

EFFECT OF Pb DOPING ON THE ENERGY BAND GAP AND ELECTRICAL PROPERTIES OF CdS THIN FILMS GROWN WITHIN POLYMER MATRIX IN CHEMICAL BATH DEPOSITION TECHNIQUES

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Cadmium sulphide thin films, doped with Pb, were deposited at room temperature, on glass substrates within a polymer matrix using chemical bath deposition technique and the effect on the energy band gap and electrical resistivity of films studied. Cadmium and sulphur ions were derived from aqueous solution of CdCl₂ and (NH₂)₂CS respectively while dopant was introduced from small quantity Pb(NO₃)₂ that gave its relative abundance X with respect to Cd²⁺ of X:100 where 1<X<8. Four point probe technique used to obtain the resistivity of film showed marked decrease in resistivity of deposits with little doping. Spectrophotometric analysis done on deposits deciphered the absorption coefficients and hence film band gaps to reveal that such doping broadens CdS band gaps in favour of IR absorption.

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1. Introduction

Cadmium sulphide is a hexagonal closed-packed II-VI semiconductor with many applications in electronic devices and solar cells. Its wide band gap of about 2.42eV makes it an optical window material together with several semiconductors such as CdTe, Cu₂S, CuInSe₂ [1]. It has piezoelectric properties and has potentials for laser applications [2,3]. Thin films of CdS are of considerable interest for their use in the fabrication of solar cells [4,5]. But CdS has poor conductivity, as low as 10⁻⁸ Ω⁻¹m⁻¹ [6] and therefore has to be doped to improve its electrical characteristics. Several researchers have doped CdS with a wide variety of elements (Zn, In, Al, F, Co, Sn etc) to meet demands of several application fields such as in thin film solar cells [7], electrochemical cells [8], gas sensor [9], etc.

We have doped CdS with Pb using chemical bath deposition (CBD) technique which results in ternary thin film (TF) of Cd_{1-x}Pb_xS where x<0.08. PbS belongs to the IV-VI group semiconductor with narrow band gap of about 0.41eV suitable as IR detector, photoresistant laser diode, humidity and temperature sensor material. It can also be used for decorative as well as solar control coatings [10,11]. We therefore expect tailoring of band gap of CdS by doping it with Pb ions.

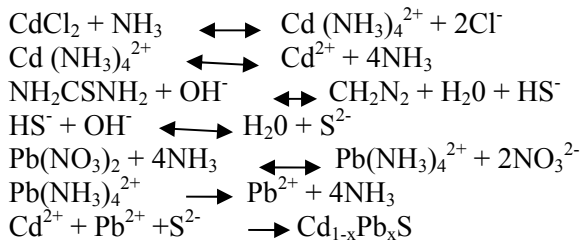
Our CBD technique is a cost effective, low temperature, electroless method that offers more affordable alternative to the widely reported but expensive techniques like molecular beam epitaxy, spray pyrolysis, quenching [12,13], etc. Our depositions were within a polyvinyl alcohol(PVA) polymer matrix and the effects of doping on the band gap, E_g and resistivity of the film were studied. Four Point Probe analysis [14] was used to obtain resistivity of our deposits while spectrophotometric analysis was applied to obtain the absorption coefficients of same deposits within the frequencies 200 – 1100nm from which the band gaps of the Pb doped TF deposits were deduced.

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2. Experimental details

We fabricated CdS thin film by mixing 5ml of 0.7M CdCl₂, 5ml of NH₃(aqu.) solution, 5ml of 0.9M thiourea(NH₂CSNH₂) and 35ml of polyvinyl alcohol(PVA) in a 50ml beaker, the solutions being continuously and vigorously stirred for 30 seconds. Substrates of plane glass slides that were previously degreased in concentrated HCl, washed in detergent solutions, rinsed with distilled water and drip dried in dust free environment were vertically inserted into the solution and suspended from a synthetic foam that rested on top of the beaker. The chemical bath was left for 2hours 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.

