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Characterization of Spray Deposited CdO - CeO_2 Mixed Thin Film.

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ABSTRACT

Mixed CdO and CeO_2 thin films were deposited on to the pre- heated glass substrates by spray pyrolysis technique. The polycrystalinity and cubic fluorite structure of both CdO and CeO_2 are observed from the X-ray diffraction studies. The crystallite size was found to be 40 - 45 nm. The morphological studies conforms the formation of closely packed uniform spherical shape nanocrystallites. From optical studies the band gap was found to be ~ 3.24 eV. The chemical composition was identified through energy dispersive X-ray analysis technique.

Keywords: CdO, CeO_2, Spray pyrolysis, XRD, EDAX.

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INTRODUCTION

Ceria (CeO_2) thin film is a wide band gap material with multiple applications, such as smart window devices because of its high optical transparency in visible light region and interceptor property from ultraviolet region [1-3], electrolytes or electrodes in solid oxide fuel cells (SOFCs) [4-7], and silicon-on-insulator structures [8] and as well as gas sensors [9]. CeO_2 films were prepared by PVD or CVD method such as PLD [8], EB-PVD [10], magnetron sputtering [11], MOCVD [12], etc. CeO_2 films are capable of corrosion protection of metals and as coating for use as a catalyst support [13]. Due to high chemical stability and high diffusion coefficient for oxygen, CeO_2 is used as oxygen sensor [14]. The ionic and electrical conductivity properties of CeO_2 were strongly depend upon nanostructure size and in turn depend on processing conditions [15]. Various undoped , doped and mixed metal oxide semiconductors such as CeO_2 [16], CeO_2 doped SnO_2 [17], Ce doped CdO [18], CeO_2-mixed ZrO_2 [19], CdO-mixed In_2O_3 [20] are studied. However much work has not reported on CdO mixed CeO_2 thin films, where CdO is a transparent conductive oxide, which have been extensively used in semiconductor optoelectronic device technology [21]. Other application of CdO includes gas sensor devices, photo diodes, transparent electrodes, photo transistors and photo voltaic devices [22]. CdO shows very high electric conductivity due to the existence of shallow donors caused by intrinsic interstitial cadmium atoms and oxygen vacancies [23]. In the present work, CdO mixed CeO_2 thin film was prepared by spray pyrolysis technique which is simple, cost effective and requires less purity precursor materials. The structural, morphological and optical properties of CdO mixed CeO_2 thin film were reported.

EXPERIMENTAL

Mixed CdO and CeO_2 thin films were prepared by home built spray pyrolysis technique [24]. Intially, 0.05 M of Cerium acetate anhydrate ($Ce(CH_3COO)_3$, 99.99% purity, Sigma Aldrich) and another 0.05 M of cadmium acetate dihydrate ($Cd(CH_3COO)_3$. $2H_2O$, 99.8% purity, Nice chemicals) were taken as precursor salts and were dissolved in 25 mL of deionized water each, to make it a 50 mL of required precursor solution. The glass slides were cut into 25 mm x 15 mm x 1.5 mm in dimensions and were pre-heated at 503 K. Large number of samples were prepared and the different spray parameters are listed in the Table 1. The solution was sprayed on the preheated substrate with the help of pressurized carrier gas which converts the solution into aerosols and sprayed through the spray nozzle. To avoid spilling of precursor solution the angle of spray gun should be optimized and the distance between spray nozzle and preheated substrate should be maintained. The spray time and break time were maintained at 5 s and 75 s interval for each successive deposition for the nucleation and growth process of the films. The films were annealed for 1 hour at 573 K and were cooled till room temperature and were used for further characterization.

RESULTS AND DISCUSSION

Structural studies

The structural properties of prepared thin films were carried out through X' Pert PRO Diffraction system (XRD) at a scanning angle of 20° to 80°. Fig 1(a) shows that CeO_2 film is amorphous in nature. Fig 1(b) shows the polycrystalline nature of CdO, all the diffraction peaks were matched with the standard JCPDS data of CdO [05-0640] with preferential orientation along (1 1 1) plane. In the closely packed cubic structure of mixed oxides, the lattice was made up of oxide ions where the tetrahedral sites were occupied by Cd^{2+} ions and another half of octahedral sites were occupied by Ce^{4+} ions and from the obtained X-ray diffraction data, it conforms the existence of two cations in a single lattice. Fig 1(c) shows the X-ray diffraction pattern of mixed CdO and CeO_2 thin film.

