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## Properties of Chemical Bath Deposited Pb-Doped CdS Thin Films Grown Within Polymer Matrix in Chemical Bath Deposition Techniques: Effect of pH Adjustments

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**ABSTRACT:** *The effects of pH variation on properties of chemical bath deposited Pb-doped CdS thin films are studied and here presented. Cadmium chloride was used to release  $Cd^{2+}$ ,  $(NH_2)_2CS$  was used to release  $S^{2-}$  and dopant (lead) was introduced from small quantity  $Pb(NO_3)_2$  that could only give Pb of relative abundance X with respect to  $Cd^{2+}$  of X:100 where  $X \leq 4$ . Ammonia was introduced in various quantities that ensured good reaction complexation and determined different pH of baths. Successfully grown thin films of Pb-doped cadmium sulphide were characterized for their elemental, structural and optical properties which revealed that pH increase of bath increased the thin film optical absorbance but decreased the refractive index as well as the energy gap.*

**KEYWORDS:** *CdS, chemical bath deposition, complexation, doping, spectrophotometry.*

### I. INTRODUCTION

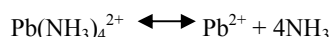
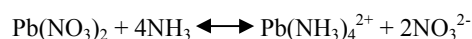
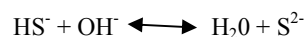
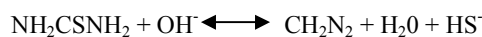
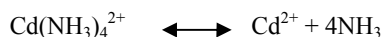
It is now well known that cadmium sulphide (CdS) is a very useful semi-conducting II – VI thin film material because of its wide range of applications in various optoelectronic, piezo-electronic and semi-conducting devices [1]. Its wide direct band-gap (2.42 eV), refractive index (2.5) and n-type semi conductivity [2] makes it very useful as window material in CdTe,  $Cu_2S$  and  $CuInSe_2$  devices for the fabrication of solar cells [3]. It has piezoelectric properties and has potentials for laser applications [4]. CdS however has poor conductivity, usually as low as  $10^{-8} \Omega^{-1}m^{-1}$  and has to be doped [5]. Pb-doped CdS has been variously fabricated using several techniques that included chemical bath deposition (CBD). The acidity of the chemical bath has always been essential in determining the possibility of precipitation in particular and in general the overall properties of fabricated films. The significance of potentiometric hydrogen ion concentration (pH) value in the preparation of CBD thin films has been presented elsewhere [6]; [7]; [8]. The researchers observed that the effect of pH on the properties of chemical bath deposited polyaniline thin film was too profound to be ignored with respect to the film surface morphology, conductivity, refractive index and band gap. This article carries the results of pH variation on the chemical bath deposited Pb-doped CdS thin film.

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## II. MATERIALS AND METHODS

The chemical deposition bath used in this exercise comprised 50 ml beaker onto which was mixed 4.5ml of 0.7M CdCl<sub>2</sub>, 3ml NH<sub>3</sub> (aqu.) solution, 4.7ml of 0.8M thiourea (NH<sub>2</sub>CSNH<sub>2</sub>) and 36 ml of polyvinyl alcohol (PVA). The solution was vigorously and continuously stirred for 30s. 4ml of 0.1M Pb(NO<sub>3</sub>)<sub>2</sub> was added to the bath, while still stirring vigorously; this small quantity nitrate maintained a low ionic ratio of Pb<sup>2+</sup>:Cd<sup>2+</sup> of X:100 where X ≤ 3 since only a small doping level is necessary to alter semi-conductor properties without significantly altering its lattice structure. Ammonia acted as a complexing agent in the controlled precipitation that was basically the hydrolysis of thiourea in alkaline solution containing cadmium and lead salts. The PVA was prepared by adding 450 ml of distilled water to 0.9 g of solid PVA and stirring at 90°C for 1h. The temperature of the resulting solution was then allowed to drop to room temperature [9]. PVA presented a matrix for orderly formation of CdS crystallites. A substrate of plane glass slide that was previously degreased in concentrated HCl, washed in detergent solutions, rinsed with distilled water and drip dried in dust free environment was vertically inserted into the solution and suspended from synthetic foam that rested on top of the beaker. The bath which had a pH of 9.0 was left for 2h at room temperature. When the ionic product exceeded the solubility product, controlled precipitation of grayish lead-doped CdS occurred on the surface of the glass substrates which was removed, rinsed in distilled water and left to drip dry in dust free air and labeled 16A. Aqueous ammonia, as a base with a pH of 11.5, was used to increase the pH of the bath. When in water, however, NH<sub>3</sub> can dissociate into NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> and hence decrease the pH. The exact pH value of chemical baths used was taken with a digital pH meter.

