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

Modaffer. A. Mohammed*, Ali M. Mousa*, and J. P. Ponpon**

***Abstract*—$Pb_xCd_{1-x}S$ films are prepared in the composition range of $0.05\leq x\leq 0.25$, using a chemical bath deposition growth technique under optimum conditions amide at realizing good photo response. The x-ray diffraction results show that the films are of PbS-CdS composite with individual CdS and PbS planes. The films exhibit two direct band gaps, 2.4 eV attributed to CdS, while the other varies continuously from 2.4 eV to 1.3 eV. The films surface morphology is smooth with crystallite, whose grain size increases with increasing mole fraction (x). The decrease in band gap with increase in lead concentration suggests inter-metallic compound of PbS (Eg=0.41 eV) with CdS (Eg=2.4 eV)**

***Index Terms*—Chemical bath deposition, $Pb_xCd_{1-x}S$ film, optical properties**

I. INTRODUCTION

There is considerable interest in the deposition of ternary derivative 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], 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].

Thin films of lead and cadmium sulfate are a promising photo voltaic materials as their 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 shows that a monotonic decrease in the band gap of the semiconductor alloys was obtained as the Pb ratio was increased, and the composition of films was very close to the composition of the deposition mixture.

In this paper a more comprehensive investigation of the optical and photocond- uctive properties of $Pb_xCd_{1-x}S$ on high cadmium composition.

II. EXPERIMENTAL

The starting materials in the preparation are of lead cadmium sulfate ($Pb_xCd_{1-x}S$) includes cadmium acetate $[Cd(CH_3COO)_2.2H_2O]$, lead acetate $\mathbf{[Pb(CH_3COO)_2.2H_2O]}$, ammonnia ($NH_3$), 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+}), are thiourea was the source of anion (S^{3-}). NH_3 was used

Manuscript received May 11, 2009; revised Jun. 11, 2009.
* Material Research Unit, Department of Applied Sciences University of Technology P.O.box 3051, Baghdad, Iraq
** InESS, umr 7163 CNRS/Universite Louis Pasteur B.P.20, F67037, Strasbourg, France
E-mail : alzuhery2000@yahoo.com

Table 1. summarizes the deposition condition

Material	Molarities	Volume
$Cd(CH_3COO)_2.2H_2O$	0.1 M	10 ml
NH_3	6 M	35 ml
Thiourea	1 M	20 ml
$Pb(CH_3COO)_2.2H_2O$	0.1 M	(0.5, 1.1, 1.75, 2.5, 3.3) ml

to provide an alkaline medium needed for maximum growth.

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

The crystal structure of the films was determined by XRD (using Cu Kα radiation λ=1.54 A°).The film thickness (d) was measured by interference microscope. In a single dip, the thickness obtained was ~40 nm.To get higher thickness; the films were dipped into a fresh bath four times. The final thickness was 0.16 μ.Optical transmission (T) was measured using a double beam spectrophotometer (PYE UNICM 8-100) over the spectral 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:

$$\alpha = 1/d \ln 1/T$$
$$\alpha h\nu = A (h\nu - E_g)^{n}$$

where d is the film thickness and A is a constant.

