

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

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Abstract

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 300-900nm 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 0.65eV and 0.75eV 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. Both films had fairly steady refractive index of 2.64 for 170nm thick PdS/CdS of 38.7nm crystal grain size and 2.50 for 154nm thick CdS/PbS of 40.1nm grain size.

Key words: PbS, CdS, CdS/PbS, PbS/CdS, heterojunction, Thin films, band gap.

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 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 CuS, Sb₂S₃ [5], BaS [3] and CdS [6] and ternary heterojunction nano films like CdS/CuS [4,7]

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 has poor conductivity, usually as low as 10^{-8} [6]. 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 a 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.

1) 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 1mm³ 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 CdCl₂, 5ml of NH₃ (aq) solution, 5ml of 1M thiourea (NH₂)₂CS, 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(NO₃)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 (NH₃) acted as 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 CuK α radiator of $\lambda = 0.15406\text{nm}$ to scan continuously as 2θ varies from 0 – 100° at a step size of 0.02° 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 Pellaton 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 result of the XRD scan 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 reveal 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 Sherer's formula [12-15]

$$D = 0.9\lambda/BCos\theta \quad (1)$$

where λ is the wavelength of X-rays, B 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 40.1nm and that for PbS/CdS is 38.7nm.

3.2 Spectroscopic Analysis

Figures 2 and 3 show the absorbance, A and transmittance, T spectra of the stack ternary films PbS/CdS and CdS/PbS as well as those of their binary parents: PbS and CdS. All films show high absorbance in UV. PbS retains this high absorbance in the visible and NIR while other films show 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. We can see from figures 2 and 3 that the optical characteristics of CdS/PbS follows the trend of variation of CdS binary films though its transmittance is lower from 460nm onwards. The same trend can be seen in the reflectance spectra of figure 4 where the films show reflectance of between 18 and 19% in the visible and near IR, and as low as 7% in the UV range.

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

$\alpha = \text{Ln}T^{-1} \times 10^6 (\text{m}^{-1})$ (2) were calculated for each thin film sample and shown in figure 5. Values 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, E_g of a semiconductor as [17-22]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where A is a constant, $h\nu$ is the photon energy and α is the absorption coefficient. For direct allowed transition, $n = 1/2$ 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 $h\nu$ will show E_g as intercept on $h\nu$ 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 is 2.42–2.58eV while that for Galena (PbS) is 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 shifts the fundamental absorption edge of PbS from 1.37eV to 1.83eV, CdS/PbS shifts that of CdS from 2.3eV to 2.55eV thus providing tuning effect to the band gap for special applications. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ as in figure 7 also provides the indirect band gap for PbS/CdS and CdS/PbS to be

0.75eV and 0.65eV respectively as read off in the intercept on the $h\nu$ (axis).

Refractive index, n is given in terms of the reflectance, R of the thin films that have $k^2 \ll n^2$ (where k is extinction coefficient) as [25-28] as:

$$n = (1 + \sqrt{R}) / (1 - \sqrt{R}) \quad (3)$$

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

3.3 RBS Results

The results of Rutherford Backscattering analysis are as shown in figure 9 for PbS/CdS sample which 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 157nm.

