# SYNTHESIS AND SOME PROPERTIES OF MOCVD LEAD SULPHIDE AND LEAD CADMIUM SULPHIDE THIN FILMS

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The single solid source precursors, bis-(morpholinodithioato-s,s')-Pb and bis-(morpholinodithioato-s,s')-Pb-Cd were prepared by direct reaction of metal chloride solution and ammonium morpholinodithiocarbamate. Lead sulphide and lead cadmium sulphide thin films were deposited on sodalime glass substrates using Metal Organic Chemical Vapour Deposition (MOCVD) technique. Preparation of the films was achieved by the pyrolysis of the prepared precursors at 400 °C with a flow rate of 2.5 dm$^3$/min for 2 hours deposition period. The deposited films were characterized using Ultraviolet-Visible spectroscopy, X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX). A direct optical band gap of 0.46 eV was obtained from the analysis of the absorption spectrum for lead sulphide and 2.17 eV for lead cadmium sulphide thin films. XRD revealed that both films are polycrystalline in nature, with face-centred cubic phase in PbS film and the presence of cubic and hexagonal phases of CdS and cubic phase of PbS in the PbCdS film. SEM micrographs also revealed polycrystalline nature with uniformly distributed grain estimated to be less than 1 µm in size for both films. It also showed that both films have textured surfaces. The EDX showed that both deposited films are non-stoichiometric and are cation deficient.

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## 1. Introduction

PbS is a group IV-VI semiconducting material that has attracted considerable attention due to its small direct band gap of 0.41 eV [1], p-type conductivity with low resistivity [2], large excitation Bohr radius of about 18 nm [3] and polycrystalline cubic structure [4]. It is one of the earliest semiconducting materials and has been employed in various technological applications such as solar absorber [5], photography [6], sensors [7], optical switch [8], infra-red detectors [9, 10] among others.

CdS belongs to group II-VI semiconductor with energy gap covering the visible spectra range and has been considered to be a good alternative that can be used in silicon devices [11]. It is one of the most useful semiconducting materials with wide range of applications in semiconducting devices such as Field Effect Transistor, photovoltaic technology [12], piezo-electronic and optoelectronic devices [6]. It is highly sensitive to light and has high absorption coefficient which makes it useful in visible light emitting diode and laser [13, 14].

Pb-Cd-S has attracted a great deal of attention because of its applications in optoelectronics, solar control coatings, gas and humidity sensor and photoelectrochemical solar cells [15, 6]. It also has large spectrum of applications in selective coatings for efficient photo-thermal conversion to obtain absorbance in the UV-VIS region and reflectance in IR region [16, 4].

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Studies have shown that Pb-Cd-S is polycrystalline in nature with the presence of cubic phase for CdS and PbS, and hexagonal phase for CdS alone [17, 18] with the crystal size depending on the ratio of lead to cadmium. [19] in their work, revealed that the deposited Pb-Cd-S films were cadmium rich with high coefficient of absorption ($10^4$ $cm^{-1}$) and a direct allowed type of transition with energy band gap decreasing continuously from 2.47 eV to 0.49 eV as the composition of lead to cadmium increases.

PbS thin films have been prepared by various techniques. Such techniques include Successive Ionic Layer Adsorption and Reaction (SILAR) [20], Electrochemical Atomic Layer Epitaxy [21], Atomic Layer Deposition (ALD) [22], Chemical Bath Deposition (CBD) [23] and so on. On the other hand, Pb-Cd-S has been prepared by various methods such as spray pyrolysis [24], chemical bath deposition [25, 4], physical and electrochemical method [26, 27], chemical vapour deposition [28], vacuum deposition [29] and so on.

The properties of thin film materials depend on the method of preparation among other parameters such as the substrate, impurity level and post-deposition processing. Thin films of miscible systems have been prepared using different techniques and these techniques have their different deficiencies. The use of MOCVD technique has received much attraction due to its great potential application to fabricate high quality films. It is a preparative method well-suited to large scale continuous production which is simple and cost effective when compared with other deposition methods.

In this work, we report the preparation of single solid source precursors bis-(mor-pholinodithioato-s,s')-Pb and bis-(mor-pholinodithioato-s,s')-Pb-Cd and the deposition of PbS and PbCdS thin films from these precursors through MOCVD method on sodalime glass substrate at deposition temperature of 400°C. Surface morphology, optical and structural characterization of the films is also reported.

## 2. Experimental

### 2.1. Preparation of Precursor

The single solid source precursor, bis-(morpholinodithioato-s,s')-Pb and bis-(morpholinodithioato-s,s')-Pb-Cd were prepared using the procedure which has been reported elsewhere [30]. The intermediate complex, ammonium morpholino-dithiocarbamate was prepared according to the method reported by [30].

For bis-(morpholinodithioato-s,s')-Pb, ammonium morpholinodithiocarbate (6.78 g, 0.0376 mol) was dissolved in 80:20 of an acetone-water solvent. Lead acetate (6.12 g, 0.0188 mol) was completely dissolved in 50 $cm^3$ of methanol. The solution of lead acetate in methanol was gradually added to the solution of ammonium morpholinodithiocarbate in acetone-water and vigorously stirred. The product obtained as a precipitate was filtered off and later dried in a dessicator.