III. Results and Discussion

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

1. Structural and Morphological Investigation

The structural properties of the films were studied

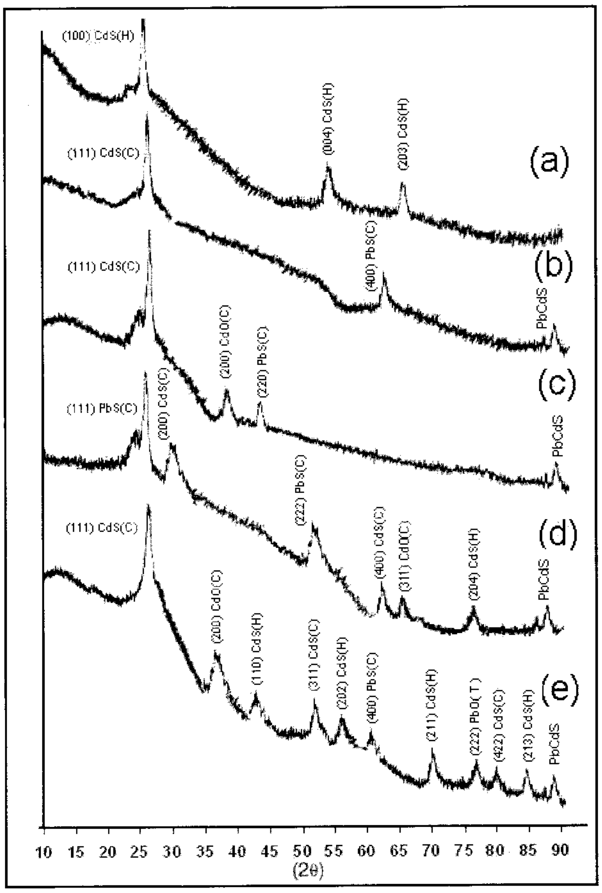


Fig. 1. X-Ray diffraction patterns and Miller indices of $Pb_xCd_{1-x}S$ (a) x= 0.05, (b) x=0.1,(c) x= 0.15,(d) x= 0.2,(e) x= 0.25.

using XRD.The XRD results for films with different composition show that the films are polycrystalline. Fig. 1 (a-e) shows the scan over a range of 10 °≤ 2θ ≤ 90 °, diffractograms 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 lead oxide planes. The dominant peaks are (111), and (200). Additionally, there exist a plane at 2θ = 89°, which does not belong to either PbS or CdS. Thus, there must be intermetallic formation of the kind ($Pb_xCd_{1-x}S$) in the composition. Table 2 lists the measured 2θ, hkl, d values for the samples. The lattice parameters are evaluated from hkl and 2θ values. Polycrystalline texture has smooth surface and is clearly defined by grains for all samples. The optical micrographs Fig. 2 (a-e) show a globular structure composite of two single types of small micro crystals. It is seen that the average crystallite size keept

Table 2. analysis of the X R D study of ($Pb_xCd_{1-x}S$) for $0.05 \le x \le 0.25$

Composition	*d(A°) observed*	*d (A°) ASTM*	*2θ 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	-	-

increasing with increasing Pb percentage in the bath.

2. Optical Properties

The optical transmition and absorption spectra of various deposited films were obtained and analyzed over wavelength range from 350-900 nm at room temperature. The samples show high coefficient of absorption ($\alpha > 10^5$ cm^{-1} for $\lambda < 500$ nm), and (10^4 cm^{-1} 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 photon energy by the following equation

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

where A is constant depending on transition probability, E_g is the band gap of the material and n has different values depending on the absorption process. It was found that n=1/2 is the best fit for our result. The plot of $(\alpha h\nu)^2$ versus hν was made to determine the optical gap. These are shown in Fig. 4 (a-e) for representive samples. The plots exhibit two well defined absorption edges for all values of (x). The first absorption edge at (2.4 eV) corresponds to the fundamental optical transition in CdS. The fundamental optical transitions of PbS (0.41 eV) is not observed in these films, presumably because of complete alloying of PbS with CdS forming a uniphase ternary inter-metallic compound of the type $Pb_xCd_{1-x}S$.

It seems that the band gap 'corresponding to the low photon energy' decreased monotonically with the film composition parameter x, as shown in Fig. 5 (a-e). The band gap decreases from 2.4 eV for CdS to less than 1.3 eV for the Pb_xCd_{1-x} S inter-metallic. Thus, decrease in optical gap is mainly attributed to the alloying of PbS with CdS, in agreement with the behavior shown pre

