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Structural and Optical Properties of $Pb_xCd_{1-x}S$ Thin Films Prepared by Vacuum Evaporation Technique

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ABSTRACT

Thin films of ternary $Pb_xCd_{1-x}S$ compounds were prepared by vacuum evaporation technique having composition ranges of x=0.1 on corning glass substrate at substrate temperatures 150°C and different annealing temperatures (RT- 300°C) of thickness 300 nm. The X–ray diffraction measurements (XRD) for $Cd_{1-x}Pb_xS$ thin films showed that all films have polycrystalline structures with cubic and hexagonal phase. Atomic force microscopy (AFM) measurement shows that average crystallite and roughness are increased with increasing of annealing temperature. The structure is uniform, densely packed and nano-tube structure, and it shows that the morphology of these films has larger number of grain size and is homogeneously distributed. The deposited films were optically characterized by UV-Visible spectroscopy, and it have direct energy gab. The energy band gaps of thin films increases with increasing annealing temperatures while the optical constants decrease.

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INTRODUCTION

The ternary semiconductor thin films are considered to be an important technological material due to its prime applications in various optical and electronic devices. The II-VI and IV-VI group compound materials having specific physical properties like high efficiency, high optical absorbance and direct band gap, are considered to be potential materials in respect for a wide spectrum of optoelectronic applications such as photo detectors, photovoltaic devices, photo-electrochemical cells, lasers, IR devices, solar control coatings, , solar cells (Barote, M.A., 2011; Suryavanshi, K.E., 2014). Cadmium sulfide (CdS) is a II-VI group semiconductor with energy gap covering the visible spectral range, which is used in many applications such as visible light emitting diodes and lasers, photovoltaic and photo-conductive devices. On the other hand PbS is a semiconductor material belonging to IV-VI group suitable for infrared detection applications (Barote, M.A., 2010; Harmann, T.C., 1971; Barote1, M.A., 2013). It has also been used as photo resistance, laser diode, humidity and temperature sensors, decorative coatings and solar control coatings. However, only a limited number of studies have been conducted on ternary II-IV-VI compounds. These materials have attracted a great deal of attention, both from the fundamental and applied point of view. These materials are used in optoelectronics, solar control coatings, gas and humidity sensors and photoelectrochemical solar cells. Harman and coworkers reported that bulk crystals of $Pb_{1-x}Cd_xS$ could be prepared beyond the stable phase boundary limits by quenching.

In the last five years, PbS has attracted considerable attention. PbS, a material of interest with a narrow band gap energy (Eg = 0.41 eV) and large excitation Bohr radius of 18 nm (Singh, J., 1995; Joshi, R.K., 2006) has been alloyed with many other binary sulfides to form variable band gap ternary semiconductors over wide wavelength range. Considering that the band gaps of bulk PbS and bulk CdS are 0.41 and 2.4 eV, respectively, a bulk ternary alloy of the type $Cd_{1-x}Pb_xS$ should show a variation of the band gaps between the limiting values of 0.41 and 2.4 eV.

Recently, growth of mixed thin film structures and nanocrystals of $Cd_{1-x}Pb_xS$ has attracted immense interest, because it offers the advantage of tuning the optical and the opto-electronic properties of $Cd_{1-x}Pb_xS$, viz. band gap, electrical conductivity, thermoelectric power, etc., in a controlled manner (Popescu, V., 2006; Thangavel, S., 2010; Herna´ndez-Borja, J., 2011). However, the solubility