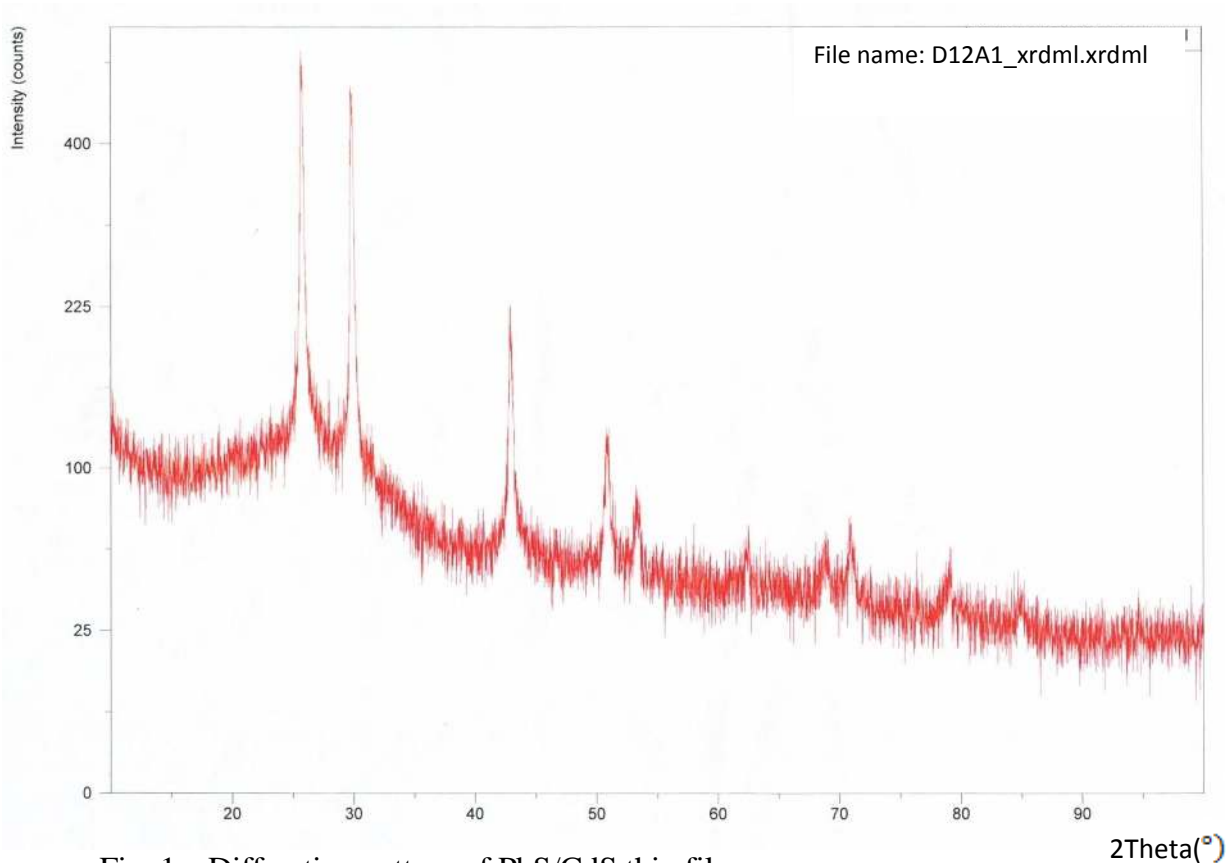


Fig. 1a: Diffraction pattern of PbS/CdS thin film

