Chemical synthesis and study of structural and optoelectronic properties of CdS thin films: Effect of SILAR growth cycles

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ABSTRACT

CdS thin films were deposited on glass substrates by using successive ionic layer adsorption and reaction (SILAR) method at room temperature. The effect of SILAR growth cycles on structural, morphological, optical and electrical properties of the films has been studied. The thickness of the deposited film is measured by employing weight difference method. The X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) studies showed that all the films exhibit polycrystalline nature and are covered well with glass substrates. The values of average crystallite size were found to be 53 nm, 58 nm, 63 nm and 71 nm corresponding to the thin films deposited with 30, 40, 50 and 60 SILAR growth cycles respectively. From the UV–VIS spectra of the deposited thin films, it was seen that both the absorption properties and energy bandgap of the films changes with increasing number of SILAR growth cycles. A decrease of electrical resistivity has been observed with increasing SILAR growth cycles.

Indexing terms/Keywords

Polycrystalline thin film, structural properties, optical properties, electrical properties.

Academic Discipline And Sub-Disciplines

Science, Physics;

SUBJECT CLASSIFICATION

Physics, Material Science

TYPE (METHOD/APPROACH)

Synthesis and Characterisation of material

Council for Innovative Research

Peer Review Research Publishing System

1. INTRODUCTION

During last three decades II-VI class of semiconducting compounds has been comprehensively studied due to its optoelectronic properties and uses. Because of the good optical transmittance, wide band-gap (2.43 eV) and electrical properties, polycrystalline CdS thin films are extensively used as one of the most ideal material for their application to solar cell fabrication, optoelectronic devices such as light detector, photoconductor, display panel and LED etc. [1–4]. CdS is one of the important semiconductors used as window layer in heterojunction solar cells based on CdTe, CuInSe$_2$ and Cu$_2$S [5-7]. Thin films of this material can be prepared by a variety of techniques such as chemical bath deposition [8], chemical pyrolysis deposition (CPD) [9], evaporation [10], sputtering [11], spray [12], pulsed laser deposition [13] and electrodeposition [14]. Since the last two decades preference is given to cost effective deposition technique for the deposition of thin films, hence we preferred successive ionic layer adsorption and reaction (SILAR) technique for the deposition of CdS thin film. Because SILAR technique is a simple, low cost, convenient and useful for large area industrial applications. Another advantage of SILAR method with respect to other methods is that SILAR does not require high quality substrates nor does it require vacuum at any stage, which is a great advantage if the method will be used for industrial application, the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles [15].

The present study has utilized this chemical method for growing CdS thin films at room temperature under normal pressure. Also, here we have presented systematic investigation on the effect of number of SILAR growth cycles on the physical properties of CdS films such as structure, surface morphology, optical and electrical properties using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), optical absorption and electrical resistivity measurements respectively.

2. EXPERIMENTAL DETAILS

2.1 Preparation of the glass substrate

A glass micro slides (supplied by Blue star, Mumbai) of the dimensions 75mm×25mm×1.10mm is used as substrate. Before deposition process, the glass substrates were cleaned with double distilled water, boiled in chromic acid for 2h. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with double distilled water. This process is done to ensure a clean surface, which plays an important role in the deposition of thin films.

2.2 Thin film preparation

The study finds that SILAR is the most promising, simple and cost effective technique among all thin film deposition techniques. SILAR method is one of the chemical methods which is used for deposition of uniform and large area thin films, which is based on immersion of the substrate into separately placed cations and anions. Thin films of cadmium sulfide have been grown by SILAR technique using cadmium acetate, sodium sulfide, TEA and ammonia (AR garde).

The cationic and anionic precursor solutions were 0.025 M cadmium acetate [Cd(CH$_3$COO)$_2$, 2H$_2$O] and 0.05 M sodium sulfide (Na$_2$S), respectively and 25% aq. Ammonia was used as a complexing agent and TEA to control the pH of the cationic precursor solution to 6. For the deposition of CdS thin films each SILAR growth cycle involved the following steps:

(i)   Immersion of the cleaned substrate in first reaction beaker containing cationic precursor solution 0.025M [Cd(CH$_3$COO)$_2$, 2H$_2$O] for 30s. Cadmium ions were adsorbed on the surface of the substrate.

(ii) This substrate was rinsed by high purity deionized water for 15s.

(iii) The substrate was then immersed in the anionic precursor solution 0.05 M (Na$_2$S) for 30s. The sulfide ions reacted with adsorbed cadmium ions on the active center of the substrate.

(iv) Again the substrate was rinsed in deionized water for 15s to remove loosely bound ions present on the substrate.

