STUDY OF OPTICAL PROPERTIES OF CdS/PbS AND PbS/CdS HETEROJUNCTION THIN FILMS DEPOSITED USING SOLUTION GROWTH TECHNIQUE

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Using solution growth technique, ternary stack thin films of CdS/PbS and PbS/CdS were deposited on plane glass substrates at room temperature. Both heterojunction films as well as their binary components: PbS and CdS, that make up the stacks were subjected to 300-900 nm range spectrophotometric analysis which provided the absorbance and transmittance data from which the absorption coefficient, α and other optical constants of the films were estimated. Structural characterization was also done on these films using X-ray diffraction which clearly showed nearly similar diffraction patterns and peaks for both heterojunction deposits. Direct bandgaps of 1.83eV, 2.55eV, 1.37eV and 2.35eV were obtained for PbS/CdS, CdS/PbS, PbS, and CdS deposits respectively while indirect band gap values of 1.72eV and 1.45eV were revealed for CdS/PbS and PbS/CdS stacks respectively. It is seen that whereas both heterojunction thin films differed in their band gaps, either value was closer to the band gap of the deposit binary film away from the substrate. Fairly steady refractive index of 2.5 for 170nm thick PdS/CdS of 28.7nm crystal grain size and 2.6 for 154nm thick CdS/PbS of 30.1nm grain size were revealed.

1. Introduction

The science of controlled condensation of the individual atomic, molecular or ionic species by either physical process or chemical (or electrochemical) reaction to form thin films of ordered compounds is well documented [1-3]. The techniques usually employed in growing such films include: Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), Electrochemical Deposition (ECD) and Chemical Bath Deposition (CBD) [4]. The CBD technique, also called Solution Growth Technigue has gained prominence in recent time for its simplicity, low cost and applicability for large area and irregular surface film deposition coverage This technique has been previously used successfully to deposit binary metal chalcogenides like CdSe, CuS, Sb_2S_3 [5], BaS [3] and CdS [6] and ternary heterojunction nano films like CdS/CuS [5-7].

Cadmium Sulphide (CdS) is a very promising II-VI thin film material because of its wide range of applications in various optoelectronic, piezo-electronic and semi-conducting devices [8]. Its wide band-gap makes it very useful as window material in CdTe devices for the fabrication of solar cells [9]. CdS, however, has poor conductivity, usually as low as 10^{-8}. Efforts have progressively been made to alter its conductivity and tune its band gap for improved solar energy sensitivity and other device applications.

We, in this work, therefore contribute by successfully fabricating CdS-PbS heterojunction thin films on plane glass substrates using CBD techniques. We deposited CdS/PbS and PbS/CdS stacks and studied the structural and optical properties of both.

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2. Experimental Details

Chemical bath deposition technique was used to fabricate stacks of CdS and PbS on plane glass substrates. The substrates were plane glass slides of 75 x 25 x 1mm^3 dimension which were previously degreased in concentrated hydrochloric acid, washed in detergent solutions, rinsed with distilled water and left to dry in dust-free environment. Two chemical baths were used − bath A was used to deposit CdS while bath B was used to deposit PbS thin films. Bath A was prepared by mixing 4ml of 0.8M CdCl$_2$, 5ml of NH$_3$ (aq) solution, 5ml of IM thiourea (NH$_2$)$_2$CS, and 30ml distilled water in a 50ml beaker, these contents being vigorously stirred for 20 seconds. The substrates were vertically inserted in the solution and suspended from a synthetic foam which rests on top of the beaker. The bath was left for three hours at room temperature, after which the glass slides covered with yellowish CdS deposits were removed, rinsed in distilled water and left to drip-dry in dust-free air.

Bath B was prepared by mixing into it 10ml of 0.1M Pb(NO$_3$)$_2$, 5ml of 1M NaOH, 6ml of 0.6M thiourea, the mixture being vigorously stirred. Distilled water was added to make the mixture up to 40ml that was still vigorously stirred into a homogenous solution. The prepared microscope slides were similarly loaded into bath **B** and left at room temperature for 20 minutes after which the glass, now covered by dark PbS deposits, were removed and similarly rinsed and dried.

Both films were deposited basically by the hydrolysis of thiourea in an alkaline solution containing Cadmium (Bath A) and lead salts solution (Bath B). Ammonia (NH$_3$) acted as a complexing agent in bath A while NaOH did same in bath **B**.

The deposition of PbS thin film on top of CdS to form the PbS/CdS stack is achieved by dipping substrate(glass) with CdS deposit on fresh bath of B while CdS/PbS is similarly achieved by dipping substrate with PbS on fresh bath A. Formation of heterojunction continued up to two hours after the end of second deposition [4].

The energy band gaps, Eg. of the heterojunction thin films as well as their refractive indices were determined from their absorbance and transmittance data as carried out on them using UNICO UV−2012 PC spectrometer on the 300-900 nm range of light at normal incidence to samples. Structural characterizations were also done on the deposited films using the X'PERT−PRO diffractometer which used CuKα radiator of λ = 0.15406nm to scan continuously as 2θ varies from 0 - 100° at a step size of 0.02^o and at a scan step time of 0.2s.

