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Cadmium sulfide thin films with capping agent of EDTA for oxygen gas sensor applications

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The Cadmium sulfide/Ethylene-diamine-tetra-acetic acid (CdS/EDTA) nanostructure thin film was prepared on a glass substrate using spin-coating method and it was used for gas sensor applications. The structure properties of CdS/EDTA were comparatively characterized. The nanostructured thin film was found both in hexagonal and cubic structure with an average crystallite size of 41 nanometer (nm). The stretching and vibration mode of CdS/EDTA was confirmed through Fourier transform infrared spectroscopy. The surface morphology of the nano particles was investigated using scanning electron microscope, which showed uniformly distributed crystalline surface. The values of band gap energy for CdS and CdS/EDTA are respectively, 4.20 and 4.17 eV. The Photoluminescence spectra of the CdS/EDTA films were exhibited green and yellow band emissions. Oxygen was suitably tailored to verify the sensor response over a concentration range of 20-100 ppm at room temperature. The observed results reveals that the performance, response, and recovery time of sensors were increased by chelating agent of CdS/EDTA thin film.

Key words: Spin coating method, Thin films, Gas sensor, AFM.

Introduction

Gas sensors have gained much attention due to their sensitized reactions to different gases such as CO2, H2, O2, NO2, and CO. Alternatively, oxygen sensors are used to find extensive applications in a variety of fields. The oxygen sensors are used in mines and in hospital incubators to detect the presence of oxygen, in largescale furnaces for combustion control and analytical instruments in various research and development fields. Further, the development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. It is well known that chemical gas sensor performance features such as sensitivity, selectivity, time response, stability, durability, reproducibility, and reversibility are largely influenced by the properties of the sensing materials used [1, 2]. Among these, a working sensor can be typically characterized by three parameters: sensitivity, selectivity and response time. Sensitivity is the ability of the sensor to quantitatively measure the test gas under given conditions. It is governed by the inherent physical and chemical properties of the materials used. Selectivity of a sensor is its ability to sense a particular gas free from interference. Response time is a measure of how quickly the maximum signal change is achieved with

gas concentration changes. [3, 4].

The synthesis and characterization of semiconductor nano crystals are significant interest from both fundamentals and applied research, due to their tunable electronic, optical and catalytic properties arising from the size confinement effect. Cadmium sulfide (CdS) thin film is a technologically important II-VI semiconductor with a direct optical band gap of 2.42 eV at room temperature are used. It is a promising material and extensive research has been done on CdS thin films [5, 6]. Cadmium sulfide (CdS) thin films have been intensively investigated including solar cells, photo resistors, transistors, piezoelectric transducers, electronic and optoelectronic devices [7]. Many methods, such as electro deposition, screen printing, physical vapor deposition, spray pyrolysis, molecular beam epitaxial, chemical bath deposition, successive ionic layer adsorption and reaction, sonochemical and spin coating method, are available for preparing CdS thin films. Among them, solgel method is more suitable to permit molecular-level mixing and processing of precursors material at relatively lower temperature. It facilitates nano-structured bulk, powders and thin films. Furthermore, sol-gel is a very attractive method which produces CdS film for photovoltaic applications for which large-area devices are required at low cost [8].

A number of chelating agents, Like EDDHA, EDDS, CDTA, DTPA, HEDTA, EGTA, EDTA and NTA have been investigated for their potential to dissolve components of metals and boost up the take by plants. Among these,

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EDTA (ethylene-damien-tetra-acetic acid) is one of the successful and admired chemical regents recoverable and comparatively bios table cheater which has ability to remediate soil [9]. The process of EDTA addition is considered as an important aspect controlling the leaching of metals. It has been used in several process involving CdS colloid or cadmium particles. Then, it affects the adsorption and desertion processes of cadmium in red soil (ferrisoils) including growth of CdS crystalline thin films [10].

In this work, CdS/EDTA nano particles and Poly Vinyl alcohol (PVA) solutions are prepared using solgel method. The CdS/EDTA thin films is coated onto a glass substrate with multi layer to develop a functional oxygen sensor while working at room temperature based on CdS/EDTA thin films prepared by spin coating technique. The optical properties of these thin films were examined to evaluate their potential for use in oxygen gas sensing applications.