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of the two sulphides at room temperature and normal pressure is very low (experimental solubility of wurtzite CdS in rock salt (RS) PbS is ≈0.017% and the solubility of PbS in CdS is probably even less, While incorporation of substantial amounts of CdS into the PbS lattice is not thermodynamically favourable at room temperature, it can be frozen in the metastable state under suitable preparation conditions. Annealing metastable $Cd_{1-x}Pb_{x}S$ samples prepared from quenched, high temperature solid state reaction, as well as $Cd_{1-x}Pb_xS$ films deposited by chemical bath deposition (Herna´ndez-Borja, J., 2011; Seghaier, S., 2006; Modaffer, A.M., 2009) has been shown lead to phase segregation, as expected from thermodynamic considerations. Because of the phase separation, the band gap energy of chemically prepared $Cd_{1-x}Pb_xS$ nanocrystals varies only in a narrow wavelength range (700-1000 nm). In addition, the lattice parameters of $Cd_{1-x}Pb_xS$ nanocrystals from wet chemical method remained almost the same with variation of *x* value, indicating inhomogeneous composition in the chemically alloyed $Cd_{1-x}Pb_xS$ nanocrystals. Therefore it is significant to take an alternative physical method to prepare surface clean and homogeneous alloyed $Cd_{1-x}Pb_xS$ nanocrystals, which could demonstrate tunable intrinsic optical spectrum or band gap energies at mid IR wavelength region and continuous lattice parameter change with variation of chemical composition (*x*). Ternary alloys prepared out of binary semiconductors provide a class of semiconductors in which the lattice parameter, energy band gap, and other operational parameters could be continuously varied within specified limits by alloying appropriate binary constituents with changes in their relative concentrations, there has been interest in tailoring the properties of semiconductors and, therefore, various ternary semiconducting materials have been developed and utilized for variety of applications.

Due to the optical, electrical and photoelectrical properties of $Cd_{1-x}Pb_xS$ is one of the promising materials having large spectrum of applications in selective coatings for efficient photothermal conversion to obtain absorbance in the UV-VIS region and reflectance in IR region. These films can be used for controlled absorption and reflection of solar light. Thin films of lead and cadmium sulfate show promise in many physical applications, such as ptoelectronics, infrared photo detectors, optical switches, and solar cells. Thangavel *et al*., Herna´ndez *et al*. and Seghaier *et al*. Mixed thin film structures of PbS and CdS ($Cd_{1-x}Pb_xS$) have generated significant interest because they offer the advantage of tunable optical and opto-electronic properties of PbS, viz., its band gap electrical conductivity, and structural properties (Ubale, A.U., 2007). In nanocrystallites, electrons confined within a narrow potential well exhibit extraordinary optical and electrical properties (Alex, P.G., 2008). Thus, when the width of such a confining potential is very small, that is, in the order of a few hundred angstroms, quantum size effects increase. Doping of PbS by Cd has been found to influence film growth and result in reductions in crystallite size Thangavel *et al*. Increases in the optical energy band gap (Eg) of thin films can be attributed to quantum size effects, as expected from thin films with a nano-crystalline nature Alex *et al*. (2008).

The objective of present work is to optimize various preparative parameters to synthesize the ternary $Cd_{1-x}Pb_xS$ thin films by vacuum evaporation technique and studies the optical properties by spectroscopic measurements to know thin film composition in order to make them suitable candidate for various optoelectronic and nano-device application and studies the effect of variation of annealing temperatures on these films.

Experimental method:

Thin $Cd_{1-x}Pb_xS$ films have been evaporated by using Edward (E306A) coating system under vacuum of about 2×10^{-5} mbar, from CdS and PbS powder purity of about 99.999% manufacturer by Balzers Switzerland at x content of (0.1). These films deposited on 7059 corning glass slides with (300) nm thickness at substrate temperature (150°C). The prepared films have been annealed at (100, 200, 300) °C. The thin $Cd_{1-x}Pb_xS$ films structural analysis was examined by using Phillips X-Ray diffractometer system with CuKα source (λ = 1.54056A^0) in the 2θ range from 20^0 to 60^0.. The surface morphology of the prepared films is investigated by means of atomic force microscopy (AFM). The optical studies were carried out using UV-VIS spectrophotometer in the 300-1200 nm wavelength range.

