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Structural, morphological and optical properties of spray deposited Mn-doped CeO_2 thin films

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ABSTRACT

Cerium oxide and manganese (Mn) doped cerium oxide thin films on glass substrates were prepared by home built spray pyrolysis system. The effect of Mn doping on the structural, morphological and optical properties of CeO_2 films were studied. It was found that both the undoped and doped CeO_2 films were polycrystalline in nature but the preferential orientation and grain size changed upon doping. Atomic force micrograph showed a complete changeover of surface morphology from spherical to flake upon doping. A water contact angle result displayed the hydrophobic nature of the doped CeO_2 film. Optical properties indicated an increase in band-gap and a decrease in transmittance upon doping owing to Moss–Burstein effect and inverse Moss–Burstein effects. Other optical properties such as refractive index, extinction coefficient and dielectric constant as a function of doping were analysed and reported.

1. Introduction

The electrical and physical properties of metal-oxide thin films can be determined by knowing its optical parameters. In particular, the band-gap of the material can be determined by measuring the absorption coefficient at various wavelengths. The knowledge of band-gap is instrumental in knowing about the electrical properties of the material. This paper provides an insight of the optical properties of Mn-doped cerium oxide (CeO_2) thin films prepared by spray pyrolysis technique. CeO_2 thin films have a potentially wide range of applications [1–4]. Most notable among them are its uses in optoelectronics. Reports have confirmed that CeO_2 has similar lattice parameter to that of silicon and hence can be used as a replacement for silicon as dielectric layers in the integrated circuits [5]. Because of its high transparency in the visible region, CeO_2 thin films also find applications in smart window devices due to their ability to insert/extract large charge densities [5]. Pure and doped CeO_2 thin films also exhibit variable electrical conductivity and high catalytic activity [6]. CeO_2 thin films exhibit high ionic and electronic conductivity and hence find applications in solid oxide fuel cells [6,7]. There are also reports of CeO_2 thin films being used as humidity sensors [8]. CeO_2 thin films also exhibit ferromagnetic behaviour and hence can be used in spintronic applications [9]. Ultra-thin films of CeO_2 were also used in FeRAM applications [10].

Ceria being an optically wide band-gap material exhibits high electric breakdown and hence finds applications in power electronics sector. The effect of manganese doping in ceria powders have been reported by few authors. Pereira et al. [11] reported that doping CeO_2 with manganese decreases the sintering temperature of CeO_2. The mixed conductivity of CeO_2 powders can be further enhanced by doping it with a transition metal such as manganese [7]. Thus, Mn doping alters and improves the properties of CeO_2. However, no reports have emanated so far describing the effect of Mn doping on the optical and morphological properties of CeO_2 thin films providing us the motivation to carry out this work. Several methods to prepare CeO_2 thin films have been reported. Debnath et al. [12] reported the deposition of CeO_2 thin films by electron beam evaporation. Sol–gel method has also been used for the preparing CeO_2 mixed oxides thin films [13]. Ming-hua et al. [10] deposited CeO_2 thin films by RF magnetron sputtering. Zhang et al. [14] reported the preparation of Mn-doped CeO_2 nanospheres by template free solvothermal method. Tan et al. [15] investigated the facile synthesis of Mn-doped CeO_2 microrods and its magnetic property.

In this work, thin films of CeO_2 and Mn-doped CeO_2 prepared by home built spray pyrolysis technique and its structural, morphological and optical properties were studied. The use of

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spray pyrolysis offers the advantage of larger deposition area at lower costs when compared to other thin film deposition techniques and was therefore adopted in our work. It also offers better control of film properties and traits by effective manipulation of spray parameters such as nozzle size, distance between the spray gun and the substrate, carrier gas pressure, precursor type and deposition temperature.

2. Material and methods

CeO_2 thin films were deposited by home-built spray pyrolysis system from aqueous solution of cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) precursor salt which was obtained from Sigma Aldrich (99.9% pure), and was used as such without further purification. The details of the home built spray pyrolysis system can be found in previous report [16]. A 50 mL of 0.05 M aqueous solution of cerium nitrate hexahydrate was prepared and was stirred for 10 min at room temperature (~30 °C). This solution was then sprayed as a fine mist onto the glass substrates which were maintained at a temperature of 250 °C. The nozzle to substrate distance was maintained at 45 cm and was sprayed at an angle of 45°. In order to deposit the doped films, 99.9% pure manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$) precursor obtained from Sigma Aldrich was used. Manganese salt concentration in the precursor solution was varied from 1 wt% to 4 wt%. The deposited films were then subjected to annealing at 350 °C and were cooled slowly to room temperature.

The structural analysis of the films were carried out using a X-ray diffractometer (Model XPERT-PRO) employing Cu Kα_1 radiation (λ = 1.5406 Å) with continuous scanning mode and range of 2θ varying from 20° to 60° to detect the possible peaks. The morphology of the films was obtained using atomic force microscope (SPM-9500J2). The water contact angle over the film surface was obtained using goniometer (ramé–hart model 250). The optical properties of the films were carried out using the data obtained from UV–Visible spectrophotometer (Lamda 35). From the transmittance and absorbance data obtained, different optical parameters such as optical band-gap, refractive index, dielectric constant and extinction coefficient were obtained.