At the end, the first SILAR growth cycle is completed. Deposition was carried out at room temperature. For this particular study we have deposited CdS thin films with 30, 40, 50 and 60 SILAR growth cycles.

The preparative parameters used for the deposition of CdS thin films are summarized in Table 1.

Table 1. Optimized preparative parameters for the deposition of CdS thin films

Parameters	Precursors solutions	
	Cadmium acetate [Cd(CH$_3$COO)$_2$, 2H$_2$O]	Sodium sulfide (Na$_2$S)
Concentration (M)	0.025	0.05
pH	6	12
Immersion time (s)	30	30
Temperature (^{o}C)	27	27

2.3 Characterisation of CdS thin films

The SILAR coated thin films of CdS were characterised for structural, optical and electrical properties. The CdS thin film thickness measured by using weight difference method. X-ray diffraction (XRD) patterns of the film were recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20-80° (2θ) using Cu Kα radiations with wavelength 1.5405 Å. S-48500 Type-II (HITACHI HIGH TECHNOLOGY CORPORATION Tokyo, Japan) field emission scanning electron microscope (FESEM) with an energy dispersive spectrometer (EDS) attachment was used for the determination of morphology and chemical composition. To study the optical characteristics of the film, absorbance and transmittance spectra were recorded in the range 400-900 nm by means of JASCO UV-VIS spectrophotometer (V-630). The resistivity of the CdS thin films was determined by two-probe method.

3. RESULT AND DISCUSSION

3.1 Kinetic Study

In order to study the growth rate, SILAR coated CdS thin films were deposited for various deposition cycles on glass substrates. After depositing, the films thickness was measured by employing gravimetric weight difference method. Figure.1 represents CdS film thickness as a function of the SILAR growth cycles. It is found that the film thickness increases almost linearly with the deposition cycles, while within 30 cycles the thickness increases slightly faster. The average growth rate was calculated as 5.9 nm/cycle, while the rate reaches 6.2 nm/cycle within 30 cycles. This finding is different from earlier investigations [16]. Wherein Lokhande et. al.used cadmium acetate and sodium sulfide as precursors of cadmium and sulphide ions and the deposited rate is 1.75 nm/cycle. Similar results were observed by Garadkar et.al. [17] for SILAR deposited CdS thin films by using cadmium acetate and thiourea as precursors of cadmium and sulphide ions. The difference of this growth rate may be attributed to the different concentrations of the used precursors.
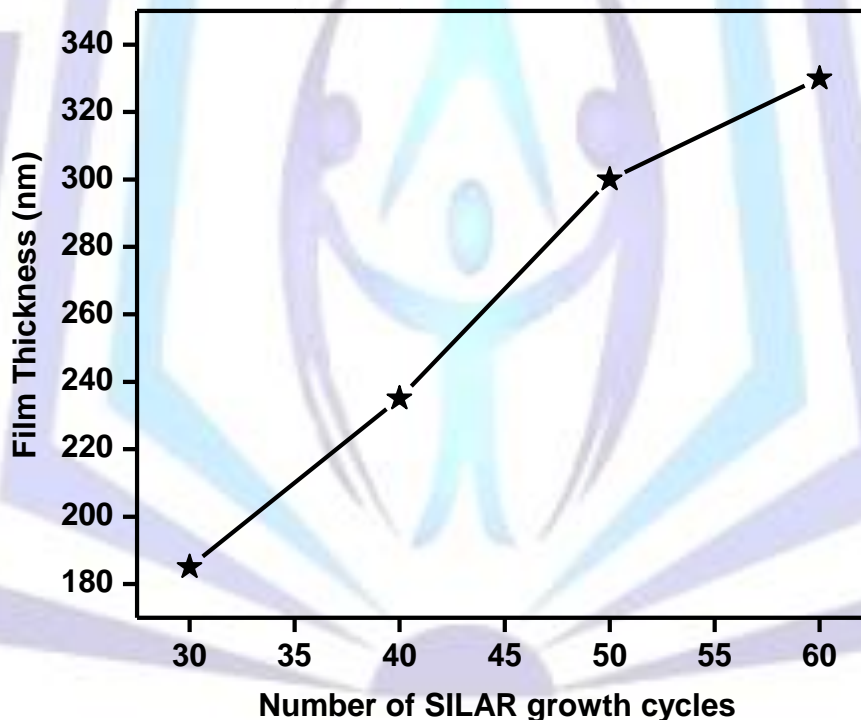

Fig. 1 Plot of thickness of the CdS thin film as a function of SILAR growth cycles.