The same procedure was followed for bis-(morpholinodithioato-s,s')-Pb-Cd, ammonium morpholinodithiocarbate (5.60 g, 0.031 mol) was dissolved in 80:20 of an acetone-water solvent. Lead acetate (5.04 g, 0.0155 mol) was completely dissolve in 50 $cm^3$ of methanol and Cadmium acetate (3.57 g, 0.0155 mol) was also dissolved completely in 50 $cm^3$ of methanol separately. The solution of Lead acetate was gradually added to the solution of ammonium morpholino-dithiocarbamate in a flask on a hot plate and vigorously stirred while adding. Then, the solution of Cadmium acetate was gradually added to the complex formed earlier while still stirring vigorously. The product obtained as a precipitate was filtered off and later dried in a dessicator.

### 2.2. Thin Film Deposition

The thin films of lead sulphide and lead cadmium sulphide were prepared by pyrolysing their respective precursors on sodalime glass substrate using a previously reported MOCVD technique [30]. The set up for the deposition is shown in Fig. 1. Prior to the deposition of the lead sulphide thin films, the dried precursors were grounded to fine powder which can be easily transported from the unheated receptacle to the reaction chamber where the film deposition takes place.

The fine powder of the precursor was poured into an unheated receptacle and nitrogen gas dried over calcium chloride was blown through the fine powder precursor at 2.5 $dm^3$/min flow. The nitrogen borne precursor was transported into the hot working chamber maintained at 400 °C by an electrically heated furnace. The process was carried out inside a fume hood in order to minimize the handling problems associated with lead and sulphur.

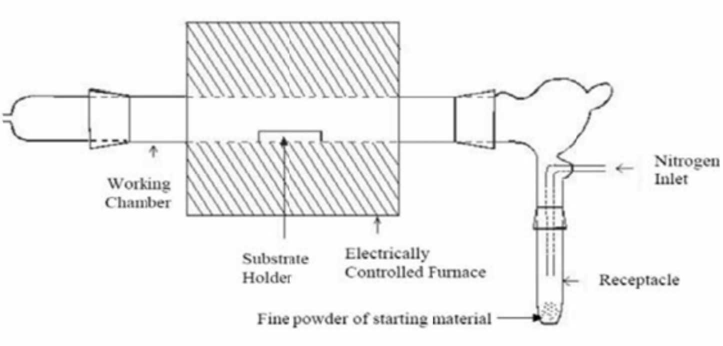


*Fig. 1 Apparatus for Pyrolysis of the Precursor*

### 2.3. Surface Morphology and Chemical Characterization

The surface morphology and elemental analysis were carried out using a Carl Zeiss Scanning Electron Microscope (Model: EVO / MA10) with Energy Dispersive X-ray (EDX) facility attached to it. The samples were cut into dimension 1 cm x 1 cm. The micrographs of both PbS and PbCdS films were taken at an accelerating voltage of 20.07 kV.

### 2.4. Structural Characterization

X-Ray Diffraction (XRD) analysis of the thin films was carried out using Radicon X-Ray Mini-diffractometer (Model: MD-10). The diffractometer used a high voltage source of 25 KV with radiation of $CuK_{\alpha_{avg}}$ line of wavelength 1.5406 nm. The diffraction angle of detection, 2θ ranges from 16° to 72°. The scanning of the films was done for 20 minutes. Phase identification of the films was performed by using a computer based system with the standard powder diffraction file embedded in the machine (i.e. by comparing diffraction data with a database maintained by the International Centre for Diffraction Data (ICDD)).

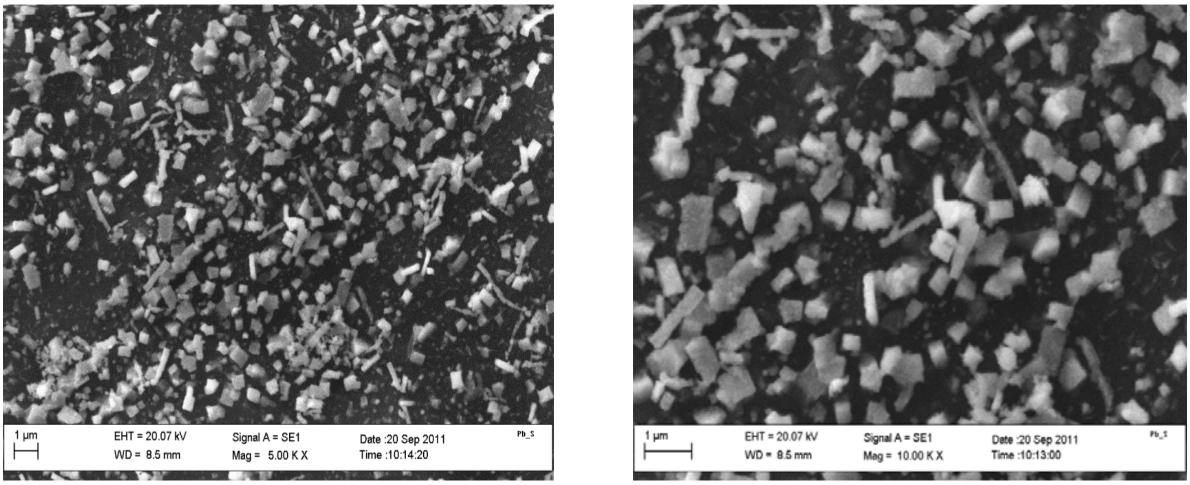
### 2.5. Optical Characterization

The absorbance spectra of the thin films were obtained using a double beam PYE UNICAM SP8-400 UV 1 – Visible spectrophotometer V1.30 at normal incidence. All measurements were made at room temperature with blank sodalime glass substrate in the reference beam path. Standardization (optical balancing) was done by first replacing the coated substrate with a plain substrate in the sample position; thus we had plain against plain substrate.