Similar chemical baths were set up except that between 2 to 10ml of 0.1M Pb(NO₃)₂ was added to each bath, while stirring vigorously, in small incremental quantity that maintained low ionic ratio of Pb²⁺:Cd²⁺ of X:100 where 1<X<8, since only a small doping level is necessary to alter semiconductor conductivity without significantly altering its ordered crystal structure. Ammonia acted as a complexing agent in the controlled precipitation that is basically the hydrolysis of thiourea in alkaline solution containing cadmium and lead salts. Other complexing agents that can be used, like sodium hydroxide, sodium borohydride and hydrazine have been reported [15,16]. The PVA was prepared by adding 450ml of distilled water to 0.9g of solid PVA and stirring at 90⁰C for 1hour. The temperature of the resulting solution was then allowed to drop to room temperature. Ammonia complexed the basic reaction as follows:



When the ionic product exceeds the solubility product, controlled precipitation of grayish lead doped CdS occurred on the surface of the glass substrates.

The structure of thin films deposits was determined with Phillips X'Pert PRO diffractometer which used CuK α radiator of $\lambda = 0.15406\text{nm}$ scanning continuously from $2\theta = 10$ to 99° in step size of 0.017° at a room temperature of 288K.

Spectrophotometric analysis done on the thin film in the 200 – 1100nm range provided the film absorption coefficient, α at various frequencies from which the band gap, E_g is deduced from the well established relation [17,18]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A is a constant, $h\nu$ is the photon energy and α is the absorption coefficient. For direct transition, $n = \frac{1}{2}$ or $\frac{2}{3}$ 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 $h\nu$ shows E_g as intercept on $h\nu$ axis for direct transition.

Rutherford Back Scattering elemental characterization was done on the films as part of the Proton Induced X-ray Emission (PIXE) analysis from a Tandem Accelerator Model 55DH 1.7MV Pellaton by NEC (National Electrostatic Corporation, USA). The analysis deciphered the elements in both substrates and deposits as well as the atomic percentages of such elements. It also obtained the substrate and deposit thicknesses. We used Four Point Probe technique to obtain the resistivity of film deposits.

3. Results and Discussion

3.1. XRD Study

The typical X-ray pattern of the deposited ternary sulphide thin film is as shown in figure 1a. Prominent peaks manifest at 2θ values of approximately 26° and 30° . The first corresponds to (111) plane which JCPDS card No. 80-0019 confirms as referring to CdS hexagonal crystal. These peaks are more pronounced in figure 1b which also has additional peaks at 43° and 50° . The peaks at 30° in figure 1b corresponds to (200) reflections of card No. 03-065-0365 which is the crystal preferred orientation of PbS [19,20]. Some peaks like in 30° and 50° corresponding to reflections (200) and (311) respectively with card No. 03-065-6623 reveal the presence of cadmium lead sulfide ($\text{Cd}_{1-x}\text{Pb}_x\text{S}$)

3.2. RBS Results

Rutherford backscattering analysis results are as shown in figure 2 for the case of deposit of dopant relative abundance $X = 2$. It shows the micrograph as well as elements and their atomic percentage contents in both the substrates and TF deposits as provided in the figure. It also deciphered the TF thicknesses as well as that of the substrate. Such RBS results were also obtained for deposits of $X = 0, 3, 4, 5.5$ and 7.5 (figures not shown) and included in table 1. Values for substrates remain the same in all analysis.

3.3. Band Gap and Resistivity Study

Figure 3 shows the plot of $(\alpha h\nu)^2 \text{ eV}^2\text{m}^{-2}$ versus photon energy, $h\nu(\text{eV})$, the absorption coefficient, α having been obtained from the spectrophotometric analysis results. As usual, the extrapolation of the linear portion of the graph to the horizontal axis provides the band gap for the thin film deposit. The band gaps, E_g are therefore shown in figure 3 for $X = 0, 2, 3, 4$ and 5.5 (7.5 not shown) and included in table 1. The average resistivity of thin film for each dopant atomic abundance X is also included in the table. It can be seen from the table and from figure 4 that only a little doping is required to lower the resistivity which decreased from $105\Omega \text{ cm}$ to as low as $27\Omega \text{ cm}$ as X increased from 0 to 4.7, beyond which further doping actually increased the resistivity. The same table 1 as well as figure 5 show that the band gap of deposit films decreased from 2.4eV as dopant concentration increased but appears to approach a minimum value of about 1.92eV at about $X = 7.5$.