3.2 Structural analysis

In order to study crystal structure of CdS thin film deposited by SILAR technique, X-ray diffractogram of the film on the glass substrate was examined. Figure 2 shows the XRD pattern of CdS thin films deposited on glass substrate at room temperature as a function of SILAR growth cycles. XRD pattern revealed that all the CdS thin films were polycrystalline in nature with hexagonal crystal structure match with JCPDS card no. 06-0314. XRD pattern of the CdS thin films showed sharp peak (1 1 0) and (2 0 4) along with two other minor peaks corrsponding to (2 0 2) and (2 1 0) planes. Diffraction peaks corresponding to 2θ =34.11^o, 37.97^o, 39.67^o and 64.70^o was observed corresponding to impurities like Cd(OH)$_2$ which is attributed to low temperature deposition of CdS thin film. As exhibited in figure 2, with increasing number of SILAR growth cycles, no significant shift in the peak position was observed, but intensity of these peaks becomes more intense and sharper. This is due to the crystallite size becoming larger with increasing the SILAR growth cycles which

might be occurred due to the increasing film thickness. The crystallite size (D) in the films has been evaluated by using Scherrer's formula:

$$D = \frac{k\lambda}{\beta cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Where k is constant (0.94), λ is the wavelength of X-ray, β is the full width at half of the peak maximum in radians and θ is Bragg's angle. It is observed that the crystallite size increases from 53 nm to 71 nm as SILAR growth cycle's increases from 30 to 60.
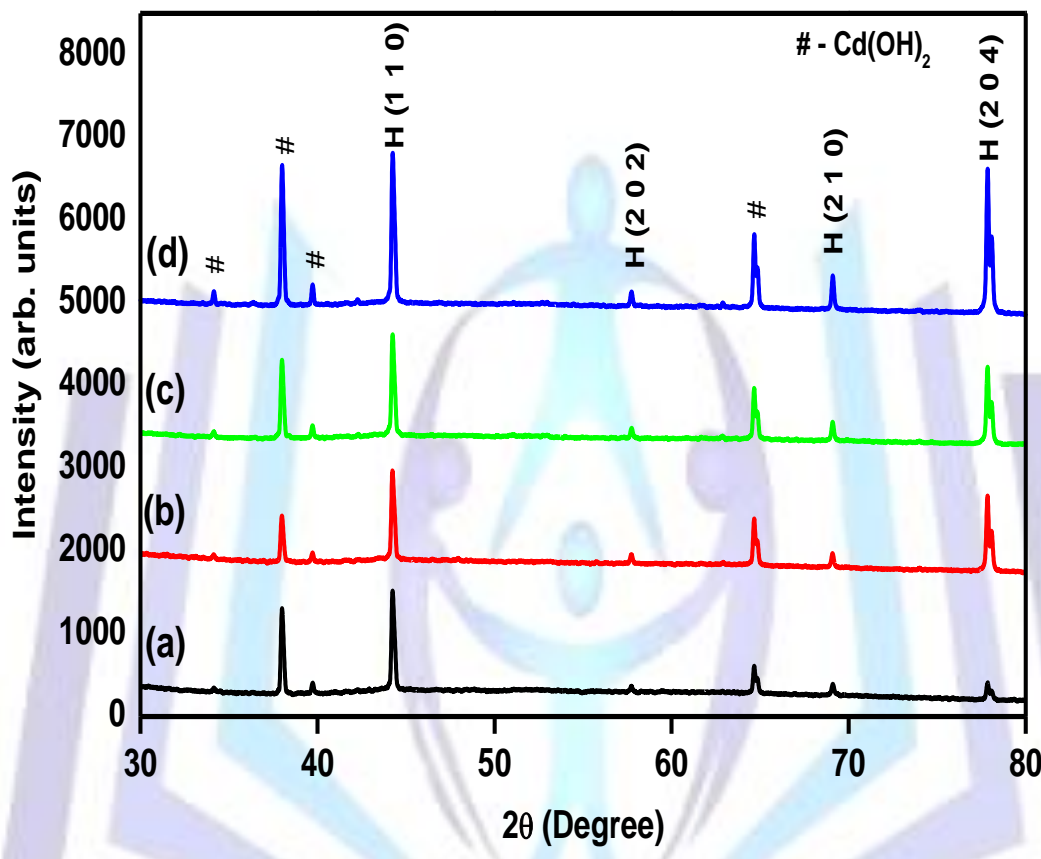
Fig. 2 X-ray diffraction (XRD) pattern of CdS thin film deposited with a) 30, b) 40, c) 50 and d) 60 SILAR growth cycles.

