Optical and Optoelectric Properties in PbCdS Ternary Thin Films Deposited by CBD

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Abstract

$Pb_xCd_{1-x}S$ films have been prepared in the composition range of $0.05 \leq x \leq 0.25$ by using a chemical bath deposition growth technique under optimum conditions to deposit good photo response. X-ray diffraction study results show that the films are of PbS-CdS composite with individual CdS and PbS planes. The films exhibited two direct band gaps, 2.4 eV belongs to CdS, and the second varies continuously from 2.4eV to 1.3eV. The surface morphology of the films is smooth with crystallite of increasing grain size with increasing the mole fraction (x). The decrease in the band gap with increase in lead concentration suggests that the Composite of PbS (Eg=0.41eV) with CdS (Eg=2.4eV).

Keywords: Ternary Thin Films Chemical Bath Deposition

الخصائص البصرية والكهروبصرية للاغشية الثلاثية PbCdS المرسبة بطريقة الحمام الكيميائي

الخلاصة

تم ترسيب غشاء رقيق لمركب($Pb_x\ Cd_{1-x}\ S$) وبتراكيز تتراوح مابين ($x \leq 2.5$ ≤ 0.05) باستخدام تقنية الترسيب بالحمام الكيمياوي وباعتماد الضروف المثلى للحصول على أستجابية ضوئية جيدة. قياسات حيود الأشعة السينية اضهرت إن المركب (PbS-CdS) يشتمل على مستويات (PbS و CdS) المنفردة .اضهرت الأغشية قيمتين لفجوة الطاقة المباشرة (eV 2.4) عائدة لكبريتيد الرصاص و الثانية تتغير من (2.4 eV) إلى (1.3 eV) . سطح الأغشية كان صقيل مع زيادة في الحجم الحبيبي بزيادة الكسر المولي (x). النقصان بقيمة فجوة الطاقة مع زيادة تركيز الرصاص يؤدي إلى تكوين مركب من (CdS) و (PbS) .

1- Introduction

There is considerable interest in the deposition of ternary derivatives material, due to the potential of tailoring both the lattice parameters and the band gap by controlling depositions parameters [1, 2]. Many techniques have been successfully employed for these purposes: CVD [3], successive ionic layer and reaction (SILAR) [4], and sol-gel methods [5]. Many researcher have deposited ternary derivatives material in thin films $Cd_{1-x}\ Zn_xS$ [6], PbS-Cu_xS [7], Bi_2S_3-Cu_xS [8],CdS-Cu_xS[9] and Bi_2Se_3-Sb_2Se_3[10], by using chemical bath deposition (CBD), which meets the criteria of cheap reproducible and relatively simple process. They even offer an opportunity for a 'do-it –yourself ' approach to the production of device and coating [1].

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Thin films of lead and cadmium sulfate are a prospective photo voltaic material as its variable band gap could be adjusted to match the ideal band gap (~1.5 eV) required for achieving a most efficient solar cell [11]. Extensive studies of the electrical and optical properties of $Pb_{1-x}Cd_xS$ have been made by many researchers [11-17]. These films generally have been prepared by chemical bath deposition from solution with high lead molar fraction in solution ($0 \leq x \leq 0.2$).
Among the numerous papers, the investigation by Skyllas-Kazacos et al [18] is the only one which gives detailed data on high cadmium mole fraction in solution. Their analysis show that a monotonic decrease in the band gap of the semiconductor alloys was obtained as the Pb ratio was increased, and the composition of was films very close to the composition of the deposition mixture .

In this paper a more comprehensive investigation of the optical and photoconductive properties of $Pb_xCd_{1-x}S$ have been made, experiments have at present been focused on high cadmium composition.

2- Experimental:

The starting materials in the preparation of lead cadmium sulfate ($Pb_xCd_{1-x}S$) includes cadmium acetate [$Cd(CH_3COO)_2.2H_2O$], Lead acetate [$Pb(CH_3COO)_2.2H_2O$], ammonia (NH_3), thiourea [$(NH_2)_2.CS$] and distilled water . The lead acetate was the source of cation (Pb^{2+}), cadmium acetate was the source of another cation (Cd^{2+}), thiourea was the source of an ion (S^{2-}). NH_3 was used to provide an alkaline medium needed for the maximum growth.