Proton Induced X-ray Emission (PIXE) scans were done on the samples from a Tandem Accelerator Model 55DH 1.7MV Pellatron by National Electrostatic Corporation (NEC), USA which effectively performed Rutherford Back Scattering (RBS) elemental characterizations on both deposits and substrates. These also deciphered the thicknesses of deposits as well as substrates.

3. Result and Discussion

3.1. X-ray Diffraction (XRD) Analysis

The results of the XRD scans done on PbS/CdS and CdS/PbS stack samples are as shown in figures 1a and 1b respectively. Nearly the same pattern and peaks can be observed for both films. Prominent peaks manifest at 2θ values of approximately 26°, 30°, 43°, 50° and 53°. The most prominent at 26° corresponds to (111) plane which appeared with JCPDS card No. 80–0019 of the CdS crystal. Another prominent peak at approximately 30° corresponds to (200) reflections of card No. 03–065–0346 which is the crystal preferred orientation for PbS [10,11] .Some peaks like 30°, 50° corresponding to reflections (200) and (311) respectively with card No. 03-065-6623 revealed the presence of Cadmium Lead Sulphide which most probably grew in the junction. Efforts are being made to determine the relative abundance of Cd, Pb and S and hence the exact molecular formula of the ternary compound.

The average grain sizes, D of the heterojunction films were obtained using Sherrer's formula [12-15]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

where λ is the wavelength of X-rays, β the full width at half maximum (FWHM) of the peak with the highest intensity and θ is the diffraction angle. Hence D for CdS/PbS was 30.1nm and that for PbS/CdS was 28.7nm.

File name: D12A1_xrdml.xrdml
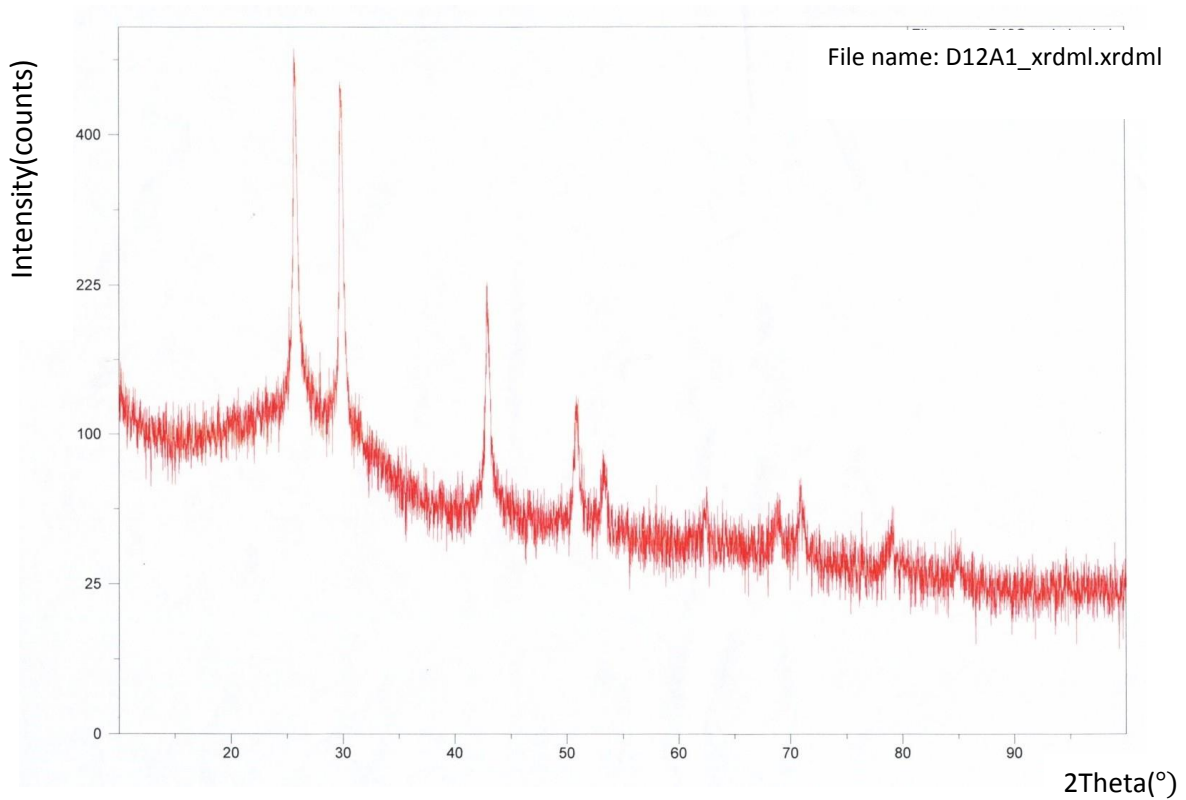
Fig. 1a: Diffraction pattern of PbS/CdS thin film