3.3 Surface morphology analysis by FESEM

Field Emission Scanning Electron Microscopy (FE-SEM) was used to investigate the effect of the SILAR growth cycles on thin film surface properties because the surface properties directly affect the electrical and optical properties of the films [18]. The SEM images of the CdS thin films deposited with different SILAR growth cycles are presented in Fig. 3. It is observed from fig. 3a-d that all the thin films were homogenous, without cracks and pinhole free with spherical grains and with dense surface morphology covering entire substrate surface area and strong adherence to the substrates. The grains were irregular in size and shape. From the FESEM images, agglomeration of the grains was found with increase in SILAR growth cycles, which results in increase in grain size which may be due to the fusion of grains to form cluster type structure.

The quantitative analysis of the film was carried out by using the EDS technique for all SILAR grown CdS thin films deposited on a glass substrates in order to study the stoichiometry of the film. Fig. 4 shows a typical EDS pattern of CdS thin films deposited with 60 SILAR cycles. The elemental analysis was carried out only for Cd and S.

Fig. 5 shows the average atomic ratio of Cd/S as a function of SILAR growth cycles. It was seen that Cd/S ratio decreases from 1.86 to 0.98 with increasing SILAR cycles from 30 to 50 and again it increases to 1.21 for the film deposited with 60 SILAR cycles. EDS results indicate that the average atomic ratio of Cd/S is nearly stoichiometric ratio (Cd/S ≈ 1) for film which is deposited with 50 SILAR cycles.
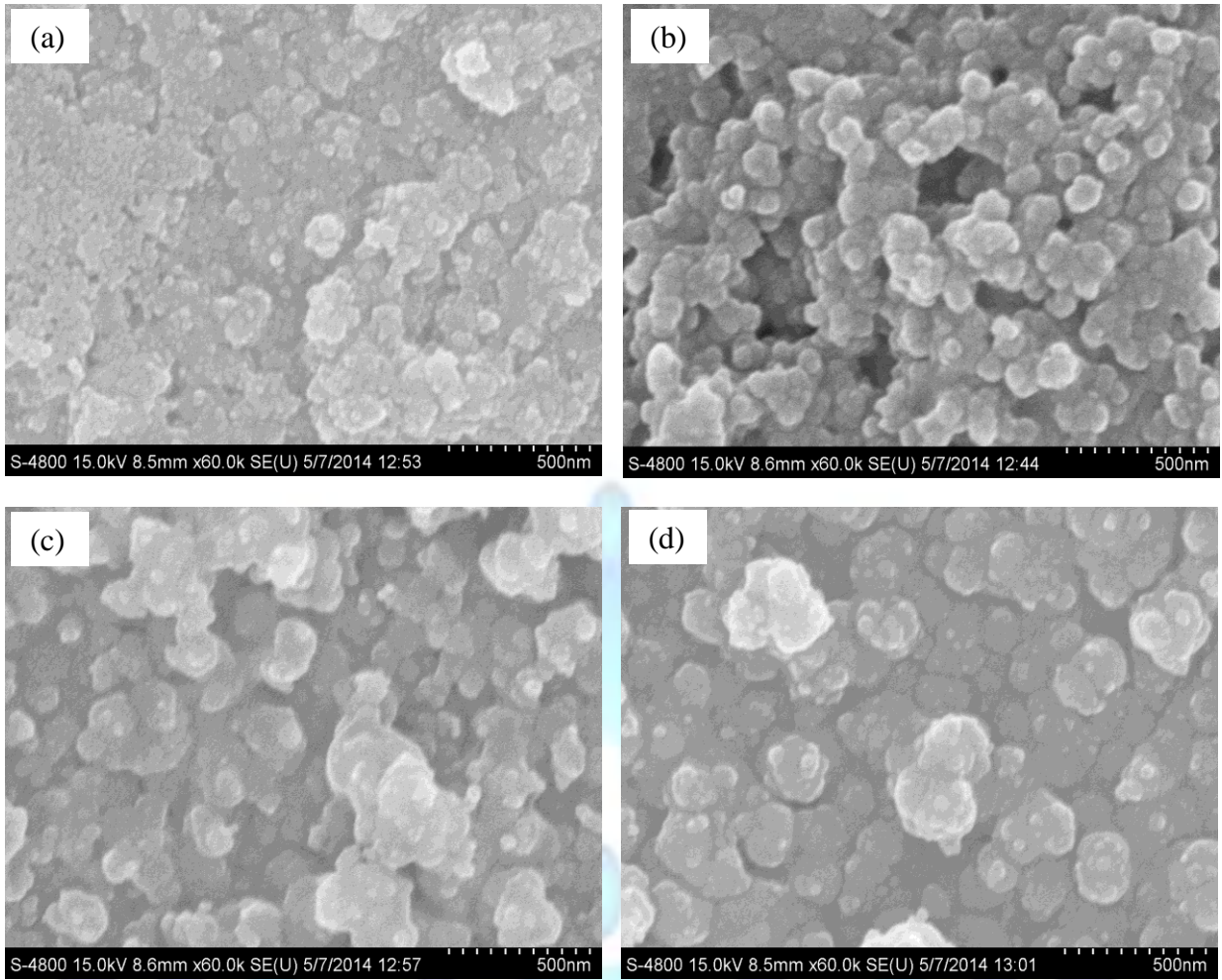
Fig. 3 Surface Morphology of CdS thin film synthesized with: a) 30, b) 40, c) 50 and d) 60 SILAR growth cycles.
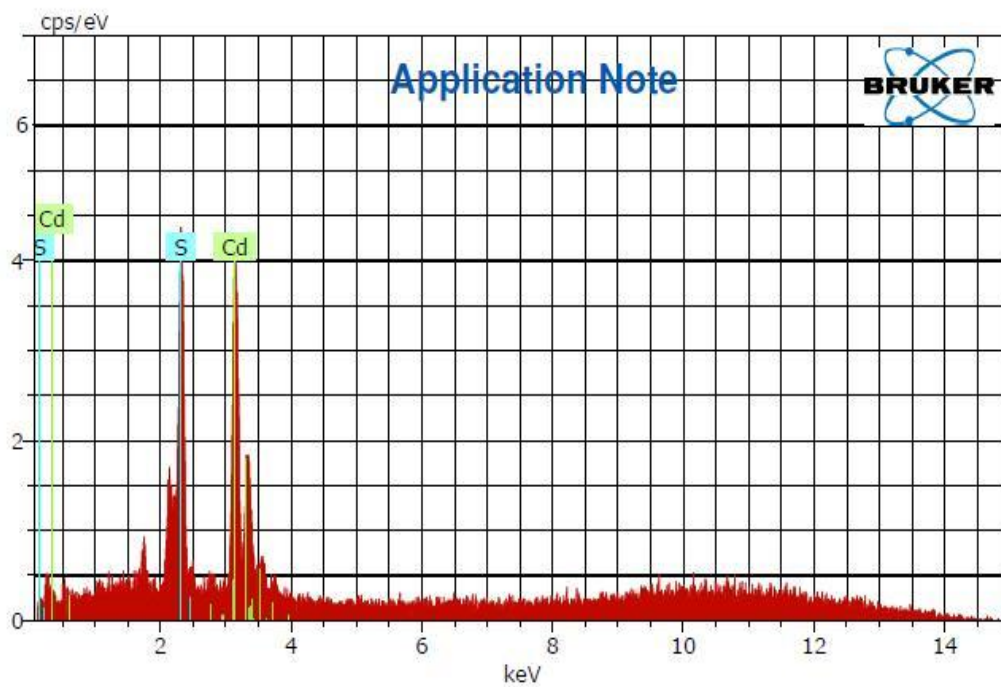