The deposition steps start with the mixing of lead and cadmium acetate with amonuia.The solution was made up to 100ml with distilled water and heated up to 50˚ C .The double glass substrate was immersed vertically and then 20ml thiourea was added drop by drop and the bath was slowly heated up to 75 ˚C and kept at this temperature for 75 minutes, substrates were taken out, washed with distilled water and dried. The substrates in our study were ultrasonically cleaned glass slide.

The crystal structure of the films was determined by XRD (using Cu Kα radiation λ=1.54A˚).The film thickness (d) was measured by interference microscope. In a single dip, the thickness obtained was ~40nm.To get higher thickness; the films were dipped in a fresh bath two times. The final thickness was 0.16μm.Optical transmission (T) measured using a Cecile CE 7200 double beams Spectrophotometer by Aquarius Company in the range of 350-900 nm.

Substrate absorption was made by placing an identical uncoated glass substrate in the reference beam. The transmition was directly measured while absorption coefficient (α) and band gap (E_g) were obtained by computations using [19-20]:

$$a = \frac{1}{d} \ln \frac{1}{T}$$

$$\alpha h\nu = A\,(h\nu - E_g)^{n} \qquad \ldots\ldots(1)$$

Where d is the film thickness and A is a constant. N has different values depending on the absorption process>

3- Result and Discussion

Specular and excellent adhesive thin films were grown by CBD growth technique.

3-1 Structural and Morphological Investigation

The structural properties of the films were studied using XRD.The XRD results for films with different composition show that the films are composite and polycrystalline .Figure (1a-e) shows the scan over a range of $10^{\circ} \leq 2\theta \leq 90^{\circ}$, diffrograms reveal the polycrystalline nature of the films, irrespective of Pb mole fraction over the whole range. Both CdS and PbS exhibit hexagonal wurtzite and cubic zinc blend structure, such results are reported by Deshmukh. et al (10) . Increasing the mole fraction of lead was accompiend by the appearance of cadmium oxide planes. The dominant peaks are (111), (200). Additionally, there existed plane at $2\theta = 89^{\circ}$ which do not belong to either PbS or CdS. Thus, there must be solid solution formation of the kind ($Pb_xCd_{1-x}S$) in the composition .Table (2) lists the measured 2θ , hkl, d values for the samples.

Polycrystalline texture has smooth surface and clearly defined grains for all samples. The optical micrographs (fig.2 a-e) show a globular structure composite of two single types of small crystals. It is seen that the average crystallite size went on increasing with increasing Pb percentage in the bath.

3-2 Optical Properties

The optical transmition and absorption spectra of various deposited films were obtained and analyzed in wavelength from 350 - 900 nm at room temperature. The samples show a high coefficient of absorption ($\alpha > 10^5 cm^{-1}$ for $\lambda <$ 500 nm), (10^4 cm^{-} for $\lambda >$ 500 nm) . The variation in the absorption coefficient with the film composition is shown in Fig (3 a-e). It is clear that the value of α increases with increasing photon energy. Absorption coefficient is related to the photon energy by the equation (1). It was found that n=1/2 is the best fit for our result (direct allowed transition). The plot of $(\alpha h\nu)^2$ versus $h\nu$ was concentrated to determine the optical gap. These are shown in Fig (4 a-e) for representive samples. The plots exhibit two well defined absorption edge for all values of (x). The first absorption edge at (2.4eV) corresponds to the fundamental optical transition in CdS. The fundamentals optical transitions of PbS (0.41eV) is not observed in these films. It seems that the band gap 'corresponding to the low photon energy' decreased monotonically with the film composition parameters x , as shown in Fig(5). The optical band gap decreases from 2.4 eV for CdS to less than 1.3eV for the Pb_xCd_{1-x} S thin films. It is found that the band gap (Eg) in electron volts decreases with x as:

$$E_g (Pb_x Cd_{1-x} S) = E_g (CdS) - 4.6x$$

The spectral photo current characteristic of each of the alloy films was tested, and the result are shown in Fig (6 a-e) increasing the lead percentage gives rise to increase in photo current over the entire investigated spectral range. The variation in the photo current with alloy composition is very significant with a Pb mole fraction of (15-20 %) Fig (7). It can also seen from these figures that the maximum in the photo current appears at energy greater than the band gap of the films. In general, photo current is directly related to the photo excitation rate, the change in life time of the career and the change in mobility. Since in the percent case all films were exposed to the same light, it is expected that a longer life time

in the (15-20 %) mole fraction is responsible for the observed higher photo current.

4. Conclusions

1. The films consist of multicomponent composite structures for the rang of composition parameter studied as suggested by structural studies.
2- The optical band gap of $Pb_xCd_{1-x}S$ lies within the band gap of PbS and CdS.
3- At a given composition in the range of 0.05- 0.2 high photo responsivity. would be achieved.
4-The influence of Pconcentration in the growth solution on the formation CdO shows that beyond $x \geq 0.15$ CdO starts to deposit.

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Table (1) summarizes the deposition condition

Material	Molarities	Volume (ml)
$Cd(CH_3COO)_2.2H_2O$	0.1	10
NH3	6	35
thiourea	1	20
$Pb(CH_3COO)_2.2H_2O$	0.1	(0.5, 1.1,1.75,2.5,3.3)

Table (2) Analysis of the X R D study of ($Pb_xCd_{1-x}S$) thin films for $0.05 \leq x \leq 0.25$

Composition	*d(Å) observed*	*d (Å) ASTM*	*2q degree*	*hkl planes*				
				CdS (C)	*CdO (C)*	*CdS (H)*	*PbS (C)*	*PbO (T)*
$Pb_{0.25}Cd_{0.75}S$	3.356	3.36	26.5	111	-	-	-	-
	2.349	2.349	38.3	-	200	-	-	-
	2.072	2.068	43.6	-	-	110	-	-
	1.757	1.753	51.9	311	-	-	-	-
	1.582	1.581	58.2	-	-	202	-	-
	1.478	1.482	62.8	-	-	-	400	-
	1.324	1.327	71.0	-	-	211	-	-
	1.226	1.226	77.8	-	-	-	-	222
	1.188	1.186	80.7	422	-	-	-	-
	1.150	1.158	84.0	-	-	213	-	-
$Pb_{0.2}Cd_{0.8}S$	3.432	3.429	25.9	-	-	-	111	-
	2.90	2.90	30.8	200	-	-	-	-
	1.714	1.714	53.3	-	-	-	222	-
	1.456	1.453	63.8	400	-	-	-	-
	1.421	1.416	65.5	-	311	-	-	-
	1.224	1.224	77.9	-	-	204	-	-
$Pb_{0.15}Cd_{0.85}S$	3.355	3.360	26.5	111	-	-	-	-
	2.342	2.349	38.4	-	200	-	-	-
	2.094	2.099	43.1	-	-	-	220	-
$Pb_{0.1}Cd_{0.9}S$	3.352	3.360	26.5	111	-	-	-	-
	1.474	1.484	62.9	-	-	-	400	-
$Pb_{0.05}Cd_{0.95}S$	3.58	3.58	24.8	-	-	100	-	-
	1.668	1.679	55.0	-	-	004	-	-
	1.389	1.398	67.2	-	-	203	-	-