All the diffraction peaks were indexed to (1 1 1), (1 1 1), (2 2 0), (2 2 0) as compared with standard bulk CeO_2 [JCPDS: 34-0394] and CdO [JCPDS: 05-0640]. The strong orientation was along (1 1 1) peak which conforms the polycrystalline nature with fluorite-type face centered-cubic structure of Cadmium oxide [24]. The average crystallite size D of the films were estimated from the X-ray diffraction patterns using the Sherrer formula [25].

$$D = \frac{K\lambda}{\beta \cos\theta} ----------(1)$$

Where K is the shape factor (0.94), λ is the wavelength of Cu- $K\alpha_1$ (1.5406 Å) which is the source of X- ray, β is the full width at half maxima (FWHM) in radians and θ is the diffraction angle in radians. The average crystalline size was varied from 40- 45 nm respectively and was good agreement with scanning electron microscope data. The texture coefficient (T_c) was used to quantify the preferential orientation of the deposited film using the following relation

$$T_C(hkl) = \frac{I(hkl)/Io(hkl)}{N^{-1}\sum_n I(hkl)/Io(hkl)} ----------(2)$$

T_c Where I is the measured intensity , I_0 is the joint committee on powder diffraction standards, (JCPDS) standard intensity and N is the number of diffraction peaks. It is maximum for (111) plane and its value is 1.54. With the addition of CdO to CeO_2 thin film, the amorphous nature of CeO_2 thin film changes to polycrystalline with orientation peaks along (111) and (111) planes for CeO_2 and CdO.

Morphological studies

The morphological studies of the prepared thin film was realized through field emission- scanning electron microscopy (FE-SEM, JSM - 6701F). Fig 2. shows the scanning electron micrograph of thin film and it conforms the formation of closely packed uniform spherical crystallites. The grain size distribution is observed in the range of 40 – 45 nm.

Elemental identification

Energy dispersive X-ray analysis (EDAX) technique was used to analyze the chemical components in a material under scanning electron microscopy (SEM). Figure 3. Shows the existence of cerium (Ce), cadmium (Cd) and oxygen (O) in the annealed thin film. The weight% of Ce, Cd and O were 53.65%, 33.13% and 7.72% respectively.

Optical studies

The optical studies of the annealed thin film was carried out using UV-Vis Spectrophotometer (Lambda 35 with scan speed of 480.00 nm/min). Fig 4. shows the optical absorption characteristics as a function of wavelength and as expected maximum absorption occurs in the visible region. The maximum absorption was at 450 nm.

The optical band gap E_g was calculated from the Tauc's plot by relating the incident photon energy (hv) with absorption coefficient (α) as [26].

$$(\alpha h\gamma)^{1/n} = A(h\gamma - E_g) --------(3)$$

where A is a constant, E_g is the band gap of the material and for different values of n different type of transition will occur. For n=1/2, 2, 3/2 and 3 the transition will be of direct, allowed indirect, forbidden direct and forbidden indirect respectively. Absorption coefficient (α) is calculated from Lamberts law.

$$\alpha = 2.303 * \frac{A}{t} --------(4)$$

Where A is the optical absorbance and t is the thickness of the film. According to the solid band theory, the relation between the absorption coefficient α and the energy of the incident light hv is used to determine the optical band gap and is shown in Fig 5. The optical band gap obtained as ~3.24 eV respectively. The band gap of mixed metal oxide was close to the band gap of crystalline CeO_2 which is equal to 3.2 eV [27]. With the addition of CdO to CeO_2 thin film, the optical absorption edge slightly shifts towards lower wavelength region which may be attributed to the decrease in the grain size and results in the increase of band gap from 3.2 eV to 3.24 eV [27].

