Effect of Deposition Time on Morphology and Optical Properties of Nanocrystalline CeO_2/CdS Thin Films Grown by Chemical Bath Deposition

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Abstract. CeO_2/CdS thin films were prepared using a two-step growth technique. The effect of deposition time on the morphology and optical properties of the CeO_2/CdS thin films were systematically studied. The morphology and composition of the CeO_2/CdS films deposited on FTO substrates were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrum analysis (EDXA), respectively. The optical properties of the films were studied by UV–vis absorption and photoluminescence (PL) spectroscopy. The optical band gap values of the CeO_2/CdS films was found to be 2.13 - 2.45 eV as estimated from the UV-Vis absorption spectra. A strong blue emission band was observed in the room temperature photoluminescence spectrum for CeO_2/CdS thin films. The estimated lifetime from decay curve analysis shows enhanced lifetime for CeO_2/CdS films with an increase in deposition time. The enhanced absorbance and strong visible luminescence suggest its future application as energy conversion device and phosphor.

Keywords: CeO_2/CdS thin films, CBD, spin coating, FESEM, Optical properties.

INTRODUCTION

An increasing demand for energy and contemporary conventional energy crisis are encouraging factors for the rising importance of solar energy harvesting researches. Rare earth oxide nanomaterials are widely used for electronic, optoelectronic and energy conversion devices, due to their unsaturated electronic structure and wide band gap. Cerium oxide (CeO_2) nonmaterial, a rare earth oxide, exhibits ample applications such as photocatalytic activity, hydrogen production, oxygen storage, solar cells and other energy-related applications [1-2]. The extent of applications of cerium oxide nanomaterials is restricted in the visible spectrum because of its wide band gap of 3.2 eV [3]. Hence, to sense the visible light, narrow bandgap semiconductors are combined with cerium oxide nanomaterials. So it has been used as a window material combined with various semiconductors such as CdS, PbS, CdTe, CdSe, InP, Cu_2S, and CuInS [4]. Among the II-IV semiconductors, CdS is the most promising candidate with a reasonable band gap of 2.40 eV. The thin film polycrystalline semiconductor devices have been achieved much attention due to their exceptional applications in electronic and energy devices [5]. Size, crystallinity, and morphology of CeO_2/CdS thin film can be controlled by the synthesis technique used and optimizing various synthesis parameters like deposition time, the concentration of precursor and pH of the precursor solution. Various synthesis methods are used to deposit CdS thin film such as chemical bath deposition (CBD), electrodeposition, spray pyrolysis, vacuum evaporation, flash evaporation, sputtering and chemical vapor evaporation (CVD) [6]. Among these methods, CBD is a low temperature, simple, aqueous technique to deposit homogeneous films. The crystalline quality of CdS layers deposited by the CBD method is poor, but the films possess the best photoconductivity and morphological properties as compared with the films processed by other deposition techniques [5]. In this work, the preparation and deposition of CeO_2/CdS thin films on FTO substrates by a two-step spin-coating and CBD method are discussed. The effects of deposition time on morphological and optical properties of the as-prepared CeO_2/CdS thin films are also reported.

EXPERIMENTAL SECTION

Materials

Cerium chloride heptahydrate ($CeCl_3.7H_2O$), citric acid monohydrate ($C_6H_8O_7.H_2O$), ethanol (C_6H_5OH), cadmium acetate dihydrate ($Cd(CH_3COO)_2$)), Thiourea (N_2H_4CS) were obtained from Sigma Aldrich chemicals Pvt. Ltd. All materials were used without any further purification.