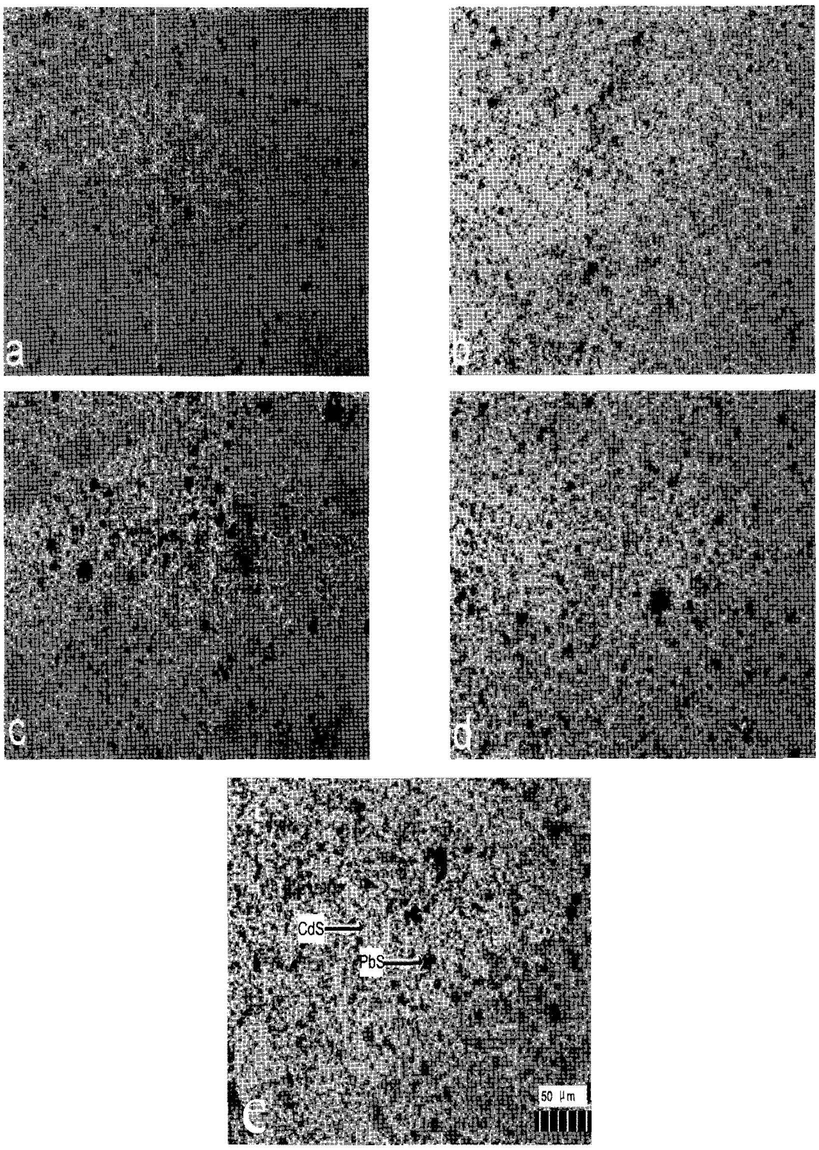


Fig. 2. Optical Micrograph (X300) of five typical composites (Pb_xCd_{1-x} S): (a) x=0.05, (b) x=0.10, (c) x=0.15, (d) x=0.20, (e) x=0.25.

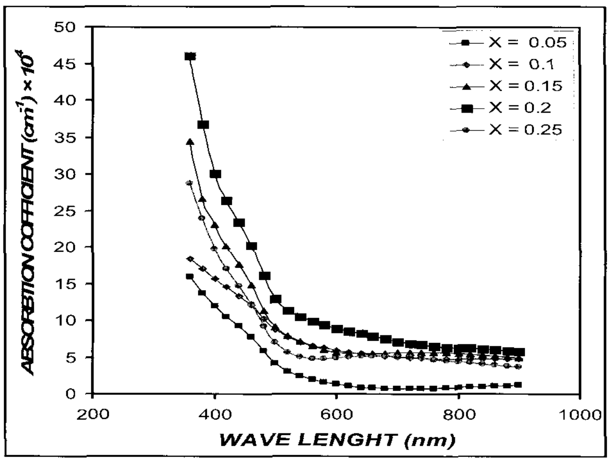


Figure (3)

Fig. 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.

viously [18]. 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 characteristics of each of the inter-metallic films were tested, and the results are shown in Fig. 6 (a-e). There was no significant difference with the spectral response. All photocurrent spectra have the following common features: A peak response exists at λ = 0.5-0.52 μm. Increasing the lead percentage gives rise to increase in photo current over the entire investigated spectral range. The increase in photocurrent is probably due to the excess carriers in the grains introduced by the absorption of above energy gap radiation and the