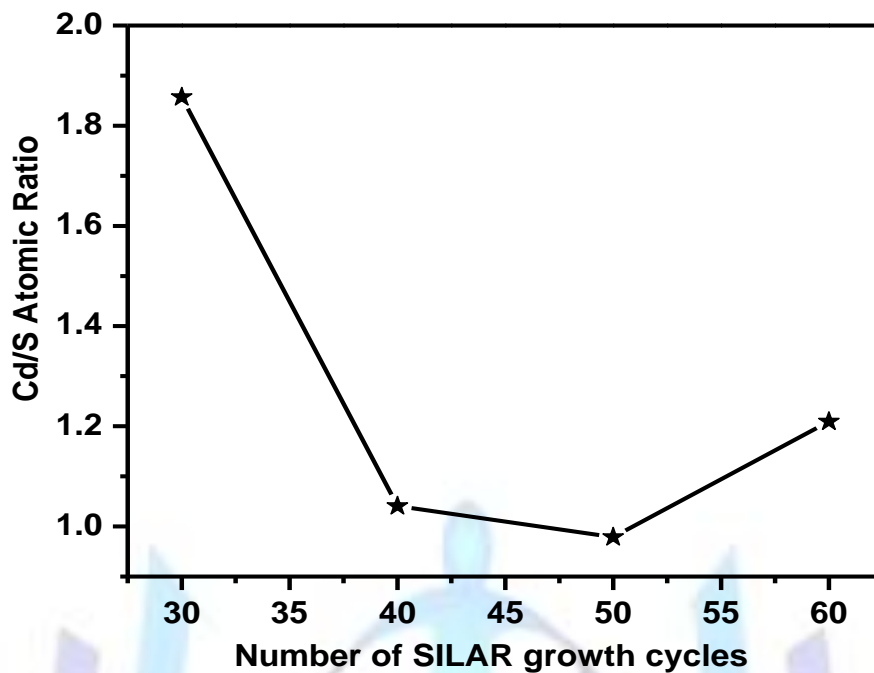**Fig. 4 Typical EDS pattern of CdS thin films deposited with 60 SILAR cycles.**

Fig. 5 shows the average atomic ratio of Cd/S as a function of SILAR growth cycles.

