Available online at www.worldscientificnews.com

World Scientific News

An International Scientific Journal

WSN 91 (2018) 73-85 EISSN 2392-2192

Effect of Time Immersion of Thiourea on Structural and Optical Properties of CdS Deposited by SILAR

Raid A. Ismail[1], **Nadir F. Habubi**[2,*] and **Kameran Y. Qader**[2]

[1]Department of Applied Sciences, University of Technology, Baghdad, Iraq

[2]College of Education, Mustansiryah University, Baghdad, Iraq

*E-mail address: nadirfadhil@uomustansiriyah.edu.iq

ABSTRACT

Successive ionic layer adsorption and reaction (SILAR) technique was used to prepare (CdS) thin films on glass substrate, by changing the immersion time in thiourea solution. XRD patterns proved that the as deposited thin films were polycrystalline structure with an average crystallite size ranging from 14.1 nm to 5.6 nm depending on immersion time. The EDX confirm the existence of CdS. Scanning electron microscopy reveals that the deposited films have a nanorod structure.Atomic force microscopy has shown that the values of average roughness and the root mean square roughness increase upon increasing the immersion time. The transmittance spectra reveal that as the immersion time increase, the value of transmittance decrease.

***Keywords*:** CdS, Optical Properties, SILAR

1. INTRODUCTION

In the past few decades, attention has been paid to the preparation of semiconducting chalcogenide thin films due to their wide application in various scientific and technological fields, causing a significant reduction in the cost of production of semiconductor devices. The films prepared from chalcogenide have been studied closely for their important applications in electronic, optical, and superconductor devices [1-3].

(Received 02 December 2017; Accepted 20 December 2017; Date of Publication 21 December 2017)

Chalcogenide thin films are semiconductors that have a broad energy gap that causes emissions cover the blue and green spectral region in terms of technology. The importance of these membranes comes from their emissions, which are close to human eye sensitivity, so the CdS thin films is very important for photonic devices [4]. Cadmium sulphide (CdS) is a significant and useful material for optoelectronic applications. Undoped CdS thin film is always growing as n-type [5].

The CdS thin films have been used in applications such as optical window solar cells [6,7], field effect transistors, light emitting diodes [8,9], photocatalysis and biological sensors [10,11] optical coding, optical data storage and sensing [12], nonlinear integrated optical device [13]. In recent years there has been growing interest in developing techniques for preparing semiconductor nanoparticles and thin films because the properties in nano form differ significantly from those of their bulk counterparts. Therefore, there is much interest in physical properties of nanometer size (20-80 nm) semiconductor materials due to their novelties; their properties are different and often superior to those coarse grained polycrystalline materials and also amorphous alloys of same composition [14,15].

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 [16], sputtering [17], chemical bath deposition (CBD) [18], spray [19], molecular beam epitaxy (MBE) [20], and metal organic chemical vapor deposition (MOCVD) [21].

The successive ionic layer adsorption and reaction (SILAR) technique was introduced by Nicolau in the mid-1980's [22]. The method has been employed to grow selected II-VI compounds, especially CdS and ZnS. In the SILAR method, a substrate is immersed separately in 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 [22–25].

2. Experimental Procedures

2. 1. Substrates Cleaning

The cleaning of the substrate is very important because it greatly influences on properties of the films deposited on it. In this study glass slides were used to prepare the samples. This process can be summarized as follows:

1\ Glass slides were cleaned using cleaning solution and water to remove dust sticking its surfaces.

2\ rinsing the slides in chromic acid (for 24 hours) to introduce functional groups called nucleation and / or epitaxial centers, which formed the basis for the thin film growth.

3\ glass slides were dipped in a beaker contains pure solution of alcohol and put it in ultrasonic device for fifteen minutes to remove contamination such as grease.

4\ eventually, glass slides were rinsed using distilled water and then dried by hot air.

2. 2. Thin film preparation

Thin films of CdS deposited on glass substrates at room temperature by the SILAR technique. Cadmium acetate solution was used as the cationic and thiourea solution (CH_4N_2S) was used as the anion precursors; the concentration of both solutions is 0.1 M. While rinsing water is a mixture of deionized water and ammonia (NH3) with pH~10.8. Dive time in cadmium acetate solution was 5 s with changing the dive time in the thiourea solution (5, 10, 15 s), the rinsing time after each immersion process is 5 s and the number of SILAR cycles was constant at preparing all thin films.

3. RESULTS AND DISCUSSION

3. 1. Structural properties

To find the best time for rearranging crystal structure of cadmium sulfide (CdS), various thiourea deposition times have been used to improve the degree of crystallization.

3. 1. 1. XRD and SEM Studies

Fig. 1 shows the X-Ray diffraction patterns for cadmium sulfide (CdS) films prepared by SILAR technique with (5, 10, and 15s) thiourea immersing time. X-Ray diffraction results for samples show that the CdS films have polycrystalline nature, and that all CdS films are mixed phases of cubic and hexagonal structure which is well matched with standard peaks. The increasing in thiourea immersing time decrease the crystallite of prepared films and makes it amorphous film. The XRD characterization is parameters are summarized in Table 1.

