

Investigation of Optical and Structural Properties of CdS Thin Films

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CdS thin films were prepared by the successive ionic layer adsorption and reaction (SILAR) method. The optical properties of these films have been investigated as a function of temperature. The band gap energy change, steepness parameter, and Urbach energy parameters were also investigated as a function of temperature. The band gap energies were calculated at 10 K and 320 K, as 2.427 and 2.377 eV for CdS thin film, respectively. Film morphology was characterized by scanning electron microscopy and XRD measurements.

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I. INTRODUCTION

The films formed by wide gap II-VI semiconductors are of considerable interest, as their emissions cover the technologically attractive blue and green spectral region. In particular, thin CdS films deserve attention because their expected gap emission lies very close to the highest sensitivity of the human eye. Thus, one might assume that thin CdS thin films are an appealing host for photonic devices [1]. Cadmium sulphide (CdS) is an important and useful material for optoelectronic applications. Undoped CdS thin film is always grown as n-type [2]. The CdS quantum dot embedded in a glass matrix is one of the well-known quantum dot systems and its electronic and luminescent properties have been studied extensively [3, 4]. II-VI semiconductors are used as optical windows for solar cells [5]. Recently there has been extensive work on the deposition of thin film materials such as CdS. This material was prepared by several methods including evaporation [5], sputtering [6], chemical bath deposition (CBD) [7], spray [8], molecular beam epitaxy (MBE) [9], and metal organic chemical vapour deposition (MOCVD) [10]. The successive ionic layer adsorption and reaction (SILAR) technique was introduced by Nicolau in the mid-1980's [11]. The method has been employed to grow selected II-VI compounds, especially CdS and ZnS. In the SILAR method, a substrate is immersed separately into precursor solutions and washed in between by water to get rid of the loosely bound species. Thus the content of one SILAR-cycle is adsorption of cationic precursors, rinsing with water, adsorption of anion precursors, followed by reaction, and again rinsing. The growth rates of the thin films in the SILAR technique have varied between a quarter and a half of a mono layer depending on the experimental conditions [11–14].

This growth rate shows that aqua ligands at least partially stay intact during adsorption, thereby lowering the density of cations and anions in one layer. However the growth of a thin film can be controlled at an accuracy of one SILAR-cycle. The successive ionic layer

adsorption and reaction (SILAR) technique due to its sequential reaction steps of saturated surfaces facilitates the growth of multi-layers.

In this present work CdS thin film was grown using cadmium chloride and sodium sulphide solutions by the SILAR method. Optical properties of the CdS thin film have been investigated as a function of temperature. Using the optical measurements the band gap, Urbach energy, and steepness parameter has been calculated as a function of temperature. Film morphology was characterized by scanning electron microscopy and XRD measurements.

II. EXPERIMENTAL PROCEDURE

In this study CdS thin film was prepared on glass substrates by the SILAR technique. Cadmium chloride solution was used as the cationic and sodium sulphide was used as the anion precursors. The pH of the cadmium chloride and sodium sulphide solutions were 5.9 and 12, respectively. The substrate was cleaned using an ultrasonic bath with acetone and a water-ethanol (50:50) solution and then dried.

The adsorption, reaction, and rinsing times were chosen experimentally so that the deposition occurred layer wise and resulted in a homogeneous thin film structure. Rinsing times for CdS were 40 s for cationic adsorption, 150 s for water, 40 s for anion adsorption, and 150 s for water.

The optical properties of these films have been investigated as a function of temperature. The absorption measurements were carried out in the temperature range 10-320 K with a step of 10 K. The optical measurements as a function of temperature were made in a closed-cycle He cryostat. For optical measurements, the Perkin Elmer UV/VS Lambda 2S Spectrometer was used, the sensitivity of the spectrometer was approximately better than ± 0.3 nm. The band gap energy changing, steepness parameter and Urbach energy parameters were investigated as a function of temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD diffraction of CdS thin film grown by the SILAR method. The thin film's X-ray diffraction patterns are given in Table I.

X-ray diffraction analysis showed that the CdS thin films on glass substrate were polycrystalline. The main reflection can be assigned from the (002) reflection. Nicolau has reported that CdS films grown by the SILAR method on glass and ITO covered glass were hexagonal, as studied by grazing-incidence XRD [17]. Chemical bath deposition produces usually randomly oriented CdS thin films, and major reflections fit both to the cubic and hexagonal structure [16]. The XRD data were taken over $2\theta = 10 - 100^\circ$.

The energy band gaps of these films were calculated with the help of the absorption spectra. To determine of the energy band gap, we plotted $(\alpha hw)^2$ versus hw . Where α is the absorption coefficient and hw is the photon energy. The absorption coefficient α is

TABLE I: Comparison between observed, standard, and reference 'd' values for CdS thin film.