File name: D12A2_xrdml.xrdml
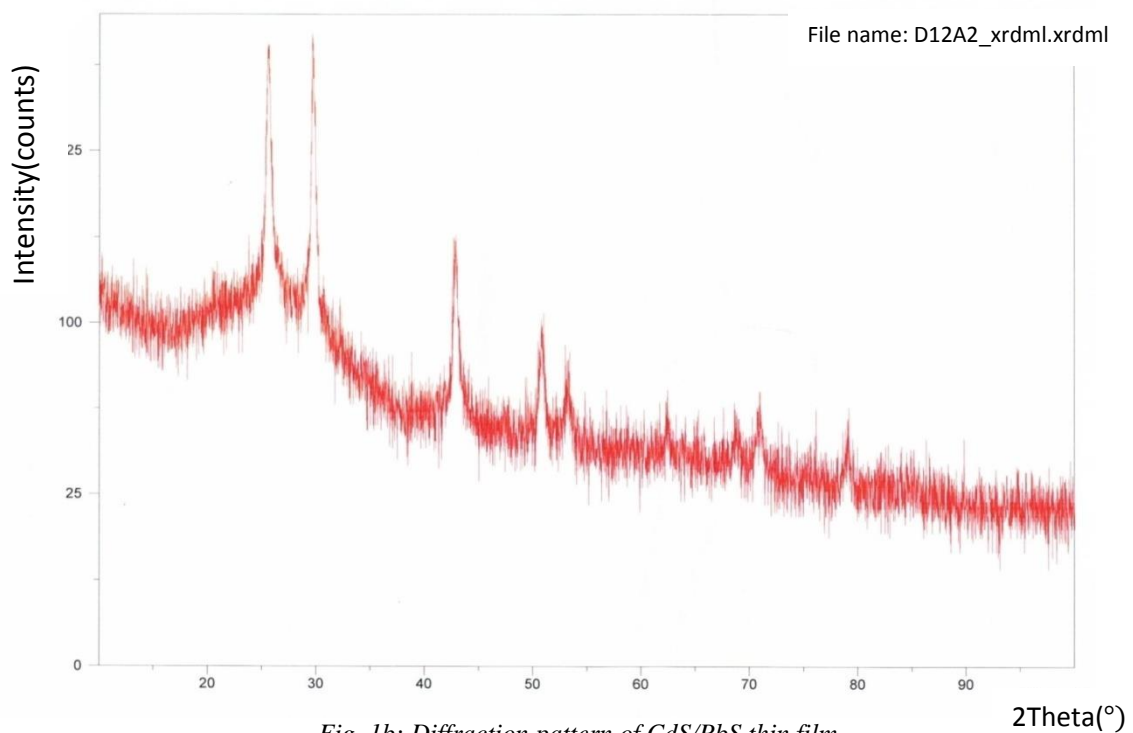
Fig. 1b; Diffraction pattern of CdS/PbS thin film

3.2. Spectroscopic Analysis

Figs. 2 and 3 show the absorbance, A and transmittance, T spectra of the stack ternary films of PbS/CdS and CdS/PbS as well as those of their binary parents: PbS and CdS. All films exhibited high absorbance in UV. PbS retained this high absorbance in the visible and near IR while other films showed reduced absorbance in the same range of wavelength, the most remarkable being CdS. PbS/CdS generally showed higher absorbance than CdS/PbS in all frequencies except in UV ranges. Transmittance spectra of figure 3 shows CdS/PbS transmitting higher than PbS/CdS for most frequencies. It can be seen from figures 2 and 3 that the optical characteristics of CdS/PbS followed the trend of variation of CdS binary films though its transmittance was lower from 460nm onwards. The same trend can be seen in the reflectance spectra of figure 4 where the films exhibited reflectance of between 18 and 19% in the visible and near IR, and as low as 7% in the UV region.
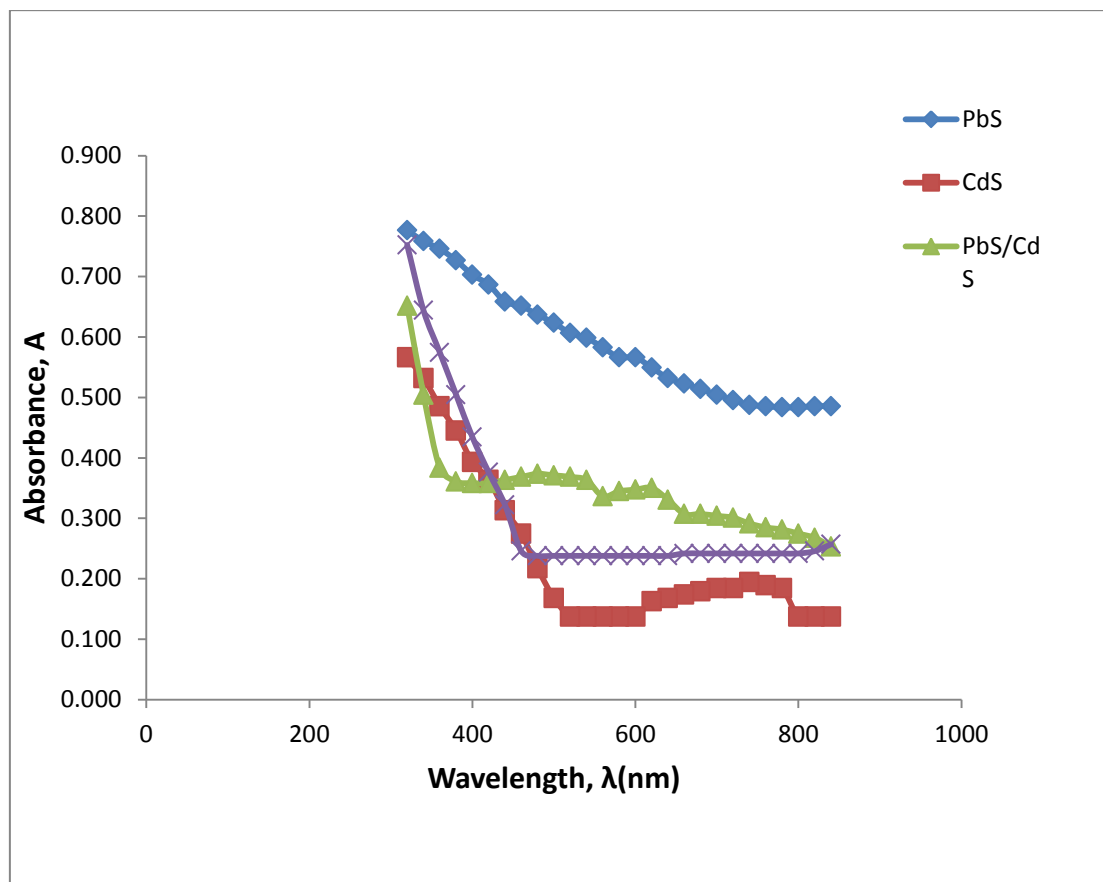