Table 1. Summary of X-Ray parameters for CdS thin films deposited at different thiourea deposition time

Time (s)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl
5	27.9614	0.5790	3.1884	14.1	(101)
	36.7189	1.1580	2.4456	7.2	(102)
	43.8118	0.9409	1.6647	9.1	(110)
	48.4439	1.3027	1.8775	6.7	(103)
	52.2075	1.5199	1.7507	5.8	(201)
10	43.8386	0.8802	1.6635	9.7	(110)
	51.6870	1.1003	1.7671	8.0	(201)
15	43.9120	1.5404	1.6602	5.6	(110)

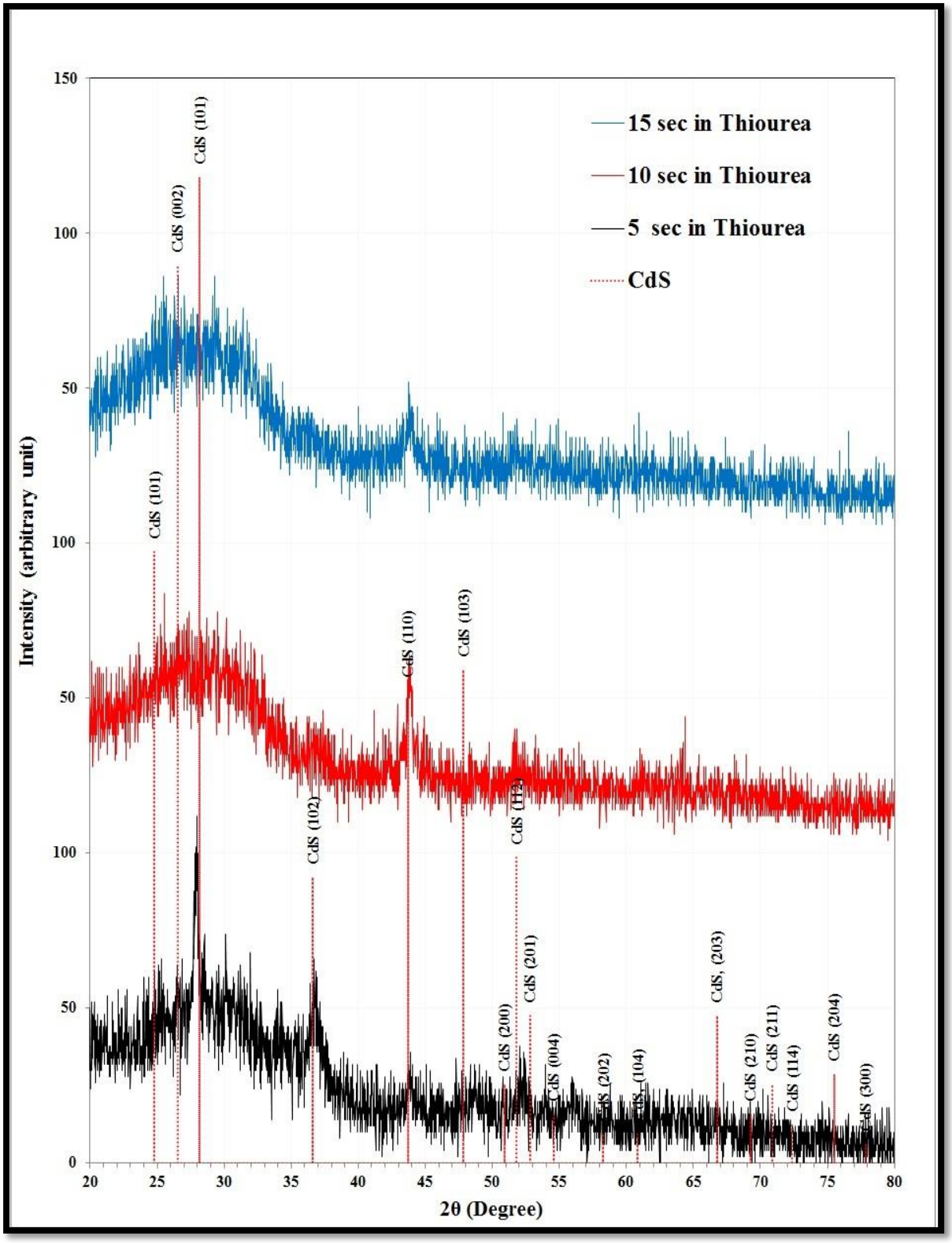

Fig. 1. X-Ray diffraction patterns of CdS thin films at different thiourea deposition time

Figure 2 shows the energy dispersive X-Ray (EDX) spectrum of the deposited CdS nanostructure films on the glass substrates. The contents in CdS films at different immersion time in thiourea solution (5, 10, 15 s). This figure shows that the atomic percentage of cadmium decrease while the atomic percentage of sulphide increase, the ratio Cd/S decrease when the immersion time in thiourea solution was increased. Table 2 shows the atomic ratio of Cd and S in these films and sure formation CdS films. It can be stressed here that the long time of immersion leads to enhance the film stoichiometry.