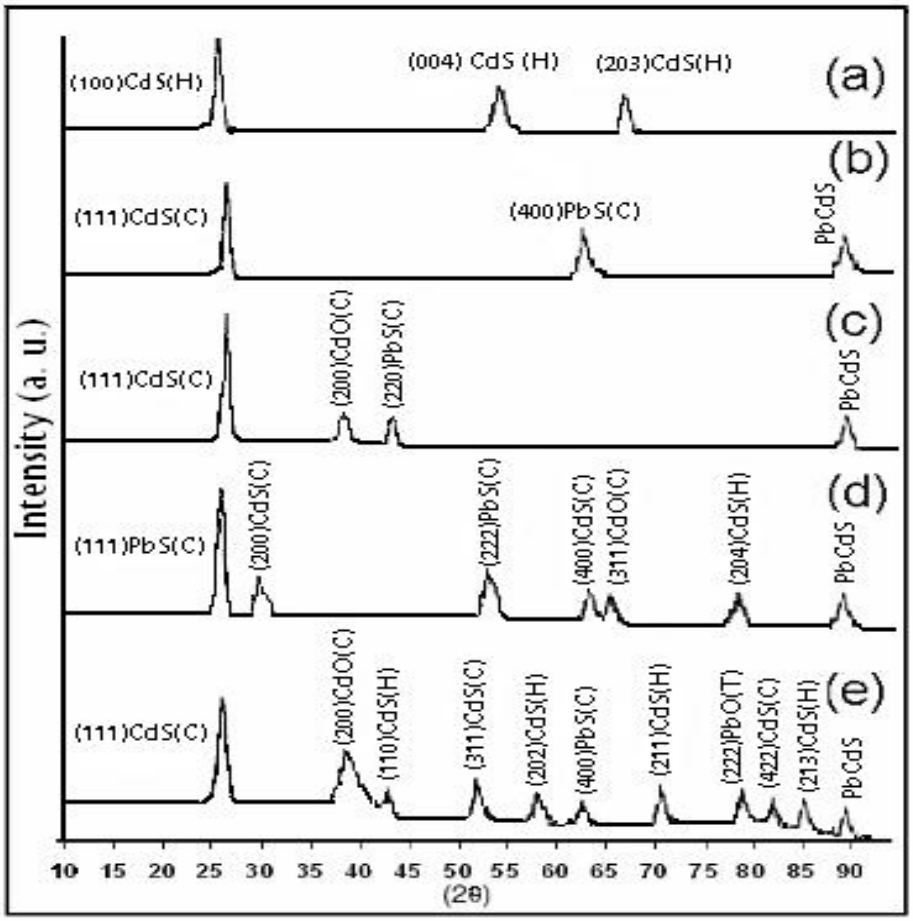

Figure (1) X-Ray diffraction patterns and Miller indices of (Pb_xCd_{1-x} S) thin films: (a) x=0.05, (b) x=0.10, (c) x=0.15, (d) x=0.20, (e) x=0