Synthesis

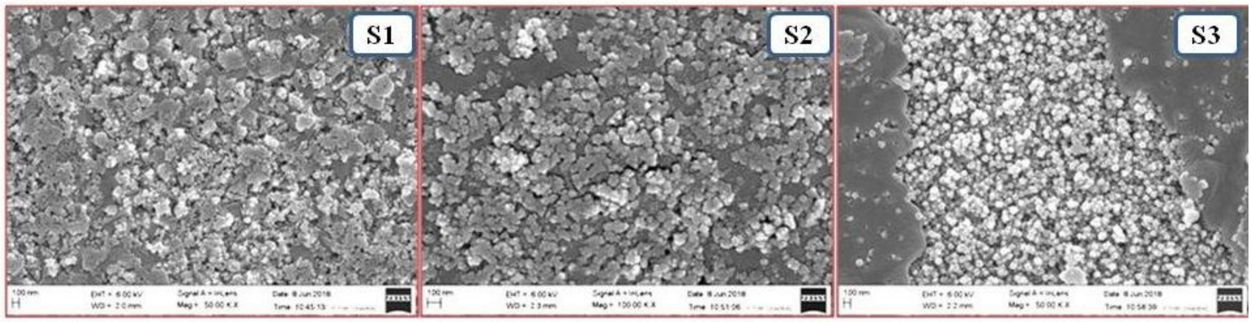
CeO_2/CdS thin films were deposited on FTO substrates by a two-step growth method. First, the CeO_2 film was deposited on FTO substrate by a spin coating technique [7]. In a typical process, 0.01 mol of $CeCl_3.7H_2O$ was added in 30 ml of ethanol. Then 0.01 mol of $C_6H_8O_7.H_2O$ was added into it and the solution was stirred for 1h at room temperature. FTO substrates were washed with acetone, ethanol and dI water each for 15 minutes. Then the sol was spin coated on the washed substrates at 3000 rpm for 30s. Subsequently, the samples were annealed at 400°C for 5 minutes. In order to deposit CdS on CeO_2 film, we followed a chemical bath deposition method. Two aqueous solutions of 32.5 mM $Cd(CH_3COO)_2$ and 65 mM of N_2H_4CS were prepared separately. Then both the solutions were mixed and stirred at 80°C. The CeO_2 coated substrates were mounted vertically on the beaker containing the solution. The substrates were removed from the bath and dried in air for 2 minutes after the deposition completed. Subsequently, the substrates were dried in a hot oven at 50 °C for 10 minutes. Substrates with homogeneous and well-adhered films were obtained. The CeO_2/CdS thin films were prepared with different CdS deposition time (Table 1). The morphological study was investigated by field emission scanning electron microscopy (FESEM) images obtained from FESEM Supra 55 (Carls Zeiss, Germany) microscope with an EDX spectroscopy. The optical absorption spectrum was recorded in the range of 200-800 nm using an Agilent Carty 5000 UV-VIS-NIR scanning spectrometer. The photoluminescence (PL) emission spectra and lifetime studies were carried out with an Horiba 2500 lifetime spectrophotometer using a xenon lamp as the excitation source (λ_{ex}= 270 nm).

TABLE 1. Deposition time of CeO_2/CdS thin films and their corresponding band gap values.

Sample Name	Deposition time (h)	Band gap E_g(eV)
S1	1 h	2.13 eV
S2	1.5 h	2.22 eV
S3	2 h	2.45 eV

RESULT AND DISCUSSION

The scanning electron microscopy technique is well-known for the study of surface morphology of thin films. The CeO_2/CdS thin films with different deposition time were used for FESEM analysis. Figure 1 shows the FESEM micrographs of CeO_2/CdS thin films prepared by chemical bath deposition method. The micrograph of sample S1 confirms that the film is uniform, homogeneous and well adherent to the substrate. The FESEM image of sample S2 confirms the formation of spherical nanosized grains that covers the substrate. The agglomeration decreased with increase in deposition time for S2. The grains formed on the substrate for sample S3 are more crystalline and less agglomerated with uniform spherical nanoparticles. Thus the deposition time for CdS on FTO/CeO_2 surface can be varied to obtain thin films with required size and crystallinity. So the nanocrystalline nature of thin films was confirmed from FESEM micrograph. The quantitative composition of the CeO_2/CdS thin films deposited on FTO substrates was determined by EDXA technique. The EDX spectra confirm the presence of Ce, O, Cd and S in the samples which indicates its purity. The EDX spectra recorded at other parts of the film yields the same result which again confirms the homogeneity of the samples.