Experiments

In this study, cadmium sulfate $(CdSO_4)$ sigma Aldrich (AR), sodium sulfate (Na_2SxH_2O) Loba Chemie, Ethylene-diamine-tetra-acetic acid $(C_{10}H_{14}K_2O_8N_2.2H_2O)$, Poly Vinyl Alcohol (PVA) Sd (Fine-Chem Ltd, Mumbai) and de-ionized water were used without any purification.

Preparation of CdS/EDTA thin films

CdS and CdS/EDTA thin films were deposited by sol gel-spin coating method. Initially, 25 ml of 0.1 M cadmium sulfate was mixed with 25 ml of 0.1 M sodium sulfide under constant stirring for 20 min. Further, 25 ml of 0.01 M EDTA was added into above obtained reaction mixer under stirring for 30 min which resulted in a cloudy yellow solution. During this process, yellow colour wet precipitation was obtained instantly. Then, it was dried in a hot air oven at 353 K for 48 h and obtained the yellow coloured CdS/blender EDTA nano powders. Similarly, CdS nanoparticle was prepared without EDTA.

Nanostructured Thin Film Fabrication

1 g of Poly Vinyl Alcohol (PVA) was dissolved in 25 ml de-ionized water. Then, 0.1 g of as prepared CdS or CdS/blender EDTA nanopowders was individually mixed in above solution and sonicated for 10 min at room temperature to obtain a homogeneous suspension. The prepared homogeneous suspension was coated on an identical glass substrate $(1.5 \times 8 \text{ mm})$ using spin coater (SM-180-BT; Sawatec, Ruggell) at 1000 rpm. Before coating process, the identical substrate was cleaned using chromic acid and sodium hydroxide pellet in de-ionized water and then washed with acetone. After washing, the glass substrate was airdried to remove any surface contaminants. Then, the

nanostructured coated thin film was allowed to air-dry for 30 min and heat treated at 60 °C for 48 h until evaporation of solvent.

Characterization

The structural properties of the CdS sample was determined by X-ray diffractometer (XRD, X'Pert Pro; PANalytical, Netherlands) using Cu Ká as a radiation source ($\lambda = 15406$ Å) which operated at 30 kV and 15 mA. The samples were scanned in the (2θ) range from 10 to 80°. The average crystallite sizes of all the samples were calculated from 20 position of FWHM by Scherrer's formula [7]. X-ray fluorescence spectrometry (XRF, EDX-720, and Shimadzu, Japan) was employed to identify the concentration of the elements presented in nano powder by using qualitative and quantitative measurements. The infrared (IR) absorption spectra of all samples were recorded at room temperature using the fourier transform infrared spectroscopy (FTIR; Spectrum 100; PerkinElmer, USA) in the wave number range from 4000 to 400 cm⁻¹. The study was carried out with KBr material to explore the present functional groups. The optical properties of the prepared thin films were determined based on their optical spectra, obtained using a UV-visible spectrometer (V-570; JASCO, Japan) in the wavelength range from 200-900 nm. The Photoluminescence spectrum (Cary Eclise WinFLR) was investigated as a sample to the wavelength range from 300-550 nm. The thickness of the prepared thin films was measured using a surface profilometer (SJ-301; Mitutoyo, Japan). The surface morphology of CdS nano particles was inspected using a scanning electron microscope (SEM, JSM-6390LV; JEOL, Tokyo, Japan) with an accelerating voltage of 20 kV. The surface topography of the film was measured through AFM. The TEM (CM200; Philips, USA) was operated at 120 kV and provided information about the individual nanoparticles up to high magnitude of 1,000,000X with a better resolution of less than 1 nm.