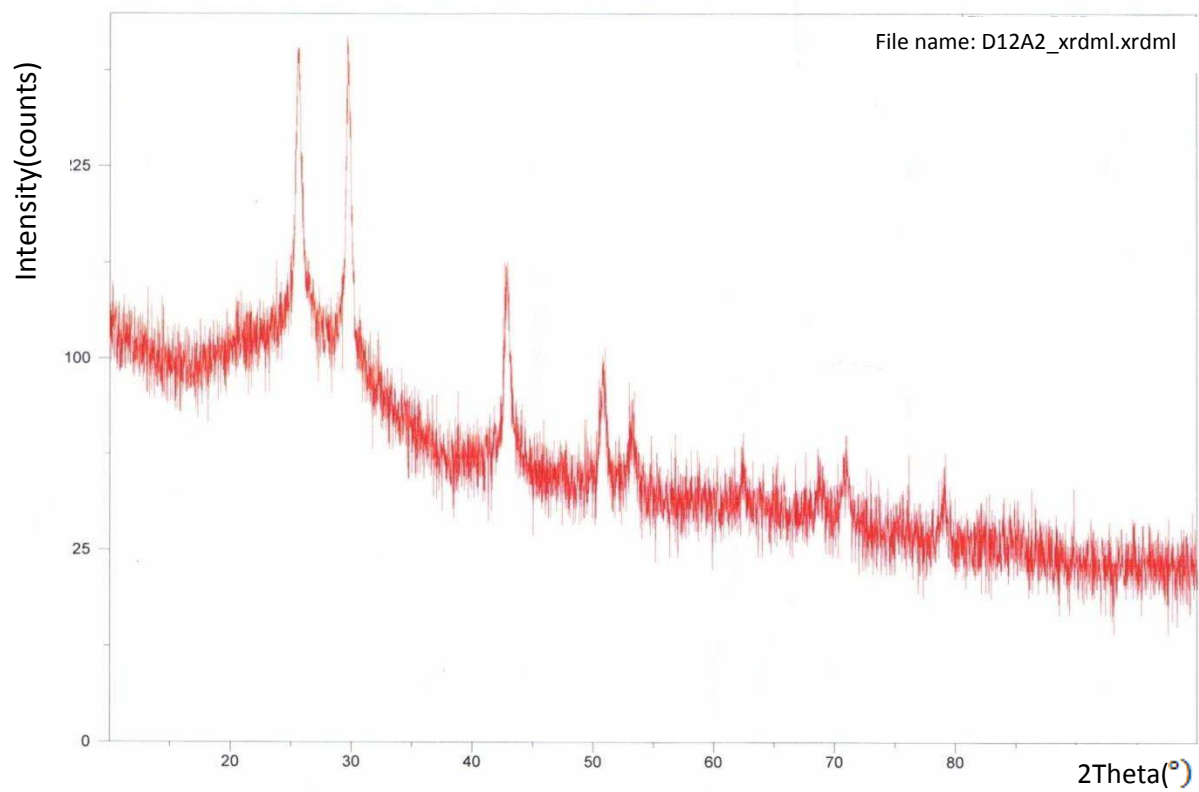
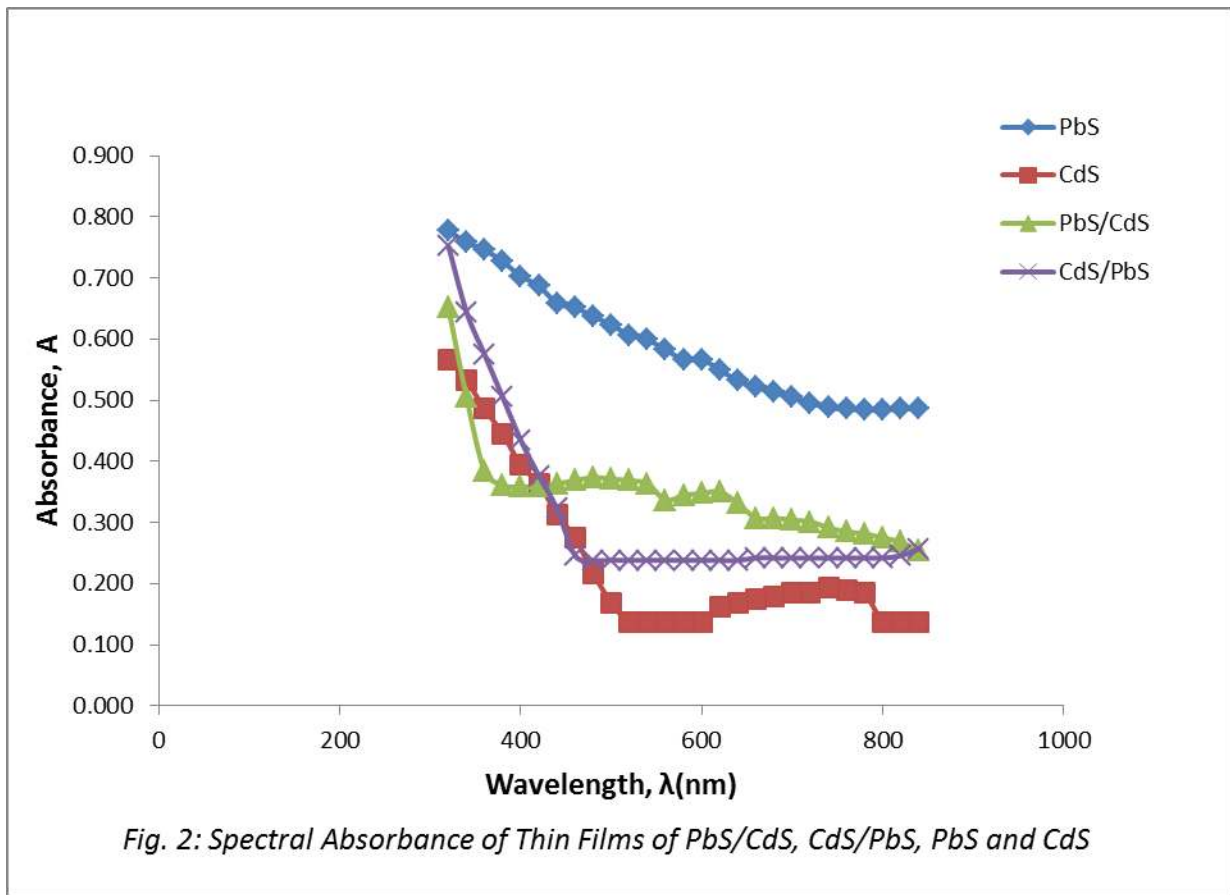