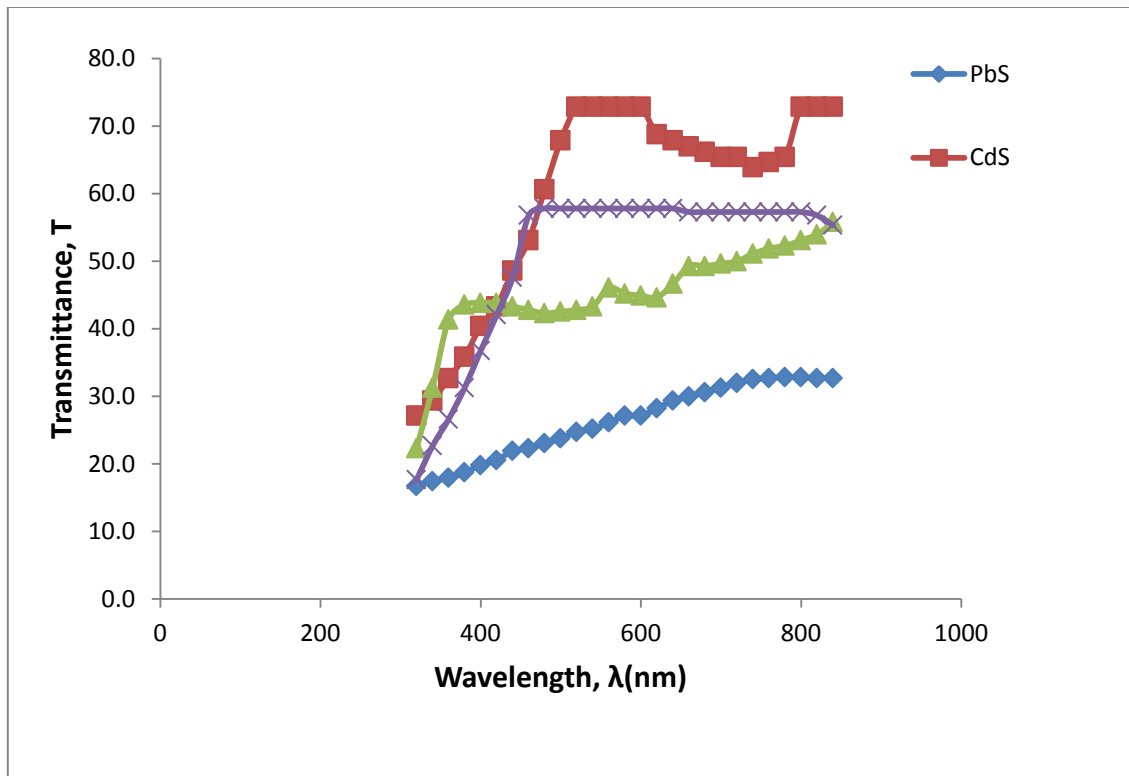*Fig. 2: Spectral Absorbance of Thin Films of PbS/CdS, CdS/PbS, PbS and CdS*

