Structural and Optical properties of Cerium oxide thin films prepared by Spray Pyrolysis technique

D.Govindarajan* and C.K.Nithya

Abstract: CeO_2 thin films with different molar concentrations are prepared on glass substrate at 350°C using hepta hydrate cerium chloride ($CeCl_3.7H_2O$) as precursor solution. The structural and optical properties of these films are studied by XRD, UV- Vis spectroscopy and SEM techniques. XRD analysis revealed that the films are well crystallized in nature having cubic fluorite structure with a grain orientation along (111) plane. Molar concentrations affect the crystallinity and structural parameters like crystallite size, dislocation density and lattice constant. An average transmittance exceeding 70% is reached for the film with thickness of 112 nm. SEM micrograph shows that the particles are in spherical shape.

Keywords: CeO_2, Spray pyrolysis, Thin films

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1. INTRODUCTION

Thin film deposition using rare earth materials have received much attention because of their enhanced optical and electrical properties which are highly desirable for applications such as electrochemical systems, fuel cells and opto electronic devices. Among the materials, Ceria (CeO_2) is a well known material because of its unique properties and various engineering and biological applications. CeO_2 have fascinating optical properties, such as high refractive index, good transmission in the visible and infrared regions and a wide band gap of 3.2 eV [1]. Thin film of CeO_2 is an attractive material because of its potential applicability as passive counter electrode in electro chromic smart windows. The cerium ion in the CeO_2 film exhibits both +3 and +4 oxidation states, which are suitable for valency change switching process   [2, 3].

There are many literatures reported the structural, optical and electrical properties of CeO_2 thin films by different methods such as thermal evaporation [4], electron beam evaporation [5], laser ablation deposition [6], pulsed-laser deposition [7], and reactive DC magnetron sputtering [8]. Among the different method spray pyrolysis was mainly

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used because of its simple, low cost, capability to produce large area films with uniform thickness, easy doping with desirable composition.

In the present work, CeO_2 thin films were prepared on glass substrates using the spray pyrolysis method. The effect of film thickness on the structural and optical properties was investigated in detail.

2. MATERIALS AND METHODS

The CeO_2 thin films are prepared by the spray pyrolysis process from a solution containing hepta hydrate cerium chloride ($CeCl_3.7H_2O$) in distilled water. The $CeCl_3.7H_2O$ solution is sprayed with a solution spray rates of 2ml/min on to a preheated glass substrate maintained at 350°C temperature, using compressed air as a carrier gas. Before spraying, the glass substrates are properly cleaned and annealed at 100°C for 30 min, in order to eliminate water molecules. The nozzle to substrate distance is about 20 cm. The CeO_2 thin films thus obtained are transparent exhibit good adherence to the substrate surfaces. X-ray diffraction (XRD) patterns were recorded with a "Xpert PRO" X-ray diffractometer using $CuK\alpha$ radiation. The optical transmittance and absorption characteristics were determined with a LAMDA 25 PERKIN ELMER spectrophotometer in the wavelength range of 300 – 900 nm. The surface morphology of CeO_2 thin films were examined by SEM (JEOL Model, JSM-5610LV). The Mitutoyosurftest SJ-301 is a stylus-type instrument was used for measuring the thickness of the films.

