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Characterization of CdS thin films synthesized by SILAR method at room temperature

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ABSTRACT

CdS thin films have been deposited by using very simple SILAR method in an aqueous alkaline medium at room temperature. Thin films of CdS were characterized by X-ray diffraction, Scanning electron microscopy, EDAX, UV-visible spectrophotometer techniques and electrical conductivity measurement. X-ray diffraction studies showed that CdS thin films are polycrystalline in nature; average particle size of the material was calculated by using Scherrer's formula and found to be 18 nm. The lattice parameters were found to be a = 4.11 and c = 6.76 Å. Optical studies showed that, it has a high absorption coefficient, and the band gap of the CdS thin film were found to be 2.39 eV.Electrical conductivity measurement indicates that it has semiconductor in nature, the specific conductance was in the order the of 10^{-4} to 10^{-2} (Ω cm)⁻¹.

Keywords: Thin film; SILAR; Nanocrystalline; X-ray Difraction; Band Gap.

INTRODUCTION

CdS is one of the very important II–VI group semiconductor, plays an important role in optoelectronic devices such as lasers, light emitting diodes and solar cells. Among these materials, Cadmium Sulphide (CdS) is a representative due to its wide band gap at room temperature, good photoconduction, high electron affinity and inexpensive preparation [1-3], n-type CdS used as the window material for hetero-junction in solar cells usually has a high absorption coefficient causing the reduction of the useful current delivered from the cell to the load. [4]. It is a technologically useful material, as many devices based upon photconducting sensors, Cd^{+2} ion selective sensors have come up in the recent years [5]. In last decade, considerable efforts have been made to synthesize CdS nanostructure thin films by several methods such as electrochemical synthesis [6-7], chemical bath deposition [8-9], solvothermal

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route [10], thermal evaporation [11], chemical vapor deposition [12], vapor-liquid-solid growth [13], pulsed laser deposition [14], spray pyrolysis etc [15]. The methods of preparation of CdS also significant impact on the thickness, particle size which is important for photocatalytic applications, [16] room temperature LPG gas sensor [17]. The reported method are expensive and requires sophistication as compared with SILAR method, so we have impressed on SILAR method due to its simplicity with the tailor made properties can be achieved in the material.

The successive ionic layer adsorption and reaction (SILAR) method is a step-wise process of chemical deposition of thin films from aqueous precursor solutions. It is a unique method in which thin films of compound semiconductor can be deposited by alternate dipping of a substrate into the aqueous solutions containing ions of each component. This method provides the control of the film thickness at atomic level, which is difficult by any other conventional methods. The film formation takes place when ionic product exceeds the solubility product this also results into the precipitate formation and control over the procedure is lost. To avoid such difficulties SILAR method is developed, it consists dipping of substrate into cation and anion precursor separately rinsing with water to avoid homogeneous precipitation [18-21]. In this communication, we are reporting the deposition of CdS thin film by SILAR method at room temperature which is very effective reported than earlier methods [22-23]. The SILAR technology provides the optimum size and thickness of the film that can fine tuned to satisfy the desired expectation for the application of CdS.

MATERIALS AND METHODS

2.1. Preparation of CdS Thin films.

All the chemicals used for the preparation were of analytical grade. It includes cadmium acetate, thiourea and aqueous ammonia. All the solutions were prepared in Millipore water obtained from Millipore water system. For the preparation of CdS thin films cationic precursor (0.1M) cadmium acetate (25 mL) has been taken in a 100 mL beaker, then the anionic precursor (0.1M) thiourea (25 mL) was taken in a separate beaker. For the deposition of CdS thin film, well cleaned glass substrate was dipped into the cationic precursor (cadmium acetate) for 20 sec adsorption of Cd⁺² ions on the surface of the glass substrate, and then the substrate was dipped into the 1:1 ratio of water and ammonia acts as a complexing agent for 10 sec to form cadmium ammonia complex. Then it was dipped into the Millipore water for 10 sec to avoid precipitation and also to remove the loosely bounded cations. The substrate was then immersed into the anions (S²⁻) for 20 sec, reacted with cadmium ions on surface of the glass substrate. The procedure was carried out at room temperature. Successive cycles repeated upto 125 cycles, to get the well adherent and homogeneous CdS thin films.

2.2. Characterization of CdS thin films

The X-ray diffraction of the thin film samples were measured on PW-1710 X-ray Diffractometer by using monochromatic CrK α radiation in the range of 2 θ from 10-80°. Surface morphology of the samples were carried out on a Scanning Electron Microscope (JEOL,JED-2300, JAPAN) with EDAX facility, before scanning, the samples were sputter coated with platinum of 15 nm thickness in order to increase conductivity of films. UV-Visible spectrum was recorded on UV-VIS-NIR Spectrophotometer (UV-3600 SHIMADZU, JAPAN). Surface Profile Analyzer (Ambios XP-1, India) was used to measure the thickness of the thin film.