## 3. Results and discussion

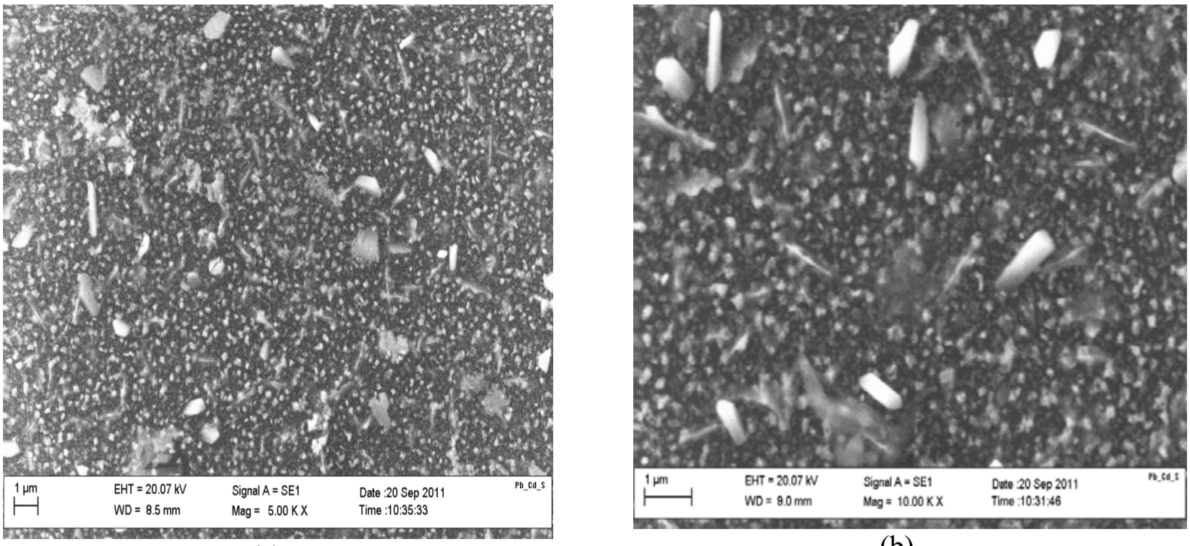
### 3.1 Surface Morphology and Chemical Characterization

The SEM micrographs of lead sulphide films are shown in Fig. 2 (a) and (b) at different magnifications. The micrograph revealed that the lead sulphide films appear to have highly smooth and homogenous surface morphology with densely packed cubic grains, well distributed over the entire substrate suggesting that the film is crystalline and adhered well to the substrate without any crack. At higher magnification (10,000X), it is apparent that the films are crystalline with identifiable cubic structure, pin-hole free and continuous with very scanty rod. This is in accordance with the work of [31] but without the formation of the cubic structure. IMAGEJ software was used to analyze the micrograph in order to obtain the dimensions of the grains. The grain size was estimated to be 0.338 µm. The SEM micrographs of Pb-Cd-S films at magnifications 5,000X and 10,000X are shown in Fig. 3 (a) and (b). The micrographs also revealed that the deposited Pb-C-dS film is crystalline in nature with uniformly distributed grains which covers the substrate very well. It can also be seen that small crystals fused together to form bigger crystals and grown into rods during the deposition temperature. The rods in this case are more than that in lead sulphide micrograph.



(a) (b)

*Fig. 2 Scanning Electron Micrograph of lead sulphide Thin Film*
*(a) Magnification at 5000 X; (b) Magnification at 10000 X*



(a) (b)

*Fig. 3 Scanning Electron Micrograph of Pb-Cd-S Thin Film*
*(a) Magnification at 5000 X; (b) Magnification at 10000 X.*

The micrographs were also analyzed using IMAGEJ software to obtain the dimension of the rods. The average length of the rods was estimated to be 0.948 µm.

Fig. 4 shows the elemental analysis of the lead sulphide thin film done by Energy Dispersive X-ray spectroscopy (EDX). The spectrum confirmed the presence of the expected Pb and S atoms. Other signals in the spectrum are due to the elements in the sodalime glass substrate. The elements present in glass substrate are O, Na, Mg, Al, Si, K and Ca as shown in the EDX spectrum of the sodalime glass substrate (Fig. 5). The ratio of the elements in the prepared films obtained from the EDX was found to be Pb:S = 48.63:51.37. The result shows that the deposited film is non-stoichiometric in composition as also reported by [17]. It is richer in sulphur than lead (i.e. it is cation deficient). The deviation in the composition may be due to the higher reactivity of $S^{2-}$.