Sample	Reflection planed (<i>hkl</i>)	Standart 'd' values (Å)	Reference 'd' values (Å)	Observed 'd' values (Å)	I/I_{max} (%)
CdS	002	3.357	3.357 [15]	3.373	87
	200	2.907	2.825 [15] 2.909 [16]	2.947	74
	110	2.068	2.068 [15]	2.069	46
	201	1.731	1.731 [16]	1.754	32

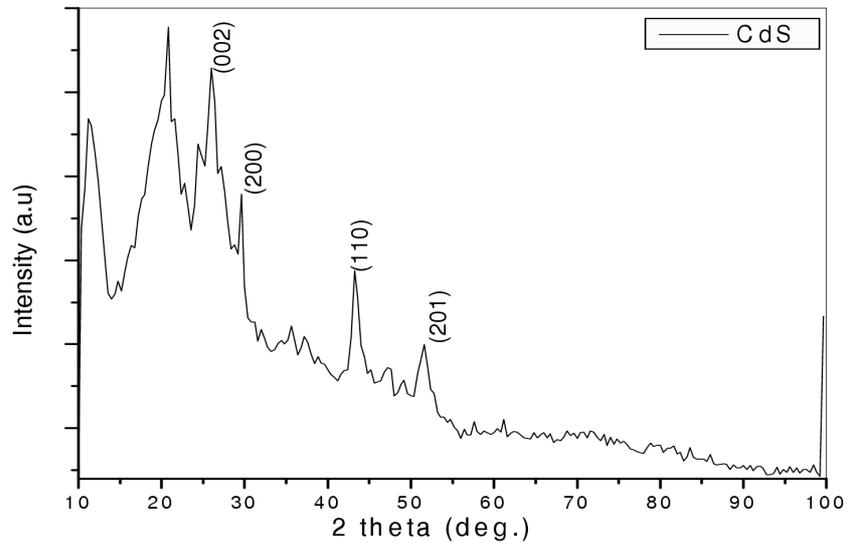


FIG. 1: XRD patterns of CdS thin film.

proportional to

$$\alpha(\hbar\omega) = B(\hbar\omega - E_g)^n, \quad (1)$$

where B is a constant and n is an index ($n = 1, 2, 3, \dots$).

The graphs of α^2 versus $\hbar\omega$ are given in Fig. 2. Using these values, the band gap energies of CdS thin films were calculated. Energy band gap values are given in Fig. 3 and Table II for different temperatures.

As can be seen in Fig. 3, the band gap energy in CdS is decreasing with increasing temperature. The band gap energies of CdS thin films are given in Table II, at 10, 80, 160, 240, and 320 K sample temperatures. The decrease in Bandgap energy is about 50 meV with increasing temperature.

The band gap energy was found to be 2.44 eV by [20], 2.40 eV by [21], and 2.42 by [22] for CdS. Our results are in agreement with this literature.

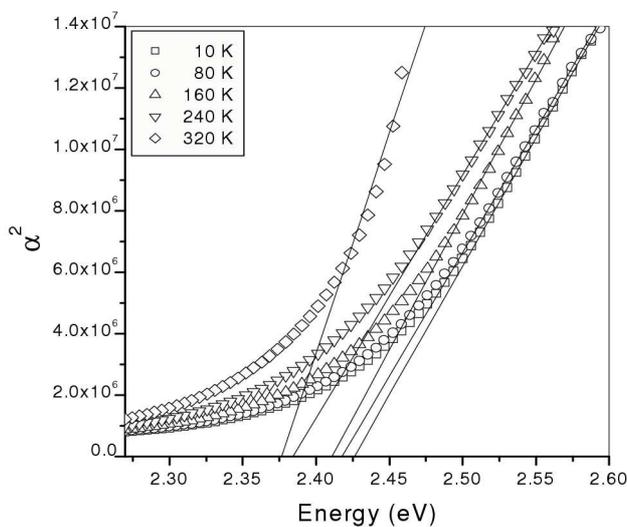


FIG. 2: α^2 versus $h\nu$ for CdS thin film.

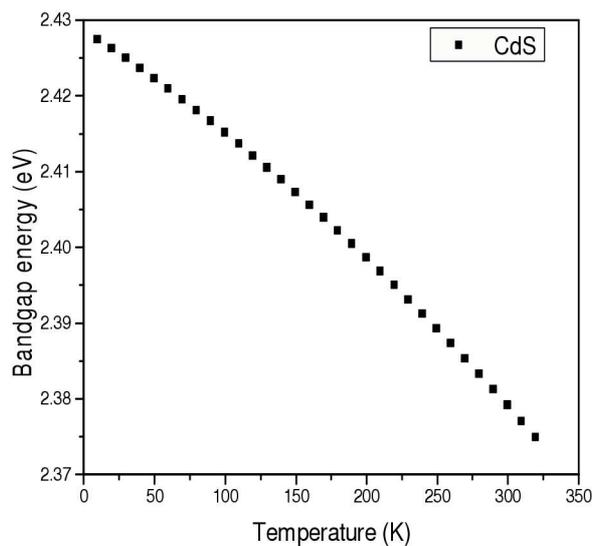


FIG. 3: Bandgap energies of CdS thin film as a function of temperature.