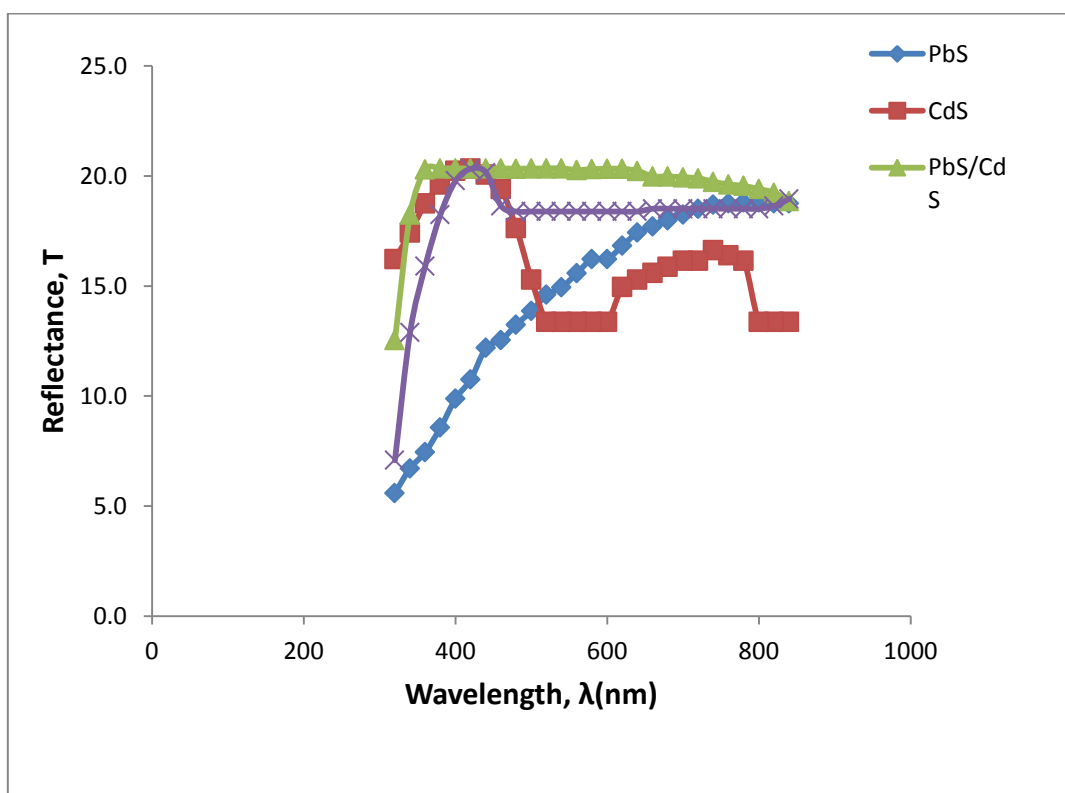*Fig. 3: Spectral Transmittance of Thin Films of PbS/CdS, CdS/PbS, PbS, and CdS*

Fig. 4: Spectral Reflectance of Thin Films of PbS/CdS, CdS/PbS, PbS and CdS

The absorption coefficients, α is related to the transmittance, T as [16]:

$$\alpha = LnT^{-1} \times 10^6 (m^{-1}) \qquad (2)$$

and is plotted against photon energy for each thin film sample as in figure 5. Values of α for CdS/PbS are higher than those of PbS/CdS in the UV range but lower in the visible and near infra red (NIR). This absorption coefficient is related to the energy gap, Eg of a semiconductor as [17-22]:

$$\alpha h\nu = A(h\nu - Eg)^n \tag{3}$$

where A is a constant, hν is the photon energy and α is the absorption coefficient. For direct allowed transition, n = ½ while for indirect ones, n = 2 or 3 depending on whether they are allowed or forbidden respectively. Hence a linear graph of $(\alpha h\nu)^2$ versus hν will show Eg as intercept on hν axis. Figure 6 reveals such direct energy gap of 1.37eV, 1.83eV, 2.35eV and 2.55 eV for the PbS, PbS/CdS, CdS and CdS/PbS thin films respectively. Values for bulk CdS, as widely reported are 2.42–2.58eV while those for Galena (PbS) are 0.34–0.37eV [23,24]. It can be seen that the band gap of either stack heterojunction film is closer to that of second binary component (further away from substrate). Whereas PbS/CdS shifted the fundamental absorption edge of PbS from 1.37eV to 1.83eV, CdS/PbS shifted that of CdS from 2.3eV to 2.55eV thus providing tuning effect to the band gap for novel applications. Plot of $(\alpha h\nu)^{1/2}$ versus hν as in figure 7 also provides the indirect band gap for PbS/CdS and CdS/PbS to be 1.45eV and 1.72eV respectively as read off in the intercept on the hν (axis).
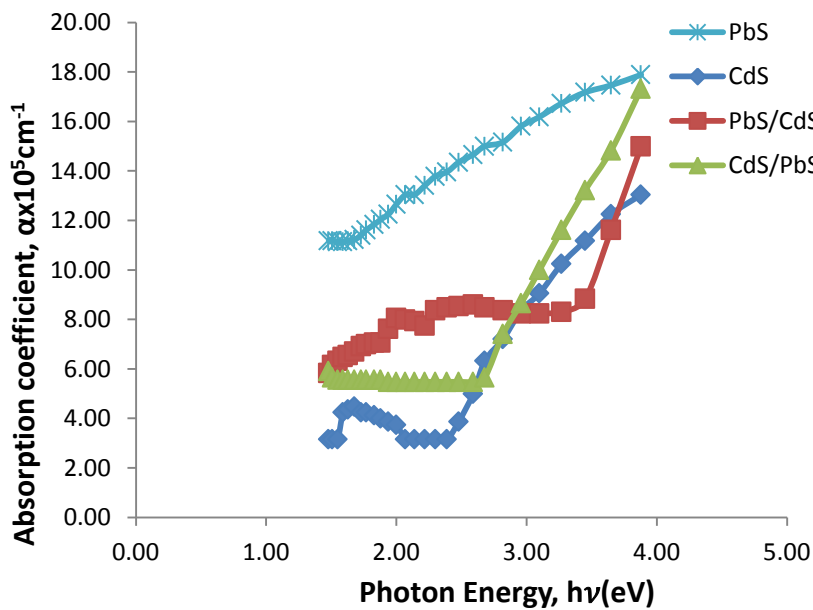