3. RESULTS AND DISCUSSION

3.1. Structural properties

Figure 1 shows the XRD patterns of CeO_2 films with different molar concentrations prepared at 350°C on glass substrates. The strong and sharp diffraction peaks indicate the good crystallization of the samples. XRD results indicated the formation of single phase CeO_2 with a cubic fluorite structure [JCPDS data (81-0792)]. No additional peaks were observed, revealing the high purity of the prepared CeO_2 thin films. From the figure 1, it is clear that the solution molarity in the range 0.01 to 0.05 M lead to the formation of well crystallized CeO_2 strongly oriented along the (111) plane.
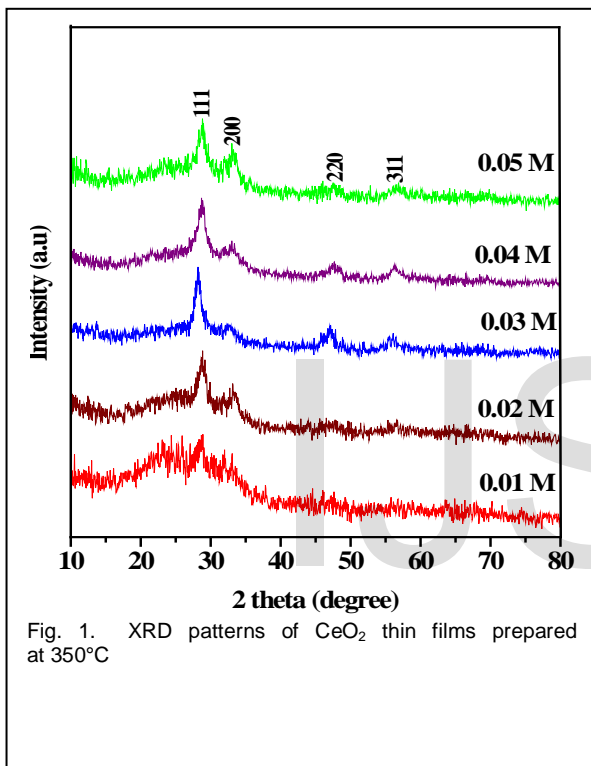

Fig. 1. XRD patterns of CeO_2 thin films prepared at 350°C

Grain sizes are calculated from XRD data using Scherrer's formula as given below [9].

$$\text{Average grain size (D)} = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the Crystallite size perpendicular to the normal line of (hkl) plane, β is the full width at half maximum of the (hkl) diffraction peak, θ is the Bragg angle and λ is the wavelength of incident X-ray. Various structural parameters like dislocation density, micro strain and lattice constant [10] of the films were calculated with different molar concentrations and listed in the table 1. The average sizes of CeO_2 crystallites are all in the nanometer scale and found to vary with film thickness. This change in size with film thickness is well in agreement with other researchers [11,12].
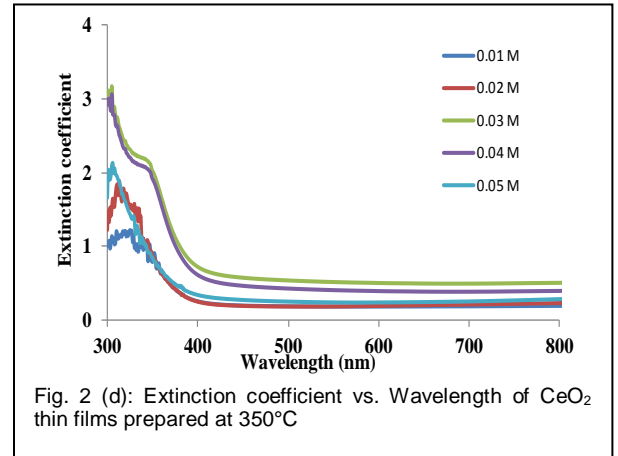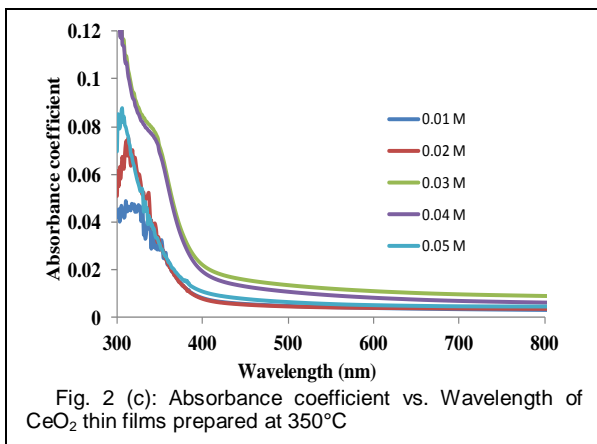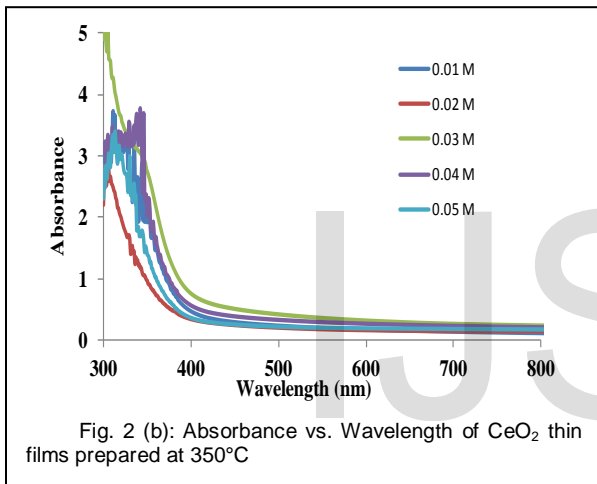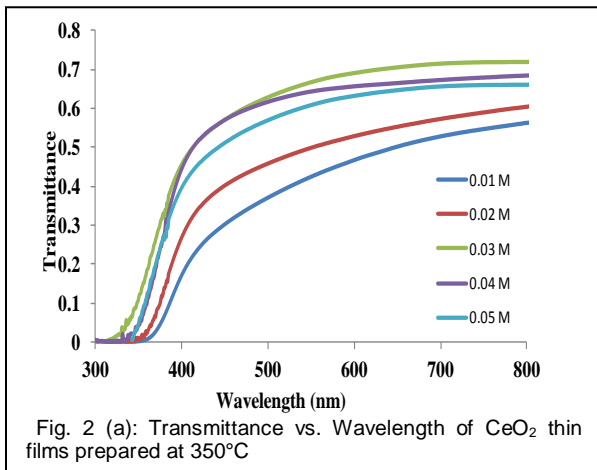
TABLE 1:

THE STRUCTURAL PARAMETERS OF CeO_2 THIN FILMS PREPARED AT 350°C

| Mole Concentration (M)	Thickness (T)	D (nm)	N ($\times 10^{15}$)	Dislocation Density ($\times 10^{14}$ lines /m^2)	Microstrain ($\times 10^{-4}$)	Lattice constant (Å)
0.01	98	120	56	0.69	0.053	5.394
0.02	110	110	82	0.82	0.030	5.410
0.03	112	75	265	1.77	0.764	5.440
0.04	114	92	146	1.18	0.045	5.421
0.05	120	115	78	0.75	0.053	5.379

From table 1, an increase in the lattice parameter and dislocation density was observed with a decrease in crystallite size. As a general rule, nanoparticles of oxides exhibit a lattice expansion with reduction in particle size while metal nanoparticles exhibit a lattice contraction [13]. This lattice expansion with concentration is attributed to the lattice strain induced by the increase of Ce^{3+} ions due to the formation of oxygen vacancies [14].

3.2 OPTICAL PROPERTIES

Figure 2 (a) and 2 (b) shows the transmission and absorption spectra of CeO_2 films with thickness of 98, 110, 112, 114 and 120 nm. These measurements were conducted in the wavelength range of 300 – 900 nm at room temperature using glass substrate as background. The prepared films are mainly transparent in the visible region and indicate that the films are uniform and well adherence to the glass substrates. An average transmittance exceeding 70% is reached for the film with thickness of 112 nm. It is crystal clearly observed that the transmission decreases with increased film thickness.

Fig. 2 (a): Transmittance vs. Wavelength of CeO$_2$ thin films prepared at 350°C

Fig. 2 (b): Absorbance vs. Wavelength of CeO$_2$ thin films prepared at 350°C

Fig. 2 (c): Absorbance coefficient vs. Wavelength of CeO$_2$ thin films prepared at 350°C

Fig. 2 (d): Extinction coefficient vs. Wavelength of CeO$_2$ thin films prepared at 350°C

The extinction coefficient of the CeO$_2$ films was calculated using the relation $k = \frac{\alpha\lambda}{4\pi}$ where λ is the wavelength and α is the absorption coefficient value and the results are shown in fig 2 (d). The observed value of k is high in the wavelength range of 325 - 400 nm and low in the higher range of 450 - 800 nm. The rise and fall in the extinction coefficient is directly related to the absorption of light.