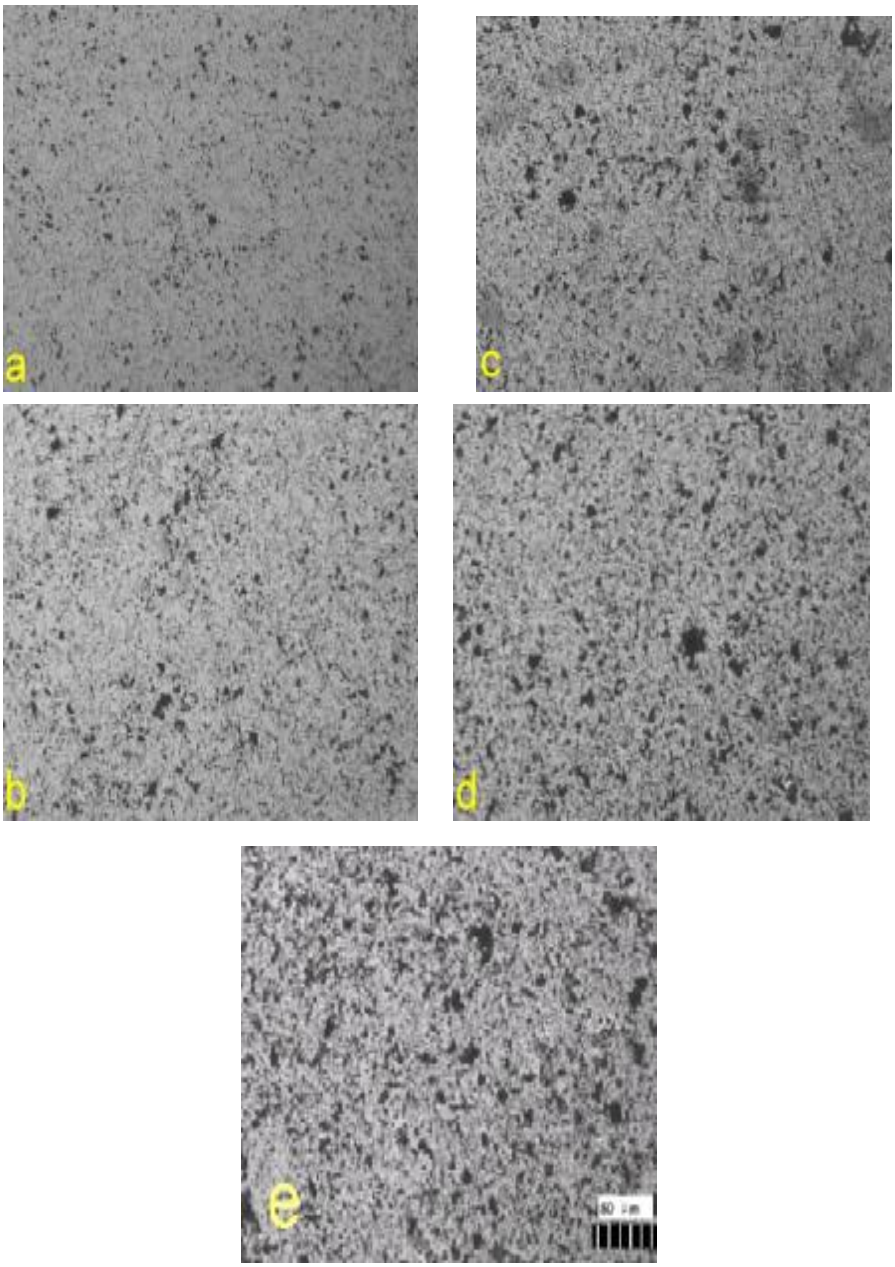

Figure (2) Optical Micrograph (X300) of five typical composites (Pb_xCd_{1-x} S) thin films: (a) x=0.05, (b) x=0.10, (c) x=0.15, (d) x=0.20, (e) x=0.

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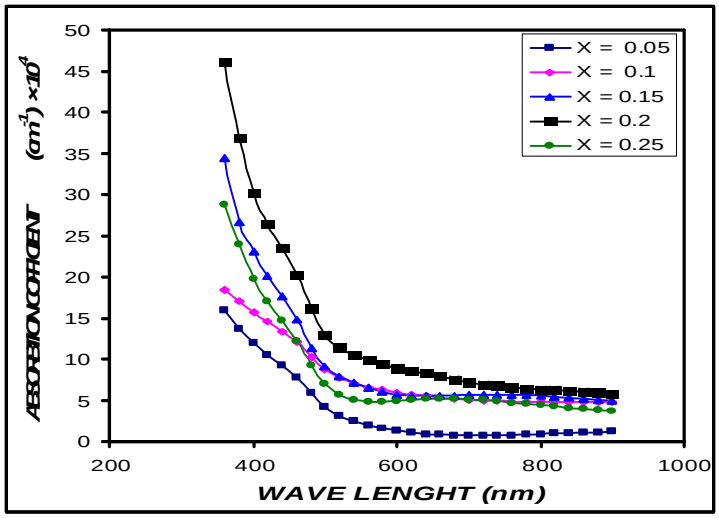
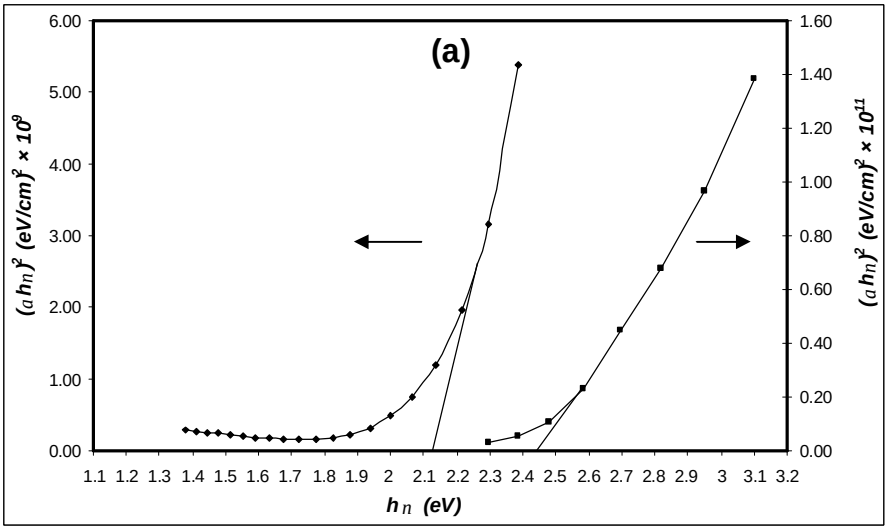