The ammonia complexation was as follows:



Hence Cd<sup>2+</sup>, Pb<sup>2+</sup> and S<sup>2-</sup> became available for the precipitation of initial monomers that progressed to the thin film semiconductor. Similar growth processes were repeated four other times except that different quantities of ammonia added were 5 ml, 7 ml, 9 ml and 11 ml which resulted in bath pH of 9.3, 9.5, 10.4 and 10.8 respectively and in successfully grown Pb-doped CdS thin films labeled 16B, 16C, 16D and 16E respectively.

The structure of thin films deposits was deciphered with Philips X'Pert PRO diffractometer which used a radiator of λ = 0.15406 nm (CuKα) which scanned sample thin films continuously from 2θ = 10° to 99° in step size of 0.017° at a room temperature of 288 K. The optical properties were analysed by taking the thin film absorbance with a UV-VIS-NIR spectrophotometer in the 200nm – 1100nm range from which film transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, dielectric constants and band gap, Eg were deduced. Reflectance is defined in terms of absorbance, A and transmittance, T knowing that energy is always conserved as:

$$R = 1 - A - T \quad (1)$$

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Absorption coefficient,  $\alpha$  is related to T as:

$$\begin{aligned}\alpha &= \ln\left(\frac{1}{T}\right) (\mu\text{m}^{-1}) \\ &= \ln\left(\frac{1}{T}\right) \times 10^{-6} (\text{m}^{-1})\end{aligned}\quad (2)$$

The band gap,  $E_g$  of thin film semiconductor, absorption coefficient,  $\alpha$  and the incident energy  $h\nu$  have a well established relation [10-14] as:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (3)$$

where A is a constant,  $n = \frac{1}{2}$  for CdS [15]. Hence a linear graph of  $(\alpha h\nu)^2$  versus  $h\nu$  shows  $E_g$  as intercept on  $h\nu$  axis.

The reflectance of an absorbing surface of refractive index,  $n$  and extinction coefficient,  $k$  in air for normal incidence is given as [16]:

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

If  $k^2 \ll (n-1)^2$  as is this case of thin film semiconductors and all insulators:

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

Hence,

$$n = \frac{(1+R)^{\frac{1}{2}}}{(1-R)^{\frac{1}{2}}} \quad (9)$$

The extinction coefficient,  $k$  is deduced using the well-known relations [13]:

$$k = \frac{\alpha \lambda}{4\pi} \quad (10)$$

$$n_c = n - ik \quad (11)$$

Also, 
$$n_c = \frac{c}{v} \quad (12)$$

where  $c$  is the speed of light in vacuum and  $v$  is the speed of the electromagnetic wave in the medium. Semiconducting or insulating thin film has dielectric properties and we can define its complex dielectric constant by:

$$\varepsilon = \varepsilon_r + \varepsilon_i \quad (13)$$

where  $\varepsilon_r$  is the real part while  $\varepsilon_i$  is the imaginary part, but:

$$\begin{aligned}\varepsilon &= (n + ik)^2 \\ &= n^2 - k^2 + 2ik\end{aligned}\quad (14)$$

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Hence,

$$\epsilon_r = n^2 - k^2 \quad (15)$$

and

$$\epsilon_i = 2ki \quad (16)$$

Proton induced X-ray emission (PIXE) technique from a Tandem Accelerator (Model 55DH 1.7MV-NEC) was applied to obtain Rutherford backscattering elemental characterization of films. This deciphered the elements in the substrates and deposits as well as the atomic percentages of such elements. It also obtained the substrate and deposit thicknesses.

## III. RESULTS AND DISCUSSION

### 3.1. X-ray Diffraction Result

The X-ray pattern obtained for the typical sample of the thin film at bath pH of 9.5 was as shown in Fig. 1. A prominent peak manifest at  $2\theta$  value of approximately  $26^\circ$  and correspond to (1 1 1) plane which JCPDS card No. 80-0019 revealed as hexagonal CdS crystal

### 3.2. Rutherford Backscattering Results

The RBS analysis result deciphered the elements to be Pb, Cd and S in elemental abundances of 1.86%, 54.60% and 43.54% respectively. The low relative abundance of Pb with respect to Cd, that is, 3.41% could explain that lead appeared only as dopant impurity that would not alter a known hexagonal phase of cadmium sulphide semiconductor. The alteration of pH of bath within normal range of 9.0 – 10.4 did not visibly alter film crystallinity and composition but beyond a pH of 10.4, there was no precipitation and hence the RBS result did not reveal any deposit for sample 16E. Beyond 10.4, it is expected that the pH value of the bath affected ionization of reacting solutions such that ionic product no longer exceeded the solubility product.