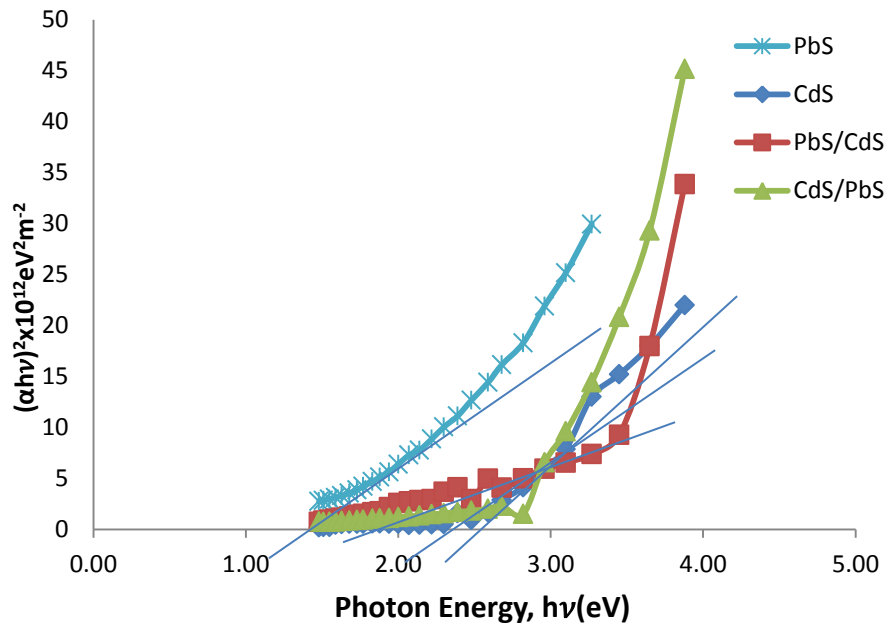*Fig. 5: Plot of absorpion coefficient, α against energy hν for thin films of PbS/CdS, CdS/PbS, PbS and CdS*

Fig. 6: Plot of (αhν)²x10¹²eV²m⁻² versus hν showing the band gaps of thin films PbS/CdS, CdS/PbS, PbS and CdS

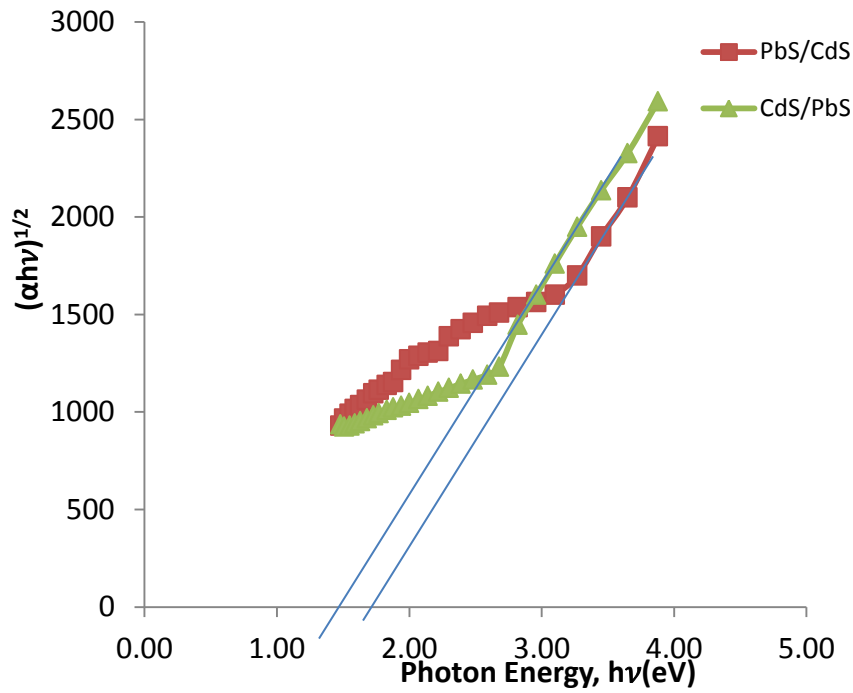*Fig.7: Plot of (αhν)¹/² versus hν for thin films of PbS/CdS and*

Refractive index, n is related to the reflectance, R and extinction coefficient k of the thin films as [25-28] :

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad (4)$$

For semiconductors and insulators, $k^2 << n^2$ and

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$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (5)$$

