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EFFECT OF DEPOSITION CYCLES ON OPTICAL, STRUCTURAL AND ELECTRICAL CHARACTERIZATIONS OF SILAR DEPOSITED CADMIUM SULPHIDE THIN FILMS

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Abstract:
The CdS thin films were prepared on cleaned glass substrates by SILAR deposition technique using cadmium acetate and thiourea as precursor solution with deposition cycles of 25, 50, and 75 dippings. The prepared samples were annealed in air. The prepared thin films were characterized for their structural, micro structural and optical properties by XRD, FESEM and UV-Visible spectroscopy. The XRD analysis shows that, the prepared samples are polycrystalline and it exhibits cubic structure. The morphology of the CdS thin films characterized by FESEM revealed that the film consisted of mixture of nanoparticles and the EDAX results showed the presence of CdS in the prepared thin films. The optical properties of the deposited films were characterized by UV-VIS. The UV-Vis results show the presence of direct transition band gap energy and it closely agrees with CdS band gap energy. The electrical properties of the CdS thin films characterized by Hall measurements. It is observed that, for 25 dippings, 50 dippings and 75 dippings samples, the resistivity decreases, conductivity and Hall mobility increases with deposition cycle increases. 75 dippings sample Shows higher carrier concentration, mobility and lower resistivity than other two samples. The paper will discuss the preparation methods and results of CdS thin films by SILAR method.

Key Words: CDS; Nano Crystalline Thin Film, SILAR Deposition Method, Deposition Cycles, Characterizations

1. Introduction:

CdS (Cadmium sulphide) is one of the important II–VI compound semiconducting material with a direct band gap of ~2.42 eV and it is being used as a opto-electronic devices [1-4] and window layer in solar cells based on cadmium telluride (CdTe), copper indium sulphide and copper indium gallium diselenide/sulphide (CIGS) as active layer [5-6]. 19.9% solar energy conversion efficiency has been reported by various researchers basically on thin film photovoltaic technology using direct band gap materials like CdTe, CuIn(SSe)2 Cu(InGa) (SSe)2 (CIGSSe) and CZTS [7-9]. Various chemical methods have been used to grow CdS films, including thermal evaporation [10], sputtering [11], molecular beam epitaxy [12], spray pyrolysis [13], electrochemical [14], chemical bath [15-16] , photochemical deposition [17] and SILAR(Successive Ionic Layer Adsorption and Reaction) deposition [18-20]. In comparison with other methods, SILAR deposition has some advantages such as easy control, simple and less expensive. In the successive ionic layer adsorption and reaction (SILAR) process the substrates are immersed into separated cationic and anionic precursor solutions and rinsed with purified water after each immersion [21]. Many kinds of thin films have been prepared by the SILAR technique [22-24]. In the present case, preparation, characterization and measurement of optical and electrical properties are reported for CdS thin films were deposited by SILAR method. The preparative parameters such as concentration of precursor's solutions, immersion time, rinsing time, number of deposition cycles, etc. are optimized.

2. Experimental:

All the chemicals used for the preparation were of analytical grade. It includes cadmium acetate and thiourea. All the solutions were prepared in Millipore water obtained from Millipore water system. Micro glass slides (6 cm x 1.25 cm) were cleaned thoroughly using soap solution to remove visible impurities and kept in chromic acid for 45 minutes. For the preparation of CdS thin films cationic precursor (0.1M) cadmium acetate (50 ml) has been taken in a beaker, then the anionic precursor (0.1M) thiourea (50 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 40 sec adsorption of Cd^{+2} ions on the surface of the glass substrate. 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 (S^{2-}) for 40 sec, reacted with cadmium ions on surface of the glass substrate. The procedure was carried out at room temperature. Successive cycles repeated and carried out for 25, 50 and 75 times separately to get the three desired films. The prepared films were dried at room temperature for 2 hours and then annealed in air at 200^{o}C for 1 hour. Phase identification and crystalline properties of the films were studied by XPERT-PRO X-ray powder diffractometer with CuKα radiation (λ = 1.5418Å). Scanning electron microscopy FE-SEM 6701 F used to study the surface morphology and to illustrate the formation of

crystallites on the film surface. UV–VIS spectrophotometric measurements were performed using a Unico UV-2102PCS spectrophotometer at room temperature. The electrical parameters were measured using Hall measurements setup (ECOPIA-HMS 3000) at room temperature with the permanent magnet of 0.57 Tesla.