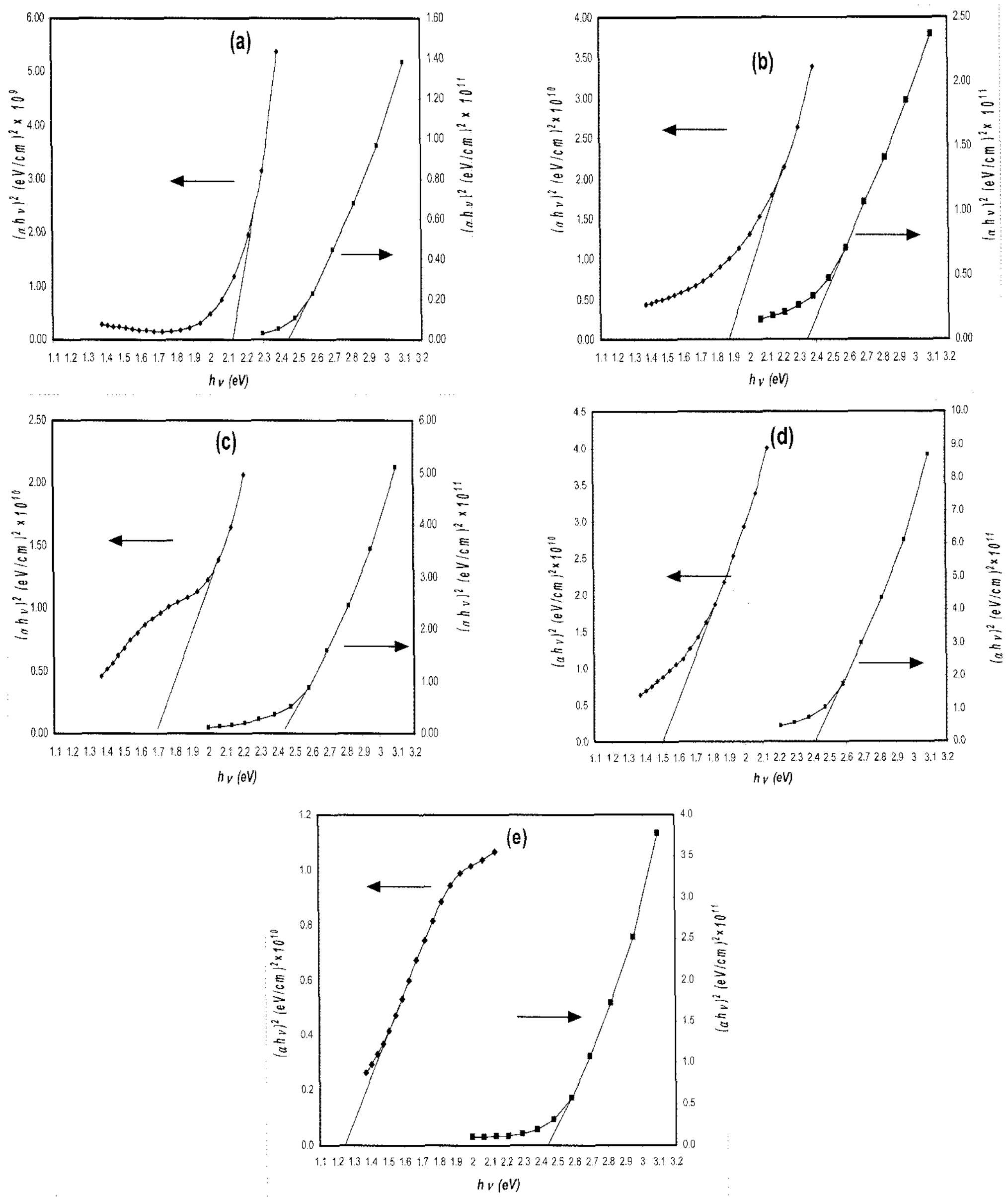


Fig. 4. Plots of $(\alpha h\nu)^2$ versus hν for films prepared with different composition (a) x= 0.05, (b) x=0.1,(c) x= 0.15, (c) x= 0.15, (d) x= 0.2, (e) x= 0.25.