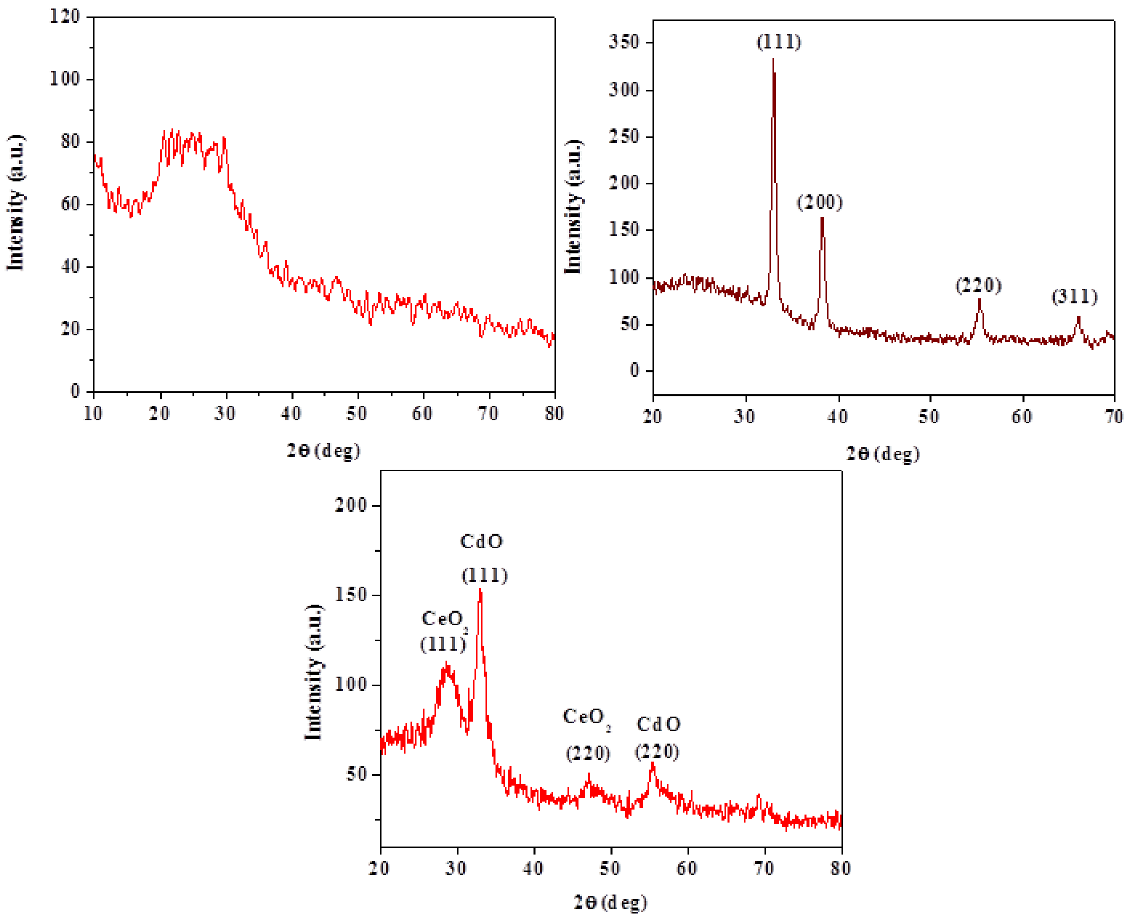

Figure 1(a) X- ray diffraction pattern for CeO_2 thin film, (b) CdO thin film , (c) mixedCdO and CeO_2 thin film.

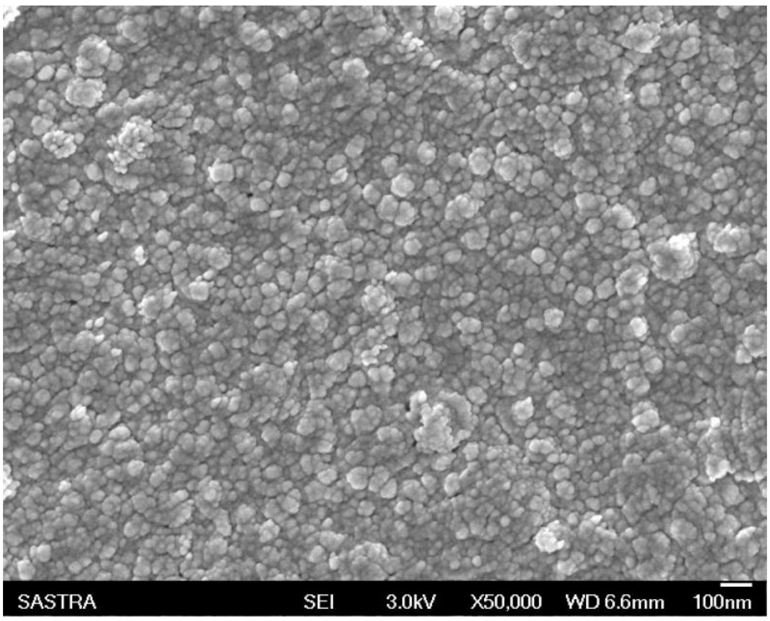

Figure 2: Scanning electron micrograph of mixed CdO and CeO_2thin film

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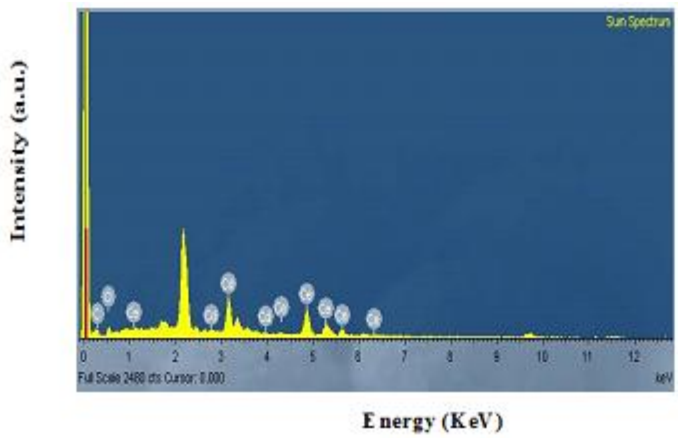