3. Results and Discussion:

3.1 XRD Analysis:

Figure 3.1 shows the typical XRD pattern of SILAR deposited CdS film. The 2θ values of diffraction peaks observed are 26.5, 30.8, 43.9, and 52.1°, these correspond [25, 26] to reflections from (111), (200), (220), and (311) planes of cubic (zincblende) CdS respectively. The diffraction pattern is good agreement with the reported standard values (ICDD No. 10-0454). In the diffraction pattern, (111) reflection was the prominent peak than the other peaks and intensity of the (111) ,(200) , (220) and (311) diffraction peaks were increased with increasing the deposition cycles, which indicates that ions deposition process is increasing with the deposition cycles. In order to determine lattice parameter of the thin films, JANA2006 code was used in the Le-Bail mode. The calculated lattice parameters of thin films were tabulated in Table 3.1.

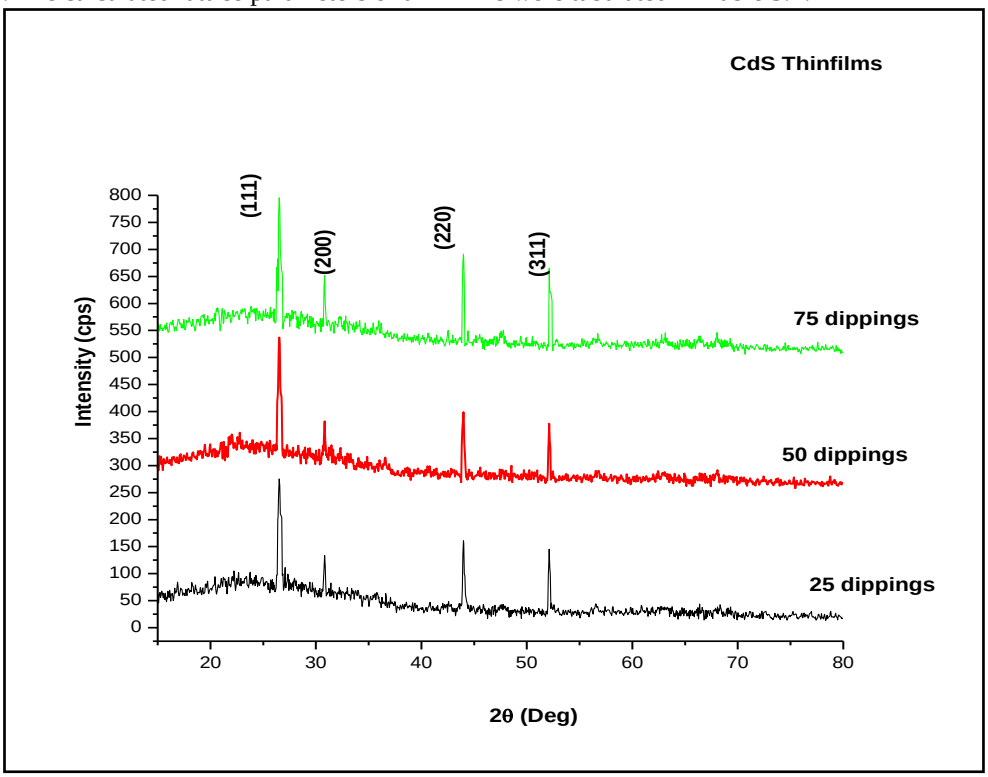

Figure 3.1: XRD pattern of CdS thin films prepared for various (25, 50 and 75) deposition cycles.

No of Deposition cycles	Crystallite Size(nm)	a (Å)
25	11.467	5.816
50	12.066	5.818
75	13.231	5.819
average	12.264	5.817

Table 3.1: Microstructural properties of ZnO

The calculated average value of lattice parameters are 5.817Å and this value is found in good agreement with the corresponding values of 5.818Å [ICDD No. 10-0454]. It can also found that, with the increase of the deposition cycles lattice constant (a) increased linearly from 5.816 to 5.819. The crystallite size of the SILAR deposited CdS thin films has been calculated using Scherer formula [27] given in equation (1), The FWHM values of the samples were derived from their highest intensity peak broadening by pseudo-voigt peak fitting.

$$\text{Crystallite size } D_{ave} = 0{\cdot}94\lambda/\beta \cos\theta \quad \text{-----} \quad (1)$$

Where D_{ave} is the mean crystallite size, β the full width at half maximum of the diffraction line, θ angle of diffraction, and λ the wavelength of the X-ray radiation. The maximum crystallite size of ~13.2 nm is found for 75 deposition cycles and the minimum crystallite size of ~11.4 nm is found for 25 deposition cycles which is shown in Table. 3.1.