3.4 Optical analysis

Fig. 6a and 6b shows absorbance and transmittance spectra obtained from CdS thin film deposited with different SILAR growth cycles, in the range of 400 to 900 nm. It is observed from the absorbance spectra that there is a red shift in the absorption edge as the SILAR growth cycles is increased, indicating a decrease in the optical bandgap. It is also observed from the transmittance spectra that for lesser SILAR growth cycles (30), the average transmittance in the visible region is found to be 55% and it decreases gradually to about 20% for the higher immersion cycles (60) [19]. This variation in transmittance can be correlated with the thickness of the film as the thickness of the film is in direct proportion with the number of SILAR growth cycles which may cause a gradual decrease in the optical transmission. The theory of optical absorption gives the relation between the absorption coefficient α and the photon energy hν, for direct allowed transition as [20],

$$\alpha = \frac{A\left(h\nu - E_g\right)^{1/2}}{h\nu} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

where hν is the photon energy, E_g is the optical bandgap, A is a constant.

Fig. 7 shows a plot of $(\alpha h\nu)^2$ versus hν which is linear at the absorption edge, confirming the direct band gap material. The linear fit of the plot indicate the existence of the allowed direct bandgap transition. The direct bandgap of CdS thin films deposited with various SILAR growth cycles are determined by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$.

The band gap values for films deposited with 30, 40, 50 and 60 SILAR growth cycles are estimated to be 2.28, 2.26, 2.23, and 2.21 eV respectively. These bandgap values were in good agreement with the earlier reported values of bandgap for CdS thin films deposited by chemical bath deposition technique [21]. It is obvious from the results that the optical band gap decreases with the increase in the SILAR growth cycles which may be due to the quantum size effect and variation in the stoichiometry of the film.

3.5 Electrical properties

The measurements on electrical resistivity of the CdS thin film as a function of SILAR growth cycles were carried out in the temperature range 300 - 423 K on rectangular-shaped samples with typical size of 1cm x 1cm, using a standard two point probe method. The variation of log ρ versus inverse of absolute temperature (1000/T) for the films deposited with different SILAR growth cycles, shown in Figure. 8. The resistivity of all the films decreases with increase in temperature indicates semiconducting nature of the films [22]. The resistivity of the films decreased from 1.1×10^4 to 0.16×10^4 Ω.cm with increasing the SILAR growth cycles. This decrease of resistivity with the SILAR growth cycles might be due to the decrease of residual defects and increase of crystallite size in the films, which was observed in the XRD studies [23].

Generally, activation energy E_a is determined by using the following Arrhenius relation,

Note that the symbols $\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$ …………………………..(3) have usual meaning.