Hence,

$$n = \frac{1+R^{1/2}}{1-R^{1/2}} \qquad (6)$$

Figure 8 which is the plot of such refractive index against photon energies reveals n = 2.5 and 2.6 for PbS/CdS and CdS/PbS respectively in the visible and near IR region.
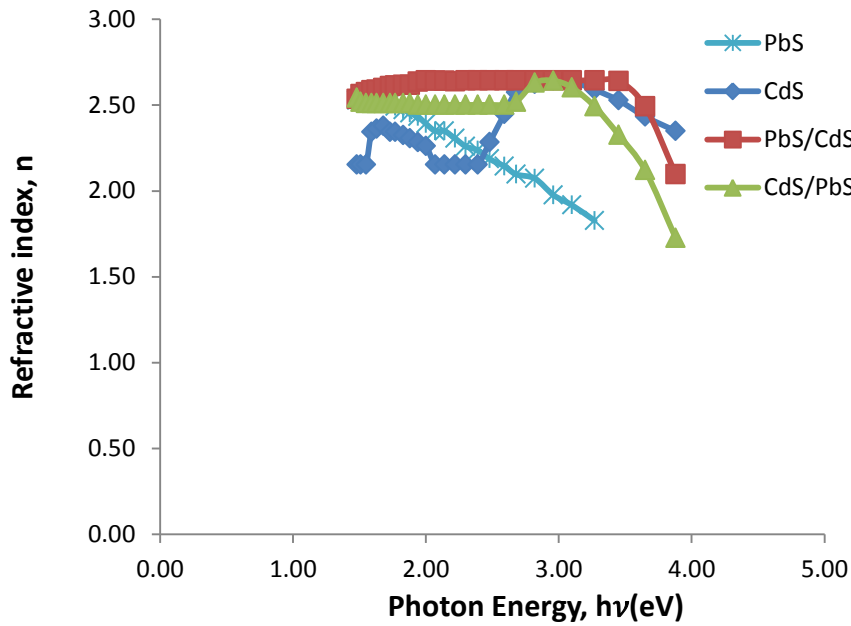

Fig. 8: Refractive index spectra of PbS/CdS, CdS/PbS, PbS and CdS thin films

3.3. RBS Results

The results of Rutherford Backscattering analysis, shown in figure 9 for PbS/CdS sample, deciphered the elements in the samples as Cd, Pb and S as expected. It also revealed the film thickness to be 170nm. Similar analysis (not shown) provided thickness of CdS/PbS sample to be 154nm and same elements as in PbS/CdS.
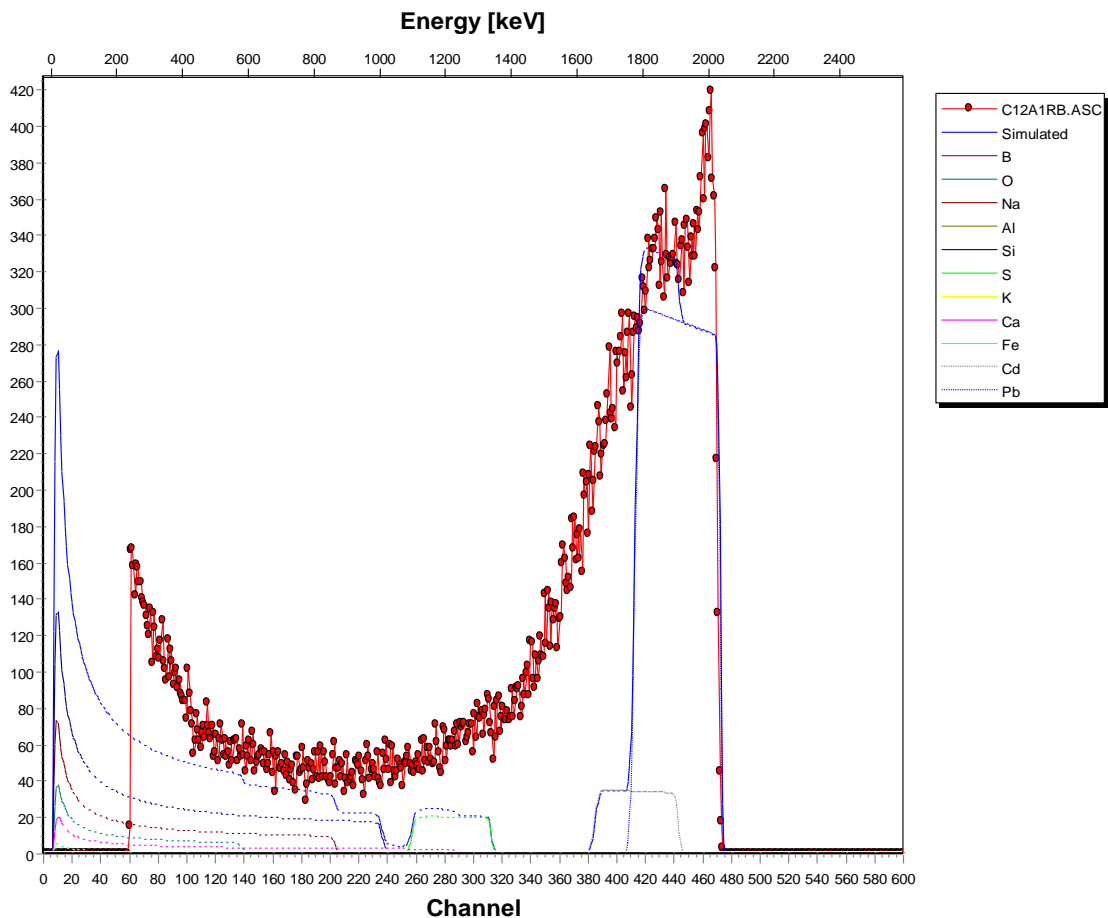
Energy [keV]