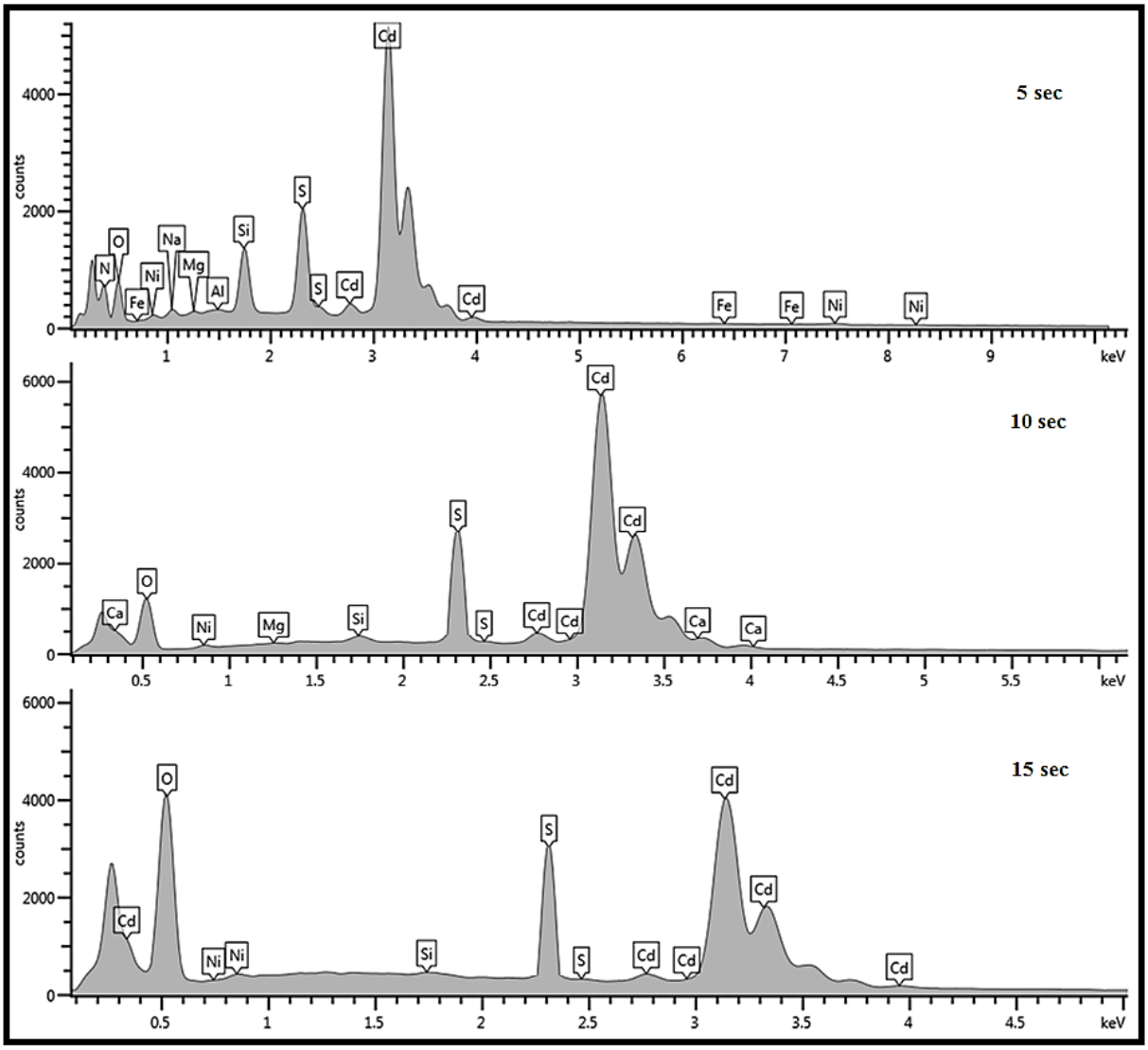

Fig. 2. EDX spectrum of CdS thin films deposited at different thiourea immersion time

Table 2. EDX data of CdS thin films deposited at different thiourea immersion time

	Thiourea time		
	5 sec	**10 sec**	**15 sec**
Cd atom%	71.87	70.042	69.855
S atom%	28.13	29.958	30.145
Cd/S	2.554924	2.338007	2.3173

3. 1. 2. Atomic Force Microscopy (AFM)

It is well known that the atomic force microscopy (AFM) is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software. The nanostructure CdS thin films are morphologically characterized using (AFM) technique; also the surface structure of a coating gains more and more importance. In the extreme case of thin films the surface roughness may be in the order of the film thickness and can influence all film properties such as mechanical, electrical, magnetically, and optical properties [26].