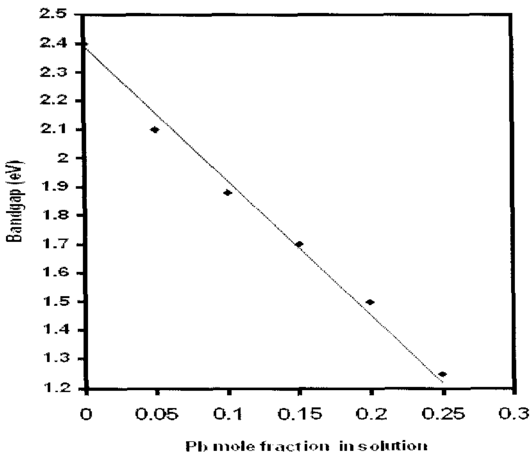


Fig. 5. The variation in band gap with Pb concentration.

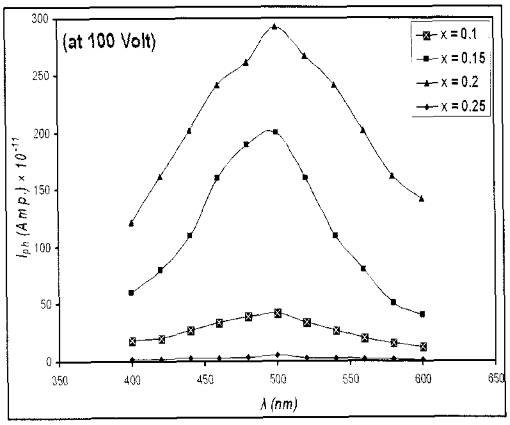


Fig. 6. Spectral photocurrent of our $Pb_xCd_{1-x}S$ Films measured at v = 100 v.

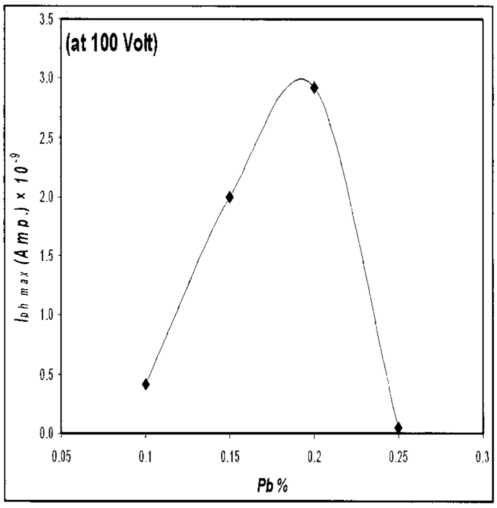


Fig. 7. Relation between the maximum photocurrent And mole fraction of lead.

lowering of potential barriers at grain boundaries [19].

The variation of the photocurrent is clearly connected with the Pb mole fraction which directly modifies the optical properties. Fig. 3 actually indicates an increase of the absorption coefficient with lead concentration up to 20% Pb, followed by a significant decrease for Pb concentration of 25%. The evolution of the photocurrent with Pb concentration can be accounted for by such variations. In addition, one can notice that it is known that the conductivity of certain semiconductors is greatly influenced by their composition [21].

IV. Conclusions

1. From the dependence of band gap on the composition, it is concluded that the $Pb_x\ Cd_{1-x}\ S$ ($0.05 \leq x \leq 0.25$) films prepared by CBD technique result from inter-metallic compound of PbS in CdS.
2. The optical band gap of $Pb_x\ Cd_{1-x}\ S$ lies within the band gap of PbS and CdS.
3. At a given composition in the range of 0.15-0.2, high photo responsivity achieved.
4. The influence of lead concentration in the growth solution on the formation of lead oxide shows that beyond $x \geq 0.15$ lead oxide starts depositing.

References

[1] B.R.Sankagal and C.D.Lokhande, Materials Chemistry and Physics; 14, (2002) 126.

[2] Rakesh K.doshi, Satish Mohan, S.K. Agarwal, and H.K.Sehgal; Thin Solid Films 447-448 (2002) 80.

[3] D.H Frigo, O.F.Z.Khan, P.Obrien, and J.Crtystal Growth 6 (1989) 989.

[4] Y.F.Nicolou and M.Dupuy, J.Electrochemical soc., 137(1990) 2915.

[5] S.C. Ray, M.K. Karanjai, and D. Dashupta, Thin Solid Films, 322(1998)117.

[6] G.K. Padam, S.U.M. Rao, and G.L.Maholtra , J. Appl. Phys. 63(1988)770.

[7] P.K.Nair and M.T.S.Nair, semicond. Sei.Technol, 4(1989) 807.

