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Structural and optical properties of EDTA capped CdS nanostructured thin films synthesized by sol-gel spin coating technique

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Abstract

In this paper, structural and optical properties of the cadmium sulfide/ethylenediamine tetra acetic acid (CdS/EDTA) nanostructure thin film was prepared on a glass substrate by using the sol-gel spin-coating technique and annealed at 573 K. The structural patterns of the nanomaterials were characterized using X-ray diffractometer (XRD), transmission electron microscope (TEM), UV-Vis spectrophotometer (UV-Vis) and photoluminscence (PL). The surface morphology of the EDTA doped CdS thin film was investigated using scanning electron microscope (SEM). The nanostructured thin film proved to have hexagonal structure with an average crystallite size of 44 nm. In addition, the PL spectra of the nanostructure thin films exhibited green emission band

Keywords: *Annealing, EDTA, Thin films, X-ray diffraction, optical properties*

1. Introduction

The thin film is a branch of science that deals with very thin structural layers of different materials. In recent years, thin film science has been developed worldwide into a major research area. The importance of thin film coating leads breakthrough in microelectronics, optics and nanotechnology. In addition, the thin film science and technology plays an important role in high tech industries [1]. Thin film technology has been developed primarily for the need of the integrated circuit industry. Furthermore, thin films of numerous materials such as metals (Au, Ag, Pt, Al), metal oxide semiconductor (SnO_2, TiO_2, Fe_2O_3, MgO, ZnO, CuO, ZrO_2, V_2O_5, CeO_2, WO_3) and metal sulphide (ZnS, SnS, CdS) find important applications due to their specific optical and electrical properties [2, 3].

Cadmium sulfide (CdS) is a direct band gap semiconductor with Eg ~2.5 eV at room temperature and large exciton binding energy, has very broad applications in photo detectors, optoelectronics and solar cell applications. A variety of resources for sulfur for preparation of CdS thin films such as sodium sulphide, hydrogen provided gas and thiourea are the most generally used for a solution based preparations of nanosized CdS [4]. CdS has crystal systems, hexagonal phase and cubic phase, besides amorphous CdS. At relatively low temperature, cubic phase and amorphous CdS are effortlessly received. As the properties of hexagonal phase CdS are much suitable than those of cubic phase CdS in the fields of photocatalysis, photoconduction and so on, and much efforts had been paid to have look at the section transition in CdS. CdS additionally possess great optical properties. A tremendous amount of effort has been devoted to the synthesis and study of optical properties of CdS nanoparticles and quantum dots [5].

Moreover, Different techniques are available to prepare CdS thin films, including sputtering, chemical vapor deposition (CVD), sol-gel and spray

pyrolysis. However, among all of these techniques, the sol-gel technique is particularly attractive due to different reasons; good homogeneity, controlled composition, low processing temperature, large area coatings, low cost efficient in producing thin, transparent, muti-component oxide layers of many compositions on various substrates [6]. A capping agent of ethylenediaminetetraacetic acid (EDTA) is an amino polycarboxylic acid and a colorless, water-soluble solid. Its conjugate base is called ethylenediaminetetraacetate and broadly used to dissolve limescale. In addition, EDTA is produced as several salts, substantially disodium EDTA and calcium disodium EDTA. Furthermore, EDTA is widely used for scavenging metallic ions in biochemistry and molecular biology, ion depletion is usually used to deactivate metallic-dependent enzymes, either as an assay for their reactivity or to suppress damage to DNA or proteins [7].

In this study focuses on the dependence of the structural and the optical properties of CdS/EDTA nano structured thin films prepared by the sol-gel method on the annealing temperature are investigated. The nanostructure thin films are coated onto a glass substrate with the multi-layer method.

2. Materials and Methods.

In this study, cadmium sulfate ($CdSO_4$) was purchased from Sigma-Aldrich, Bangalore, India. Sodium sulfide and Ethylenediaminetetraaceticacid (EDTA: $C_{10}H_{14}K_2O_8N_2.2H_2O$) were purchased from Sd Fine-Chem Ltd, Mumbai, India. Deionized water was used throughout the experiment.