Figure 3 shows that the surface morphologies are dependent on the immersing time in thiourea solution. The small spherical grains agglomerates are uniformly distributed of shape and size over the film surface. It can be seen that the film is crack-free and quite smooth with a decrease on the surface roughness [27]. Smoothening of the films is possibly due to order of surface atoms to attain a lower energy state. Table 3 shows that the root mean square and surface roughness increases, where the average grain size decreased with increase thiourea deposition time (75.74 to 59.3 nm) and increased after that.

Table 3. Values of average grain size and average roughness of CdS thin films deposited at different thiourea immersion time

Time (s)	Average grain size (nm)	Average roughness (nm)	Root mean square (nm)
5	75.74	1.79	2.12
10	59.30	2.71	3.18
15	71.55	2.95	3.5

A high grain density distribution with tightly packed grains and exhibit a higher surface roughness with uniform oriented this may correspond to the spherical grains agglomerates with uniformly distributed of shape and size along the film surface increased as increased deposition times.

The grain size obtains from AFM is larger than that obtains from XRD and SEM due to the following reasons:

1\ the effect of particle agglomeration
2\ structural defects (stress and strain)
3\ aggregation of grains

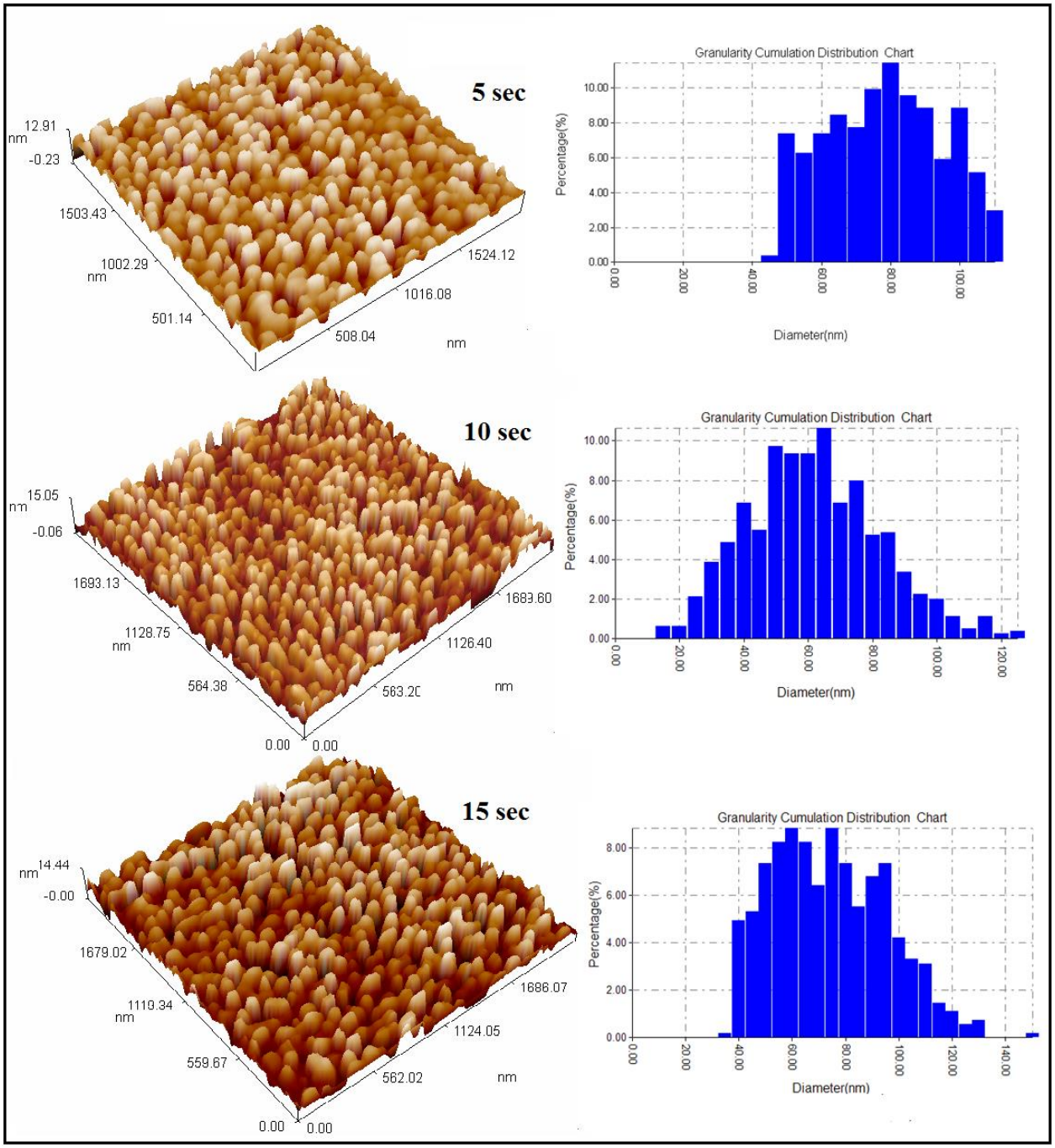

Fig. 3. 3D AFM images and granularity distribution chart of CdS thin films deposited at different thiourea immersion time

3. 1. 3 Scanning Electron Microscope (SEM)