3. Results and discussions

3.1. Structural analysis

The X-ray diffraction (XRD) patterns of the undoped and different Mn-doped CeO_2 thin films are shown in Fig. 1. The diffraction profile indicates that both the film have polycrystalline in nature. The undoped CeO_2 shows a mixed crystal structure of hexagonal (ICDD card no: 78-484) and cubic (ICDD card no: 34-394) structure. However with the increase in Mn concentration, pure cubic phase was observed. Preferential orientation of the undoped and Mn-doped CeO_2 thin film was determined using texture co-efficient relation (Eq. (1)) [16] and estimated results shown in Fig. 2(a).

$$TC = \frac{I_{(hkl)}/I_{o(hkl)}}{(1/N)\left[\sum_N I_{(hkl)}/I_{o(hkl)}\right]} \quad (1)$$

where I is the measured intensity, I_o is the JCPDS intensity and N is the number of diffraction peaks. Fig. 2(a) shows that in undoped CeO_2, preferential orientation is along both (1 1 1) and (2 0 0) planes, but in the case of Mn-doped films preferential orientation is only along (1 1 1) plane. The Lotgering factor (F) of the film was estimated using the following relation [17] and a plot is shown in Fig. 2(b).

$$F_{(hkl)} = \frac{P_{(hkl)} - P_{o(hkl)}}{1 - P_{o(hkl)}} \quad (2)$$

where $P_{(hkl)}$ is the ratio of the XRD intensity of (hkl) reflection to the sum of the reflection in a scanned range, and $P_{o(hkl)}$ is the equivalent value for a randomly oriented CeO_2 (ICDD card no: 34-394). Mn dopant inhibit the growth in (2 0 0) plane and improved (1 1 1) plane, which may due to changes of crystal structure from hexagonal to cubic phase. The XRD pattern does not show any impurity/additional peaks for any Mn doping concentration. This clearly suggests that the Mn ions occupy positions within the fluorite-lattice. The same was also reported for Mn-doped CeO_2 nanopowders by Pereira et al. [11].

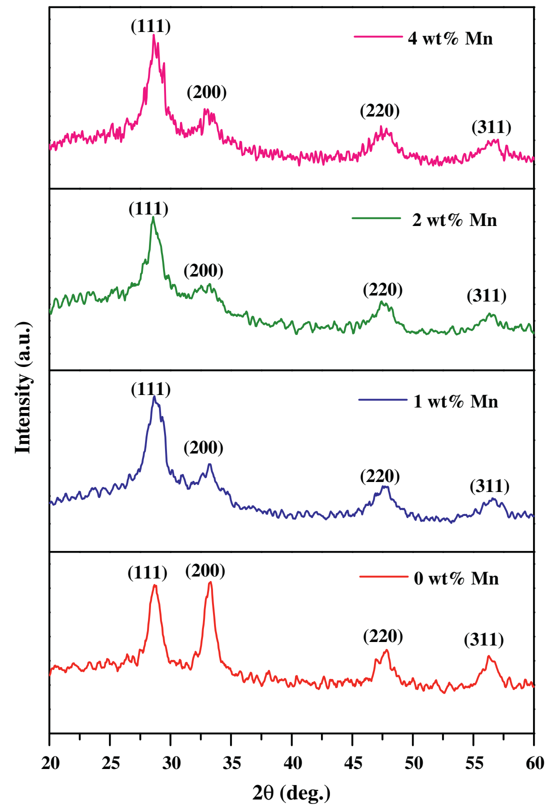

Fig. 1. X-ray Diffraction profile of 0 wt% (undoped), 1 wt%, 2 wt% and 4 wt% Mn-doped CeO_2 thin films.

Grain size and microstrain was estimated using a Williams–Hall relation,

$$\frac{\beta \cdot \cos\theta}{\lambda} = \frac{1}{D} + \varepsilon\left(\frac{\sin\theta}{\lambda}\right) \quad (3)$$

where β is the full width at half maxima (FWHM, in radian), θ is the diffracting angle (in radian), λ is the wavelength of the X-rays (1.5406 Å), D is the grain size (nm) and ε is the microstrain. The slope and intercept in the plot between $\sin\theta/\lambda$ versus $\beta{\cdot}\cos\theta/\lambda$ gives the grain size and microstrain respectively, and shown in Fig. 3. Moreover, the values of grain size (D), microstrain (ε), d-spacing, lattice parameter (a) and macrostrain obtained for undoped and Mn-doped films are shown in Table 1. The effect of doping is also observed by the narrowing of the peak (decrease in FWHM) which corresponds to the plane (1 1 1) clearly suggest that there is an increase in the grain size upon Mn doping in CeO_2. Peak shifts towards higher diffraction angles were also observed from the XRD data testifying a shrinking of unit cell volume caused due to the dopant [18]. Upon doping, grain size was found to increase up to 37 nm as Mn dopant increased. The d-spacing and lattice parameter of the films were also found to decrease with increase in Mn doping. The decrease in d-spacing and lattice constant is due to the replacement of large Ce^{4+} ions (101 pm) by the small Mn^{4+} ions (67 pm) [15]. Thus, the undoped CeO_2 film has greater strain when compared to the doped films. Also, Mn dopant stabilizes the crystal structure to cubic phase.