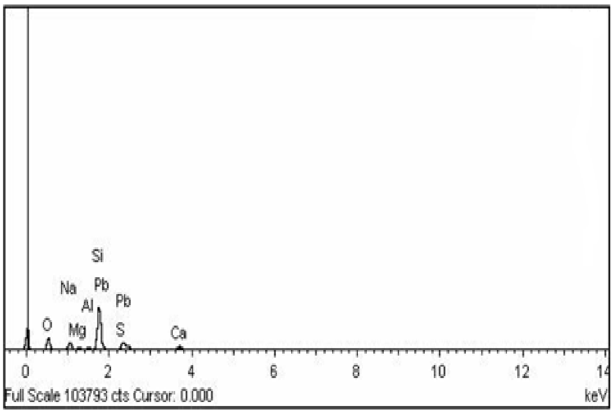


*Fig. 4 EDX Spectrum lead sulphide Film.*

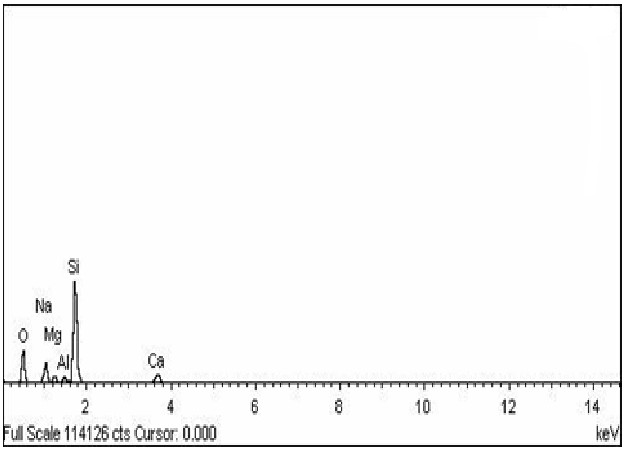


*Fig. 5 EDX Spectrum Blank glass substrate*

The EDX analysis of the deposited Pb-Cd-S thin film is shown in Fig. 6. The spectrum revealed the presence of Pb, Cd, S and other elements that are present in the glass substrate. The proportion of elements in the thin film Pb:Cd:S was found to be 30.22:17.26:52.52. The result also shows that the deposited film is non-stoichiometric in composition which is in agreement with the report of [19]. The mixture is also cation deficient, that is, the cations ($Pb^{2+}$ and $Cd^{2+}$) are together less than that anion ($S^{2-}$). The ratio gave a stoichiometry of $Pb_{(1-x)}Cd_xS_{(1+\delta)}$, where x = 0.36 and $\delta$ = 0.10. The analysis showed no traces of impurities like carbon and oxygen in the film.

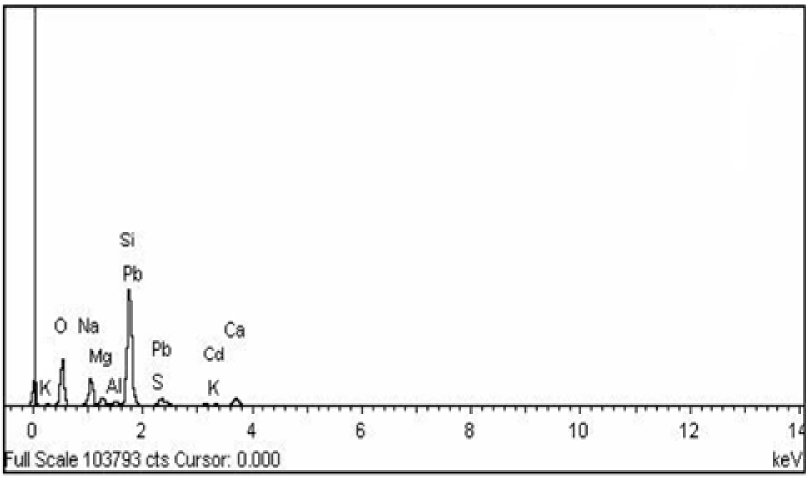


*Fig. 6 EDX Spectrum Pb-Cd-S Thin Film*

### 3.2. Structural Characterization

The structure and crystallographic orientation of deposited lead sulphide film was determined from XRD spectrum in the range of diffraction angle, 2θ from $16^{o}$ to $72^{o}$ as shown in Fig. 7. The spectrum shows diffraction peaks at 2θ values of $25.14^{o}$, $28.01^{o}$, $41^{o}$, $48.74^{o}$ and $62.83^{o}$ which correspond to the diffraction lines produced by (111), (200), (220), (311) and (400) planes of the face-centred cubic structure of PbS (Card Number 5-0592). This confirms the polycrystalline nature of the film and is in accordance with what has been reported in literature [1, 23, 2]. Diffraction along the (200) plane shows the highest intensity with well-defined sharp peak indicating the preferred orientation of the deposited lead sulphide thin film.

The average crystal size of the film was estimated to be 0.3395 μm using Debye Scherer's formula in Eq. (1).

$$D = \frac{k\lambda}{\beta_{2\theta}\ \cos\theta} \tag{1}$$

where $D$ is the crystal size, $k$ is a constant (0.94) and $\beta_{2\theta}$ is the Full Width at Half Maximum (FWHM) in radian. This result is in good agreement with the value of 0.338 μm obtained from SEM.