3.2 Surface Morphology and EDAX by FESEM Analysis:

Field Emission Scanning Electron Microscope (FESEM) images of CdS films deposited for different deposition cycles 25, 50 and 75 are shown in figures 3.2 (a), (b) and (c) respectively. Surface morphology of the films is found to improve when the deposition cycles were increased from 25 to 50. The size distribution of

grains appears to be less homogenous for 25 deposition cycles and also not fully covered the substrate. The film deposited for 50 deposition cycles shows less uniform surface with medium substrate coverage.

The film deposited for 75 deposition cycles shows poor uniformity with closely aligned nano particles and in 75 deposition cycles, the grown film almost fully covered the substrate. Although some holes indicating porosity is present, no cracks could be detected. Agglomeration of nano particles also seems to be present in the certain region on the CdS film surface. Fig 3.2 (d), (e) and (f) show the EDAX results of the SILAR deposited CdS thin films for 25,50 and 75 deposition cycles respectively, the incorporation of Cd and S were verified by the EDAX result. No, detectable change in the computational changes are observed during the increase of deposition cycles as 25, 50 and 75 dippings.

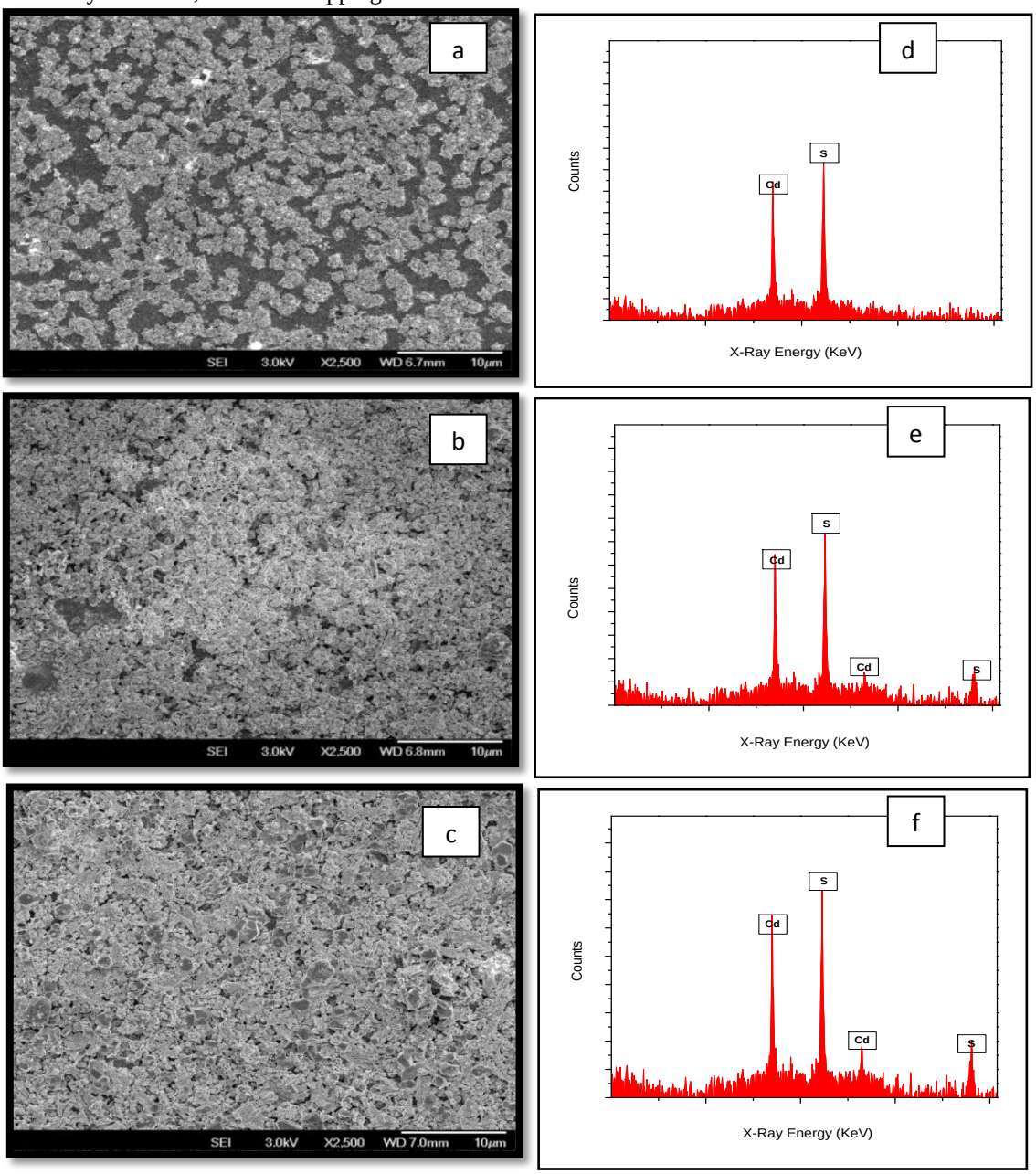