RESULTS AND DISCUSSIONS

The X-ray diffractograms of cadmium lead sulphide films ‘as-deposited’ and annealing at (100, 200, 300) °C is shown in Fig.(1). The presence of large number of peaks indicates that the films are polycrystalline in nature with cubic and hexagonal structure Both CdS and PbS exhibit hexagonal wurtzite and cubic zinc blend structure, such results are reported by other researcher [10]. Increasing the mole fraction of lead was accompiend by the appearance of cadmium oxide planes. The dominant peaks are (111), (101). Thus, there must be solid solution formation of the kind ($Cd_{1-x}Pb_xS$) in the composition. Table (1) lists the measured 2θ, hkl, d values for the $Cd_{1-x}Pb_xS$ thin films at annealing temperatures (100, 200, 300) °C at x=0.1. The spectrum shows diffraction peaks as in table 1. From this XRD result obtained, it can be inferred that the deposited $Cd_{1-x}Pb_xS$ film is a mixture of PbS and CdS with the two showing their individual planes which is in agreement with the report of (Modaffer, A.M., 2009; Ubale, A.U., 2007; Alex, P.G., 2008).

The crystallite size increases from 37.3 to 57.6 nm as annealing temperatures increases (RT- 200) °C at x=0.1. as in table 2. The increase of T_a improves the crystal structure by increasing the intensity of the planes. Such improvement in crystal structure could be attributed to the increase in crystallite size as the small crystallites join each other's in the planes by increasing heat treatments.

AFM measurements:

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 $Cd_{1-x}Pb_xS$ thin films and annealing films at (100, 300) °C were morphologically characterized using Atomic Force Microscopy (AFM) technique. Fig. 2 shows the two and three-dimensional representation of 2000X2000 nm area of as deposited $Cd_{1-x}Pb_xS$ thin films and annealing films at (300) °C. It can be seen that films are uniform, densely packed and nanotube structure, and it shows that the morphology of these films has larger number of grain size and are homogeneously distributed and have nano tube structures, which indicates the crystalline nature of the film. Initial visual investigations of the deposited film have shown that they are compact and have good adherence to the substrate. No evidence of cracking observed. The grains are made of different sizes varying from 95.24-100.95nm However, the sizes of the grains are noticed to increase as the annealing temperatures is increased as shown in Table 3. Based on AFM image (Fig. 2), the grain density reduced indicating the smaller grains agglomerate together to form larger grains of $Cd_{1-x}Pb_xS$ thin films. On the other hand, the surface roughness and Root Mean Square (RMS) of the films were measured. As in Table 3. The surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness. The surface roughness is unavoidable since the grains are grown with different sizes. It can be seen that the surface roughness and RMS values increase with increasing T_a indicating an increase in the grain size As in Table 3 and Fig. 2., and this is agreement with other literatures.

Table 1: The measured 2θ , hkl, d values for the $Cd_{1-x}Pb_xS$ thin films at annealing temperatures (RT, 100, 200) °C at x=0.1.

T_a (°C)	2θ(degree)	$d_{Exp.}$(Å)	hkl	I/I_o	type
RT	24.88	3.576	100	58	CdS H
	26.58	3.3308	111	100	CdS C
	28.22	3.1597	101	86	CdS H
	31.06	2.8769	200	48	CdS C
	43.65	2.099	220	29	PbS C
	47.5	1.89	220	30	CdS C
	51.5	1.67	311	30	PbS C
100	24.84	3.581	100	64	CdS H
	26.56	3.533	111	100	CdS C
	28.28	3.153	101	82	CdS H
	31.64	2.825	200	48	CdS C
	43.55	2.0998	220	28	PbS C
	47.66	1.89	220	28	CdS C
	51.8	1.67	311	29	PbS C
200	24.8	3.587	100	73	CdS H
	25.66	3.46688	111	72	PbS C
	26.4	3.3732	111	100	CdS C
	28.1	3.1729	101	71	CdS H
	30.88	2.921	200	79	CdS C
	43.44	2.098	220	73	PbS C
	47.36	1.89	220	28	CdS C
	51.1	1.67	311	29	PbS C

Table 2: The grain size and lattice constant for the $Cd_{1-x}Pb_xS$ thin films at annealing temperatures (RT, 100, 200) °C at x=0.1.