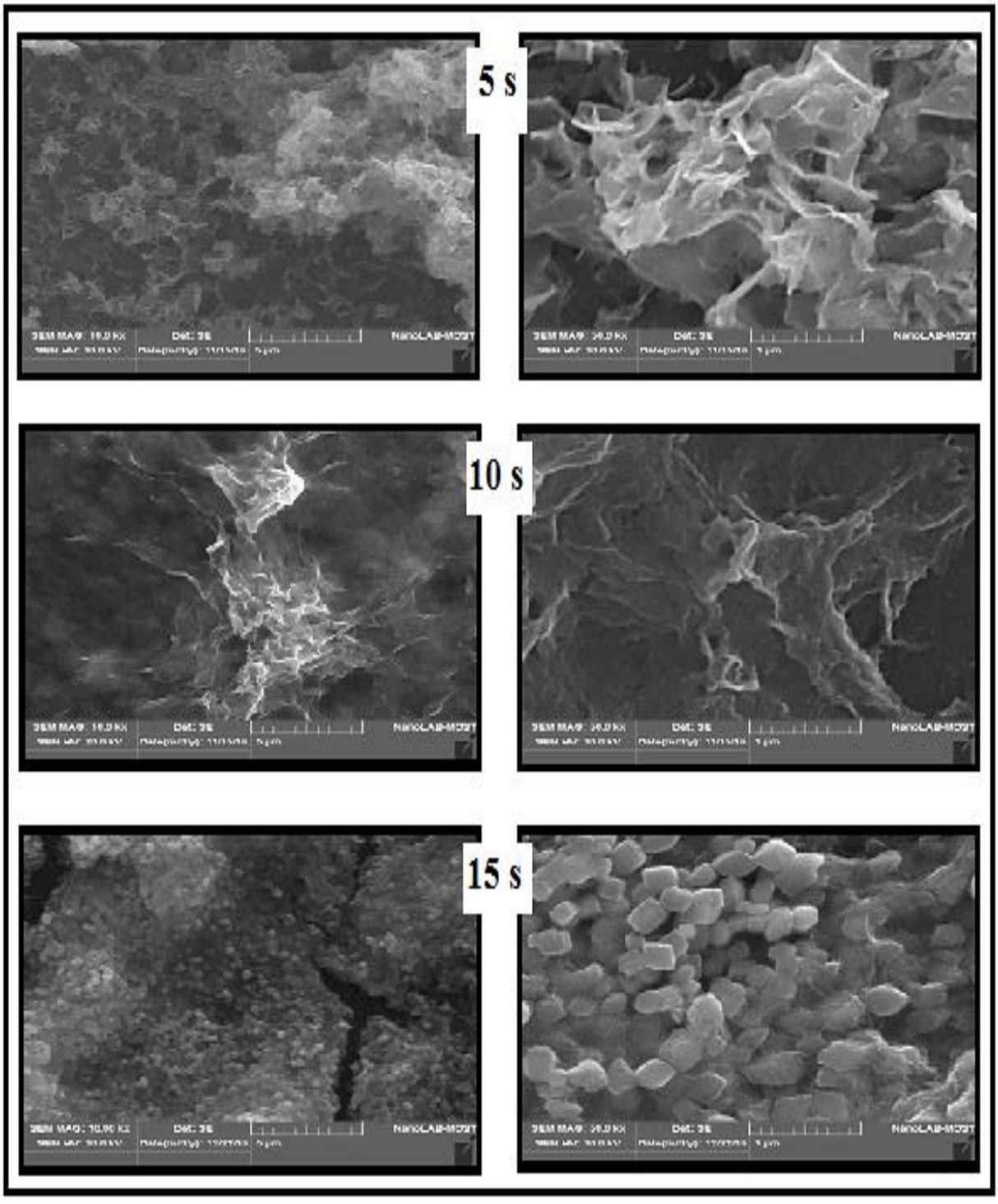

Fig. 4. SEM image with two magnification powers for CdS thin films deposited at different thiourea immersion times

The morphology of CdS nanostructures film prepared by SILAR technique is characterized by SEM investigation. Figure 4 shows the typical SEM images of the prepared CdS nanostructures films at different immersion time in thiourea solution (5, 10, 15 s) with two magnification powers. This figure shows clearly the effect of disposition time of thiourea in SEM image of CdS films. Increasing the disposition time from (5 s) to (10 s) caused to decrease the diameter of nanowires from (25 nm) to (38 nm), while increase disposition time to (15 s) leads to formation cubic and hexagonal structures with grain size around (150 nm).

3. 1. 4. Thin film thickness

To deposit nanocrystlline CdS thin film one SILAR cycle involves the following four steps: i. adsorption of Cd^{2+}, a well cleaned glass substrate is immersed in the cadmium acetate solution having Cd^{2+}, cadmium ions are adsorbed on glass substrate. ii. rinsing the unabsorbed Cd^{2+} ions are separated out by dipping the substrate in double distilled water. iii. reaction with S^{2-}, sulfides ions were adsorbed from an aqueous solution of thiourea. iv. Finally rinsing the substrate with distilled water, thus one SILAR cycle is completed. After few number of such SILAR cycles, CdS thin film is formed onto a glass substrate.