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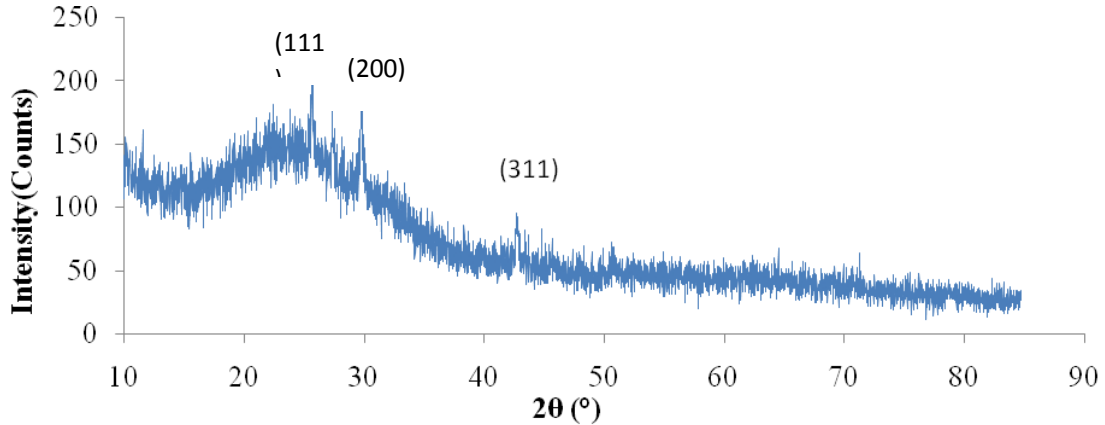


Fig. 1: XRD pattern of Pb-doped CdS thin film at pH of 9.5

3.3 Spectral Analysis Results

The absorption spectra was as shown in Fig. 2 while those of transmittance, reflectance, refractive index, extinction coefficient, absorption coefficient and dielectric constant are as shown in Figs. 3, 4, 5, 6, 7, 8 and 9 respectively for thin films grown from baths of pH 9.0, 9.3, 9.5 and 10.4. It could therefore be seen that absorbance at visible region varied from 0.15 to 0.35, with the trend being that absorbance increased with bath pH. The absorbance decreased to a very low level of about 0.06 for near infra-red. All films deposited completely absorbed ultra violet waves. Refractive index converged to the value of 2.6 for high energy waves but depended largely on bath pH for visible ranges (Fig. 5) the trend being that refractive index decreased when pH of bath increased. Rahul, et al. [17] observed that both refractive index and conductivity of CBD polyaniline thin film decreased when the pH of bath increased.

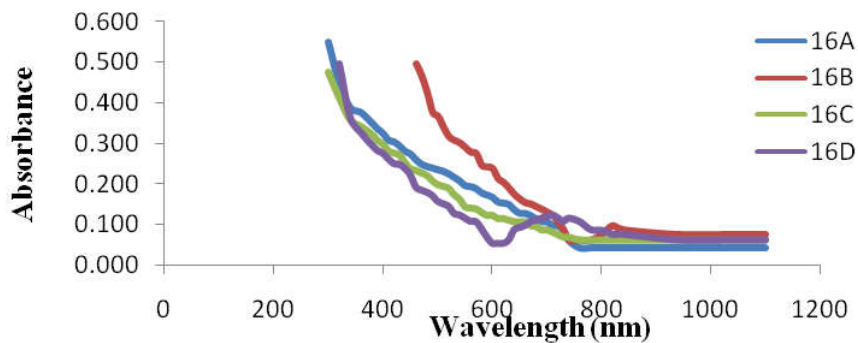


Fig. 2: Spectral absorbance of cadmium lead sulphide grown in various pH media.