The XRD spectrum of the deposited Pb-Cd-S is shown in Fig. 8. The spectrum revealed that the deposited Pb-Cd-S film is polycrystalline in nature. The spectrum shows diffraction peaks at 2θ values of $28.20^{0}$, $31.35^{0}$, $47.20^{0}$, $56.25^{0}$, $58.65^{0}$ and $68.97^{0}$. These correspond to diffraction lines produced by (111), (200), (220), (311), (222) and (400) planes from cubic CdS diffraction data file (Card Number 21-0829). Hexagonal CdS structure also deduced from the intense diffraction peaks and the corresponding planes are $24.79^{0}$ (100), $26.57^{0}$ (002), $28.20^{0}$ (101), $34.07^{0}$ (102), $47.80^{0}$ (103), $54.48^{0}$ (004), $58.07^{0}$ (202), $60.88^{0}$ (104), $66.92^{0}$ (203), $69.42^{0}$ (210) and $70.73^{0}$ (211) of Card Number 41-1049. It also exhibit cubic PbS with diffraction peaks at 2θ values of $25.85^{0}$, $29.80^{0}$, $41.00^{0}$, $50.48^{0}$, $53.36^{0}$ and $70.74^{0}$ corresponding to (111), (200), (220), (311), (222) and (420) planes with diffraction data file of card number 78-1901.

From this XRD result obtained, it can be inferred that the deposited Pb-Cd-S film is a mixture of PbS and CdS with the two showing their individual planes which is in agreement with the report of [18, 19, 17].

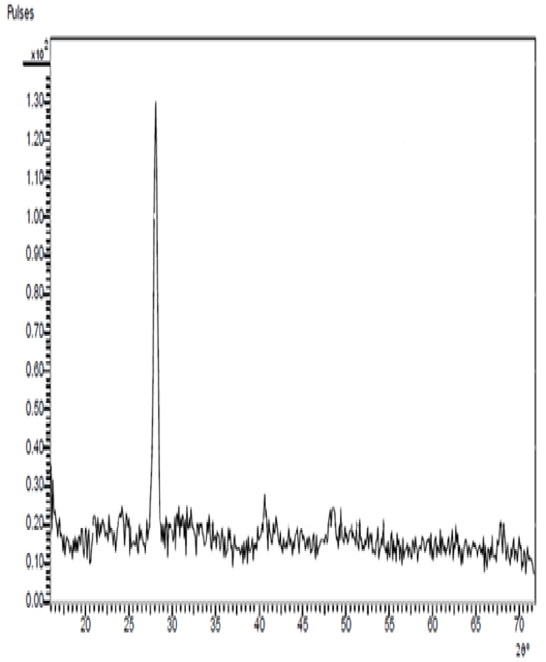


Fig. 7 XRD Spectrum of Deposited Lead Sulphide Film

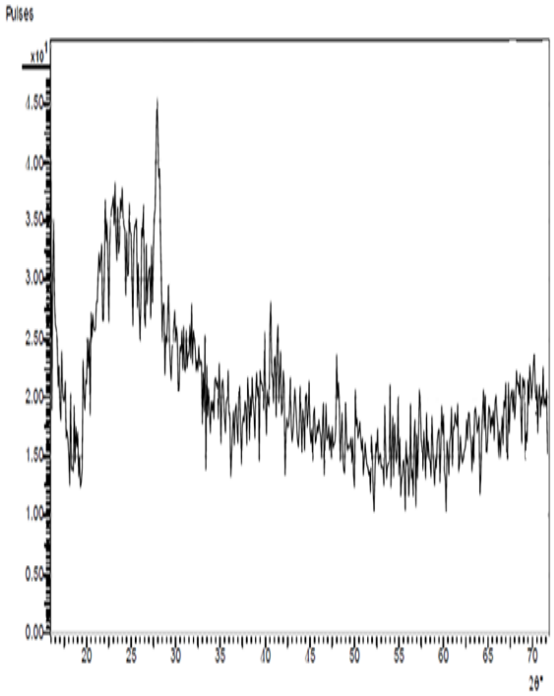


Fig. 8 XRD spectrum of Deposited Pb-Cd-S Film

### 3.3. Optical Characterization

The UV-visible spectrum of the deposited lead sulphide thin film is shown in Fig. 9. The spectrum is a plot of absorbance against wavelength obtained at room temperature. The spectrum shows that the deposited lead sulphide thin film starts absorbing at wavelength of 290 nm which then increases until it reaches a maximum at 310 nm before it starts to decrease. The absorption edge lies in the near Infrared region.

The absorption coefficient $\alpha$ was calculated using the expression in Eq. (2)

$$\alpha = \frac{1}{t_p}\ln(\frac{1}{T}) \tag{2}$$

where $t_p$ is the thickness of the film, $T = 10^{-A}$ is the transmittance and $A$ is the absorbance. The absorption coefficient, $\alpha$ also varies with photon energy, $E$ for different allowed transition as in Eq. (3)

$$\alpha = \mathrm{B}(hv - E_g)^n \tag{3}$$

where $B$ = proportionality constant, $h$ = Planck's constant, $v$ = frequency, $E_g$ = energy gap and the exponent, $n$ = ½ for direct allowed transition. A plot of $\alpha^2$ against energy (in eV) is shown in Fig. 10. The intercept on the energy axis when the linear region is extrapolated gave the optical band gap energy of 0.46 eV. This agrees fairly well with the value of the band gap of 0.41 eV as reported by [1]. From the energy band gap, high absorption is expected to occur when the incident photon energy is sufficient to excite the valence electrons into the conduction band. Photon with less energy will not be absorbed, such materials are generally transparent ($\alpha$ = 0) and are referred to as a Tauc plot [32].