2.1. Preparation of CdS/EDTA Thin Films

CdS/EDTA-573K nanostructured thin films have been deposited on an identical glass substrate by using sol-gel spin coating method. Firstly, the identical substrate changed into wiped clean the use of chromic acid and sodium hydroxide pellet solution and then washed with acetone. Initially, 30 ml of 0.1 M cadmium sulfate turned into mixed with 30 ml of 0.1 M sodium sulfide under constant stirring for 45 min. In addition, 30 ml of 0.02 M EDTA changed into brought into the above received reaction mix under stirring for 40 min which ended in a cloudy yellow solution. The yellow solution was through sonication for 10 min at room temperature, with the intention to obtain a homogeneous suspension. The organized homogeneous suspension changed into coated on an equal glass substrate (1.5 × 8 mm) the use of spin coater (SM-180-BT; Sawatec, Ruggell) at 2000 rpm. Further, the glass substrate changed into air dried to cast off the residual iron contaminants. The prepared thin film become allowed to dry inside the air for 45 min and heated at 60°C for 48 h until evaporation of the solvent. Finally, the sample changed into annealed at 573 K for 1 h at air atmosphere.

2.2. Characterization

The structural properties of the CdS/EDTA samples have been decided via the usage of X-ray diffractometer (XRD, X'Pert Pro; PANalytical, Netherlands) the usage of Cu Kα as a radiation supply (λ=1 5406 Å) which operated at 30 kV and 15 mA. The samples have been scanned inside the (2θ) range from 10 to 80°. The average crystallite sizes of all the samples have been calculated from the 2θ position of FWHM the use of Scherrer's formulation. The TEM (CM200; Philips, USA) was operated at 120 kV and provided information about the character nanoparticles upto high importance of 1,000,000X with a better resolution of less than 1 nm. The selected area electron diffraction (SAED) pattern became observed to expect the crystalline nature of the samples. The infrared (IR) absorption spectra of all samples have been recorded at room temperature the usage of the Fourier transform infrared spectroscopy (FTIR; Spectrum 100; PerkinElmer, USA) within the wavenumber range from 4000 to 400 cm^{-1}. The samples are accomplished with KBr pellet to discover the presence of functional groups. The optical properties of the prepared thin films have been determined based totally on their optical spectra, obtained the use of a UV-visible spectrometer (V-570; JASCO, Japan) within the wavelength range of 200-900 nm. X-ray fluorescence spectrometry (XRF, EDX-720, and Shimadzu, Japan) changed into employed to discover the concentration of the factors supplied in nano powder by using the usage of qualitative and quantitative measurements. The photoluminescence spectra (Cary Eclise WinFLR) turned into investigated for the samples, the wavelength variables are numerous from 300-550 mm. The surface morphology of CdS/EDTA samples has been inspected the use of a scanning electron microscope (SEM, JSM-6390LV; JEOL, Tokyo, Japan) with an accelerating voltage of 20 kV. The particle size of the sample was analyzed in the range of 1–100 nm at the scattering angle of 90° using the particle analyzer. Three dimensional photon cross-correlation techniques were used for the simultaneous measurement of particle size.

3. Results and discussions

The X-ray diffraction pattern of CdS/EDTA-573K thin film is shown in Fig. 1. The diffraction peaks observed at 24.94°, 26.07° 28.33°, 35.57°,

43.03°, 43.95°, 51.14°, and 58.97° corresponding to (100), (002), (101), (102), (110), (103), (112) and (202) crystal planes which are well agreed with the hexagonal structure of CdS [JCPDS No. 41-1049]. The corresponding lattice parameter become a = 4.140Å and c = 6.719Å. The common crystallites size of the thin films determined to be 44 nm in step with the Scherrer equation. In addition, the important intensity peaks of CdS thin film exhibit (101) and (002) plane and its intensity encouraged by using strongly dependent on the annealing temperature at 573 K, then it's well crystallized CdS crystalline [8].