Fig. 9: Showing RBS micro graphs of PbS/CdS thin film. LAYER 1: Thickness. 170nm.
Compo: Pb, Cd, S. Layer 2: Tickness. 677899nm. Compo: Si. O, Na, Ca, Al, K, Fe, B,

4. Conclusion

Chemical bath deposition technique was applicable in growing stack heterojunction thin films of CdS/PbS and PbS/CdS. The band gap of each stack is closer to that of the binary component thin film away from the substrate. The structural characteristics of both stacks are virtually same though they have different band gaps. Transmittance of both stack films are good, over 50% in the VIS and UV ranges even though PbS alone is a natural absorber in these ranges. Their band gap tunings from their binary film origins offer them for several new applications, such as in solar cell technology, selective surfaces and optoelectronic devices.

References

[1] K. L. Chopra, S.R. Dans, Thin Film Solar Cells, Plenum Press, New York,
   New York (1983).
[2] F. I. Eze, Turk J. of Physics **105** (2005).
[3].L. Eckertova, Physics of Thin Films, Plenum Press, New York (1986).
[4] F. I. Ezema, D. D. Hile, S. C. Ezugwu, R. N. Osuji, P. U. Asogwa,
   Journal of Ovonic Research **6**(3), 99 (2010).
[5] Y. Rodriquez-Lazcaro, M. T. S Nair, P. K. Nair, Thin Films. J. of Crystal Growth
   223, 399 (2000).
[6] S. C. Ezugwu, P. U. Asogwa, F. I. Ezema, R. U Osuji, Journal of Non-Oxide Glasses

2(2), 121 (2010).

[7] P. U. Asogwa, S C. Ezugwu, F. I. Ezema,A. B. C. Ekwealor, B. A. Ezekoye, R. U. Osuji, J. Optoelectron. Adv. Mater. **11**(7), 940 (2009).

[8] V. V. Stefko, Sov. J. Commun. Technol. Electron **36**.(1991).

[9] P. K. Nair, D. O. Gomez Daza, A. A. Readigos, M. T. S. Nair, Semicond. Sci. Technol. **16,** 651 (2001).

[10] D. O. Eya, Pacific Journal of Science and Technology **7** (2) (2006).

[11] J. C. Osuwa, C. I. Osuwa, F. I. Ezema, Advances in Natural and Applied Sciences **3**(2) (2009).

[12] A. B. C. Ekwealor, Digest J. Nanomater. and Biostructures **9**(1) 423 (2014).

[13] L. Sujatu Davi, K. Nomita Davi, B. Indrajit Sharma, H. Nandakumar Sharma, Chalcogenide Letters **9**(2) 2012.

[14] B. D. Cullity, Elements of X-ray Diffraction, 2nd. Ed. Addison Wesley, 1866 (1978).

[15] M. N. Bchnajady, N. Modirshahla, E. Ghazalian, Digest J. Nanomater. and Biostructures **6**, 689 (2011).

[16] M. Digiullo, G. Micocci, P. Sicillano, A. Tepore, Appl. Phys. **62**(10), 4231 (1987).

[17] F. Abeles, Optical Properties of Metals, North-Holland Pub. Co. Amsterdam, 97 (1972).

[18] T. S. Moss, Optical Properties of Semiconductors, Butterworth and Co. Pub. Ltd., London, 2 (1961).

[19] R. A. Smith, Semiconductors, Cambridge University Press (1959).

[20] N. Soltani, A, Debzangi, A. Kharazmi, E. Saion, W. Wahmood Mar Yunus, B. Yeop Majlis, M. Reza Zare, E. Gharibshahi, N. Khalilzabeh, Chalcogenide Letters **11**(2) (2014).

[21] R. Seoudi, A. Shabaka, W. H. Elisa, N. M. Farage, Physica B. **405,** 919 (2010)

[22] T, P, Sharma, D. Patidar, S. N. Sexana, K. Sharma, Indian J. Pure and Appl. Phys. **44,** 125 (2006).

[23] C.Kittel, Introduction to Solid State Physics, Wiley Eastern Limited, New Delhi 985 (1985).

[24] N. W. Ashcroft, N. D. Mermin, Solid State Physics, Holt, Rinehart and Winston, London (1976).

[25] J. I. Pankov, Optical Processes in Semiconductors, Prentice-Hall Inc., New Jersey, 88 (1971).

[26] A. O. E. Animalu, Inter. Quantum Theory of Crystalline Solids, Prentice-Hall Inc., New Jersey, 225 – 241 (1977).

[27] J. I. Gittleman, E.K. Sichel, Y Arie, Sol. Energy Mater. **1,** 93 (1979).

[28] W. G. Spitzer, H. Y. Fan, Phys. Rev. **106,** 882 (1957).