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Consequence of source material on the surface properties of nebulizer spray coated cerium oxide thin films

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ABSTRACT

Cerium oxide thin films are coated on glass substrates by nebulizing spray pyrolysis technique using cerium nitrate and cerium chloride as a source material. Their crystallographic structures, surface morphology, optical properties and I–V characteristics are analyzed as a function of substrate temperature (300–500 °C). XRD is used to estimate the crystallographic texture, crystalline size, strain and lattice constant. All films exhibit a cubic fluorite structure with different preferred orientation depending on the preparation conditions. All the films exhibit dense, smooth and crack-free spherical nanostructures with some uneven surfaces in the range 400 nm. PL analysis indicates the presence of indigo and blue emission in the visible region centered at ~425 and ~467 nm respectively. UV-ViS spectra revealed that the films are transparent (70%) in the visible region. Optical parameters like refractive index, optical conductivity and band gap are calculated for different Ts. XPS analysis revealed the existence of Ce, O and C in the films. It demonstrates the prevalent occurrence of Ce^{4+} rather than Ce^{3+}. I–V characteristics confirm the semiconducting behavior of cerium oxide thin films due to its linear response to applied voltage.

1. Introduction

Nanostructured metal oxide thin films have drawn significant attention from many researchers due to their assorted applications in various fields of science and technology [1,2]. These nanostructured metal oxide thin films have unique physical and chemical properties, which are importantly dissimilar from their bulk counterparts [3]. Among these metal oxide thin films, cerium oxide (CeO_2) has been of vast interest due to its excellent properties such as a high refractive index, wide bandgap, high dielectric constant, high melting point, high transparency in the VIS–NIR regions with high thermal and chemical stability [4,5]. It is one of the most abundant and reliable compound in the useful rare earth lanthanides family and has been applied to diverse technological fields like UV absorbent and high activity catalysts [6,7], sensors [8–11], electrochemical devices [12,13] and fuel cells [14]. For the future demands in the fields of catalysis, it is necessary to develop new highly active catalysts for removal of emissions from combustion of conventional as well as bio-based fuels. Ceria has been shown to be an interesting support material for noble metals in catalysts designed for emission control, mainly due to its oxygen storage capacity. Another aspect is that the use of biofuels put new demands on the emission treatment system. Several methods have been devoted to the preparation of cerium oxide thin films such as spray pyrolysis [5,15–17], electron-beam evaporation [18], sputtering [19], pulsed laser deposition (PLD) [20,21] and Chemical Vapor Deposition (CVD) [22,23]. Among these methods, spray pyrolysis is a simple and unique technique to develop high quality, uniform and adhesive thin films with low cost and simple apparatus. It only requires a simple apparatus to deposit thin films of various materials under atmospheric condition. It has the ability to control particle shape, particle size, composition and phase homogeneity of the film. Moreover, this method is compatible with large scale industry manufacturing for deposition of thin and porous films due to the wide selection of precursors and lower equipment costs for mass production.

Spray pyrolysis has been widely used to produce fine powders because it is an inexpensive and continuous, ambient pressure process. It involves the atomization of a liquid precursor containing metal salts, droplet transport towards a heated substrate and film formation of the substrate surface, evaporation of the solvent and decomposition of the deposited material. Crack-free films obtained when the deposition temperature is above 290 °C.

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This article depicts the nebulizer spray pyrolysis process for the fabrication of nanostructured cerium oxide thin films. The films are characterized by XRD, SEM, FT-IR, PL, UV-ViS, XPS and I–V characteristics.

2. Experimental details

Cerium oxide thin films are deposited on glass substrates using Cerium Nitrate hexahydrate and Cerium Chloride heptahydrate as the chemical precursor. The substrates are cleaned using Hydrochloric acid, sodium hydroxide, isopropyl alcohol and then rinsed with deionized water. 0.02 M of cerium nitrate is dissolved in ethylene glycol and stirred for 30 min. The prepared solutions are deposited on glass substrates with different substrate temperature (300–500 °C). The same process is followed for cerium chloride source material. The compressed air is used as carrier gas. The pressure is maintained at 30 Pa. The results are compared with different substrate temperature. The optimized parameters are presented in Table 1. The prepared films are characterized by UV-Vis, PL, XRD, SEM, XPS and I–V characteristics. In this method, the aerosol (cerium hydroxide) formed from nozzle undergoes successive pyrolysis due to temperature gradients, this successive pyrolysis result into decomposition of aerosol at the substrate and leads to film formation. In case of CeO_2 film formation, the substrate temperature is fixed at 300 °C.

