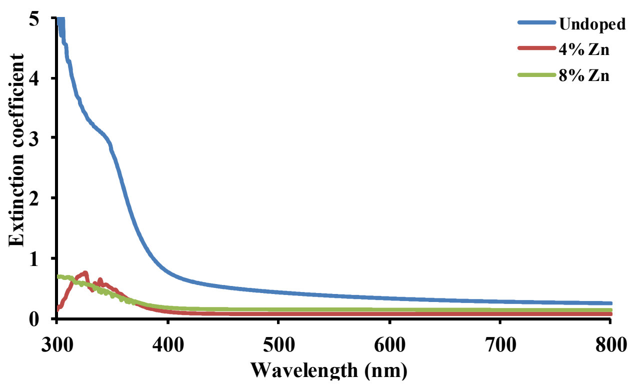

Fig. 2 (d). Extinction coefficient vs Wavelength for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

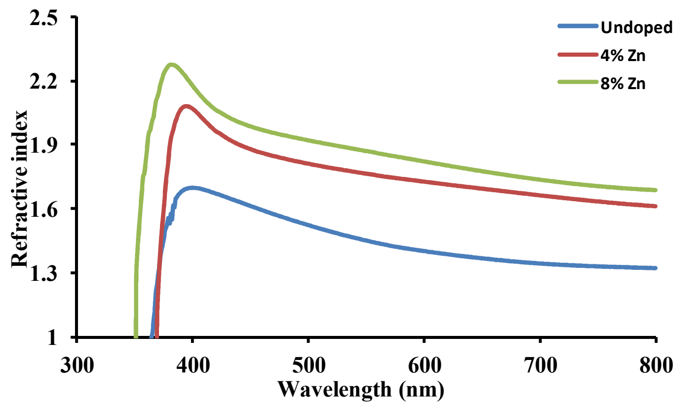

Fig.2 (e). Refractive index vs Wavelength for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

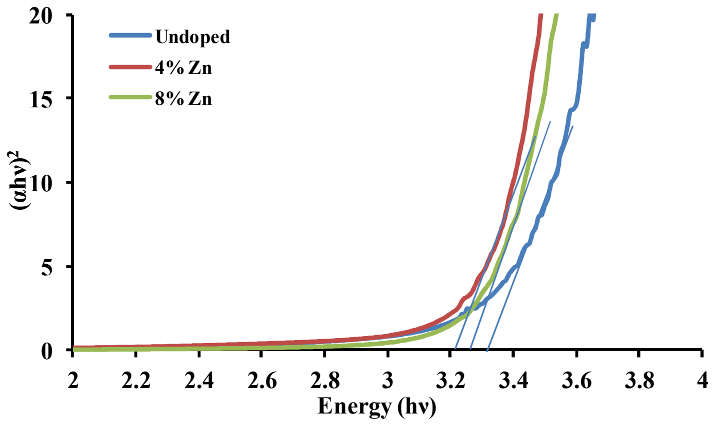

Fig. 2 (f). Energy (hν) vs $(\alpha h\nu)^2$ for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

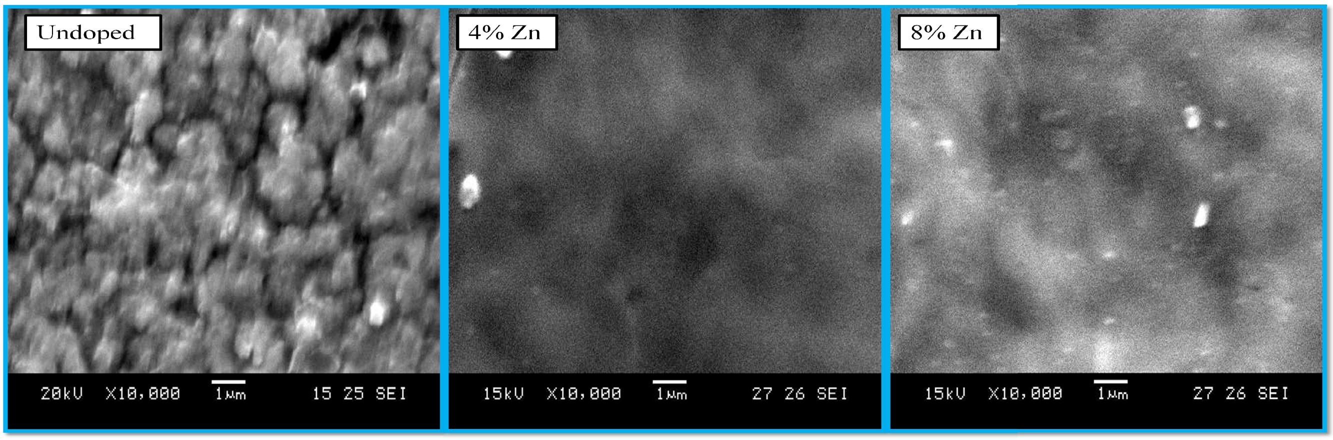

Fig. 3. SEM photographs for Undoped and Zinc doped CeO_2 thin films prepared at 350°C

Morphological characterization

Surface morphology of undoped and Zn doped CeO_2 thin films deposited at 350°C substrate temperature is shown in Fig.3. The undoped CeO_2 film image shows big size aggregates of CeO_2 particles without much individual particles. For Zn doped thin films, the image shows a smooth uniform surface oxide with fine grains.