T_a (°C)	G.S (nm).	a(A)
RT	37.3	6.1
100	45.6	6.11
200	57.6	6

Table 3: The grain size from AFM and XRD and Roughness for the $Cd_{1-x}Pb_xS$ thin films at annealing temperatures (RT, 100, 200) °C at x=0.1.

T_a (°C)	Grain size(AFM)	Grain size(XRD)	Roughness (nm)
RT	95.24	37.3	0.707
100	-	45.6	-
300	100.95	57.6	0.736

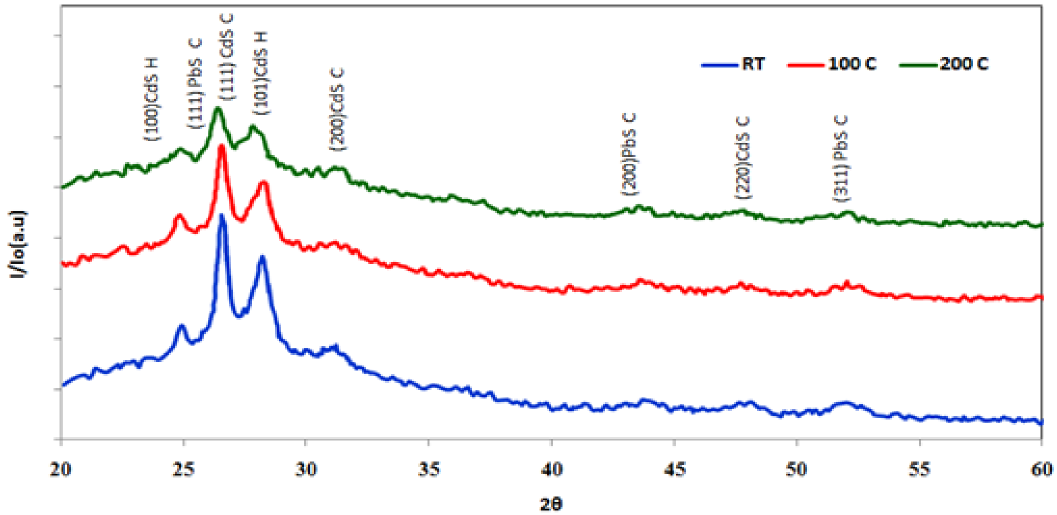

Fig. 1: XRD patterns of $Cd_{1-x}Pb_xS$ thin films at annealing temperatures (RT, 100, 200) °C at x=0.1.