Fig. 1b; Diffraction pattern of CdS/PbS thin film



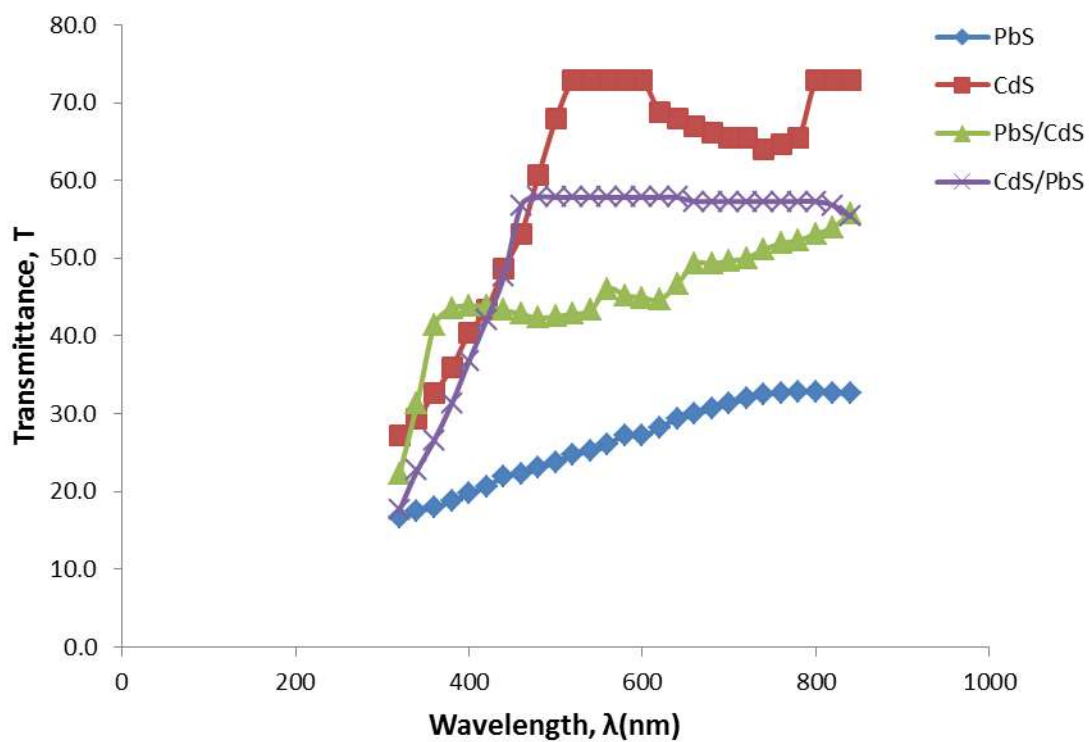