Figure 3.2 (a), (b) and (c) FESEM pictures and (d), (e) and (f) EDAX results of CdS film-25, 50 and 75 dippings

3.3 UV Visible Spectroscopy:

In Figure 3.3 we report the variation of the optical transmittance in the UV- Visible range, of films deposited with different deposition times. The transmittance of the deposited films was decreases with the deposition cycles. The reduction of the transparency in the long wavelength range (600- 1500 nm) may originate from the light scattering on the film surface in one hand and to the film thickness increases with the deposition time on the other hand. The optical band gap of CdS films can be estimated from the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) as shown in Fig 3.4, according to Tauc formula for direct bang gap semiconductor [28] $\alpha h\nu = A\ (h\nu - Eg)^{n/2}$ where A is a constant, Eg is the optical gap energy, υ is the frequency of the incident photon

and h is the Planck's constant. The optical gap of the deposited film is increased with increasing the deposition time, it varies from 2.45 to 2.50 eV for increasing the deposition cycles from 25 dippings to 75 dippings.

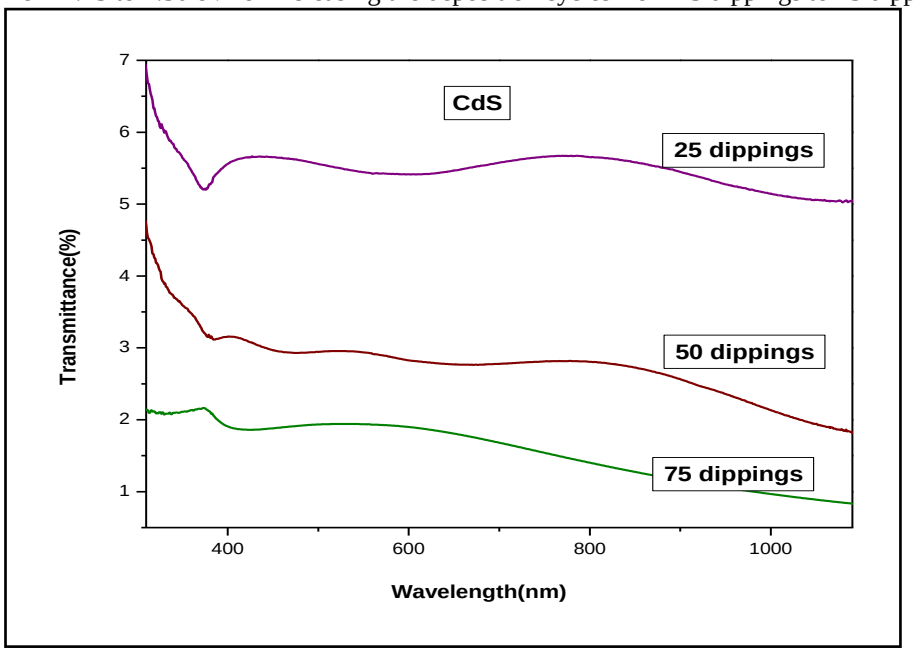

Figure 3.3: UV Transmittance graphs of SILAR deposited CdS thin films for 25, 50 and 75 dippings.