Fig. 5 shows the effect of thiourea immersion time on the thickness of CdS thin films, this figure shows that the thickness decreased at 10 s and increased at 15 s.

The thickness of the thin films reduced either by peeling of the material from the substrate or formation of outer porous layer and peeling off from glass substrate [28].

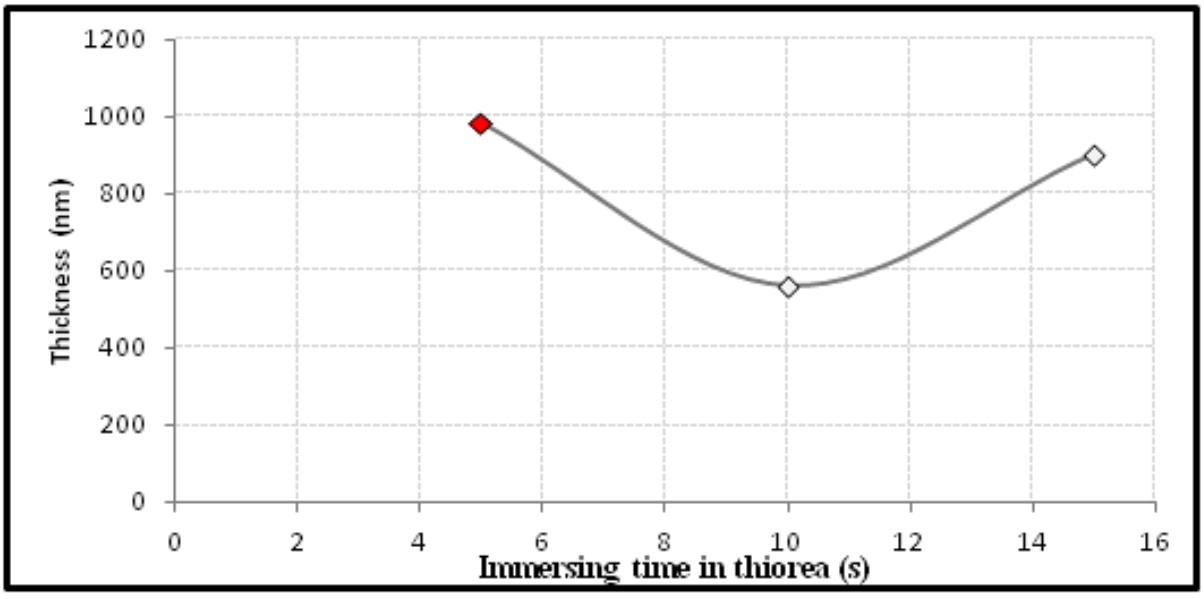

Fig. 5. Variation of film thickness with thiourea immersion time

3. 2. Optical Properties

3. 2. 1 Transmittance Spectrum

Measurements of optical transmittance of deposited CdS films were carried out for all prepared films at different thicknesses within wavelength range (350-900 nm); these films

have been prepared at different thiourea immersion time. Figure 6 shows the variation transmittance of thin films deposited at different thiourea immersion time, the transmittance reached highest value at 10 s immersion time in thiourea, It is noticed that all the deposited films exhibit transmission about 25–70% in the visible light range of (500–600) nm. Transmittance varies depending on the thickness of the films, generate localized states within the energy gap leading to an increase in the absorbance of the films and then decrease the transmittance of the films, also the cracks and pin holes play an important role in film transmittance. In some films there are no changes in the transmittance curves at low energies within a range of λ = 600-900 nm, this change is due to the low absorbance of the photons which has lower energies than that of the film. The absorbance increases or the transmittance decreases rapidly at high energies (short wavelengths) corresponding to the energy gap of the film, (when the incident photon has an energy equaling or higher than the energy gap value).