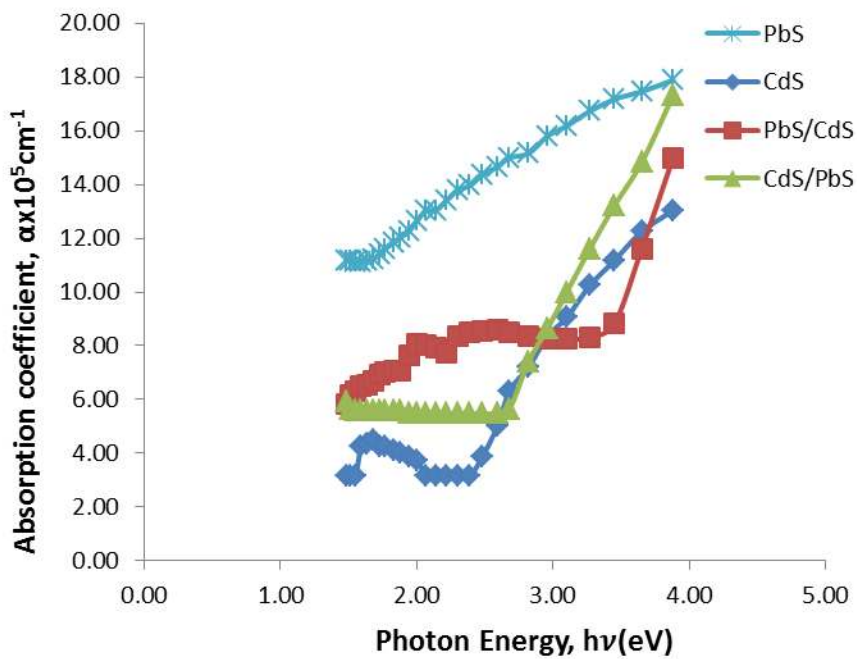
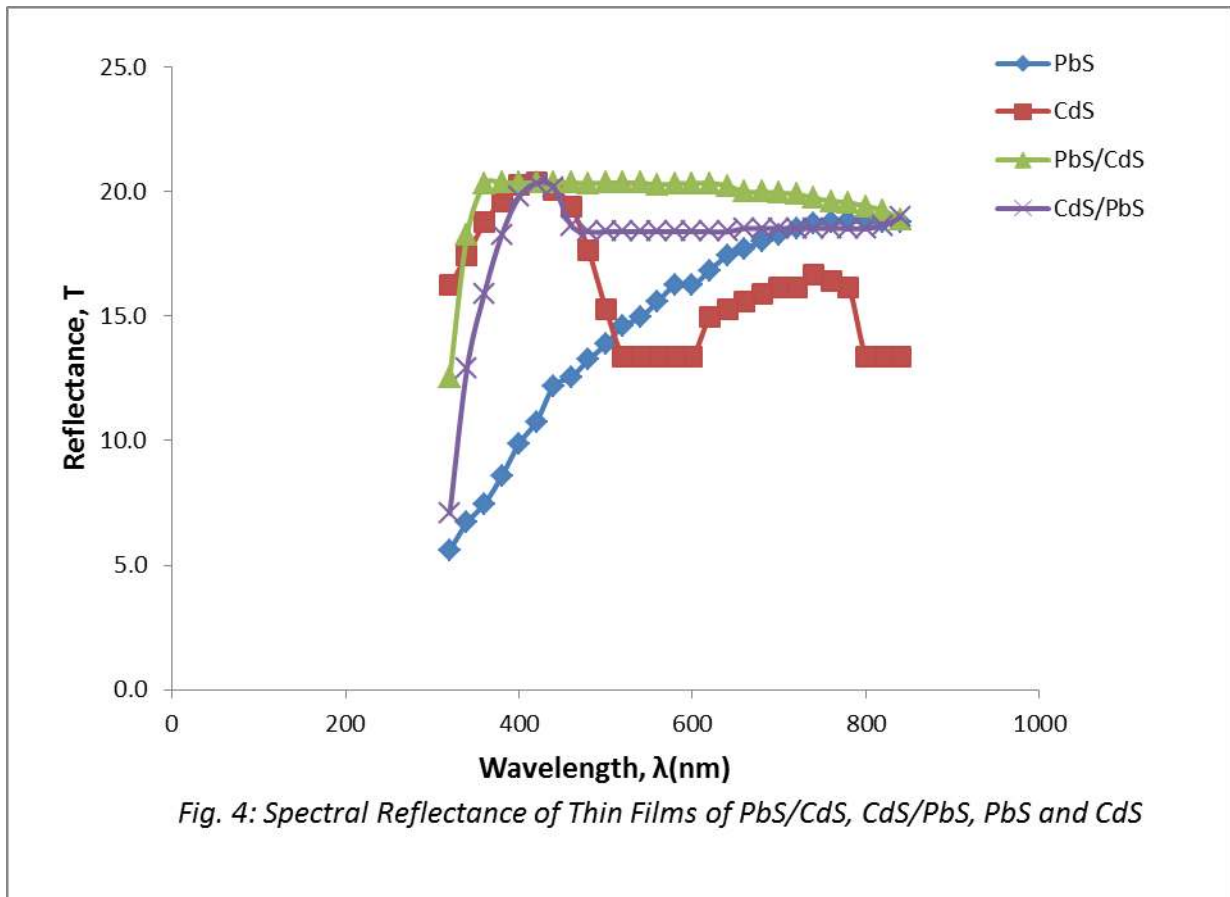