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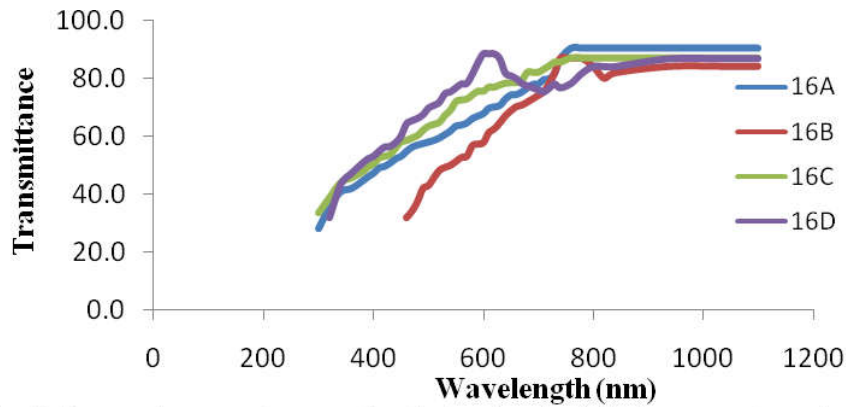


Fig. 3: Spectral transmittance of cadmium lead sulphide grown in various bath pH.

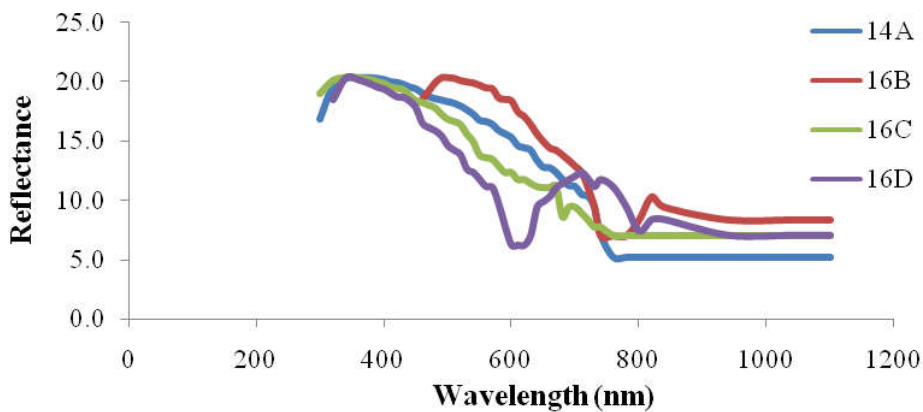


Fig. 4: Spectral reflectance of cadmium lead sulphide grown in various bath pH.