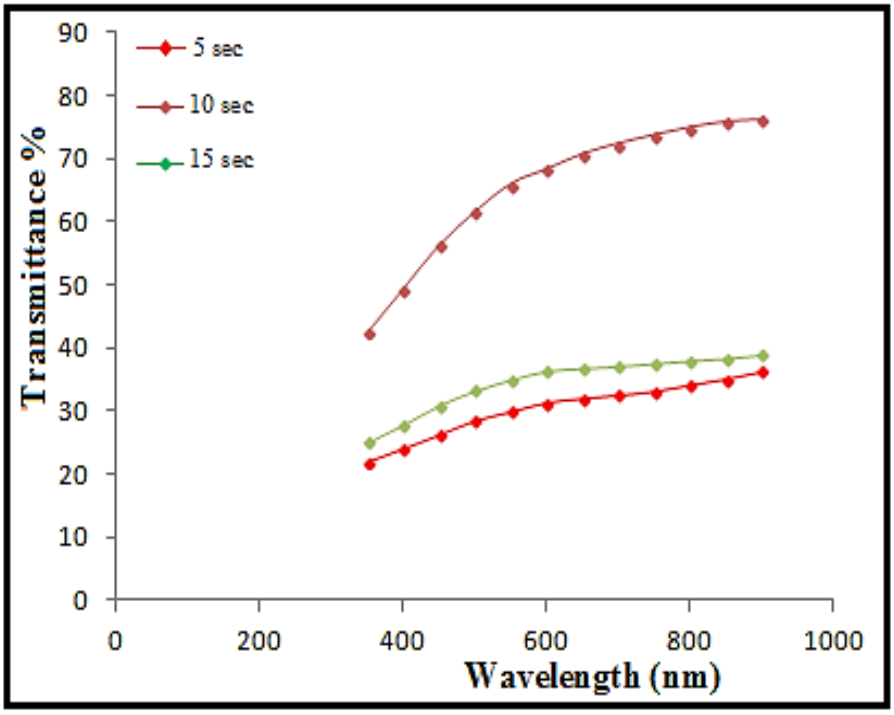

Fig. 6. Optical transmittance of CdS thin films deposited at different thiourea immersion time

Table 4. Transmittance, absorption coefficient, and extinction coefficient of CdS thin films deposited at different thiourea immersion time

Thiourea deposition time (s)	T%	α (cm^{-1})	K
5	29.289	12579	0.054
10	63.609	8219	0.034
15	33.853	12088	0.052

3.2.2 The optical energy gap

The energy band gap of prepared films is estimated by plotting the square of (αhυ) versus (hυ). The extrapolation of the straight line to $(\alpha h\upsilon)^2 = 0$ gives the value of energy gap. Figure 7 shows the energy gap of CdS thin films prepared at various deposition time (5, 10, and 15 s) in thiourea solution, It is clear that the thickness film and the sulfur ratio in it has an effect on the value of the energy gap. It is noticeable that this behavior is similar to thickness change; this change in the energy gap can be explained by the increasing proportion of new bonds resulting from the sulfur component that is compatible [29].

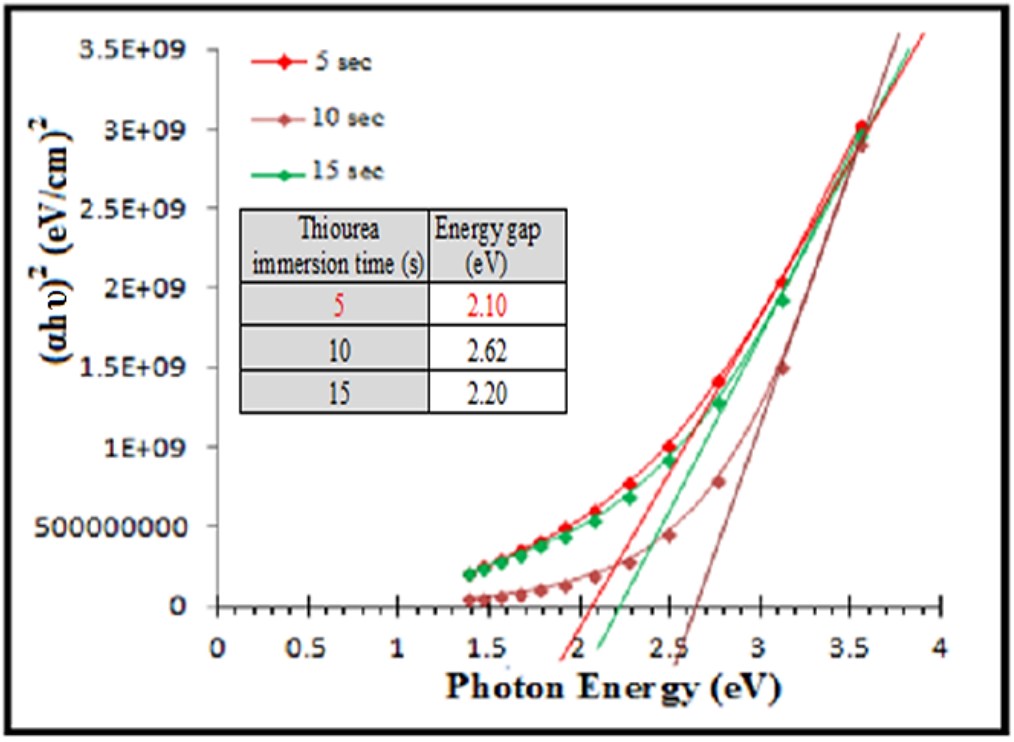

Fig. 7. Variation of energy gap for CdS thin films prepared at different immersion time of thiourea solution

4. CONCLUSION

Thin films of CdS with different time immersion of thiourea have been successfully deposited using SILAR technique. The XRD reveals that all the deposited films were polycrystalline. SEM Images assure that the deposited films were nanorod shape. All the studied parameters were affected by time immersion of thiourea.

References

[1] K.J. Rajeshwar, *Appl Electrochem* 15 (1985) 1.