These values of band gap differ from the results: $2.38\text{--}2.45\text{eV}$ reported for undoped CdS thin films [21]. There is therefore band gap shifting in favour of increased infra-red absorption as a result of our doping.

Table 1: Shows results of elemental analysis (element and atomic percentages), band gaps and resistivity of Pb-doped CdS TF as doping level, X increased.

Pb abundance X	Elements	Atomic percentage	E_g (eV)	Resistivity (Ωcm)
0.0	Cd	55.00	2.40	104
	S	45.00		
2.0	Cd	53.34	2.20	64
	Pb	1.10		
	S	45.53		
3.0	Cd	52.22	2.14	42
	Pb	1.62		
	S	46.16		
4.0	Cd	54.20	2.00	31
	Pb	2.26		
	S	43.54		
5.5	Cd	54.82	1.94	32
	Pb	3.19		
	S	41.22		
7.5	Cd	53.30	1.93	75
	Pb	4.33		
	S	42.32		

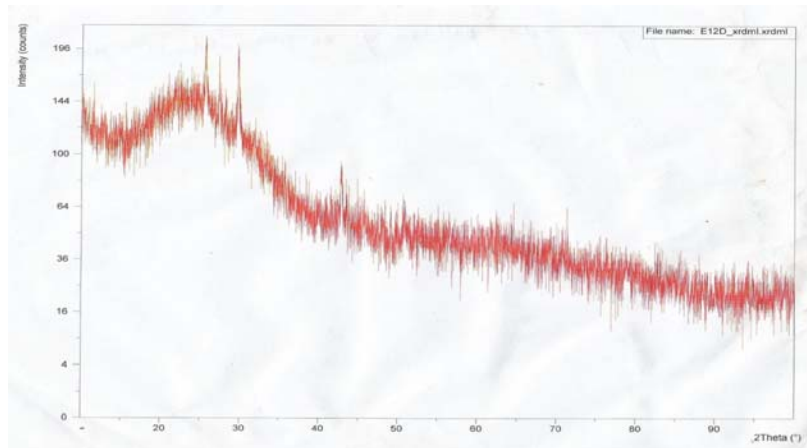


Fig. 1a: Showing the XRD pattern of as grown CdS thin films.

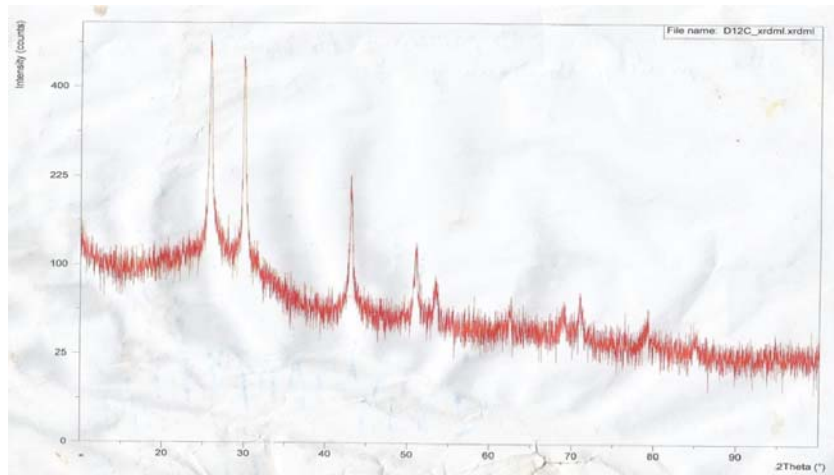


Fig. 1b: Showing the XRD pattern of Pb doped CdS for a case where percentage abundance of Pb^{2+} is $X = 2$.