Fig. 3: Spectral Transmittance of Thin Films of PbS/CdS, CdS/PbS, PbS, and CdS



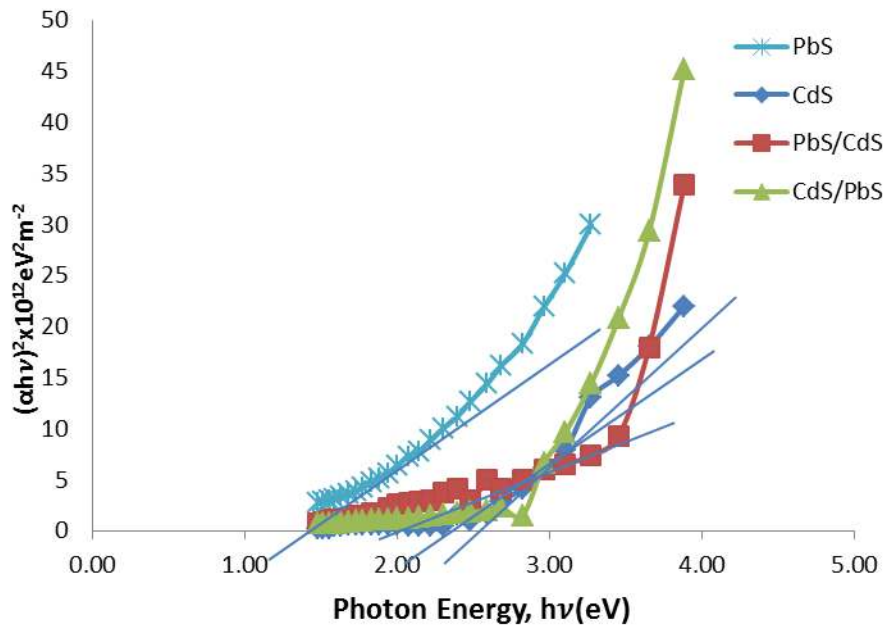


Fig. 6: Plot of $(\alpha h\nu)^2 \times 10^{12} \text{ eV}^2 \text{ m}^{-2}$ versus $h\nu$ showing the band gaps of thin films PbS/CdS, CdS/PbS, PbS and CdS