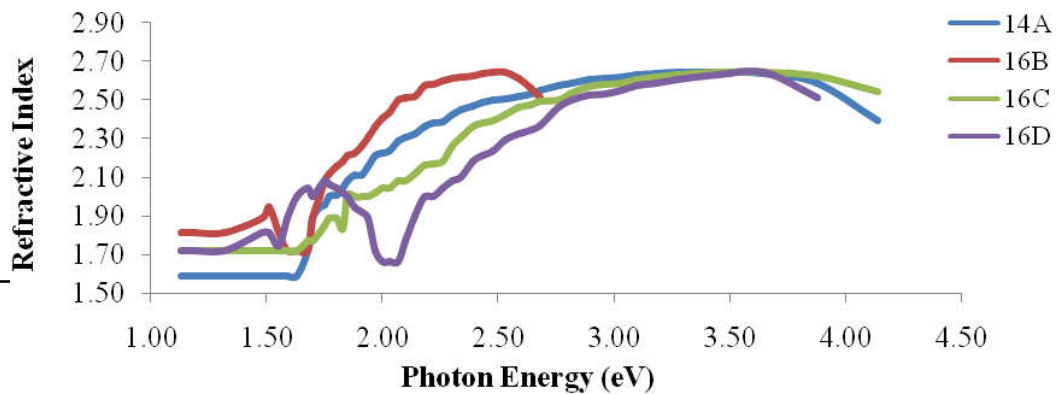


Fig. 5: Refractive index of cadmium lead sulphide grown in different bath pH

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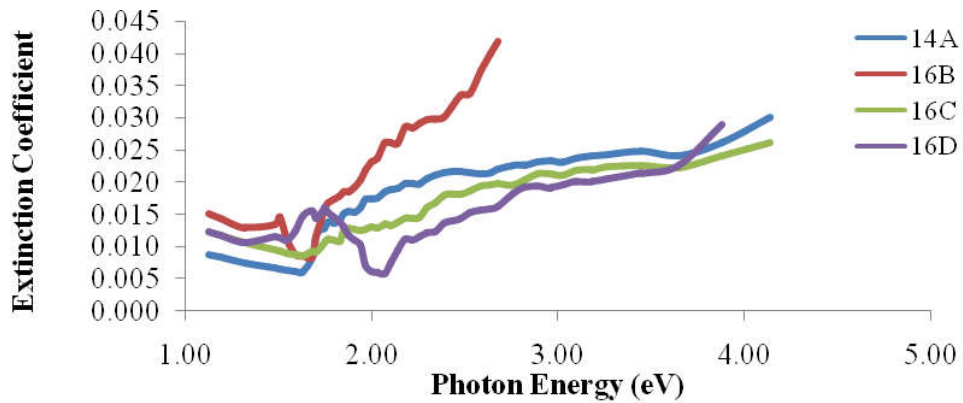


Fig 6: Extinction coefficient of cadmium lead sulphide grown in various bath pH.

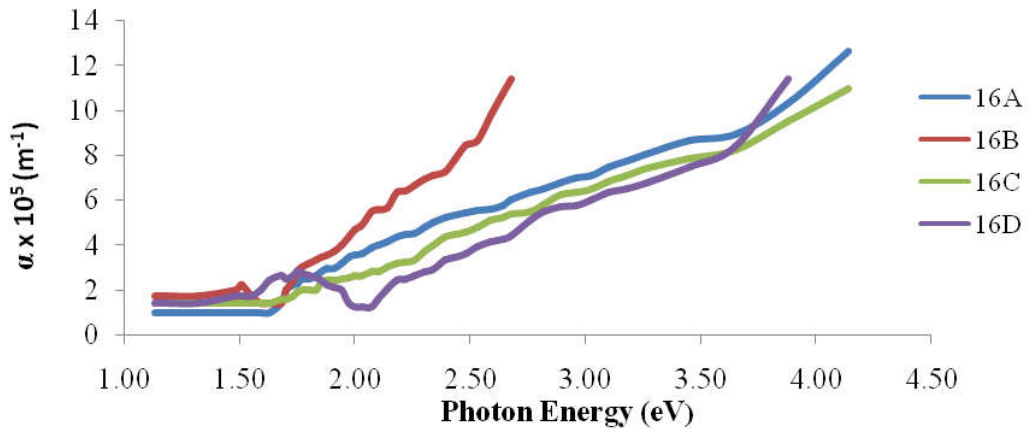


Fig. 7: Absorption coefficient of cadmium lead sulphide grown in various bath pH.

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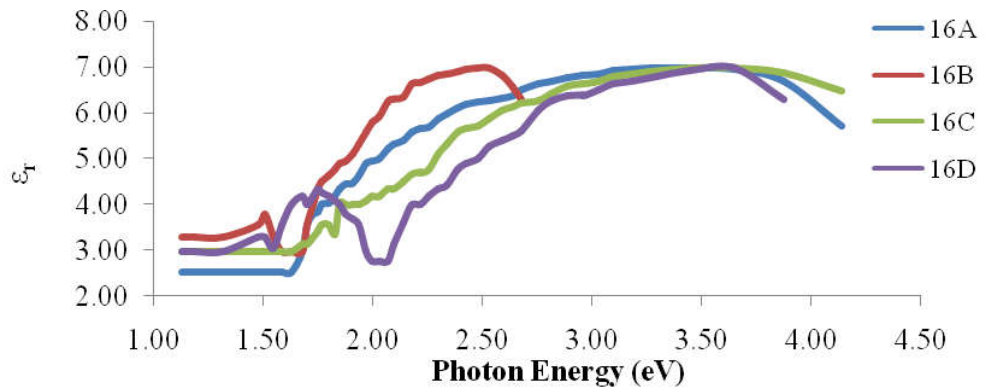


Fig. 8: Real dielectric constant of cadmium lead sulphide grown in various bath pH