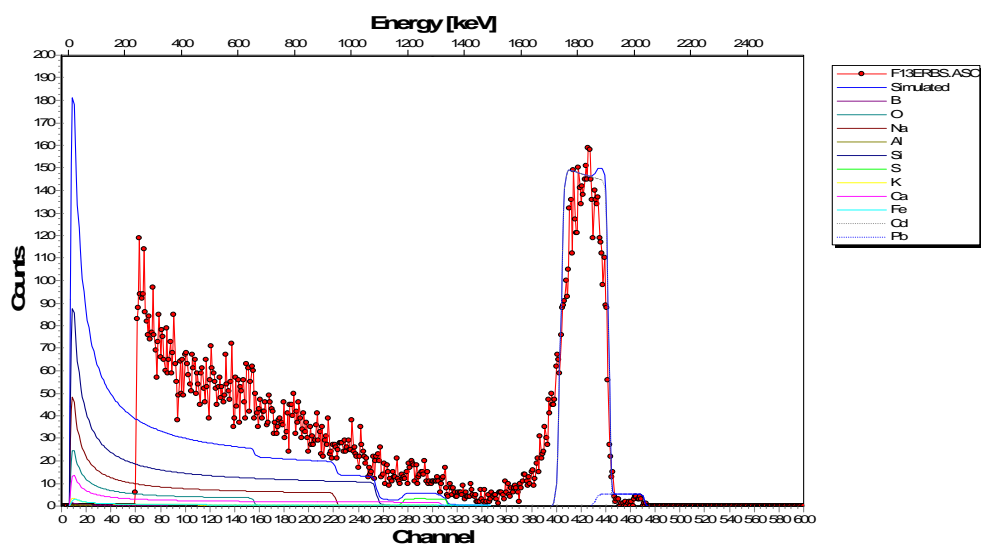


Fig. 2. Showing RBS micro graphs for Pb doped CdS for $X=2$. LAYER 1: THICKNESS 140nm. Compo: Cd 83.35%. Pb 1.10%. S 15.62%. LAYER 2: THICKNESS 677894nm Compo: Si 31.97%. O 32.89%. Na 25.85%. Ca 1.64%. Al 0.25%. K 1.05%. Fe 0.38%. B 5.89%. Layer 1 refers to thin film sample while layer 2 refers to substrate.

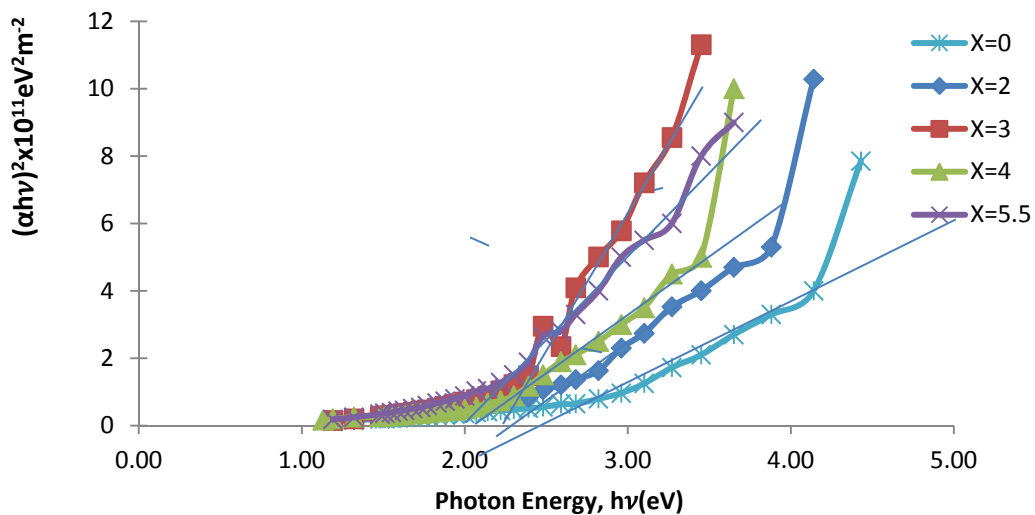


Fig. 3. Plot of $(\alpha h\nu)^2 \times 10^{11} \text{ eV}^2 \text{ m}^{-2}$ versus $h\nu$ showing the band gap, E_g for various dopant levels, X .

