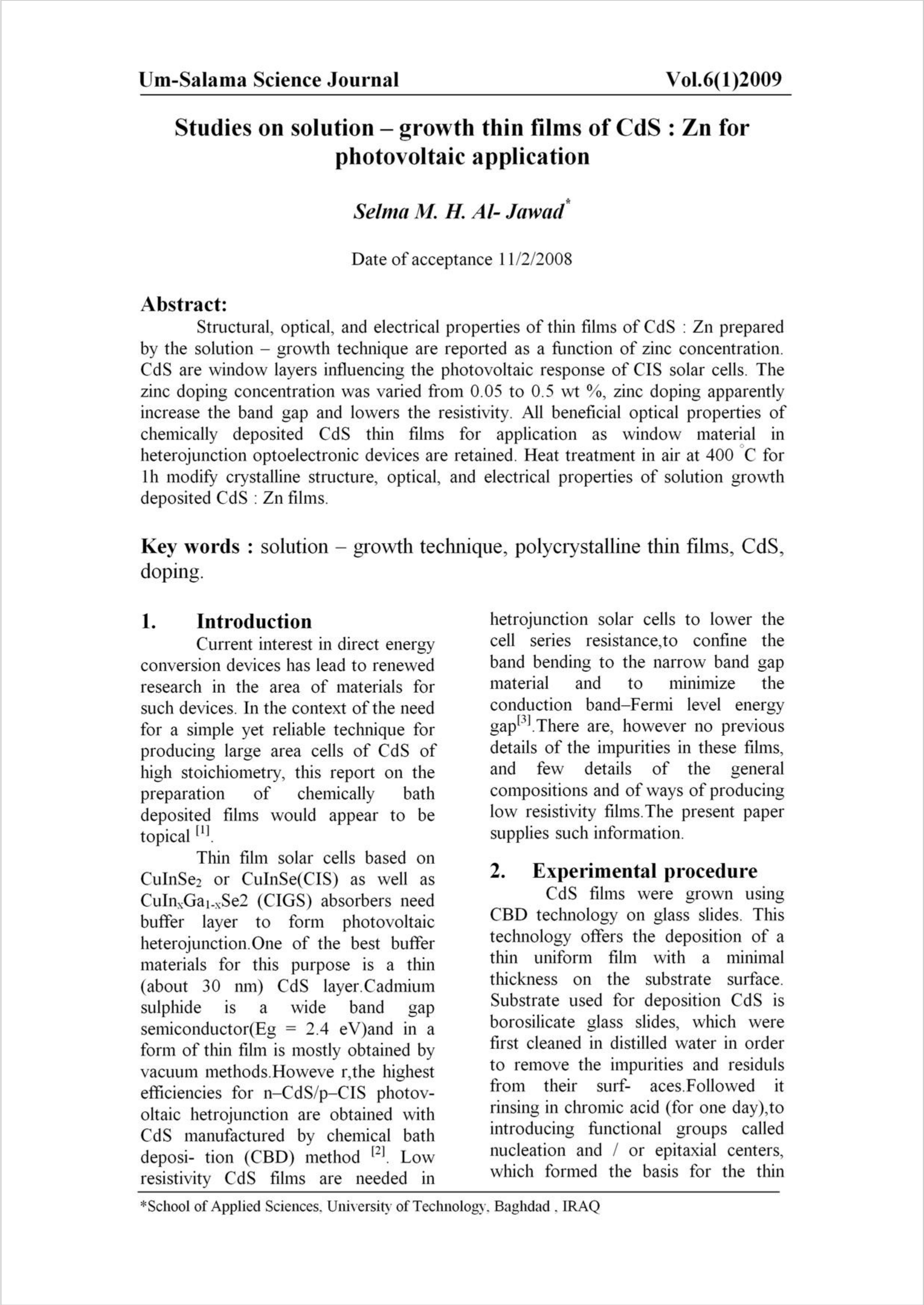
Selma M. H. Al- Jawad

Friday, December 24, 2010
4:28 PM



Um-Salama Science Journal **Vol.6(1)2009**

Studies on solution – growth thin films of CdS : Zn for photovoltaic application

Selma M. H. Al- Jawad[*]

Date of acceptance 11/2/2008

Abstract:

Structural, optical, and electrical properties of thin films of CdS : Zn prepared by the solution – growth technique are reported as a function of zinc concentration. CdS are window layers influencing the photovoltaic response of CIS solar cells. The zinc doping concentration was varied from 0.05 to 0.5 wt %, zinc doping apparently increase the band gap and lowers the resistivity. All beneficial optical properties of chemically deposited CdS thin films for application as window material in heterojunction optoelectronic devices are retained. Heat treatment in air at 400 °C for 1h modify crystalline structure, optical, and electrical properties of solution growth deposited CdS : Zn films.

