

Characteristics of sol–gel dip coated Ceria films

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Received: 20 April 2007 / Accepted: 4 June 2007 / Published online: 3 August 2007
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Abstract Cerium oxide(CeO_2) thin films were deposited by the sol–gel dip coating technique using cerium chloride, acrylamide and *N,N* bis methylene acrylamide. The as deposited films were heat-treated at different temperatures in air. X-ray diffraction studies indicated the films to be of single phase CeO_2 . Optical bandgap in the range of 3.53–3.60 eV was obtained from optical studies. Laser Raman studies exhibited Raman bands around 457 cm^{-1} .

1 Introduction

Cerium oxide is a promising material that has potential use as a solid oxide fuel cell electrolyte [1, 2]. It can also be used as promoter of automotive exhaust catalysts because it possesses an excellent high oxygen storage capacity [3, 4]. Recent work has shown that cerium oxide films with ultrafine grain size can greatly improve the resistance of metals and alloys to high temperature oxidation [5] and shows good corrosion inhibition [6–8]. Thus, low cost methods for making cerium oxide need to be developed. Several ways have so far been used to make cerium oxide films, including vapour deposition processes, i.e. reactive sputtering [9], epitaxial growth [10], electrochemical vapour deposition [11], and the aqueous precipitation method, i.e. sol–gel [12] and spin coating [13, 14], reactive direct magnetron sputtering [15], pulsed laser deposition [16], electron beam evaporation [17], wet chemical deposition [18] and electrodeposition. Electrodeposition in

aqueous solution has recently been recognized as an attractive method for making thin oxide ceramic films [19] because it offers the advantages of low temperature processing, low cost processing, and result in the production of high purity films [20, 21]. In this work, cerium oxide films were deposited by the sol–gel dip coating method using Acrylamide.

2 Experimental methods

Cerium oxide thin films were grown by the sol–gel dip coating technique using AR grade Cerium chloride, Acrylamide, *N,N* bis methylene Acrylamide and Ammonium persulphate. 100 mL of 0.15 M cerium chloride solution was taken and the pH was adjusted to a value of nine. The temperature of the solution was then increased to 70°C . 2 g of Acrylamide and 0.5 g of *N,N* bis methylene acrylamide was added to the hot solution. After 10 min, sufficient quantity of ammonium persulphate was added to this mixture, till the solution became viscous. Cleaned Aluminium foil and indium tin oxide coated substrates were dipped inside the viscous solution and withdrawn at the rate of 2 cm min^{-1} . The film coated glass substrates were dried in an oven for 15 min, followed by heating in air at different temperatures in the range $400\text{--}525^\circ\text{C}$ for 30 min. Cerium hydroxide ammonia complex was trapped in the polymer network of bis acrylamide which then breaks into the oxide after post heating in air. The thickness of the films estimated from gravimetry was in the range of $1.0\text{--}1.5\text{ }\mu\text{m}$. The films were characterized by X-ray diffraction using a Phillips X-ray diffractometer and $\text{CuK}\alpha$ radiation. Optical band gap was estimated from the absorbance data obtained using an Hitachi U3400 UV–Vis–NIR spectrophotometer.

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Laser Raman spectrum was obtained using a Renishaw laser Raman system.

3 Results and discussion

The films heat-treated at different temperatures were characterized by X-ray diffraction (XRD) studies. The XRD pattern of the films deposited on Aluminium substrates and post heat treated at different temperatures is shown in Fig. 1. It is clear from the figure, that the films heat-treated at 400 °C are mainly amorphous. As the heat treatment temperature increases, the films become more crystalline as indicated by the increase of the (200) peak intensity and the decrease of its full width at half-maximum value. The films are crystallized in the cubic structure with a strong preferred orientation along the (200) direction. These results are in good agreement with the published data [22]. The lattice parameter a is calculated from the peaks positions and its value is found to be 5.42 Å, which is close to the value reported for vacuum evaporated CeO₂ films [23]. The crystallite size determined using the Scherrer's equation varied from 40–100 nm as the heat treatment temperature increased from 400 °C to 525 °C. The optical properties of CeO₂ thin films are determined from transmission and reflection measurements in the range of 0.3–2.5 μm. All the transmittance and reflectance spectra are normalized with respect to the substrate. The films were found to be highly transparent. High transparency for CeO₂ thin films was also reported for the films deposited by reactive DC magnetron sputtering method [24]. Figure 2 shows the optical transmission of CeO₂ films

post heat-treated at different temperatures. The films exhibit a transmittance above 80% in the visible and near-infrared region with a sharp absorption edge to approximately 350 nm. According to the solid band theory, the relation between the absorption coefficient (α) and the energy of the incident light $h\nu$ is given by:

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

where A is a constant, E_g is the band gap energy and $n = 2$ for direct band transition. Figure 3 shows a plot of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ for the films heat treated at different temperatures. Band gap of the films was 3.6 and 3.53 eV, respectively. These values are higher than the earlier results [25]. The higher values may be due to the small grain size.