An exponentially increasing absorption edge in a number of insulators including ionic crystals, semiconductors, and organic crystals follows the empirical expression [18]

$$\alpha = \alpha_0 \exp(\sigma(E - E_0)/kT), \quad (2)$$

where α_0 and E_0 are characteristic parameters of the material, σ is the steepness parameter,

TABLE II: The bandgap energies, steepness parameter, and Urbach's energies of CdS thin film at different sample temperatures.

Sample temperature (T) (K)	CdS Bandgap (E_g) (eV)	Steepness Parameter (σ)	Urbach's energy (E_u) (eV)
010	2.427	7.4×10^{-4}	1.157
080	2.417	3.6×10^{-3}	1.216
160	2.411	0.011	1.252
240	2.385	0.015	1.423
320	2.377	0.018	1.480

k is the Boltzmann constant, and T is the temperature. Eq. (2) implies that logarithm of α plotted as a function of E can be approximated by a straight line in energy just below the fundamental absorption edge. The extrapolations of those lines for various temperatures usually converge at a point (E_0, α_0) , which is called the "converging point". We found that all extrapolations of the Urbach tails converge at (E_0, α_0) , 2.88 eV and $1.9 \times 10^4 \text{ cm}^{-1}$ for CdS thin film.

The steepness parameter, σ , which characterizes the steepness or width of the straight line near the absorption edge is expressed empirically as a function of temperature [19]:

$$\sigma = \sigma_0(2kT/\frac{h}{2\pi}w_p) \tanh(\frac{h}{2\pi}w_p/2kT). \quad (3)$$

σ_0 is a temperature-independent but material-dependent parameter, being inversely proportional to the strength of the coupling between excitons and phonons. Some researchers have stated that hw_p corresponds to the energy of phonons associated with the Urbach tail. The parameter σ/kT for the interaction between exciton and longitudinal-optical (LO) phonons coincides with Eq. (3) by a constant factor [19]. kT/σ is called Urbach's energy (E_u). E_u represents the thermal disorder or the occupancy level of phonon states in crystals [19]. E_u can be modelled as an Einstein oscillator, which takes into account contributions of structural and thermal disorder in the sample by considering Skettrup's theory [20, 21].

Scanning electron microscopy (SEM) is a convenient method for studying thin films. The microstructure of the CdS film is shown in Fig. 5. It was observed from the micrographs that the deposited CdS film were almost homogeneous and without many cracks and covered the substrate well. The presences of overgrown CdS particles were also observed.

The successive ionic layer adsorption and reaction (SILAR) method was applied to prepare the multilayer thin film structure of CdS. The film thickness was calculated by using the X-ray florescence (XRF) method as 8 μm . CdS layers could be detected by modern scanning electron microscopy. The film surfaces were just about flat and smooth. As a result, we can say that the SILAR method is suitable method for depositing CdS thin films. The optical bandgap energy decreased from 2.427 eV to 2.377 eV with increasing temperature. The steepness parameter and Urbach's energy also changed with temperature. Urbach's energy, E_u represents the thermal disorder, as can be seen in Fig. 4; thermal disorder increased with increasing temperature.

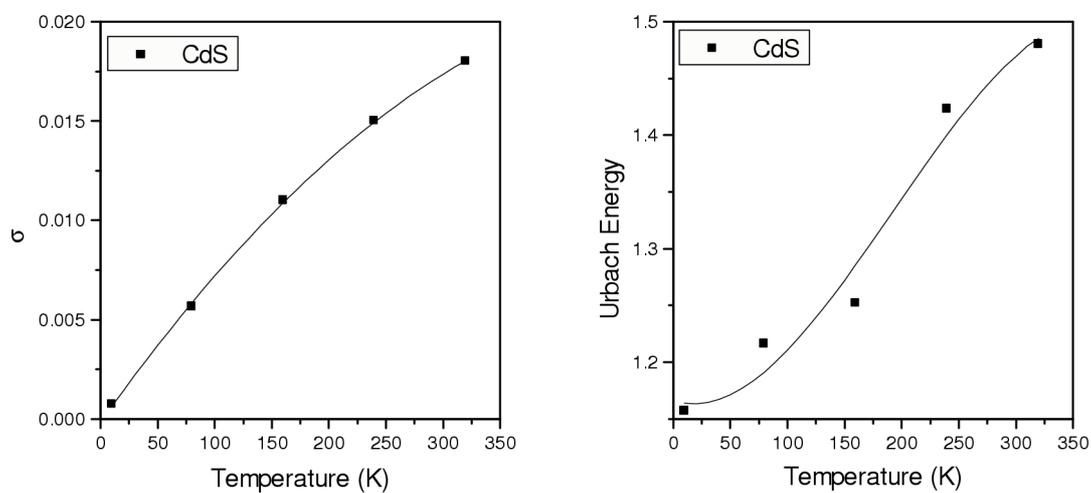


FIG. 4: Steepness parameter and Urbach's energy of CdS thin film.



FIG. 5: Scanning electron micrograph image of CdS film; status bar length is 10 μm .

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