(a) (b) (c)

FIGURE 1. FESEM images of CeO_2/CdS thin films prepared with different diposition time: (a) sample S1, (b) sample S2, and (c) sample S3.

Optical absorption study of thin films provides useful information to analyze the features concerning the band structure and optical band gap of materials [5]. The optical absorption property of CeO_2/CdS thin films was studied by absorption spectra and recorded in the wavelength range of 200 nm to 800 nm. Figure 2 shows the absorption spectra of CeO_2/CdS thin films. The absorption was found to be maximum for sample S1 with a deposition time of 1h. The absorption of light both in UV and visible wavelength range was found to be decreased with increase in CdS deposition time. A broad absorption band was observed in the visible region upto 650 nm. The absorption coefficient α satisfies the following expression [6] for optical absorption of semiconductors,

$$(\alpha h\nu) = C\left(h\nu - E_g\right)^n$$

Where C is constant, E_g is the band gap of semiconductor and n is constant, i.e; n=1/2 for direct bandgap semiconductor and n=2 for indirect bandgap semiconductor. Figure 3 shows a plot of $\alpha h\nu$ versus $h\nu$ and extrapolating the linear portion of the curve provides the optical band gap of the samples. Here, the band gap values of CeO_2/CdS films were estimated from the above plot and found to be 2.13 eV, 2.22 eV, and 2.45 eV, respectively. The band gap values increased with increase in deposition time of CdS on FTO/CeO_2 surface.

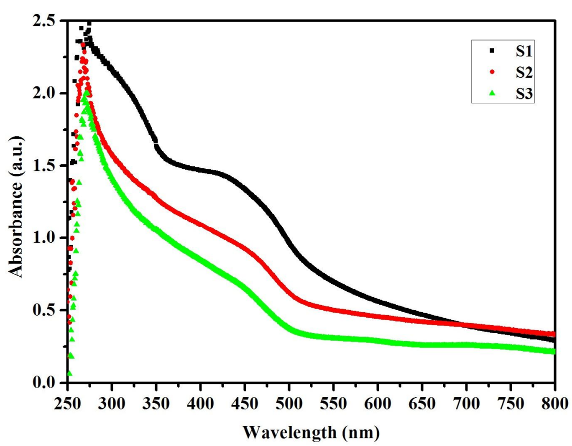


FIGURE 2. UV-Vis absorption spectra for CeO_2/CdS thin films

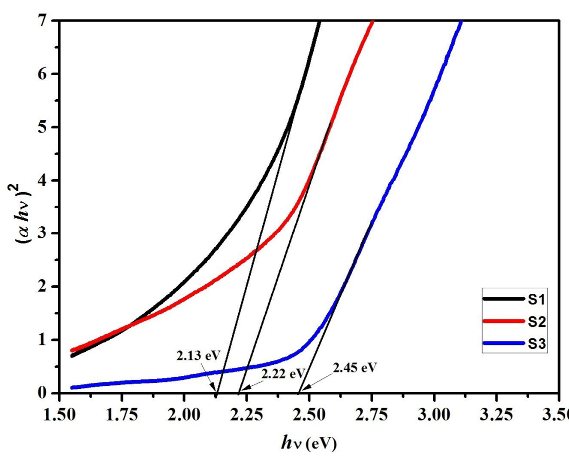


FIGURE 3. Tauc plot for CeO_2/CdS thin films.