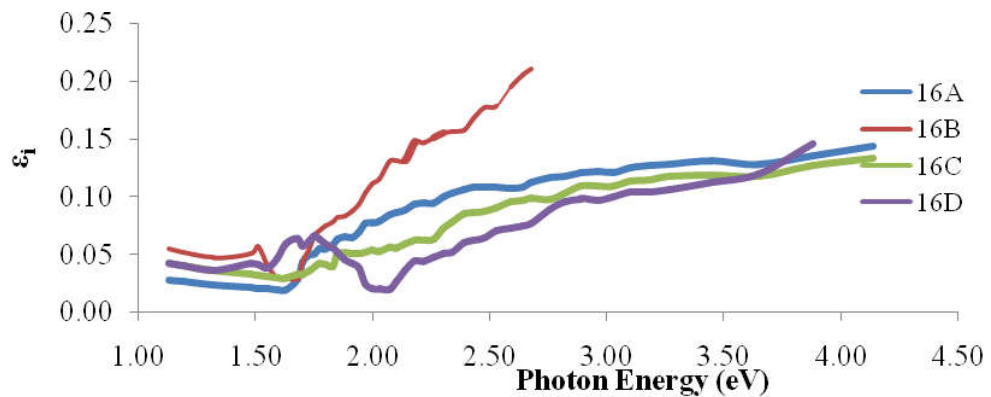


Fig. 9: Imaginary dielectric constant of cadmium lead sulphide grown in diff. bath pH



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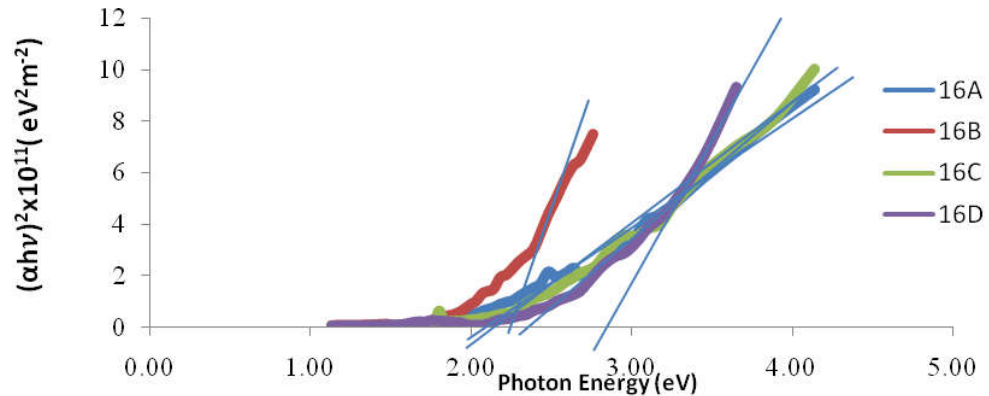


Fig. 10:  $(\alpha h\nu)^2$  vs photon energy for cadmium lead sulphide grown in various bath pH.

Fig. 10 shows the plot of  $(\alpha h\nu)^2$  ( $\text{eV}^2\text{m}^{-2}$ ) versus photon energy,  $h\nu$  (eV), the absorption coefficient,  $\alpha$  having been obtained from the spectrophotometric analysis results. As usual, and from equation 3, the extrapolation of the linear portion of the graph to the horizontal axis revealed the band gap for the thin film deposit. In the regions of low photon energies, it could be seen that the graphs were not generally linear since other absorptions processes different from inter band transition dominated. Equation 3 in which the plots were based was derived considering only inter band electronic transitions. Fig. 10 shows that bath pH indeed affected the band gap of semiconductor with the gap size decreasing with pH increase. The summary of such band gaps was as presented in Table 1. It was noted that beyond pH value of 10.4, precipitation of monomers were ineffective and stable films of measurable band gap could not be produced. These observations were consistent with the findings of Ersin and Osman [18] who determined that band gap of chemical bath deposited CdS thin films decreased with bath pH increase. They also determined that the film surface became rougher with such increase.

**Table 1: Band Gaps Of Different Pb-Doped Cds Thin Films Grown In Different Bath Ph.**

Thin film	Bath pH	Eg (eV)
16A	9.0	2.82
16B	9.3	2.30
16C	9.5	2.20
16D	10.4	2.18
16E	10.8	-

**IV. CONCLUSION**

Pb-doped cadmium sulphide thin films have been grown in chemical baths of different levels of acidity and the effect on optical properties as well as band gap studied. Rutherford backscattering analysis done on the films revealed hexagonal structure with (111) reflection plane. Growth of different grades of films were possible at bath pH of 9.0 – 10.4 beyond which no orderly precipitations and crystallizations became possible. The absorbance was found to increase with pH rise while the refractive index as well as the band gap was found to

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decrease with pH rise. The increase in pH of bath from 9.0 to 10.4 led to decrease in band gap but increase beyond 10.4 was not advisable.

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