Gas sensor setup

A gas sensor chamber was constructed using a cylindrical glass chamber, as shown in Fig. 1. The bottom end of the glass chamber was tightly closed using a rubber cork. A lead hole was made in the middle of the rubber cork to insert electrode cables for resistance measurements. After the insertion of the electrode cables, the lead hole was sealed with an airtight seal. Provisions for gas inlet and outlet were provided respectively to pass and to release the gases during the experiment. The thin film sample was clamped in-between two crocodile clamps. Thus, the set-up facilitated the sensor to detect the gas, which was incident on its front surface. The crocodile clamps were connected to the electrode cables and then inserted through the lead hole in the middle of the rubber cork. One of the two cables acted as a cathode



Fig. 1. Schematic diagram of gas sensing measurement system.

while the other as an anode. The other ends of the electrode cables were connected to an LCR-Q meter (Autocompute LCR-Q meter MT 4080 D; Aplab, Mumbai) operated at a frequency of 100 Hz. When the sensor detects the gas, an increase in resistance across the sensor surface may lead to an increase in resistance value in the LCR Q meter. Inductance, capacitance, and resistance variation across the sensor sample were measured using the LCR-Q meter. This thin film sample arrangement (connected to the electrode cables) was placed inside the bottom end of the glass chamber for gas sensing. The gas-sensing ability of the entire prepared thin film sample was measured by repeating the above experiments separately [11].

Results and Discussion

Fig. 2(a) shows the XRD pattern of CdS/EDTA thin films which reveals the presence of diffraction peaks at 24.92°, 28.20°, 36.79°, 43.75°, 51.49°, 54.72°, 58.59°, 60.50° and 66.29° corresponding to (100), (101), (102), (110), (112), (004), (202), (104) and (203) crystal planes are well agreed with the hexagonal structure of CdS [JCPDS No. 41-1049]. The main peaks are at 30.22°, 43.75°, 51.49° and 63.28° corresponding to (200), (220), (311) and (400) crystal plane which is in agreement with the cubic structure of standard CdS [JCPDS No. 89-0440]. This, CdS exhibit both the hexagonal and cubic phases in the nanosize regime [12].

Fig. 2(b), diffraction peaks of XRD correspond with 26.65 ° which can be ascribed to a cubic structure. The intensities of the peaks, the CdS thin film can be regarded to be oriented with [111] direction, which indicates the well crystallized CdS crystalline. However, weakened peak intensity and broadened diffraction peaks are obtained with the introduction of EDTA (Fig. 2(b)). This may result from the effect of nanoscale or nanostructure of the crystallites. The size of the average nanoscale is calculated about 41 nm according to the Scherrer equation [7]. The size of the grain is decreased due to



Fig. 2. XRD pattern of CdS/EDTA thin films.



Fig. 3. Optical absorption spectra of CdS/EDTA thin films.

the addition of chelating agent EDTA [13].

The UV absorption spectra of CdS/EDTA thin films at room temperature are shown in Fig 3. It is observed to be at strong peaks between 295 (Fig. 3(a)) and 297 nm (Fig. 3(b)) respectively, for the CdS/EDTA

Table 1. The CdS thinfilms of Wave length (nm) and Energyband gap (eV).

S.No	Samples	Thickness (ìm)	Wave length (nm)	Energy Bandgap (eV)
1.	CdS	5.75	295	4.20
2.	CdS/EDTA	19.46	297	4.17



Fig. 4. FTIR spectra of CdS/EDTA composite.

Table 2. Vibrational assignments of CdS nano materials with positions and intensities of absorption shown by IR spectra.

Wavelength (cm ¹)	Functional group	
615	Cd-S stretching	
994-1116	SO4 as traces	
1336-1616	Sulphate group S = O	
2920	C-H stretching	
3458	O-H stretching	

thin films. It is evident that the absorption of the CdS films in the visible region strongly depends on the chelating agent. The addition of EDTA to the CdS thin film displays high absorption in the visible region. The optical band gap values obtained from the spectra are 4.20 and 4.17 eV, respectively for 295 and 297 nm as shown in Table 1. The direct band gap measurements of the multi layered films are coated on the substrate and the optical band gap is calculated using the Maxplank energy equation [14]. The increasing absorption wave length of thin film layers leads to decrease in the band gap energy.