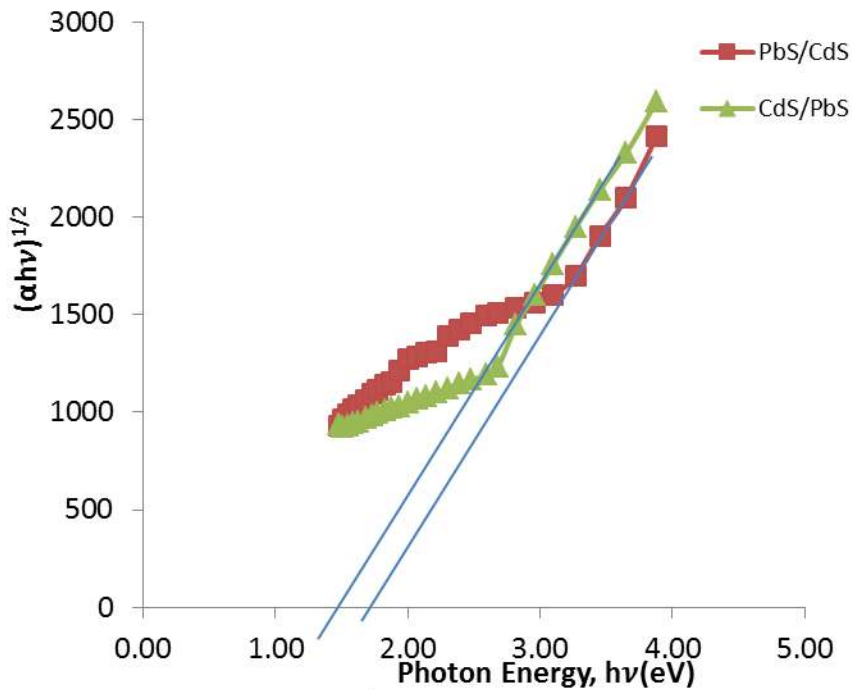


Fig.7: Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for thin films of PbS/CdS and CdS/PbS