[2] G.J. McCarthy, J.J. Rhyne (Eds.), The Rare Earths in Modern Science and Technology, Plenum Press, New York, 1978.

[3] R. Suryanarayanan, *Phys. Status Solidi B* 85 (1978) 9.

[4] B. Ullrich, D. M. Bagnall, H. Sakai, and Y. Segawa, *Solide State Commu.* 109, 757 (1999).

[5] M. Avinor and G. Meijer, *J. Chem. Phys.* 32, 1456 (1960).

[6] Maruyama T, and Kitmura R., Transformation of the wave length of the light incident upon CdS/CdTe solar cells, *Sol. Energy Mater. Sol. Cells*, 69, 61 (2001)

[7] Gerardo Larramona G., Choné C., Jacob A., Sakakura D.B., Daniel Péré D., Cieren X., Nagino M. and Bayón R., Nanostructured Photovoltaic Cell of the Type Titanium Dioxide, Cadmium Sulfide Thin Coating, and Copper Thiocyanate Showing High Quantum Efficiency, *Chem. Mater.* 18(6), 1688–1696 (2006)

[8] Wang Y., Ramanathan S., Fan Q., Yun Q., Morkoc H., and Bandyopadhyay S., Electric Field Modulation of Infrared Absorption at Room Temperature in Electrochemically Self Assembled Quantum Dots, *J. Nanosci. Nanotechnol.* 6, 2077–2080 (2006)

[9] Klevin D.I., Roth R., Lim A.K.I. and Alivisators A.P., A single electrontransistor made from a cadmium selenide nanocrystal, *Nature*, 389, 699-701 (1997)

[10] Kolvin V.I., Schlamp M.C., Alivisators A.P., Light emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature*, 370, 354-357 (1994)

[11] Alivisators A.P., Semiconductor clusters, nanocrystals and quantum dots, *Science*, 271, 933-937 (1996)

[12] Cao G., Nanostructure and nanomaterials synthesis, properties and applications, Imperial College Press, 349 (2004)

[13] Senthil K., Magalraj D. and Narayandas S.K., *Appl. Surf. Sci.* 476, 169-170 (2001)

[14] Henglein A., Small partical research; physicochemical properties of extremely small colloidal metal and semiconductor partials, *Chem. Rev.* 89, 1861-1873 (1989)

[15] Fukuka A., Sakamoto Y., Guan S., Ingaki S., Sugimoto N., Fukushima Y., Hirahara K., Lijima S. and KIkawa M., Novel templating synthesis of neckless-shaped mono and bimetallic nanowire in hybrid organic-inorganic mesoporous material, *J. Amer. Chem. Soc.* 123, 3373-3374 (2001)

[16] G. Stanly, *Appl. Solid-State Sci.* 5, 251 (1975).

[17] M. Savelli and J. Bougnot, *Solar Energy Conversion, Top. Appl. Phys.* 31, (1979), 213.

[18] H. Uda, S. Ikegami, and H. Sonomura, *Jpn. J. Appl. Phys.* 29, 30 (1990).

[19] J. Kaur, D. K. Paudya, and K. L. Chopra, *J. Electrchem. Soc.* 127, 943 (1980).

[20] J. T. Mullis and T. Tagushi, *J. Crys. Growth*, 117, 432 (1992).

[21] K. A. Dhese, J. E. Nicholls, W. E. Hagston, P. I. Wrigth, B. Cockayne. and J. J. Davies, *J. Crys. Growth*, 138, 140 (1994).

[22] Y. F. Nicolau, *Appl. Surf. Sci.* 22/23, 1061 (1985).

[23] M. P. Valkonen, T. Kannianinen, S. Lindoros. M. Leskela, and E. Rauhala, *Appl. Phys. Sci.* 115, 386 (1997).

[24] Y. F. Nicolau, M. Dupy, and M. Brunel. *J. Electrochem. Soc.* 137, 2915 (1990).

[25] S. Lindoros, T. Kannianinen, M. Leskela, and E. Rauhala, *Thin Solid Films*, 263, 79 (1995).

[26] L. L. Pan, G. Y. Li, and J. S. Lian, Structural, optical and electrical properties of cerium and gadolinium doped CdO thin films, *Appl. Surf. Sci.* vol. 274, pp. 365–370, Jun. 2013.

[27] B. J. Zheng, J. S. Lian, L. Zhao, and Q. Jiang, Optical and electrical properties of In-doped CdO thin films fabricated by pulse laser deposition, *Appl. Surf. Sci.* vol. 256, pp. 2910–2914, 2010.

[28] U. M. Jadhav, S. N. Patel, and R. S. Patil, Room Temperature Deposition of Nanocrystalline CdS Thin Film by Successive Ionic Layer Adsorption and Reaction (SILAR) Method, *Res. J. Mater. Sci.*, vol. 1, no. 1, pp. 21–25, 2013.

[29] J. Barman, J. P. Borah, and K. C. Sarma, Effect of pH variation on size and structure of CdS nanocrystalline thin films. *Chalcogenide Lett.*, vol. 5, no. 11, pp. 265–271, 2008.