Conclusion

Undoped and Zn doped CeO_2 thin films were successfully prepared by a simple and low cost spray pyrolysis technique. The structural analysis of the deposited film suggests that the thin films were cubic fluorite structure. UV-Visible spectra reveal that the transmittance of the films increased with increasing zinc concentration and the observed band gap are in the range of 3.20 to 3.35 eV. SEM image indicated that this method is useful to prepare a high quality and microcrack free films. The deposited CeO_2 thin films are used for various applications such as solid oxide fuel cell, miniature capacitors and counter electrode in smart window devices.

REFERENCES

Addou M., A. Moumin, B. Elidrissi, M. Regragui, A. Bougrine, A. Kachouane, C. Monty, Structural, optical and electrical properties of undoped and indium doped zinc oxide prepared by spray pyrolysis, *Journal of Chemical Physics,* 96 (1999) 232.

Ahalapitiya H. Jayatissa, Preparation of gallium-doped ZnO films by oxidized ZnS films Semiconductor Science and Technology 18 (2003) L27.

Bardeen J., F.J. Blatt, L.H. Hall, Proceedings of Atlantic City Photoconductivity Conference in 1954, Wiley and Chapman and Hall, New York, (1956) 146

Bougrine A., M. Addou, A. Kachouane, J.C. Bernede, M. Morsli, Effect of tin incorporation on physicochemical properties of ZnO films prepared by spray pyrolysis, *Materials Chemistry and Physics*, 91 (2005) 370

Di Giulio M., G. Micocci, R. Rella, P. Siciliano, A.Tepore, Optical absorption and photoconductivity in amorphous indium selenide thin films, *Thin Solid Films,* 148 (1987) 273

Elkorashy A.M. Optical constants of tin monosulphide single crystals in the transparency region, *Semicond.Sci.Technol.,* 4 (1989) 382

Goharshadi E.K., S. Samiee, P. Nancarrow, Fabrication of cerium oxide nanoparticles Characterization and optical properties, *J. Colloid and Interface Sci.,* 356 (2011) 473.

Hankare PP., PA. Chate, DJ..Sathe, PA. Chavan, VM. Bhuse, Effect of thermal annealing on properties of zinc selenide thin films deposited by chemical bath deposition, *J. Mater Sci Mater. Electron,* 20 (2009) 374.

Karakoti A.S., N.A. Monteiro-Riviere, R. Aggarwal, J.P. Davis, R.J. Narayan, W.T. Self, J.McGinnis, and S. Seal, Nanoceria as antioxidant: Synthesis and Biomedical Application, *Biomedical Mat. Sci.,* (2008) 33.

McAleese J., J. C .Plakatouras, B.C.H. Steele, The use of Ce(fod)(4) as a precursor for the growth of ceria films by metal-organic chemical vapour deposition, *Thin solid Films,* 280 (1996) 152.

Nakazawa T., T. Inoue, M. Satoh, Y.Yamamoto, Electrical Characteristics of Metal/Cerium Dioxide/Silicon Structures, *J.Appl.Phys.,* 34 (2A) (1995)548.

Oleynik N. and M. Adam, . Metalorganic chemical vapor phase deposition of ZnO with different O-precursors, *Journal of Crystal Growth*, 248 (2003) 14.

Prathap P., Y.P.Subaiah, K.T.Ramakirushna, Reddy, Effect of precursor molarity on physical properties of In_2O_3 films, *Optoelectron.Adv.Mater.,* 1 (2007) 252

Reintjes J.F., Nonlinear Optical Parametric Processes in Liquids and Gases, Academic, Orlando, 1984.

Roh Y.H., K.Kim, D.G.Jung, The Hysteresis Caused by Interface Trap and Anomalous Positive Charge in Al/CeO_2–SiO_2/Silicon Capacitors *J.Appl.Phys*., 36 (12B) (1997) L1681.

Rong C.F., GD.Watkins. Optically detected magnetic-resonance observation of the isolated zinc interstitial in irradiated ZnSe, Phys. Rev. Lett.58 (1987) 1486.

Ryasnyanskiy A.I., B. Palpant, S. Debrus, U. Palc, A. Stepanov, Third-order nonlinear-optical parameters of gold nanoparticles in different matrices *Journal of Luminescence*, 127 (2007) 181.

Steele B.C.H. Materials for electrochemical energy conversion and storage systems, ceram. *Int.,* 19 (1993) 269.

****