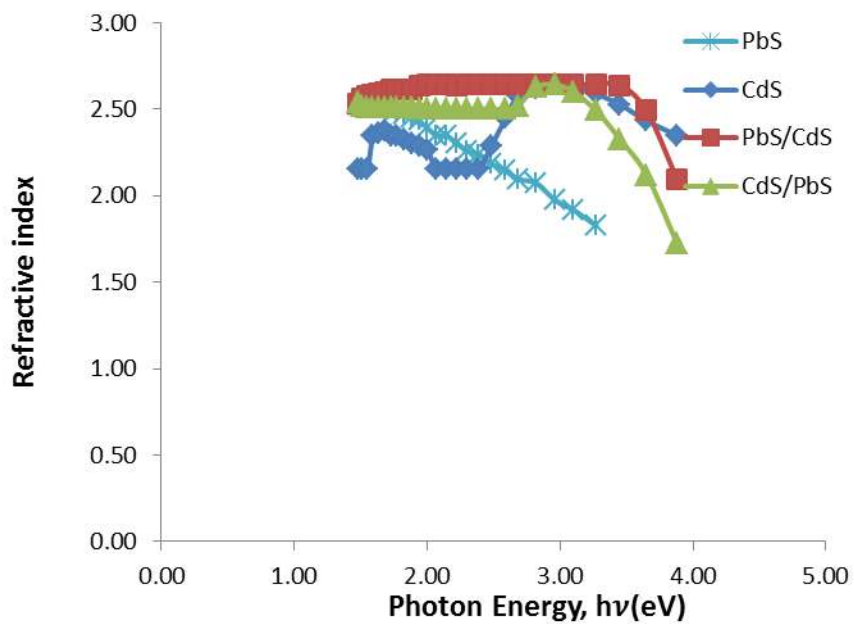


Fig. 8: Refractive index spectra of PbS/CdS, CdS/PbS, PbS and CdS thin films

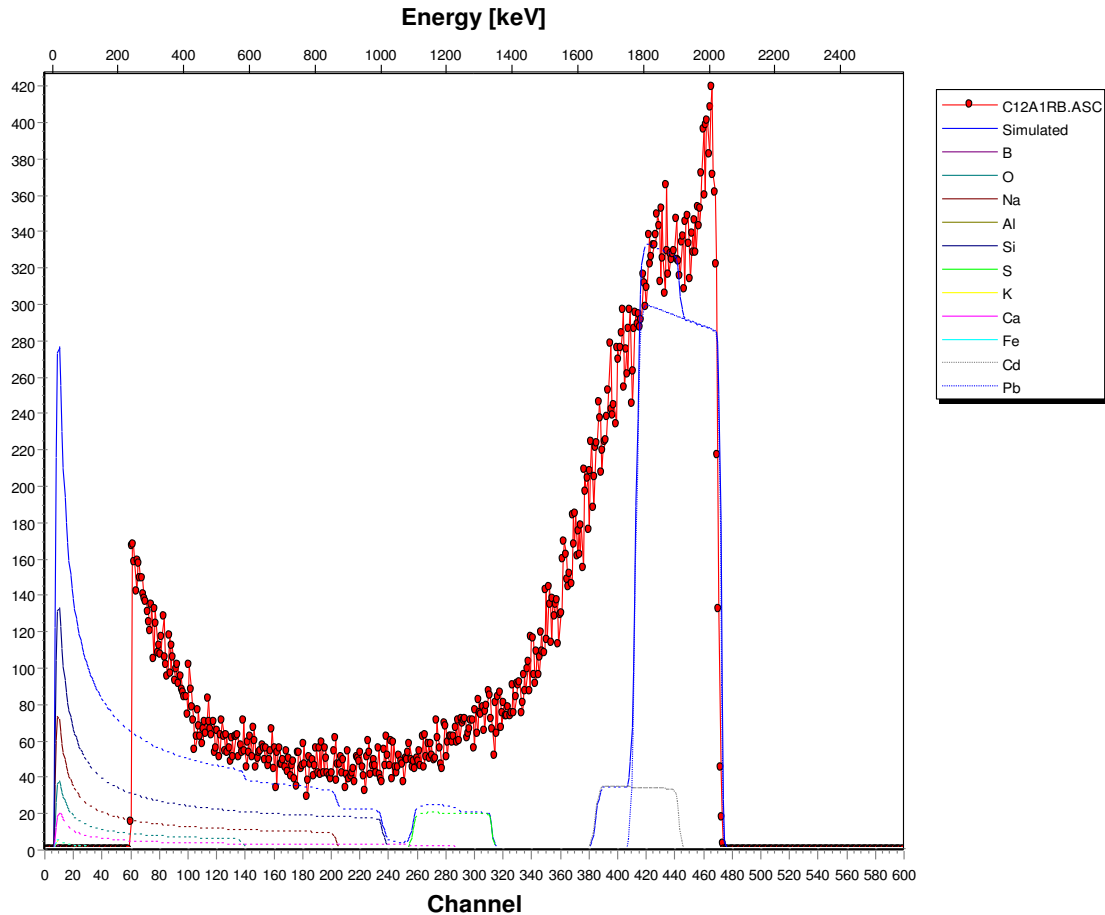


Fig. 9: Showing RBS micro graphs of PbS/CdS thin film. LAYER 1: Thickness. 170nm. Compo: Pb, Cd, S. Layer 2: Tickness. 677899nm. Compo: Si, O, Na, Ca, Al, K, Fe, B,

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 away from the substrate. The structural characteristics of both stacks are virtually same. Both are semiconductors but with 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.

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