Figure 4 shows PL spectra of CeO_2/CdS thin films deposited on FTO substrates with an excitation wavelength of 270 nm. A series of peaks were observed for the samples in the visible spectrum. The PL emission peaks corresponding to PLE peak centered around 270 nm are 438.6 nm, 458.5 nm, 481 nm, 502.4 nm, 516.7 nm, 529 nm, 557.8 nm, 570.5 nm, 590.3 nm, 624 nm and 665.5 nm. The peak positions for all the samples in PL spectra are same. On the contrary, the intensity of emission spectrum increases with increase in deposition time, with sample S3 having the most intense luminescence property. A broad emission band observed from 350 nm to 500 nm can be attributed to the transition from 4f of Ce to 2p of O. A strong peak observed at 458.5 nm can be arisen due to surface defects such as dislocations and oxygen vacancies [8]. Figure 5 shows the decay curve of CeO_2/CdS thin films deposited on FTO substrates. The lifetime of the samples corresponding to 458.5 nm emission peak from the decay curve analysis was found to be 6.07 μs, 6.16 μs and 6.18 μs for S1, S2, and S3 respectively. Consequently, the lifetime increased with increase in deposition time.

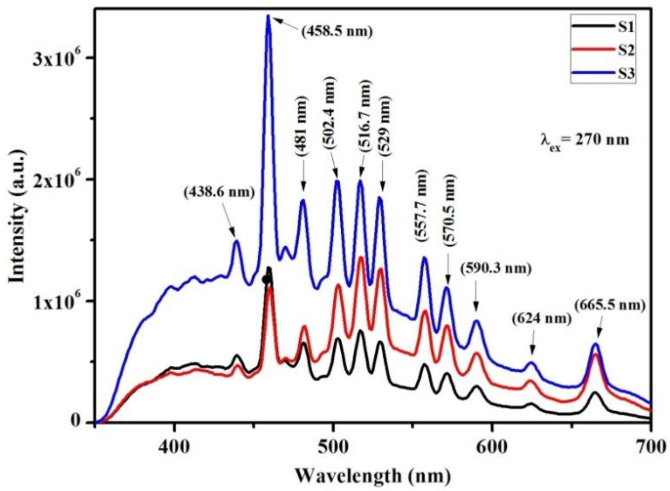


FIGURE 4. PL spectra of CeO_2/CdS thin films; (λ_{ex} = 270 nm)

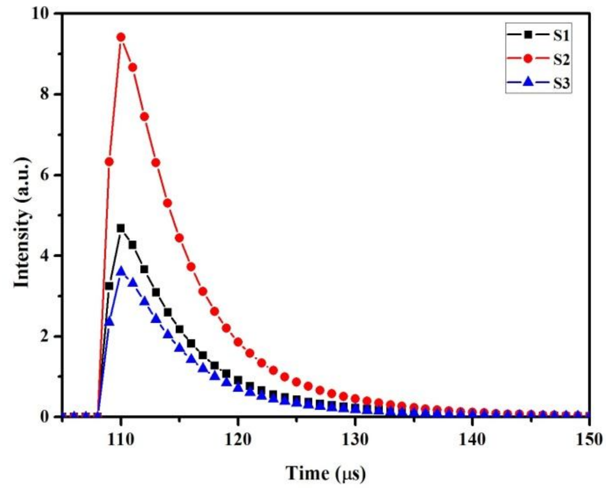


FIGURE 5. Decay time plot for CeO_2/CdS thin films.

CONCLUSION

The spin coating method along with the CBD method was followed for the preparation of CeO_2/CdS thin films on FTO substrate. The FESEM analysis reveals that the film is homogeneous, well adhered and covers FTO substrate. The grain size, uniformity, crystallinity, and agglomeration were depended on the deposition time as confirmed by FESEM analysis. The optical band gap of CeO_2/CdS thin films was found to be 2.13 eV to 2.45 eV. The broad emission band obtained from PL study signifies the importance of the films in phosphor applications. The enhanced lifetime of CeO_2/CdS thin films makes it more suitable for use in optical devices. The lifetime could also be enhanced by increasing deposition time. Further studies and experiments are being carried out for high-efficiency energy harvesting devices using CeO_2/CdS thin films.

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