The values of activation energy E_a are found to be in the range between 0.11 and 0.08 eV in the low-temperature region and 0.14 and 0.09 eV in the high-temperature region. The values of the activation energy indicate that the prepared samples are semiconductors.
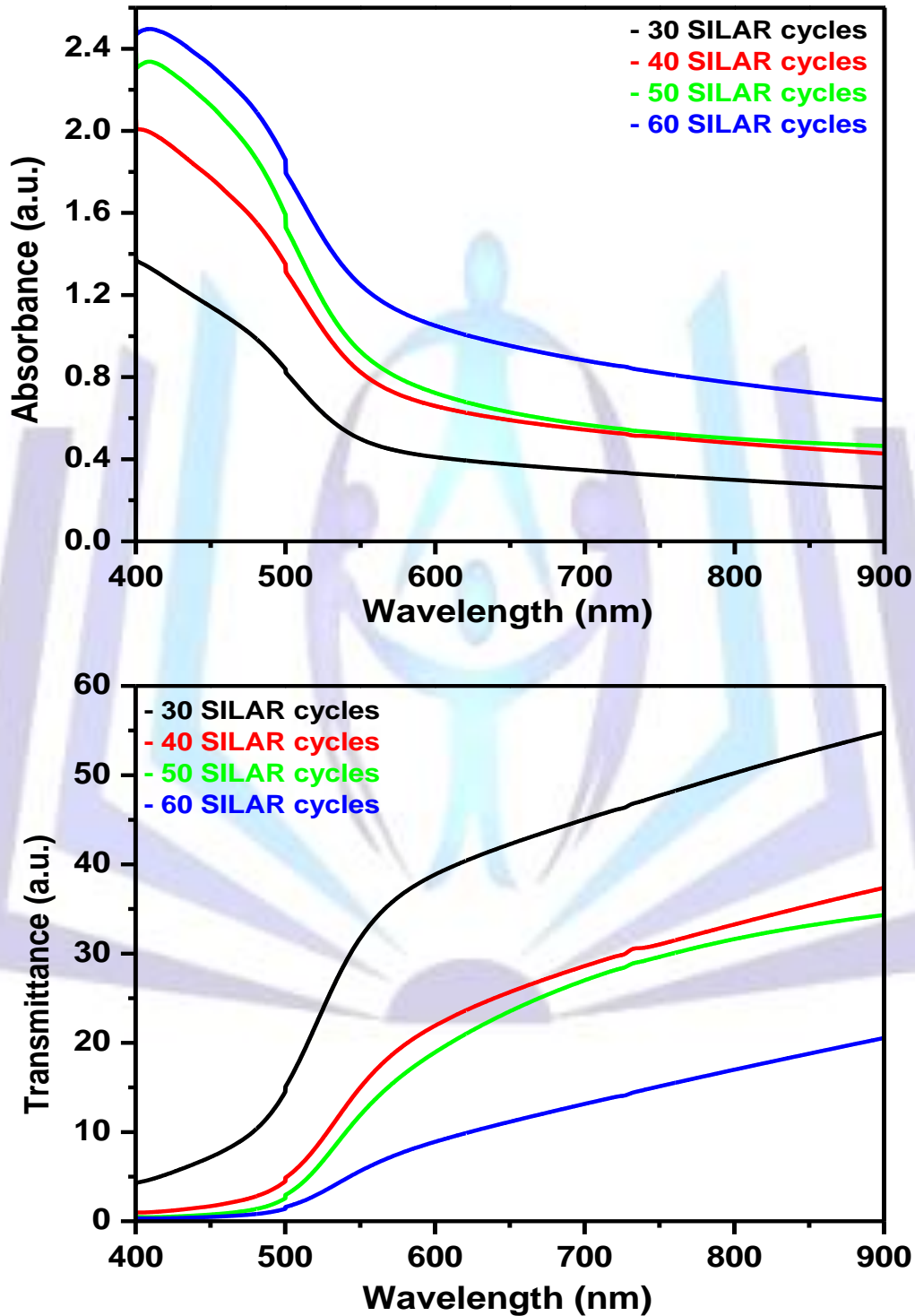