[8] V.M. Garcia, M.T.S.Nair, and P.KNair, Solar Energy Mater; 23 (1991) 47.

[9] P.K. Nair, M.T.S Nair, and J.Campos, Proc. SPIE 823 (1987) 256.

[10] L.P.Deshmukh, B.M.More, S.G.Holikatti, and P.P. Hankare, Bull. Mater.Sci.17 (1994) 455.

[11] B.B. Nayak and H.N.Acharya, J.of Mat.Sci.lett. 4 (1985) 651.

[12] L.N.Maskaeva, V.F.Markov, and A.IGusev; DOKLADY physical chemistry 390 (2003) 147.

[13] S.Bushan, M.Mukhenjee, and P.Bose, J.Mater.Sci. 13 (2002) 581.

[14] V.F.Markavov, L.N.Maskaevas, and G.A.Kitaev, Inorganic Materials 36 (2000) 1194.

[15] L.P.Deshmukh, B.M.More, S.G.Holikatti, and P.P.Hankare, Bull.Mater.Sci. 17 (1994) 455.

[16] M.Guglielmi, A.Martucci, J.Fick, and G.Vitrant, J.Sol-Gel Sci.Techn. 11 (1998) 229.

[17] K.Ashok and Jay N.Zemel, J.Appl.phys. 49 (1978) 5292.

[18] M.Skyllas-Kazacos, J.F.Mccann, and R.Arruzza, Application of Surface Science 22/23 (1985) 1091.

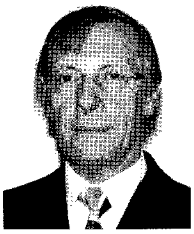
[19] T L. Chu, S.S.chu, N.Schultz, and C.Q.Wu, j.Electrochem.Soc. 139(1992) 2443.

[20] K.V.Zinoviev and O.Zelaya-Angel, Mater. Chem. Phys. 70 (2001)100.

[21] L.M.Frass, W.P.bleha, and P.Braatz, J. Appl. Phys. 46 (1995)491.

Modaffer A. Mohammed: He was born in Karbala in 1962. He had his B.Sc. in Physics from the University of Baghdad (Iraq) in 1983, and M.Sc. and Ph.D. degrees in Materials Science and Materials Technologies from University of Technology, Baghdad (Iraq) in 1990 and 2008, respectively. He had 4 published articles inside Iraq. His main field of research is preparation and characterization of semiconducting thin films by chemical bath deposition (CBD). He is member of the Iraqi Society of Physics Since 1983.

Ali M. Mousa: He was born in Baghdad in 1951. He had his B.Sc. in Physics from the University of Baghdad (Iraq) in 1973, and M.Sc. and Ph.D. degrees in Physics from University of Louis Pasteur (France) in 1980 and 1983, respectively. He had 30 published articles inside Iraq and abroad. His main field of research is laser-induced production of semiconductor structures since 1989. As well, he is heading a research group on preparation and characterization of semiconducting thin films and nanostructures by chemical bath deposition (CBD). He is member of the Iraqi Society of Physics since 1973.



J. P. Ponpon received a "Doctorat de 3ème Cycle" degree in Nuclear Instrumentation in 1972 and a "Doctorat d'Etat" in Electronic Physics in 1979 from Université Louis Pasteur, Strasbourg, France. He has been with CNRS (Centre National de la Recheche Scientifique) since 1976. His fields of interest have been the development and characterization of semiconductor materials for nuclear radiation detectors (germanium, silicon, mercuric iodide, cadmium telluride), the study of rectification at the metal-semiconductor contact, especially the instablilities in silicon Schottky barriers, the progress in silicon solar cells, the rapid thermal annealing of Pd and Ti silicides for microelectronic applications. More recently he has been involved in the analysis of the reactions occurring at the surface of mercuric iodide during etching in various solutions and in the deposition and characterization of polycrystalline lead iodide thin films for X-ray imaging applications. He published about 80 papers in international journals and presented 25 communications in international conferences. He has written a chapter in a book devoted to the experimental methods used in nuclear physics and he is the author of a book on semiconductor detectors (2007, in French). He has teached semiconductor physics, semiconductor technology and semiconductor nuclear radiation detectors at the Strasbourg University. A tens of Ph. D. thesis were carried out under his supervision.