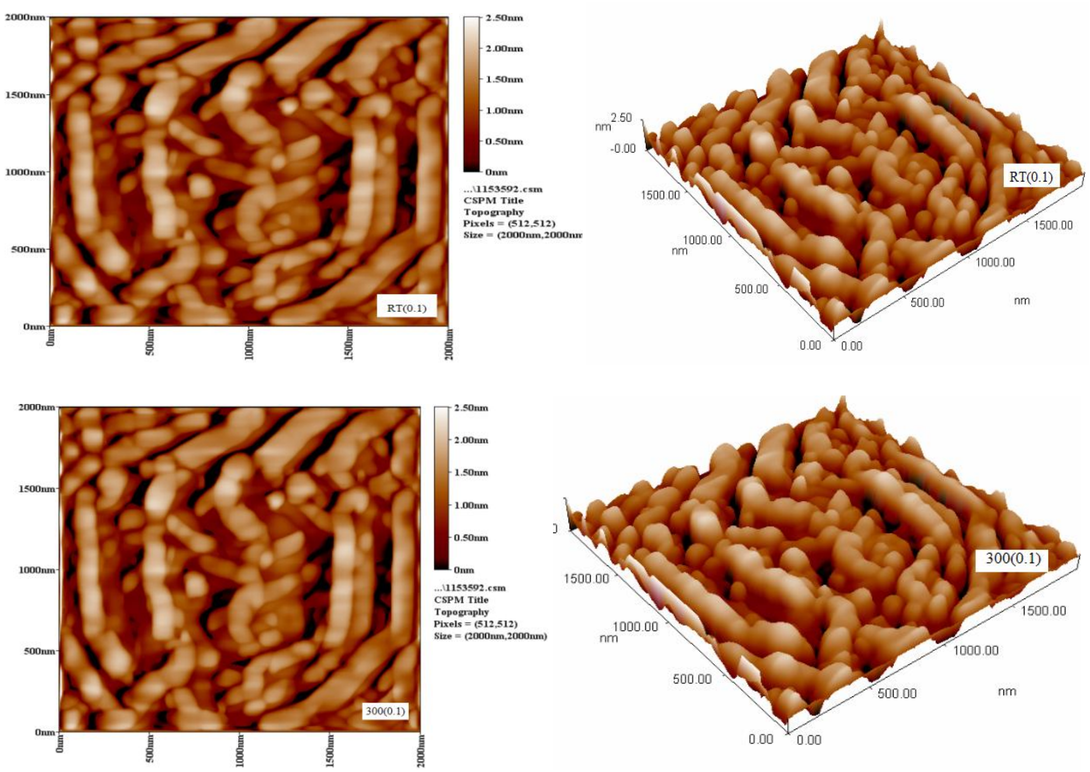

Fig. 2: The two and three-dimensional representation of the as deposited $Cd_{1-x}Pb_xS$ thin films and annealing films at (200) °C.

The optical properties of as-deposited $Cd_{1-x}Pb_xS$ thin films and annealing films at (100, 200, 300) °C by using UV-VIS spectrophotometer at room temperature were measured in the wavelength range 300-1100 nm as shown in Fig. (3). The optical studies revealed that the films are highly absorptive with a direct type of transition. The peaks of transmittance spectrum have been shifted to the shorter wavelength compared to the un annealed films. The shift in the peak position films may be attributed to the crystallite of film structure by increasing the grain size and this is in agreement with our result of XRD. Also we studied the spectrum of absorpttance and reflectance, it is obviously that its behavior is opposite to that of the transmittance spectrum and this is an agreement with other researcher.

Also the transmittance increases, whereas the absorbance and reflection decrease with increasing annealing temperatures from RT to 300C as in Table.4 and this is due to crystallization of film structure by increasing the grain size, and slightly, the absorption edge shift to smaller wavelength (higher photon energy) with increasing T_a from RT to 300C.

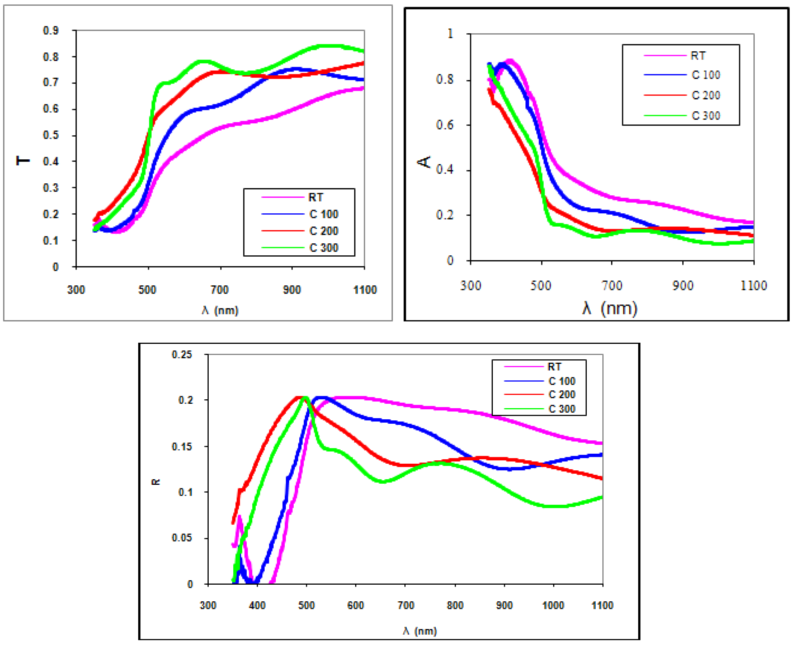

Fig. 3: The transmittance, absorptatance and ereflectance spectrum of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature at x content 0.1.