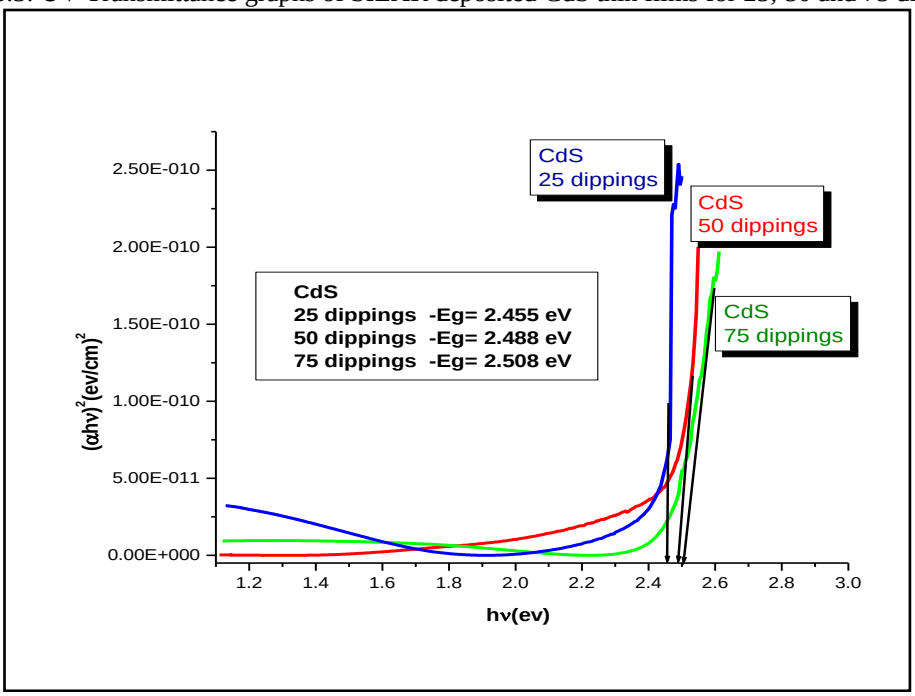

Figure 3.4: Band gap of CdS thin films.

3.4 Electrical properties - Hall Measurements:

Samples	Resistivity (Ω.cm)	Mobility (cm^2/Ns)	Carrier concentration (cm^{-3})	Hall coefficient (cm^3/coul.)	Conductivity (1/ohm-cm)
25 dippings	$3.67x10^{-1}$	2.01×10^3	8.46×10^{13}	7.38×10^3	$2.085 x10^{-03}$
50 dippings	$2.61x\ 10^{-1}$	4.50×10^3	2.32×10^{14}	1.04×10^4	$4.312 x10^{-03}$
75 dippings	$2.21x\ 10^{-1}$	7.18×10^3	5.37×10^{14}	3.63×10^4	$6.156 x10^{-03}$

Table 3.2: Resistivity, conductivity and carrier concentrations of CdS thin films

Figure 3.5 shows that, conductivity of the prepared samples increases with the deposition cycles and resistivity of the samples decreases with the deposition cycles. Fig 3.6 shows that, carrierconcenration of the films increase with deposition cycles. From the electrical studies, it is observed that, for 25 dippings, 50 dippings and 75 dippings samples, the resistivity decreases, conductivity and Hall mobility increases with dipping cycle increases. 75 dippings sample shows higher carrier concentration, mobility and lower resistivity

than other two samples. This may be due to the change in film stoichiometry (excess cadmium or sulphur vacancies, which are electron donor sites that provide the additional carriers and decrease the resistivity) [29].