Fig. 6a and 6b Absorbance and transmittance with respect to wavelength for CdS thin films synthesized with different SILAR growth cycles.
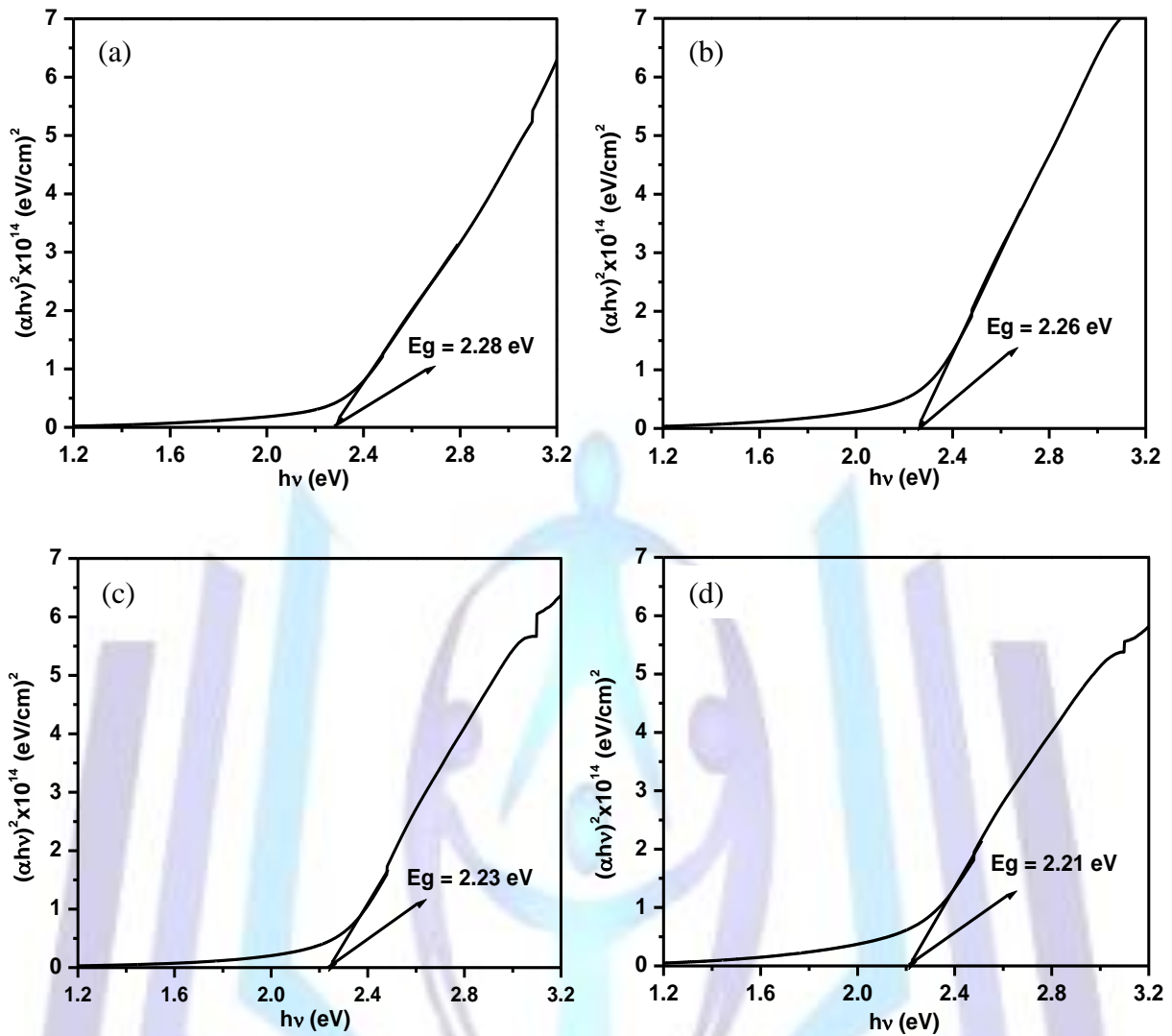
Fig. 7 Variation of (αhν)² versus hν for CdS thin films deposited with a) 30, b) 40, c) 50 and d) 60 SILAR growth cycles.
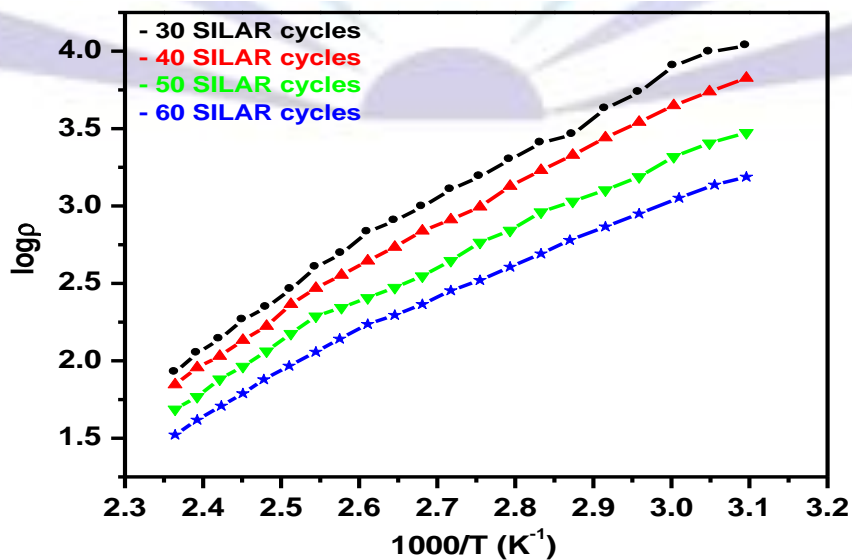

Fig. 8 Electrical resistivity as a function of Temperature

4. CONCLUSION

CdS thin films were deposited onto glass substrates by using SILAR technique as a function of SILAR growth cycles varing from 30 to 60 in the interval of 10. The effect of SILAR growth cycles on the structural properties, composition and surface morphology, optical and electrical properties of the deposited thin films were determined by using XRD, FESEM, EDS, optical absorbance and transmission spectra and two probe methods respectively. The salient conclusions arising from this study are summarized below:

i. XRD analysis revealed the polycrystalline and hexagonal structure of CdS thin films.

ii. Peak intensity increases with SILAR growth cycles and thus the crystalline quality of the films gets better and the crystallite size increases with increase of SILAR growth cycles.

iii. Surface properties of deposited thin films were improved with increasing SILAR growth cycles.

iv. EDS analysis showed that the film deposited with 50 SILAR growth cycles had nearly stoichiometric ratio (Cd/S ≈ 1).

v. The band gap energy values reduced from 2.28 to 2.21 eV with increasing SILAR growth cycles.

vi. Electrical studies showed that the films are semiconducting which may be used in optoelectronic devices.

vii. It can be concluded that influence of the SILAR growth cycles on the structural, electrical, and optical properties of the films was observed.

ACKNOWLEDGEMENTS

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