Table 4: The values of A,T and R at 0.7 µm.

T_a°C	A	T	R
RT	0.148	0.712	0.141
100	0.13	0.741	0.189
200	0.076	0.837	0.085
300	0.061	0.869	0.069

Fig.(4) shows the absorption coefficient (α) of $Cd_{1-x}Pb_xS$ thin films with different annealing temperatures (RT, 100, 200, 300)C. From these figures, α decreases with increasing annealing temperatures for all samples as shown in Table(5) and this is due to the increasing value of energy gap with annealing temperatures.

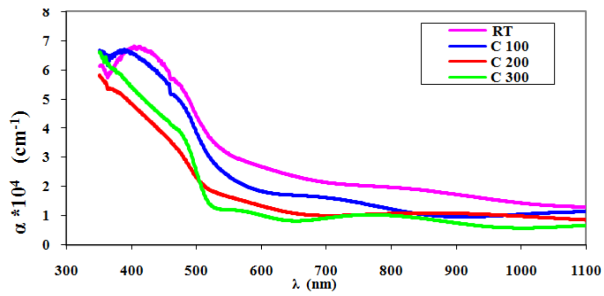

Fig. 4: The absorption coefficient of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

Table 5: The values of α , E_g and optical constant at 0.7 µm.

T_a°C	*α *10^4 (cm^{-1})*	*Eg(eV)*	*K*	*n*	*ε_R*	*ε_I*	$\sigma_{optical}$ (s^{-1}) *10^4
RT	1.137	2.34	0.063	1.986	3.939	0.252	5.395
100	1	2.4	0.056	1.889	3.566	0.211	4.515
200	0.591	2.54	0.032	1.56	3.434	0.103	2.202
300	0.467	2.61	0.026	1.451	2.106	0.076	1.622

The optical band gap (E_g) is determined using the classical relation[9]:

$$(\alpha h\upsilon) = A (h\upsilon - Eg)^{1/2} \quad (1)$$

Where ‘A’ is a constant and ‘hυ’ is the radiation energy. Fig. (5). shows the plot of $(\alpha h\upsilon)^2$ vs hυ for different annealing temperatures. The linear nature of the plots at the absorption edge confirmed that Cd_{1-}

$_x$Pb$_x$S is a semiconductor with a direct band gap. The optical band gap is varied from 2.34 eV to 2.61eV. The variation of band gap with the annealing temperatures of x=0.1 is shown in table 2. The band gap was observed to increase with an increase in annealing temperatures and this is due to the growth of grain size and the decrease in defect states near the bands and this is turn increased the value of E_g. The nature of this variation in the band gap energy may be useful to design a suitable window material in fabrication of solar cells and this corresponding with other reserchers.

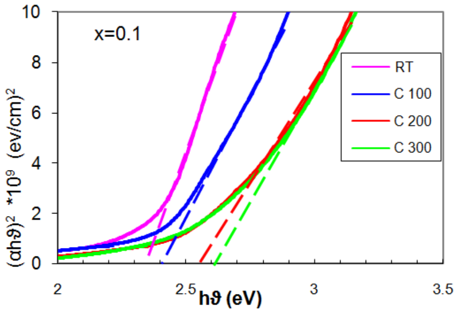

Fig. 5: $(\alpha h\nu)^2$ as a function of photon energy for $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

The optical behavior of materials is generally utilized to determine its optical constants for example the refractive index (n). Fig.6 and Table (5) show the variation of refractive index $Cd_{1-x}Pb_xS$ thin films with different annealing temperature (RT, 100, 200, 300)C of thickness (0.3)µm. It is interesting to see that n decreases with increasing annealing temperatures. This behavior is due to decrease in the reflection which the refractive index depend on it.