Fig. 4 shows the FTIR spectra of CdS nanoparticles. The FTIR spectra and corresponding function groups are reported in Table 2. An absorption peak at 3458 cm¹ is assigned to O-H stretching vibration of water molecules, due to presence of moisture in the sample [15].

Table 3. XRF chemical analysis for CdS/EDTA blender composite.

Cd	IS	CdS-EDTA		
Elements	Weight %	Elements	Weight %	
Cd	92.813	Cd	75.134	
S	6.713	S	20.811	
K	0.474	Κ	4.017	
		Zn	0.038	



Fig. 5. Surface morphology of CdS/EDTA composites.



Fig. 6. PL spectra of nanostructure CdS/EDTA thin films.

Further, CdS nano particles show that the stretching bands, asymmetric and symmetric around 2920 cm⁻¹ get associated with C-H stretching [16, 17]. The observed weak peak at 1336 and 1616 cm⁻¹ are possibly due to stretching vibrations of sulphate group [17]. Furthermore, the peak at 994 and 1116 cm⁻¹ are assigned to SO⁻ [18]. In addition, IR characteristics revealed a strong absorption band at 615 cm⁻¹, which is assigned to stretching vibration of CdS [17]. Hence, the existences of absorption spectra identify the presence of CdS with reduced impurities.

XRF elements for the samples CdS/EDTA are listed in Table 3. The analysis reveals that the precipitation route is yielded and it also confirms that the presence of CdS is around Cd (75%) and S (20%) of weight after chelating.

The surface morphology of CdS samples is shown in Fig. 5. The chelating agents of EDTA lead to very smooth film. During this process, it is believed that



Fig. 7. AFM images of CdS/EDTA thin films.

clusters by clusters deposition via CdS colloidal particles formed in the solution and ion by ion deposition via metastabe complex comprising Cd and S agents [7]. It is observed that the surface morphologies are in the form of assemblies of nanoparticles having nodular and uniformly distributed over the entire surface and it is due to the increase in average grain size which was confirmed through SEM micrographs.

The analysis of photoluminescence (PL) synthesized CdS thin film room temperature reveals various peaks and are shown in Fig. 6. Emission bands such as 360, 397, 486, 494, 520, 538 and 542 nm reveal the green emission bands in CdS/EDTA film. The observed other broad visible emission band from 360 nm (3.44 eV) and 520 nm (2.38 eV) correspond to emission of near band edge excitonic peak of CdS thin films. These exhibit green band emissions are corresponding to the defect related luminescence emission [19]. The emission band present at 486 nm (2.55 eV) is known as green band of CdS and is due to the acceptor levels related to interstitial sulphur and donor levels native defects in the CdS lattice. Further, emission band at 542 nm (2.28 eV) is known as yellow band and is ascribed to the donor level of the interstitial cadmium atoms forming surface defects leading to trap emission in CdS [8]. The PL spectrum is observed to be broad in the visible region which found emission peak around 494 nm. The films show a very high intense peak at 494 nm (2.51 eV) and it is related to excitons bound to neutral acceptors or donors [20]. In addition, the green emission band at 538 nm (2.30 eV) is associated with the emission due to electronic transition from the conduction band to an acceptor level due to interstitial sulphur ions [12]. High-energy band around 3.44 eV is known as violet band [21].

The AFM images of CdS/EDTA thin films are shown in Fig. 7. The AFM images are utilized for measuring the surface roughness and its CdS particles which are randomly distributed on the surface of the films. It is evident that speed pattern of CdS/EDTA thin film is uniform. The thickness of CdS and CdS/EDTA thin films measured using surface profilometer is determined to be 5.75 and $19.46 \mu m$ respectively.

Measurement and Calibration

Oxygen Gas Detection of CdS/EDTA thin film

The glass chamber is cleaned and the calibrated oxygen gas is passed through the inlet valve of the glass chamber at a constant pressure of 1.75 kg cm⁻². Initially, the samples are exposed to a dry compressed air to determine the base line resistance of CdS/EDTA



Fig. 8. Time dependent change in resistance of CdS/EDTA thin films to test oxygen gas.