Figure 3: Energy dispersive X-ray analysis spectrum of mixed CdO and CeO_2 thin film

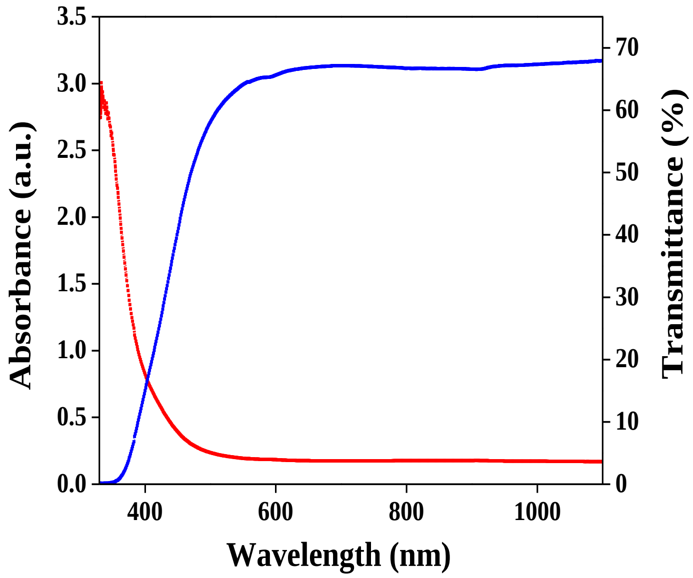

Figure 4: Optical absorption and transmission spectrum ofmixedCdO and CeO_2thin film

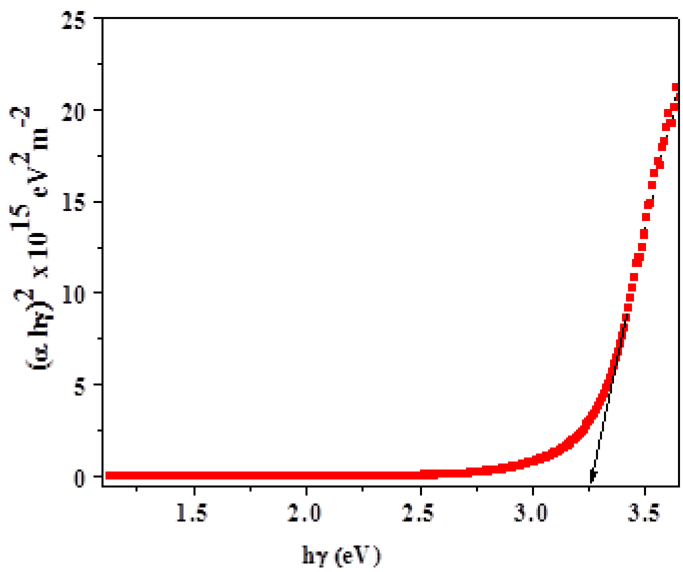

Figure 5: Optical band gap of mixed CdO and CeO_2thin film

Table 1: Optimized preparation conditions to obtain CdO mixed CeO_2 thin film in spray pyrolysis technique

Precursor salts	Cerium acetate anhydrate, Cadmium acetate dehydrate
Concentration of precursor salts	0.05 M each
Dissolving agent	50 mL of deionized water
Deposition temperature	503 K
Angle of spray gun	45°
Distance between spray nozzle and preheated glass substrate	40 cm
Solution flow rate	5 mL/min
Spray time	5 s
Break time	75 s

CONCLUSION

Mixed CdO and CeO_2 thin films were successfully deposited on glass substrates by spray pyrolysis technique. X- ray diffraction patterns conforms the formation of polycrystalline CdO with preferred orientation along (1 1 1) plane and amorphous CeO_2. With the addition of CdO to CeO_2, the structural studies shows the formation of cubic fluorite structure of both CdO and CeO_2 with the orientation planes along (1 1 1) and (1 1 1) direction. The average crystallite size is 40 – 45 nm. Field emission – scanning electron micrograph shows the formation of closely packed uniform spherical crystallites with an average crystallite size of 40- 45 nm. The EDAX spectrum conforms the existence of Ce, Cd and O in the thin film and the weight% of the elements were 53.65%, 33.13% and 7.72% respectively. The optical band gap of the film was 3.24 eV and shows good optical transmittance in the visible region.

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