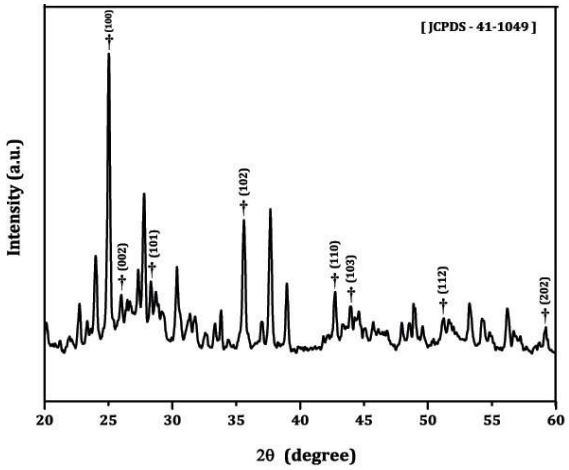

Fig. 1. *XRD pattern of CdS/EDTA nanostructured thin films at 573 K*

The FTIR spectra of CdS/EDTA nanoparticles annealing at 573K with unique absorption values are shown in Fig. 2. The CdS nano particles show that the asymmetric and symmetric stretching band at 2921 cm^{-1} and 2859 cm^{-1} is associated with C-H stretching of EDTA [9, 10]. An absorption peak at 3467 cm^{-1} is corresponding to the -OH group of water absorbed through the samples [11-13]. Further, a peak at around 1414 cm^{-1} shows that bending vibration of water molecules is because of the presence of atmospheric moisture [14] while the bands at 1600 cm^{-1} arised from aromatic C-C stretching [15]. The observed strong, broad IR absorption band at around 1106 is assigned to SO_4^{2-} functional group [16, 17]. Similar such high peaks due to C-H bending vibrations are found at about 613 cm^{-1}. Hence, it can be inferred that the capping agent passivates the surface of the nanoparticles [18].

Fig. 3 shows typical TEM images of the prepared CdS/EDTA-573K nanostructure thin films. The TEM image shows that the formation of CdS nanoparticles in an agglomeration of a size much less than 100 nm. The SAED pattern is shown as an inserted image in TEM image, verify the crystalline nature of CdS nanoparticles, which is clearly ascertained from the XRD spectral data. Thus, the above measurements truly identify the morphology, size and crystallinity of prepared CdS nanoparticle, used inside the guidance of the spin coating method.