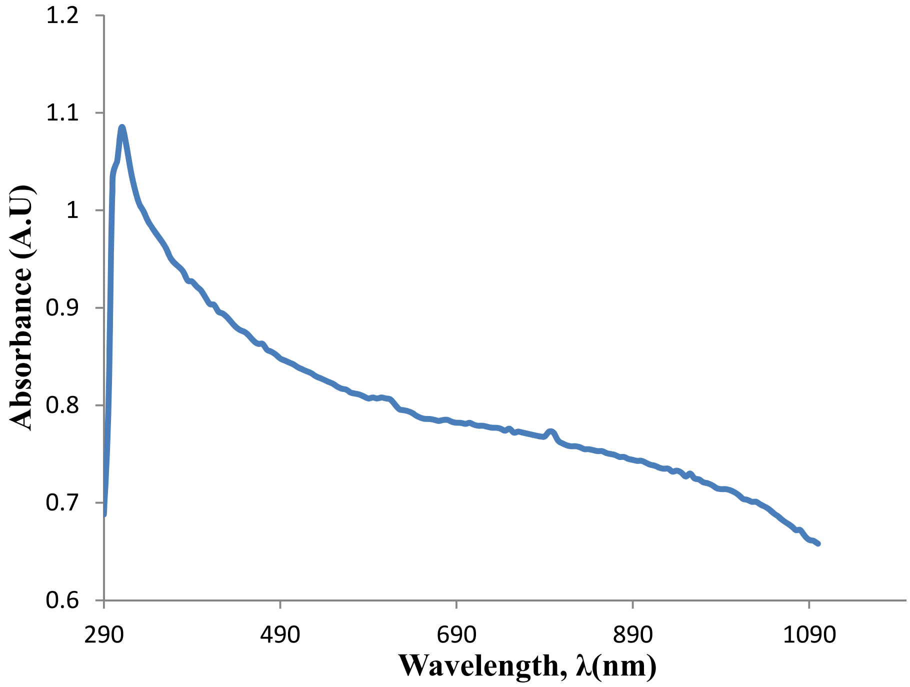


*Fig. 9 Absorbance against Wavelength of lead sulphide Thin Film*

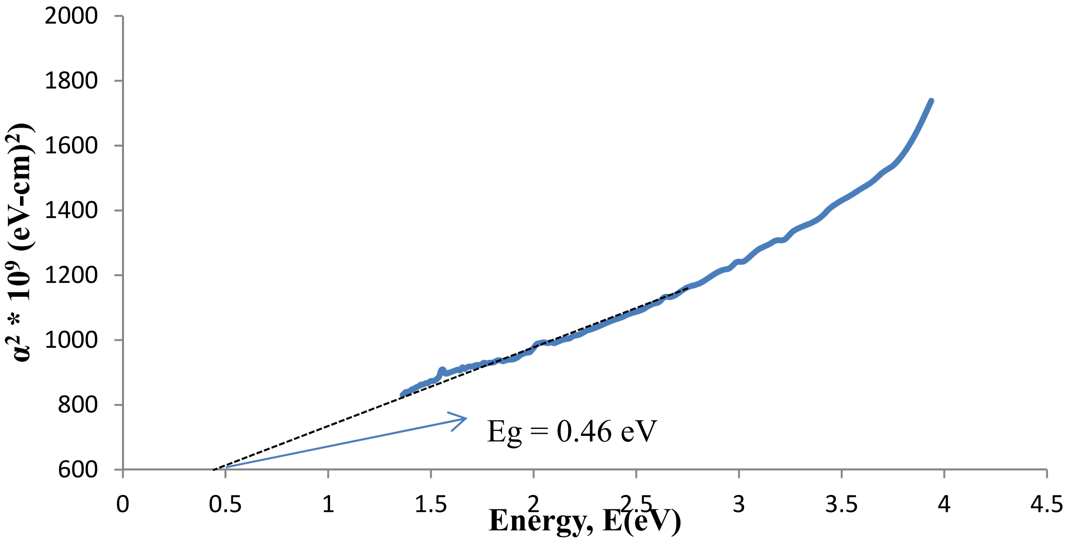


*Fig. 10 $\alpha^2$ against Energy of lead sulphide Thin Film*

Fig. 11 shows the plot of absorbance against wavelength obtained at room temperature for Pb-Cd-S thin films. The spectrum shows that the deposited Pb-Cd-S thin film also starts absorbing at wavelength of 290 nm which then increases until it reaches a maximum at 310 nm before it starts to decrease. The absorption edge lies in the visible region. A plot of the square of the absorption coefficient, $\alpha^2$ against energy for Pb-Cd-S thin film is shown in Fig. 12. An extrapolation of the linear portion to the energy axis gave a direct optical band gap of 2.17 eV for the Pb-Cd-S thin films. The band gap of 2.17 eV obtained for the lead cadmium sulphide falls between that of lead sulphide thin film (0.46 eV) and the band gap of cadmium sulphide thin film

(2.40 eV) as reported earlier by [30]. This is in agreement with the work of [19] in which the energy band gap increases with increasing Cd content.