Fig. 2 (e): Refractive index vs. Wavelength of CeO$_2$ thin films prepared at 350°C
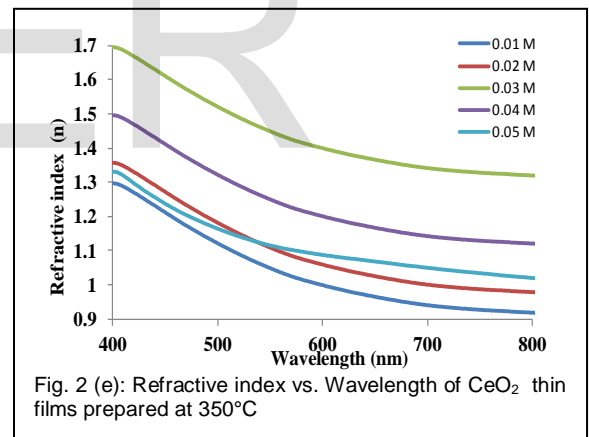
The refractive index of the films with 0.01 M to 0.05 M was calculated and found to be 1.29, 1.32, 1.35, 1.49 and 1.69 at 400 nm respectively. It was found to be decreasing with an increase in the wavelength. The main causes of refractive index variation are modes of nucleation and growth during the deposition. The increase in refractive index for 0.03 M films suggests that the films are more absorbing than other mole concentration of the films. This can be attributed to the smaller grain size   (0.03 M), which allows for closer packing, in good agreement with SEM observations (Fig.3).

Figure 2 (f) shows the plot of $(\alpha h\nu)^{1/2}$ as a function of energy (hν) of the incident photon. The band gap can be calculated by extrapolating the linear portion of the curve to

the abscissa intercept. It could be observed that the band gap energy decreased with increase of crystallite size (98 – 120 nm) due to size effect, concentration of Ce^{3+} ions and oxygen vacancies [15].
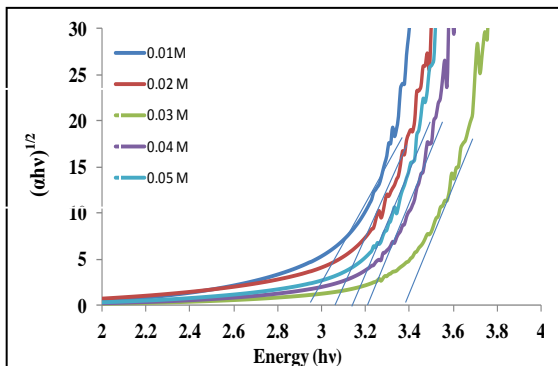

Fig 2 (f): Energy (hv) vs $(\alpha h v)^{1/2}$ of CeO_2 thin films prepared at 350°C
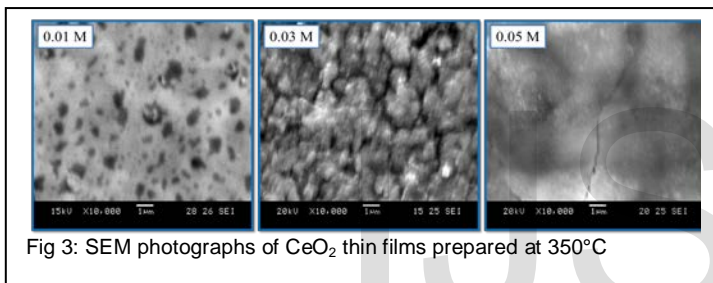
3.3 MORPHOLOGICAL STUDIES

Fig 3: SEM photographs of CeO_2 thin films prepared at 350°C

Figure 3 shows the SEM analysis of CeO_2 thin films at 350°C. It indicates that the film prepared with 0.01 and 0.03M concentrations show the spherical shaped particles with some voids. The formation of micro cracks are observed in the 0.05 M concentration of the thin film is due to the thermal stress during the deposition and the presence of unevaporated precursor solvent.

4. CONCLUSION

A spray pyrolysis technique to deposit CeO_2 thin films of different molar concentrations at 350°C has been investigated. The structural and morphological analysis of the deposited film suggests that the thin films were cubic fluorite structure, having preferred orientation of grains along the (111) direction. UV-Visible spectra reveal that the films are transparent (70%) in the visible region and the band gap are in the range 3.4 eV to 2.9 eV. Due to its nano-crystalline nature, the deposited CeO_2 thin films are used for various applications such as solid oxide fuel cell, gas sensors and catalysis.

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