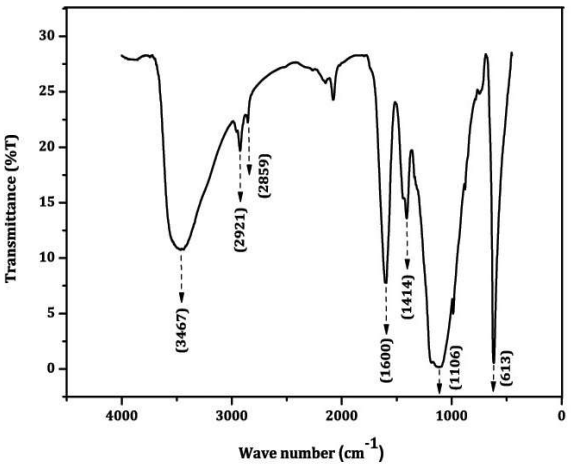

Fig. 2. *FTIR spectra of CdS/ EDTA nanostructured thin films at 573 K*

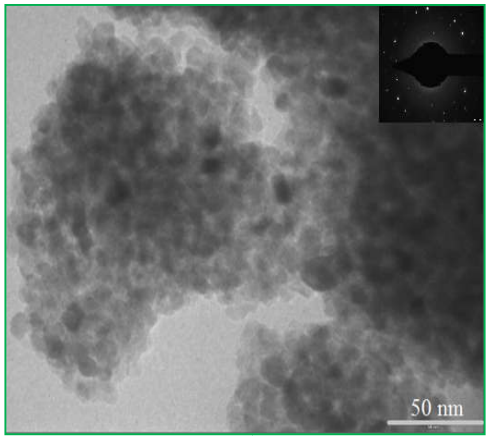

Fig. 3 *TEM image along with a SAED pattern*

The UV absorption spectra of the CdS/EDTA-573K nanostructured thin films are revealed in Fig. 4. The located consequences imply that higher absorption at 430 nm, the absorption outcomes is because of the presence of EDTA inside the CdS/EDTA nanostructured semiconductor that is tuned to a better energy band gap and extensively increasing quantum yield by means of decreasing the crystallite size of the nanoparticles. The optical band gap determined in the present investigation is found to be 2.88 eV. It is obvious that the absorption of the films in the visible place strongly depends on the chelating agent (EDTA). The adding of EDTA to the CdS thin film presentations the high absorption within the visible region. If lowering absorption

wavelength of the thin film layers results in an increase in the band gap energy [19].

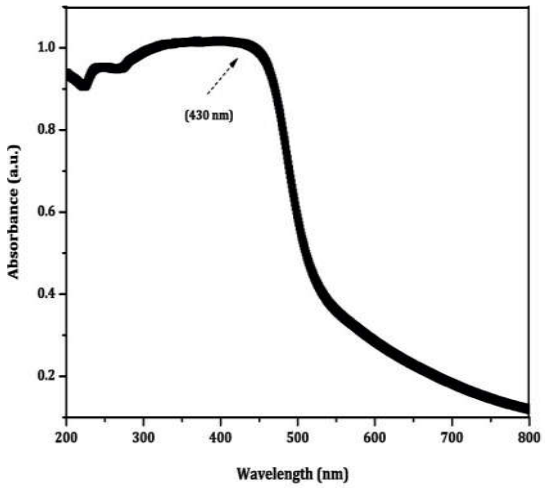

Fig. 4. *Optical absorption of CdS/EDTA nanostructured thin films at 573K*

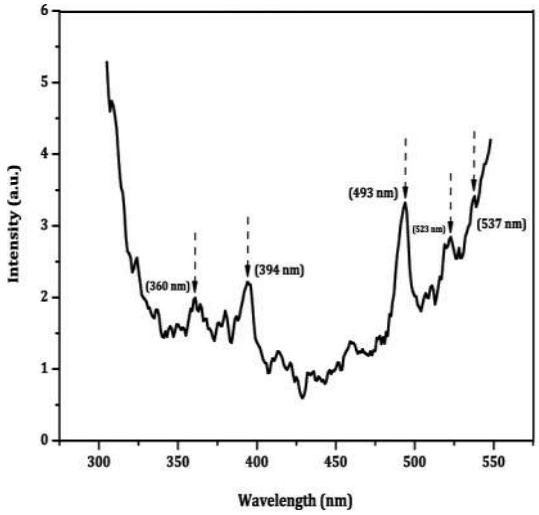

Fig. 5. *Photoluminescence spectra of CdS/EDTA nanostructured thin films at 573K*

XRF elemental analyses of CdS/EDTA-573K are indexed in Table 1. The analysis confirms that the presence of Cd and S elements along residual impurities. It is located even as increasing the annealing temperature as growth in Cd element and a lower inside the sulfur element.

Table. 1. XRF analysis for CdS/EDTA-573K thin films

Elements	Weight%
Cd	63.952
S	29.695
K	6.151
Cu	0.086
Fe	0.067
Zn	0.049

The evaluation of photoluminescence of synthesized CdS/EDTA-573K thin films reveal the numerous peaks which may be verified in Fig. 5. The Photoluminescence spectrum showed the emission peak at 360, 394, 493, 523 and 537 nm. The emission band of 493 nm corresponds to the band edge transitions of CdS, while that of 360 and 523 nm corresponds to the band edge transitions in bulk CdS thin films [20]. Further, the green emission peak at around 537 nm, which became assigned to the surface trap brought on fluorescence. This involved the recombination of electrons trapped internal a sulfur vacancy with a hole in the valence band of the CdS nanoparticles [15]. It is revealing that the band gap-resonant conduct of the surface chemical reactivity is responsible for the oxygen gas sensing applications [9].