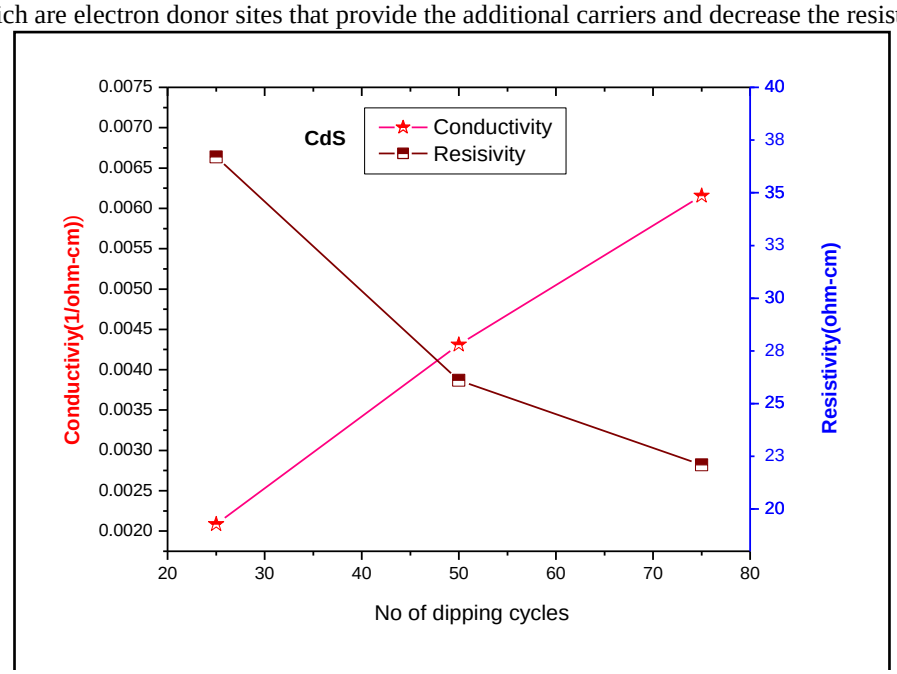

Figure 3.5: Shows the variation of conductivity & resistivity with deposition cycles.

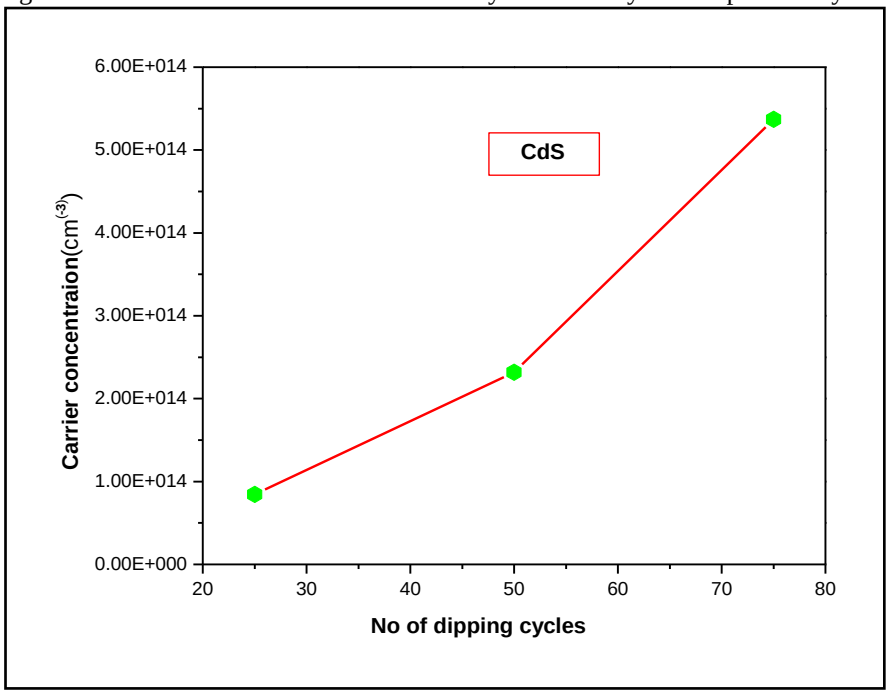

Figure 3.6: Shows the variation of carrier concentration with deposition cycles.

4. Conclusion:

CdS nano crystalline thin films have been prepared by SILAR method using cadmium acetate and thiourea. The XRD pattern confirms that samples contain the mixture of cubic nanoparticles of size 11-13 nm. The peaks indicate that synthesized product is crystalline and pure. The XRD analysis reveals that CdS is in cubic structure, the maximum grain size of the film is 13.23 nm at 75 deposition cycles. The result of UV-Vis. spectrum shows that prepared ZnO thin films have strong UV absorption ability and the optical gap of the deposited film is increased with increasing the deposition time, it varies from 2.45 to 2.50 eV for increasing the deposition cycles from 25 dippings to 75 dippings. FESEM micrograph witnesses the samples consist of regular and almost spherical shape particles at higher deposition cycles and the films are homogeneous and well covered to the substrate. EDAX analyses of the prepared CdS thin films confirm that the samples are composed of Cd and S without any impurity. From the Hall measurements, it is observed that, 75 dippings sample shows higher carrier concentration, mobility and lower resistivity than other two samples. The data presented here

concludes that in SILAR method, no of deposition cycles plays an important role in fabrication of good quality CdS nano crystalline thin films and also determining the particle size.

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