Figure (3) Plots of Spectral absorption coefficient of $Pb_xCd_{1-x}S$(a) x= 0.05, (b) x=0.1,(c) x= 0.15, ,(c) x= 0.15,(d) x= 0.2,(e) x= 0.25



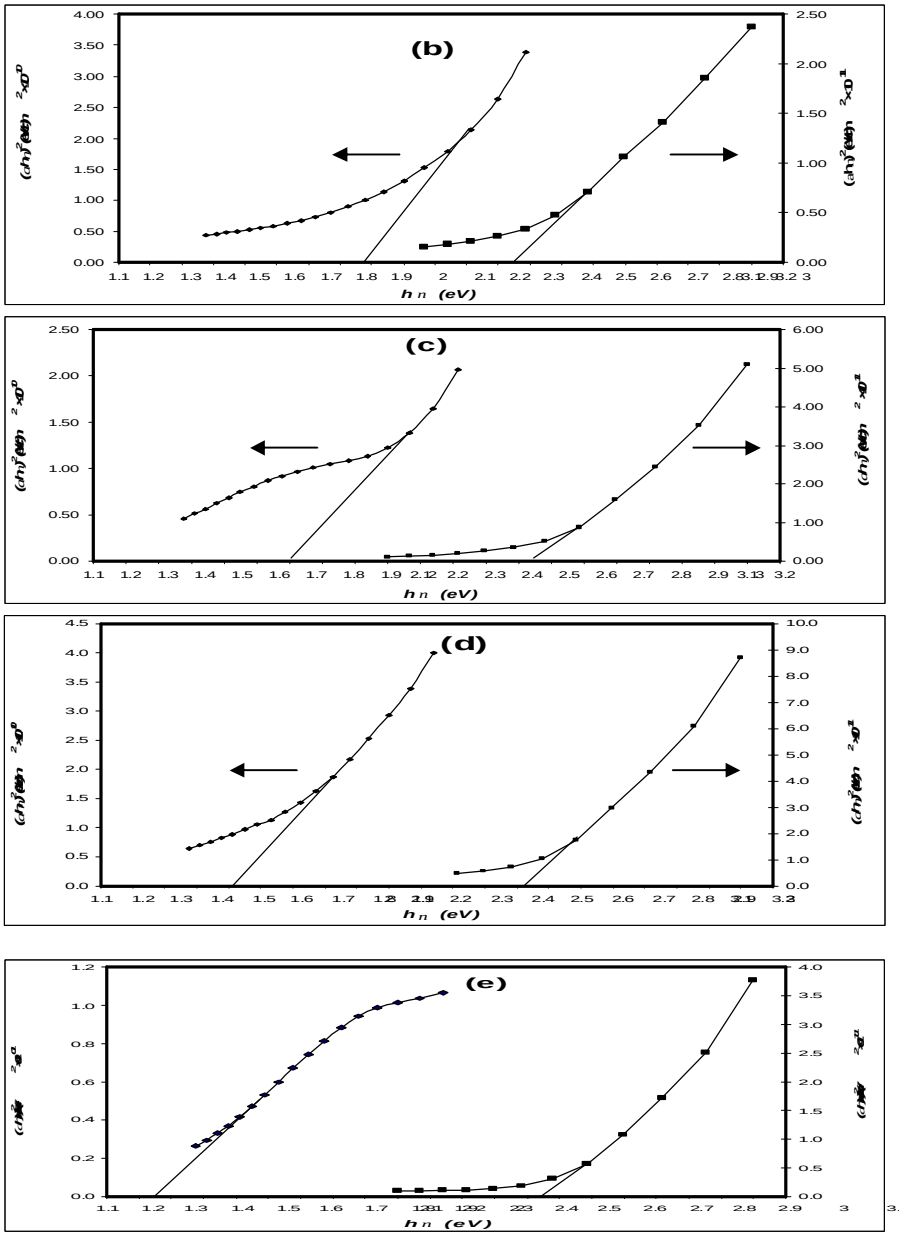


Figure (4) Photon energy dependences of the absorption coefficient squared for ($Pb_x Cd_{1-x} S$): (a) x = 0.05 (b) x = 0.1 (c) x = 0.15 (d) x = 0.2 (e) x = 0. 25