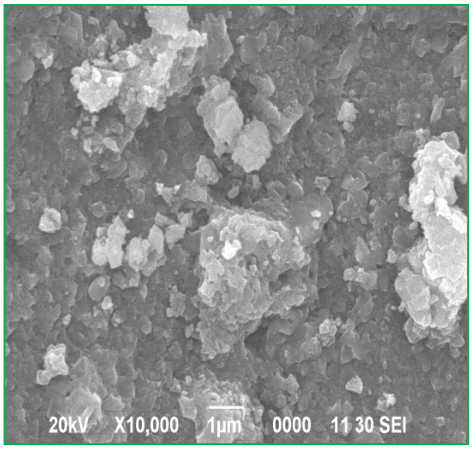

Fig. 6. *SEM images of CdS/EDTA-573K*

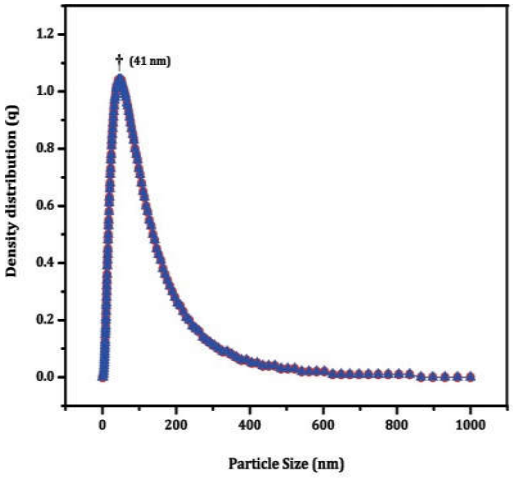

Fig. 7. *Particles size distribution of CdS/EDTA nanostructured thin films at 573K*

The structural morphology of the CdS/EDTA-573K thin film is shown in Fig. 6. It definitely

indicates that the formation of clusters with compact crystalline nature. Since annealing temperature 573K, the CdS particles are agglomerated and in flip shape clusters. The particle size distributions of CdS/EDTA-573K nanostructured thin films are revealed in Fig. 7. The average size of the particles of annealed at 573K was 41 nm. Nevertheless, the sample show around similar size of the particles without significant difference. It is more evident in the crystallite size of the particles.

The surface morphology located inside the TEM image (Fig. 3) is correlated with the micrograph of SEM image (Fig. 6). Addition of EDTA with CdS produced some changes within the crystalline nature of the thin film [21]. The difference in surface morphology and crystalline nature of CdS/EDTA-573K nanostructured thin film is known from the SEM and TEM image analysis. In XRD, the hexagonal peak exhibited high intensity (100) in comparison with that of another structure peak. It indicates the high degree of crystallinity. It additionally showed narrow band gap. Hence it is understood that hexagonal structure have affect the oxygen gas sensing performance in comparison with an additional structure [9].

4. Conclusions

The CdS/EDTA annealed at 573K has been efficaciously synthesized through sol-gel spin coating technique. Cadmium sulfate and sodium sulfide were used as a starting precursor for the preparation of CdS thin films. The structural properties of the organized sample had been measured through X-ray diffraction (XRD) with an average crystalline size of approximately 44 nm. The optical absorption peak was observed at 430 nm wavelength and the band gap calculated from absorption spectra was at 2.88 eV. CdS particles show that the asymmetric and symmetric stretching band at 2921 cm^{-1} is associated with C-H stretching of EDTA. Hence, the CdS/EDTA-573 K nanostructure thin films may be used as oxygen gas sensing applications.

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