In the present study, optical properties of thin films are analyzed using JASCO spectrometer instrument. X-ray Diffraction (XRD) is a powerful technique used to identify the crystalline phases present in materials and measure the structural properties (strain state, grain size, phase composition, preferred orientation, and defect structure) of these phases. Samples are analyzed by an XPERT-PRO, Cu Kα Bruker AXS D8 Advance X-ray diffractometer. The films are analyzed in the 0–90° (2θ) scale angle range. The thin film samples are analyzed using JEOL Model JSM – 6390LV instrument for high resolution surface imaging. Vibration stretching of cerium oxide thin films has been done with the help of IR spectra (PerkinElmer, model 783, USA) in the spectral range 700–4000 cm^{-1} with a resolution of 1 cm^{-1}. Photoluminescence (PL) measurements are measured on a Hitachi F-4500 FL spectrophotometer using a Xenon lamp as the excitation source at room temperature. The excitation wavelength is fixed at 325 nm. The optical properties of CeO_2 thin films are investigated by computer controlled UV-Visible spectrophotometer (Aquila NKD 7000V) with a 150 Watt Xe arc lamp as a light source in the range 200–1200 nm. Thin film samples are analyzed using Thermo Fisher K-Alpha electron spectrometer with Al Kα X-rays (monochromatic), with a flood gun used for charge neutralization under the base pressure 10^{-7} Pa for elemental analysis. I–V Characteristics are analyzed with the help of Keithley electrometer 6517B.

3. Results and discussion

3.1. Microstructural characterization

3.1.1. X-ray diffraction studies

Fig. 1 a and b shows the XRD patterns of cerium oxide thin films prepared from cerium chloride and cerium nitrate as a source material deposited on glass substrates at various substrate temperature 300–500 °C respectively. The films are crystalline as they are deposited at a substrate temperature 350–450 °C. It indicates the amorphous nature of the films prepared at 500 °C due to the addition of a new phase Ce_2O_3 at 450 °C and film thickness. All the films exhibit single phase crystalline and cubic fluorite structure with preferred orientation along (1 1 1) direction [24]. The minority peaks are observed at $2\theta = 33.26, 47.12$ and 56.35 corresponds to (2 0 0), (2 2 0) and (3 1 1) planes respectively. These results are compared with JCPDS data 34-0394. Substrate temperature increases the intensity of the peak (1 1 1) up to 400 °C and then decreases due to the addition of a new phase (Ce_2O_3). It shows the films prepared from cerium nitrate having better crystallinity (Sharp peaks) and crystalline size compare to the films prepared from cerium chloride as shown in Fig. 1a and b. Fig. 1c–f shows the variations of crystalline size, FWHM, No. of crystallites and lattice constant with substrate temperature. The crystalline size increases with increasing substrate temperature upto 400 °C and then decreases due to the reduction of its FWHM and addition of new phase.

3.1.2. Surface morphology analysis

Fig. 2 (right side) shows the differences in surface morphology of cerium oxide thin films deposited at different substrate temperature using cerium nitrate. At 300 °C, shows the 3D interconnected porous structure owing to the slow spreading of droplets landing on the substrate and form a dense layer. When the deposition temperature increases, the droplets landing on the substrate may be semidry and slightly spread on it and forms the cracks of the layer gradually disappear with increasing deposition temperature up to 400 °C and layer with many micro cracks are formed at 450 °C [25]. The formation of micro cracks in the films is probably due to the thermal stress during the deposition and unevaporation of precursor solvent. Films prepared at 400 °C shows the formation of golf-ball like background with spherical particles with the size in the range 600 nm Fig. 2 (left side) shows the differences in surface morphology of cerium oxide thin films deposited at different substrate temperature using cerium chloride. All the films exhibit dense, smooth and crack-free spherical nanostructures with some uneven surfaces in the range 400 nm. Films prepared at 400 °C shows the discrete agglomeration of semi porous lamellar shaped particles [26]. Cerium nitrate shows the smooth surface and homogeneous distribution of crystallites compared to cerium chloride due to the formation of golf-ball like particles can be applied to various technological fields.

3.1.3. FT-IR analysis

The IR study gives the information about the phase composition as well as the way oxygen is bound to the metal ions. Fig. 3a and b shows the FTIR spectra of cerium oxide thin films prepared from cerium chloride and cerium nitrate source material respectively. It is noted that the CeO_2 thin films exhibit a group of strong, intense bands at 992, 2921 and 2844 cm^{-1}, which may be ascribed to the presence of υ (O–H …. H) stretching mode and υ (C–H) mode of residual organic moieties absorbed from atmosphere respectively. The strong and broad bands are observed at 1691 and 1529 cm^{-1} are ascribed to the bending mode of hydroxyl groups of absorbed water. The group of weak intensity peaks at 3842 and 3719 cm^{-1} are assigned to the υ (O–H) mode of (H-bonded) water molecules and υ (CH_3) mode of organic moieties respectively. The lower intensity peaks at 2313 cm^{-1} are assigned to the υ (C–O) stretching mode of vibrations. The broad bands are observed at 1685 and 775 cm^{-1} is due to the envelope of (Ce=O) terminal stretching and phonon band of metal oxide (Ce–O) network respectively [16]. The carbonation of ceria films is unavoidable in ambient atmosphere.

Table 1
Optimized parameters of spray coated cerium oxide thin films.

Source material	Solvent	Temperature	Mole concentration	Nebulizer-substrate distance
Cerium nitrate	Ethylene glycol	400 °C	0.02 M	5 cm