Fig. 9. Oxygen gas sensing performance of CdS/EDTA composite thin film.



Fig. 10. Stability of CdS/EDTA composite thin films in dry air and oxygen.

thin films. Later, the selected oxygen gas is passed into a sensing chamber at concentrations varying from 20 to 100 ppm. The change in resistance of CdS/EDTA thin films samples is recorded and the gas response of thin films is defined as the change of electrical resistance due to the target gas. The gas response or sensitivity (S) was calculated using the following relation:

$$S = \frac{(R_g - R_a)}{R_a}$$
(1)

where R_g is the change in resistance of the sensor in presence of calibrated oxygen gas and R_a , the resistance of sensor in the presence of dry air. The oxygen gas sensor response is obtained for all the prepared sensor samples (namely CdS and CdS/EDTA) following the same procedure.

Fig. 8 (a) shows the change in resistance of CdS thin film sample when exposed to different concentrations of oxygen gas. The sharp sensor resistance peak values get increased in magnitude as the gas response to concentration of oxygen gas is varied from 20 to 100 ppm. Initially, air is allowed inside the chamber to avoid any organic and inorganic residues. Similarly to the experimental procedure oxygen gas is allowed to pass into the gas chamber through inlet valve the change in the CdS thin film resistance as a function of time at the moment of gas turn-on and turn-off is monitored. The sensor resistance value gradually gets increased when the target gas oxygen interacted with the surface of the sensor. This means that the CdS thin films have a promising response or sensitivity to the oxygen gas [4].

The time-dependent change in resistance of CdS/ EDTA sensor on exposure to oxygen is shown in Fig. 8(b). The initial resistance value starts lower compared to that of CdS sensor film, for both dry air and target gas. The resistance of this sensor gets decreased for gas concentration from 20 to 100 ppm. Since, when decreased the initial resistance values, it is observed that CdS/EDTA is higher than CdS thinfilms. However, considerable change is observed in the resistance on exposure to oxygen at a concentration from 20 to 100 ppm in CdS/ EDTA thin films.

Figs. 9(a) and 9(b) shows the oxygen response analysis of the thin film sensor samples. This plot provides some valuable insight regarding the sensitivity of the fabricated sensor to various concentrations of oxygen as well as the effect of chelating agent of EDTA. Sensor response of the sensor sample CdS thin film is found to be high oxygen, whereas there is a slight variation in percentage of sensor response with the increase of oxygen gas concentration. Similarly, the sensor sample CdS/EDTA has very high variation in sensor response with an increase in oxygen gas concentration. Thus, it is observed that the sensor sample CdS/EDTA shows higher sensor response to different concentration of oxygen gases than any other sensor samples tested.

Figs. 10(a) and 10(b) shows the stability of CdS/ EDTA composite thin films on exposure to oxygen gas at different concentrations with respect to repeatability and reproducibility. The measurements of resistance



(a) CdS



(b) CdS/EDTA Fig.11. TEM image of CdS and CdS/EDTA composite.

across the films on passing oxygen gas (20-100 ppm) are repeated for 7 days. The observation of stability of the thin films reveals fast response and good reproducibility even with small variation in gas concentration.

The TEM images of CdS and CdS/EDTA nano composite are shown in Fig. 11. It reveals randomly oriented grains in the range of nanometer size around 100 nm. It provides an evidence for non-agglomerated, well defined CdS nanoparticles with spherical shape and diameter ranging from 30 to 50 nm.

Conclusions

CdS/EDTA thin film was fabricated by sol-gel spin coating method. XRD pattern of the CdS/EDTA thin films reveals the presence of both hexagonal and cubic structure with an average crystallite size 41 nm. CdS and CdS/EDTA thin film of optical band gap were obtained respectively 4.20 and 4.17 eV. The presence of CdS nanoparticles were also identified with a strong absorption band at 615 cm⁻¹. Photoluminescence spectra of the CdS films exhibited green and yellow band emissions. The sensor sample CdS/EDTA thin film has very high variation in sensor response with an increase in oxygen gas concentration.

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