RESULTS AND DISCUSSION

3.1. Structural Studies

The X-ray diffraction pattern of CdS thin film prepared by SILAR method was shown in Fig.1. The sharp peaks reveals that the deposited thin film were polycrystalline nature. The observed interplaner distance'd' values were compared with the standard JCPD cards (Card No: 80-006, 80-0019) to determine the crystal structure. The XRD analysis reveals that the obtained films were mixed phases of hexagonal and cubic, hexagonal was more dominant than the cubic phase. CdS thin film shows prominent [002], [101], [110], [200] hkl planes. The lattice parameters were found to be a = 4.11Å and c = 6.76 Å. The average particle size of the material was calculated by using Scherrer's formula and found to be 18.0 nm.

3.2. Compositional analysis and Surface Morphological Studies

The EDAX was recorded in the binding energy region between 0 - 20 keV and was shown in Fig.2. The spectrum peak reveals the presence of Cd and S at 3.13 and 2.30 keV respectively, which confirms the presence of Cd and S in the thin film. The atomic percentage of cadmium and sulphur were found to be 64 and 36% respectively, this revels that the thin film of CdS is cation rich. The cation rich material shows (n-type) very good photocatalytic activity in the form of heterojunction [24]. The surface morphology of the thin films was recorded at two different magnifications as shown in Fig.3 (a, b). Thin film of CdS is homogeneous, well adherent and covers the glass substrate without cracks and pinholes. From the SEM micrographs it is evident that the CdS film was in the form of homogeneous fibrous structures, which was similar to the features reported in the literature [25].

3.3. Optical Properties

The optical absorption spectra of as-deposited CdS thin film samples were recorded by UV-VIS double beam spectrophotometer in the range of 400–700 nm without taking into of account the reflection and transmission losses. Fig. 4 (a) shows the variation of optical absorbance with wavelength. The optical studies show that the films are highly absorptive. The value of absorption coefficient is depending upon radiation energy as well as the composition of films. The interpretation of experimental results is most often performed with the help of formula derived for three-dimensional crystal model. The band gap 'Eg' was calculated using following relation [26-27].

$$\alpha h \upsilon = A (h \upsilon - Eg)^n$$

Where hv is the photon energy, A and n are constants. For allowed direct transition n = 1/2, direct forbidden transition n = 3/2 and indirect allowed transition n = 2. For the determination of band gap, plotted the graph $(\alpha hv)^2 vs$. hv, as shown in Fig.4b. The linear nature of plot indicates the existence of direct transition. The band gap was determined by extrapolating the straight portion to energy axis at $\alpha = 0$. The band gap was found to be 2.39 eV.

3.4 Electrical Conductivity

The dark electrical conductivity of 'as-deposited' CdS film deposited on non-conducting glass slide was measured using a two probe method, in the temperature range for 303–523 K. It is observed that the conductivity of the film increases with increasing temperature. The higher values of conductivity may be due to higher crystallanity and thickness of the film. This

indicates the semiconducting behaviour of the thin film. A plot of log (conductivity) versus absolute temperature for the cooling curve was shown in Fig.5. A plot shows that electrical conductivity has two linear regions, the low- temperature extrinsic and high-temperature intrinsic regions indicating the presence of two conduction mechanism. The high-temperature region is due to grain boundary scattering limited conduction, while a low-temperature region is due to variable range hopping conduction mechanism. The specific conductance was found to be in the order of 10^{-4} to 10^{-2} (Ω cm)⁻¹.

3.5. Thickness Measurement

Film thickness is important parameter in the study of film properties. The thickness of the CdS films was measured by Surface Profile Analyzer. Thickness of CdS thin film was depends on the number of deposition cycles. The deposition of CdS thin films, the adsorption period was 20 sec while the reaction period was 20 sec. It was observed that for each pair of adsorption-reaction period, the thickness of the thin film was increases with increasing the number of immersion cycles as shown in Fig.6. After certain limit it shows that the thickness of the thin films is saturated to almost for 130 cycles at 0.21 μ m. Initially the growth of the thickness was very fast due to chemical affinity upto the cycles of about 125. For further cycles no chemical species (Cd⁺² ions) are available for further growth of CdS thin films and the growth were saturated for about 130 cycles. Therefore the desired thickness can be achieved which is well adherent and uniform on the substrate support. This is the novelty of this technique which is easily used directly for device applications.



Fig.1 X-ray Diffraction pattern of CdS thin film.







Fig.3 a.

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Fig. 3 b. Fig.3a) SEM image of the CdS thin films at 3000 b) 10,000 magnifications



Fig.4a. Absorption spectrum of CdS thin film



Fig.4b.The plot of $(\alpha h\nu)^2$ vs. $h\nu$ of the CdS thin film







Fig.6 The variation of thickness with number of cycles for the deposition

CONCLUSION

Thin films of CdS have been deposited successively by using very simple SILAR method. It is an unique method in which thin films of compound semiconductor can be deposited by alternate dipping of a substrate into the aqueous solutions containing ions of each component. SILAR method provides the control of the film thickness at monolayer formation, which is difficult by other conventional methods. Deposited thin films were polycrystalline in nature. Optical study reveals that it has high absorption coefficient with 2.39 eV optical band gap. Electrical conductivity study shows that it has semiconductor in nature. Surface morphology of the thin film has been shown as a fibrous like structure. Good quality of the thin film has been successively deposited on glass substrate at room temperature which is very effective as cost concern.

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