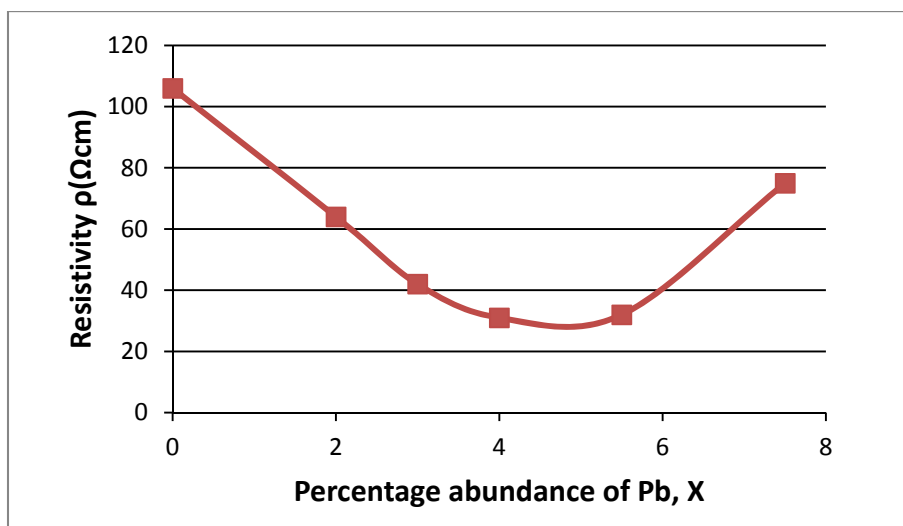


Fig. 4. Graph of resistivity, ρ against percentage abundance of Pb ions, X

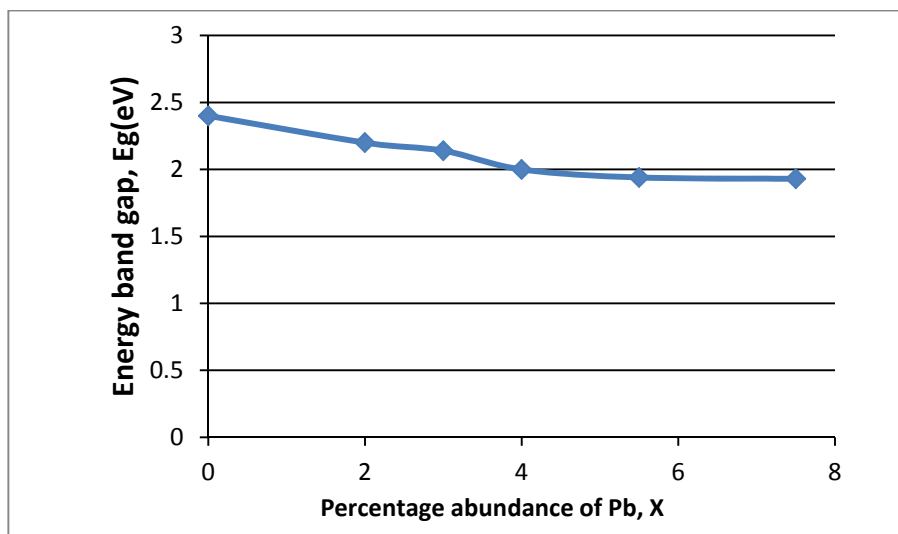


Fig. 5. Plot of thin film band gap, E_g versus percentage abundance of Pb ions, X

4. Conclusions

CdS has been successfully doped with Pb to form $\text{Cd}_{1-x}\text{Pb}_x\text{S}$. Rutherford backscattering analysis and XRD results were used to confirm the presence of the resulting ternary thin films. The energy band gaps of the thin films were deduced using spectroscopic techniques and the resistivity of the films were also deciphered using four point probe technique.

Such doping red shifted the absorption energy band gap to cover more IR ranges. It also reduced the resistivity of CdS films for very low doping but actually increased it for high doping. The doped film is therefore useful for solar meter and solar energy collector applications. Such material will also find applications in solar brooders as well as in photo electronic devices.

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