Key words : solution – growth technique, polycrystalline thin films, CdS, doping.

1. Introduction

Current interest in direct energy conversion devices has lead to renewed research in the area of materials for such devices. In the context of the need for a simple yet reliable technique for producing large area cells of CdS of high stoichiometry, this report on the preparation of chemically bath deposited films would appear to be topical [1].

Thin film solar cells based on $CuInSe_2$ or CuInSe(CIS) as well as $CuIn_xGa_{1-x}Se2$ (CIGS) absorbers need buffer layer to form photovoltaic heterojunction.One of the best buffer materials for this purpose is a thin (about 30 nm) CdS layer.Cadmium sulphide is a wide band gap semiconductor(Eg = 2.4 eV)and in a form of thin film is mostly obtained by vacuum methods.Howeve r,the highest efficiencies for n–CdS/p–CIS photovoltaic hetrojunction are obtained with CdS manufactured by chemical bath deposition (CBD) method [2]. Low resistivity CdS films are needed in hetrojunction solar cells to lower the cell series resistance,to confine the band bending to the narrow band gap material and to minimize the conduction band–Fermi level energy gap[3].There are, however no previous details of the impurities in these films, and few details of the general compositions and of ways of producing low resistivity films.The present paper supplies such information.

2. Experimental procedure

CdS films were grown using CBD technology on glass slides. This technology offers the deposition of a thin uniform film with a minimal thickness on the substrate surface. Substrate used for deposition CdS is borosilicate glass slides, which were first cleaned in distilled water in order to remove the impurities and residuls from their surfaces.Followed it rinsing in chromic acid (for one day),to introducing functional groups called nucleation and / or epitaxial centers, which formed the basis for the thin

---

*School of Applied Sciences, University of Technology, Baghdad , IRAQ

films growth[4]. Then, repeated washing in deionized water, and finally put in ultrasonic wave with distilled water for 15 min then dried

The reaction cell was a 100 ml beaker containing 0.1M $CdSO_4$ aqueous solution,0.2 M thiourea aqueous solution and 5.6 M NH_4OH in the volume ratio 1:1:1.The substrate were then suspended in the reaction cell. Reasonably good films of CdS were obtaind in 20 min at a constant temperature.

The freshly grown films were thoroughly washed by water jet, dried and kept in a vacuum. .

To prepare Cd:Zn films, $ZnCl_2$ was also added to the reaction cell being used for CdS deposition.The procedure adopted was the same as described for CdS deposition.

3. Film formation

The mechanism of CdS: Zn film formation can be assumed to proceed as follows:

i) Formation of a complex with cadmium

$$CdSO_4 + 2NH_3 \rightarrow [Cd(NH_3)_4]SO_4$$

ii) Diffusion of $[Cd(NH_3)_4]^{2+}$, OH^- and thiourea to the catalytic surface of CdS;

iii) Dissociation of thiourea in alkaline media

$$CS(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

iv) Formation of a sulphide ion

$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$

v)

$$ZnCl_2 + 2NH_4OH \rightarrow 2ZnOH + (NH_4)_2Cl_2$$

vi) $ZnOH \rightarrow Zn^+ + OH^-$ zn

vii)

$$[Cd(NH_3)_4]^{2+} + xZn^+ + S^{2-} \rightarrow CdSx.Zn^+ + 4NH_3 \uparrow$$

4- Results and discussions

4.1 Structure properties

The crystal structure of the CdS:Zn films has been determined from X-ray diffraction.The analyses established the presence of mixture of cubic, nd hexagonal (CdS) with H(002)/C(111) predominant planes of crystallization was observed for the films as shown in figure (1).And decrease doping concentration improve the degree of crystallinity of the films.This phenomenon can be explained on the basis of adsorption and its effects on crystal growth.Thus attribute the lack of polycrystalline form when manganese is added during deposition, to the adsorption of Zn ions at the surface of a growing CdS microcrystal. This then prevents the microcrystals from growing larger along the plane of the substrate (and perpendicular to it).

This is also substantiated by the observed fact that layers made with zinc addition during deposition are thinner than those made without [5].

The air annealing was carried out at 400°C for one hour.It is evident that the as prepared film is of both hexagonal and cubic phase and the air annealed film is converted cubic CdS films into the hexagonal phase with a slight shift towards lower scattering angle.The shift towards lower scattering angle is the consequence of an increase in the lattice parameter due to the relaxation of the tensile strain induced by grain boundaries along the film plane,probably due to a slight grain growth, and lets the interplanar distance increase towards its stress free value [6,7].

4.2 Optical properties

Optical transmission spectra of the films are shown in Figure (2). All the films show high optical transmittance (>70%) beyond the absorption edge. The effect of Zn doping on optical absorption and band gap was studied in the wavelength range from 375 nm to 900nm. The optical absorption coeffic- ient(α)is of the order $10^{-5}cm^{-1}$.Figure (3) sho- ws the wavelength dependence of (α) for a few sample. From the plots it can be justified that the films show higher absorption on the shorter wavelength side and the presence of an edge.