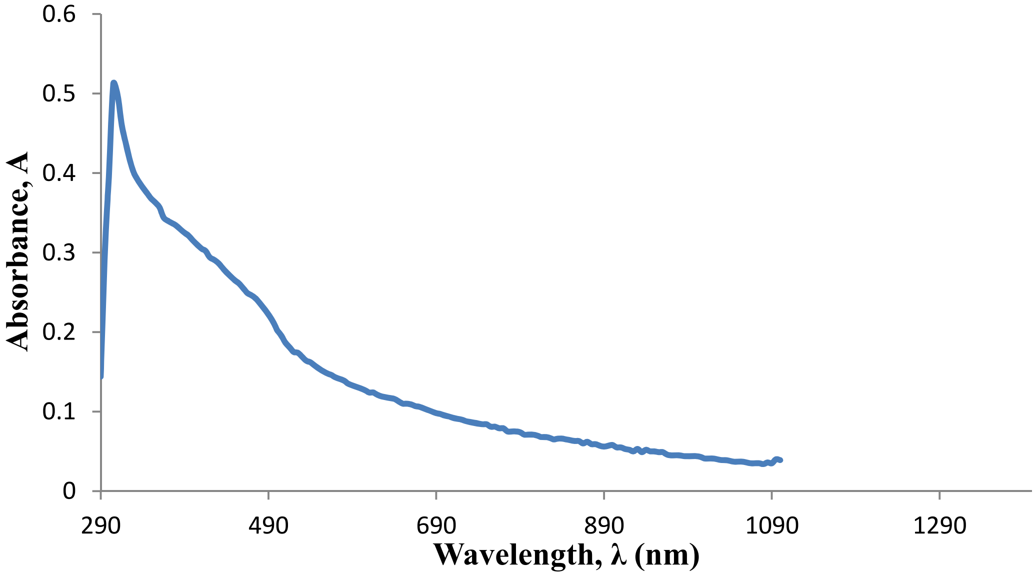


*Fig. 11 Absorbance against Wavelength of Pb-Cd-S Thin Film*

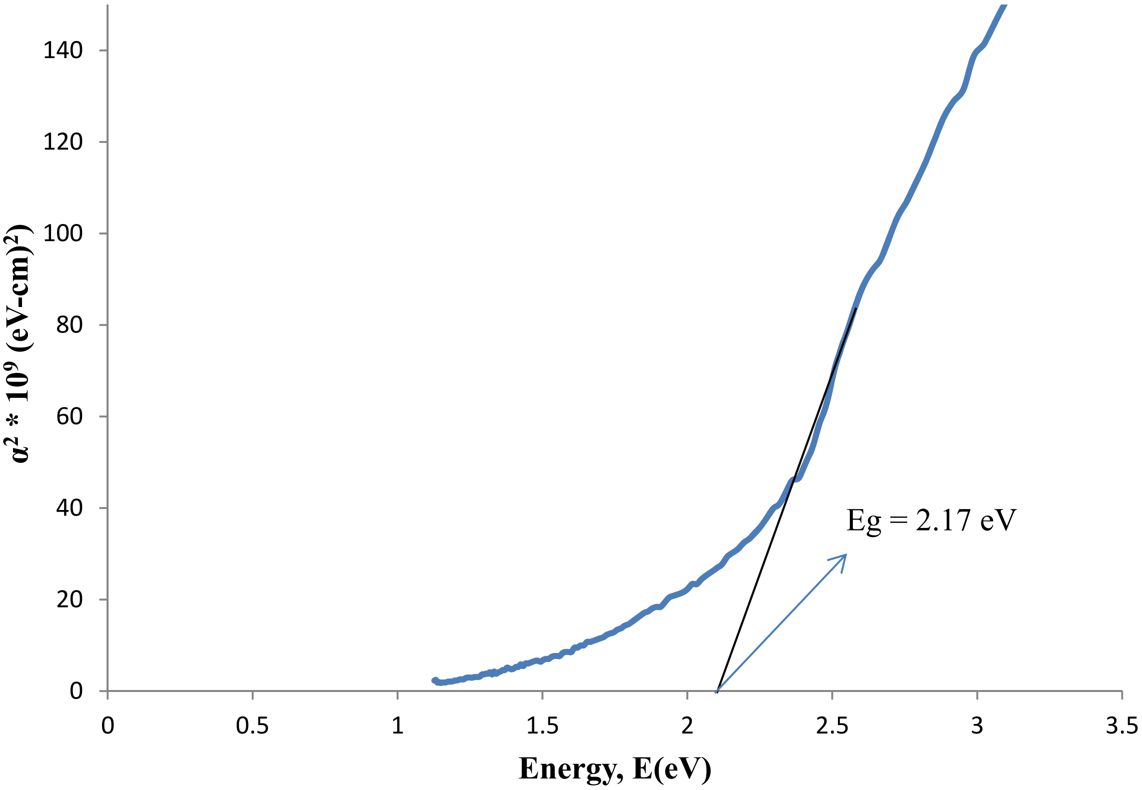


*Fig. 12 $\alpha^2$ against Energy of PbCdS Thin Film*

## 4. Conclusion

Lead sulphide and Pb-Cd-S thin films were successfully prepared through the pyrolysis of single solid source precursors, (morpholinodithioato-s,s')-Pb and (morpholinodithioato-s,s')-Pb-Cd respectively prepared from commercial reagents.

The micrographs revealed that both lead sulphide and Pb-Cd-S thin films are polycrystalline and uniformly distributed at different geometry in different sizes with some rods. The average grain size of the lead sulphide film was estimated to be 0.338 μm whereas that of Pb-Cd-S was 0.948 μm. The elemental compositions of the films as determined by EDX revealed that both lead sulphide and Pb-Cd-S films are non-stoichiometric in composition giving stoichiometry of PbS and $Pb_{(1-x)}Cd_xS_{(1+\delta)}$, where $x = 0.36$ and $\delta = 0.10$.