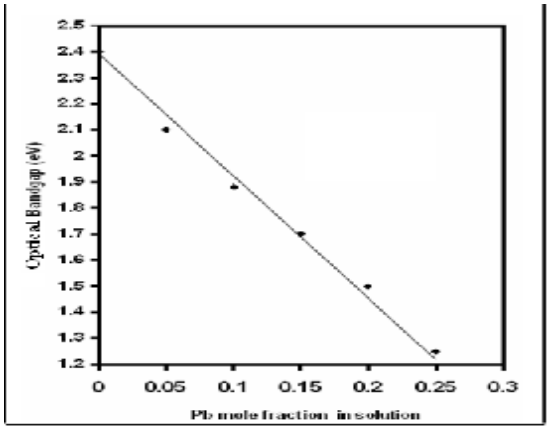


Figure (5) The variation in band gap with Pb concentration.

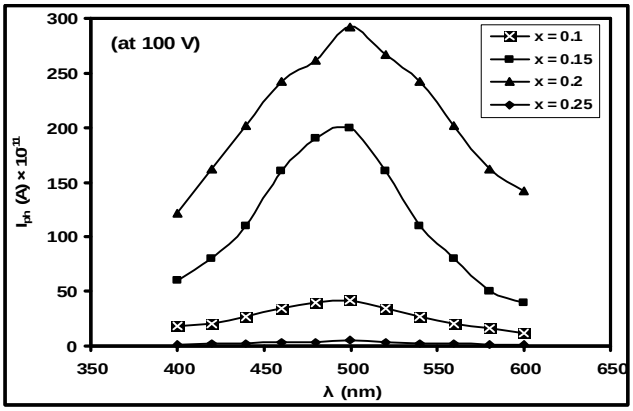


Figure (6) Spectral photocurrent of our $Pb_xCd_{1-x}S$ films measured at 100V

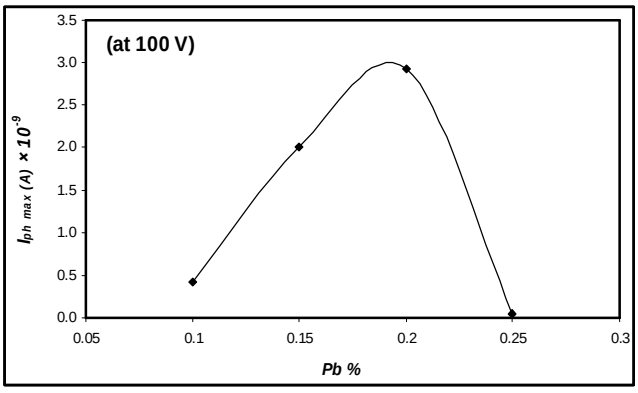


Figure (7) Relation between the maximum photocurrent and mole fraction of lead