The Raman spectrum (Fig. 4) of the CeO₂ layer on Al substrate is characterized by one intense and symmetric band at 457 cm⁻¹. In the case of the film on the ITO substrate the spectrum is characterized by two broad bands having similar intensities, one at 453 cm⁻¹ and one at 575 cm⁻¹, while recent systematic Raman studies on monodispersed CeO_x nanoparticles [26] as well as on CeO₂ thin films [27] showed that as the particle size decreases the F_{2g} mode of Ce–O symmetric vibration shifts from 464 cm⁻¹ to 450 cm⁻¹. Furthermore, the broad band (centered at 580 cm⁻¹) that appears on the Raman spectra of the CeO_x/ITO film was also observed in spectroscopic studies on solid solutions of CeO₂ with rare-earth oxides [28] and MO₂ (M: Si, Ti, Zr) [29] and was attributed to the increased oxygen vacancies that arise from the introduction of different cations. From the above discussion we can associate the Raman band at 453 cm⁻¹ for the film on ITO and the band at 457 cm⁻¹ for the film on Al to the F_{2g} mode of Ce–O bond in the fluorite-type lattice. The

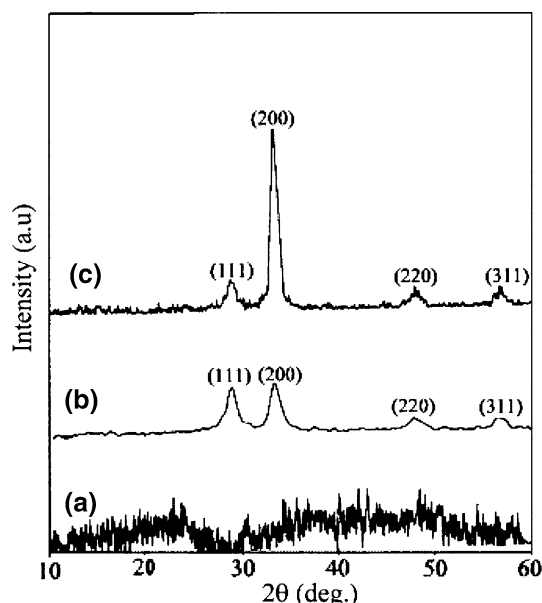


Fig. 1 XRD patterns of CeO₂ films deposited on Al substrates after heat treatment at (a) 400 °C (b) 475 °C (c) 525 °C

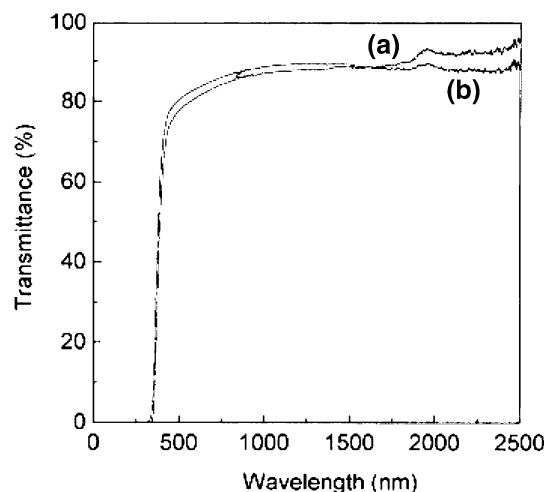


Fig. 2 Transmittance spectra of CeO₂ films on ITO substrates after heat treatment at (a) 475 °C (b) 525 °C

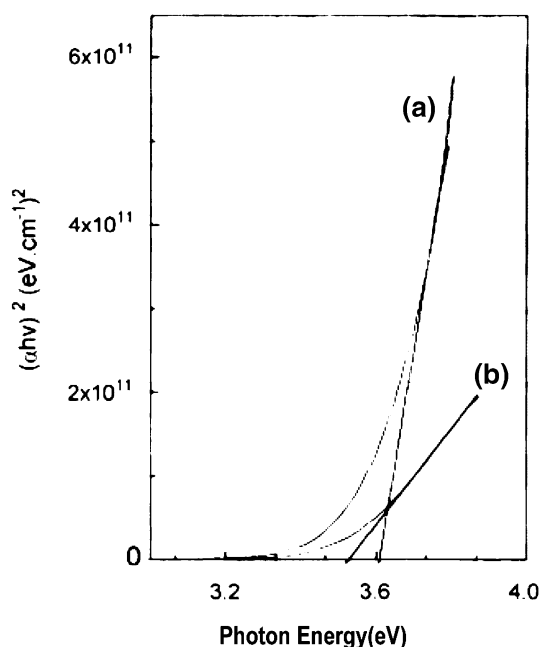


Fig. 3 $(\alpha h\nu)^2$ versus $h\nu$ plot of CeO_2 films on ITO substrates after heat treatment at (a) 475 °C (b) 525 °C

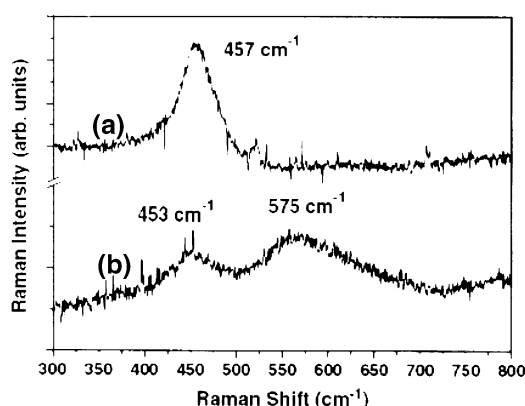


Fig. 4 Raman spectra of the films deposited on different substrates after heat treatment at 525 °C (a) Al (b) ITO

allocation of this band in smaller wave number for the case of the ITO substrate indicates its decreased particle size compared to that of the film on Al foil. This conclusion is further supported by the evolution of the band at 575 cm^{-1} , which is due to the existence of a large amount of oxygen vacancies in the CeO_x layer deposited on ITO. The increase in the molar fraction of oxygen vacancies (reduction of Ce^{4+} to Ce^{3+}) could also be due to the decrease in particle size.

4 Conclusion

The results of this investigation clearly point to the possibility of obtaining nanocrystalline CeO_2 films. CeO_2 films

with crystallite size in the range of 40–100 nm can easily be obtained by this technique. Further work is in progress to study the corrosion inhibition properties of these films on Aluminium foils.

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