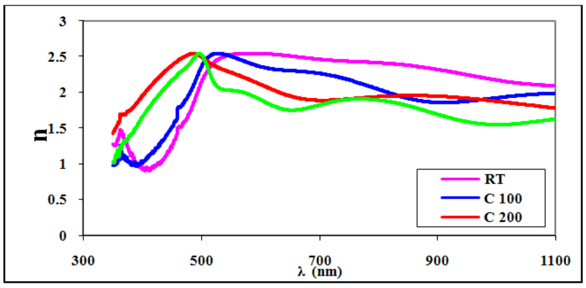

Fig. 6: The refractive index of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient as shown in Fig.(7) and Table(5) at different T_a, we can see from this Table that k decreases with increasing T_a from RT to 300C. This attributed to the same reason, which mention previously in absorption coefficient

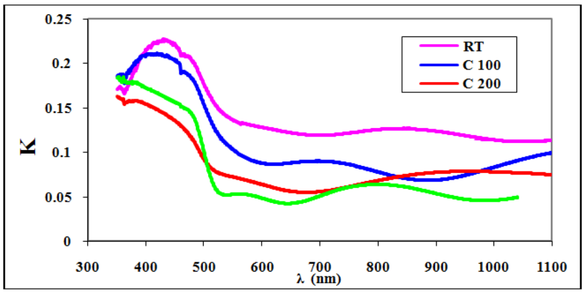

Fig. 7: The extinction coefficient of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

Fig.(8) and Table(5) shows the variation of real dielectric constant (ε_1) and imaginary dielectric constant (ε_2) with different annealing temperatures. The behavior of ε_1 is similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_2 is mainly depends on the k values, which are related to the variation of absorption coefficient. It is found that ε_1 increases with T_a, and ε_2 decrease with increasing T_a.

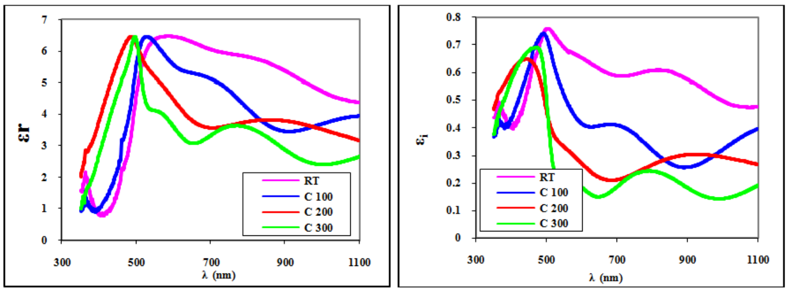

Fig. 8: The real dielectric constant (ε_1) and imaginary dielectric constant (ε_2) of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

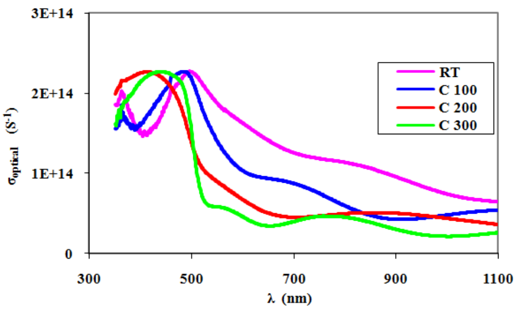

Fig. 9: The optical conductivity of $Cd_{1-x}Pb_xS$ thin films with different annealing temperature.

The optical conductivity can be shown in Fig. (9) and Table.(5), and it is decreases with increasing annealing temperatures.