The structural studies show the polycrystalline nature of both films. Lead sulphide exhibits face-centred cubic structure with preferential orientation along (111) plane. Pb-Cd-S film also exhibits the mixed cubic and hexagonal structures of CdS and only cubic structure of PbS.

UV-Visible analysis revealed that the film of lead sulphide has its absorption edges at near infrared and Pb-Cd-S at UV-Vis region. The optical absorption measurement indicates a material that is absorbing at near infrared with direct optical energy band gap of 0.46 eV for lead sulphide and a direct optical band gap of 2.17 eV for Pb-Cd-S thin film.

## References

[1] S. Seghaier, N. Kamoun, R. Brini, A. B. Amara, Mater. Chem. and Phys., **97**, 71–80 (2006).

[2] S. Mahmoud and O. Hamid, FIZIKA A (Zagreb), **10**, 21-30 (2001).

[3] J. L. Machol, F. W. Wise, R. C. Patel and D. B. Tanner, Phys. Rev. B, **48**, 2819-2822 (1993).

[4] N. Choudhury and B. K. Sarma, Bull. Mater. Sci., **32**, 43–47 (2009).

[5] T. K. Chaudhuri and S. Chatterjee, Design of thin film solar thermoelectric generator. Proc. Int. Conf. Thermo electronic, (Arlington, USA) **11**, 40 (1992).

[6] P. K. Nair, O. Gomezdaza and M. T. S. Nair, Adv. Mater. Opt. Electr., **1**, 139 (1992).

[7] H. Hirata and K. Higashiyama, Chem. Soc. Jpn., **44**, 2420 (1971).

[8] R. S. Kane, R. E. Cohen and R. Silbey, J. Phys. Chem., **100**, 7928 (1996).

[9] H. Kanazawa and S. Adachi, J. Appl. Phys., **83**, 5997-6001 (1998).

[10] R. K. Joshi, A. Kanjilal and H. K. Sehgal, Appl. Surf. Sci., **221**, 43 (2004).

[11] P. Raji, C. Sanjeeviiraja and K. Ramachandran, Bull. Mater. Sci., **28**, 233-238 (2005).

[12] A. V. Feitosa, M. A. Miranda, J. M. Sasaki and M. A. Araujo-Silva, Braz. J. Phys., **34**, 2B, 656-658 (2004).

[13] A. Pan, H. Yang, R. Yu and B. Zou, Nanotechnology, **17**, 1083 (2006).

[14] Y. Gu, E. S. Kwak, J. L. Lensch, J. E. Aller, T. W. Odom and L. J. Lauhon, Appl. Phys. Lett., **87**, 43111-3 (2005).

[15] G. B. Reddy, D. K. Pandya and K. L. Chopra, Sol. Energ. Mater., **15**, 383-390 (1987).

[16] S. Maheshwar, K. S. Ramaiah, K. Mukul, M. Neumman-Spallart, C. Levy-Clement, J. Electroanal. Chem., **436**, 49-52 (1997).

[17] M. A. Barote, A. A. Yadav, T. V. Chavan and E. U. Masumdar, Digest J. Nanomaterials and Biostructures, **6**, 979-990 (2011).

[18] M. A. Mohammed, A. M. Mousa and J. P. Ponpon, J. Semicond. Tech. Sci., **9**, 117-123 (2009).

[19] M. A. Barote, A. A. Yadav and E. U. Masumdar, Physica B, **406**, 1865- 1871 (2010).

[20] J. Puiso, S. Lindroos, S. Tamulevicius, M. Leskela and V. Snitka, Thin Solid Films, **428**, 223-226 (2003).

[21] T. Torimoto, S. Takabayashi, H. Mori and S. Kuwabata, J. Electroanal. Chem., **522**, 33-39 (2002).

[22] E. Nykanen, J. Laine-Ylijoki, P. Soininen, L. Niinisto, M. Leskela and G. Hubert-Pfalzgraf, J. Mater. Chem., **4**, 1409-1412 (1994).

[23] K. M. Gadave, S. A. Jodgudri and C. D. Lokhande, Thin Solid Films, **245**, 7-9 (1994).

[24] J. J. Valenzuela, R. Ramirez, A. Mendoza and M. Sotelo-Lerma, Thin Solid Films, **441**, 104-110 (2003).
[25] I. Pop, C. Nascu, V. Lonescu, E. Indvea and I. Bratu, Thin Solid Films, **307**, 240 (1997).
[26] P. Tyagi and A. G. Wedeshwar, Bulletin of Materials Science, **24**, 297-300 (2001).
[27] R. B. Kale and C. D. Lokhande, Appl. Surf. Sci., **252**, 929-938 (2005).
[28] N. I. Fainer, M. Kosinova, M. Rumyantsev Yu., E. G. Salman and F. A. Kuznetsov, Thin Solid Films, 280, 16-19 (1996).
[29] A. G. Rolo, U. Gonde and M. J. M. Gomes, Thin Solid Films, **318**, 108-112 (1998).
[30] O. B. Ajayi, O. K. Osutola, I. A. Ojo and C. Jeynes, Thin Solid Films, **248**, 57-63 (1994).
[31] T. Sugimoto, S. H. Chen and A. Muramatsu, Colloid Surf. A., 135, 247 (1998)
[32] M. E. Rami, M. F. Benamar, F. Chraibi and A. Ennaoui, Solid State Sci., **1**, 179-188 (1999).