Conclusions:

From above study it is concluded that thin, nano tube, uniform and adherent cadmium lead sulphide thin films with different annealing temperatures at x= 0.1 can be deposited successfully by vacuum evaporation technique. From XRD, the films are polycrystalline in nature with cubic and hexagonal structure. The grain size of thin $Cd_{1-x}Pb_xS$ films increases with increasing the annealing temperatures. From AFM measurements the average crystallite and roughness increases as the annealing temperature increase, The effect of annealing temperature on optical properties is studied. We found that the increasing in T_a shifts the peak of transmittance spectrum to the shorter wavelength compared to the un annealed films for all films. From measurement of optical energy gap, showed that the optical energy gap are direct transitions with (r) equal to (1/2). Also increasing annealing temperature lead to increase the energy gap, whereas in general the optical constants decreases.

REFERENCES

Alex, P.G., P.I. Gaiduk, A.N. Larsen, 2008. Chemical bath deposition of PbS nanocrystals: Effect of substrate. *Thin Solid Films, 516:* 3791-3795.

Barote, M.A., A.A. Yadav, E.U. Masumdar, 2011. Effect Of Deposition Parameters On Growth And Characterization Of Chemically Deposited $Cd_{1-X}Pb_XS$ THIN FILMS, 8(2): 129-138.

Barote, M.A., A.A. Yadav, L.P. Deshmukh, E.U. Masumdar, 2010. Synthesis And Characterization Of Chemically Deposited Cd1-xPbxS THIN FILMS, Journal of Non-Oxide Glasses, 2(3): 151-165.

Barote1, M.A., A.A. Yadav and E.U. Masumdar, 2013. Effect of Thickness on Structural, Optical and Electrical Properties of Chemically Grown $Cd_{0.825}pb_{0.175}S$ Thin Films, Journal of Chemical, Biological and Physical Sciences, 3(1): 510-521.

Harmann, T.C., 1971. Mass. Inst. Technol. Lincoln Lab. Rep., 3, 10.

Herna´ndez-Borja, J., Y.V. Vorobiev, R. Ramı´rez-Bon, 2011. Thin film solar cells of CdS/PbS chemicallydeposited by an ammonia-free process. *Solar Energy Materials & Solar Cells, B405:* 1882-1888.

Joshi, R.K., P. Kumar, H.K. Sehgal, A. Kanjilal, 2006. Journal of The Electrochemical Society, 153: C707-C712.

Modaffer, A.M., A.M. Mousa, J.P. Ponpon, 2009. Opticl and optoelectronic properties of PbCdS ternary thin films deposited by CBD. *J. Semiconductor Tech. and Science, 9*(2): 1-6.

Popescu, V., H.I. nascu , E. Darvasi, 2006. Optical properties of PbS-CdS multilayers and mixed(CdS+PbS) thin films deposited on glass substrate by spray paralysis", jurnal of optoelectronics and advanced material, 8(3): 1187-1193.

Seghaier, S., N. Kamoun, R. Brini, A.B. Amara, 2006. Structural and optical properties of PbS thin films deposited by chemical bath deposition. *Mat. Chem. & Phys., 97:* 71-80.

Singh, J., 1995. Semiconductor Optoelectronics: Physics and technology, McGraw-Hill international edition, electrical engineering series, McGraw-Hill, New York, 170.

Au, H.T., Y.S. Giang, S.J. Wan, W.H. Tseng, Shih, 2012. Nanotechnology, 23: 275601.

Suryavanshi, K.E., R.B. Dhake, A.M. Patil, 2014. Optical Properties Of PbxCd1-xS Thin Films Prepared By Chemical Bath Deposition Method, 4(2): 858-861.

Thangavel, S., S. Ganesan, S. Chandramohan, P. Sudhagar, Yong Soo, Kang, Chang-Hee, Hong, 2010. Band gap engineering in PbS nanostructured thin films from near-infrared down to visible range by in situ Cd-doping. *Journal of Alloys and Compounds,* 495: 234-237.

Ubale, A.U., A.R. Junghare, N.A. Wadibhasme, A.S. Daryapukar, R.B. Mankar, V.S. Sangawar, 2007. Thickness dependent structural, electrical and optical properties of chemically deposited nanopartical PbS thin films. *Turk. J. Phys., 31:* 279-286.