From the observed absorption data it is found that plots of $(\alpha h\nu)^2$ versus(hν) (Figure 4)for undoped and doped films gave fairly good straight lines indicating that the transition were direct and allowed. These observations are in agreement with the fact that the material is known to be a direct gap material. The plot of $(\alpha h\nu)^2$ against (hν) for undoped film extrapolates to (Eg) = 2.4 eV, while that for the doped film extrapolates to (Eg) = 2.48 eV.The increase in band gap from 2.4 eV to 2.48 eV upon doping with Zn has been explained by splitting of the tailed levels from the bands. Increase in band gap can also occur by filling the lower–lying conduction (valence) band levels with electrons (holes) ,thereby requiring a larger photon energy to promote an electron from the valence to the conduction band(the Burstein–Moss shift)[8,1].

The annealed samples show a relative decrease in band gap as shown in (Figure 5).These results are consistent with other published results such as results of George et al [9] who attribute this decrease in the band gap in the annealed samples to the grain size growth. Conversely Archbold[10] attributes similar results to the either phase transition from the cubic to hexagonal phase, or a reduction in strain within the film.

4.3 Electrical properties

From Hall effect,we found all the prepared films CdS : Zn have n-type condu- ctivity.The dark resistivity of zinc doped CdS films on glass deposited is shown on Fig. (6). As it can be seen, dark resistivity of CdS : Zn decrease with increase of doping concen- tration. Fig. (7) indicates the variation of the measured dark electrical resistivity (ρ) of CdS : Zn films with temperature. And Fig. (8) explains the relationship between ln ρ and 1000/T for CdS :Zn films,which can calcu- late the activation energy by using the relation ($E_{a=}$ 0.9 eV)

$$\rho = \rho_{\circ} \exp(E_a / kT) \qquad (3)$$

Where E_a is the activation energy, ρ resistivity at temperature (T), $\rho_{\circ}$ is the resistivity at room temperature, and (k) is the Boltzmann's constant. The enhancement in conductivity can be explained on the basis of formation of Cd^+ ions or Cd vacancies being formed for charge compensation, because during the film growth zinc replaces the divalent cadmium and there is evary possibility of formation of Cd^+ ions rather than the Cd vacancies as Zn and Cd are deposited simultaneously.This helps in increasing the conductivity [11].

Heating of the CdS films at 400 °C for one hour causes changes in the dark resis- tivity. This arises from cumulative effect of grain size enhancement and oxygen incorp- oration at grain boundaries. This is due to the partial conversion of CdS to CdO as seen from Figure .1.

These results are consistent with other published results such as results of Danaher et al.[12] who attribute this decrease to O_2 deso- rption,while Ramaiah et al.[13] attribute similar results to the creation of number of sulphur vacancies in the films.

5 . Conclusion

Solution growth is a sample and suitable method of obtaining adherent, specular, homogeneous and stoichiometric CdS : Zn thin films. The results confirm that the electrical resistivity of CdS films doped with zinc was dependent on doping level. And however, annealing of the sample in air has been found to be useful for lowering the resistivity down to 100 Ω. Cm.

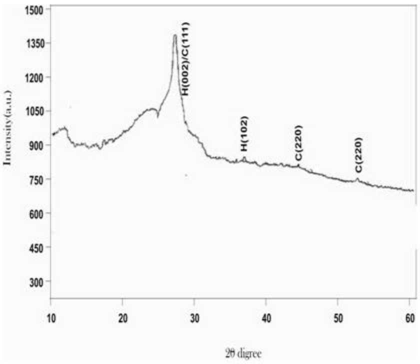


Figure 1. X – ray diffraction of CdS : Mn.

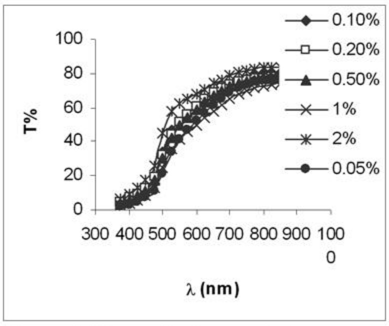


Figure 2. The optical transmission spectra of CdS films for different doping concentration.

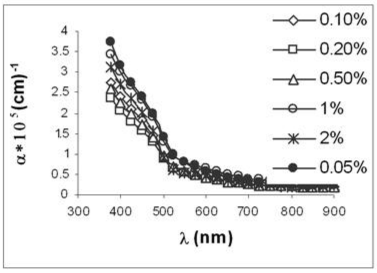


Figure 3. The optical absorption spectra for the (CdS) for different doping concentration.

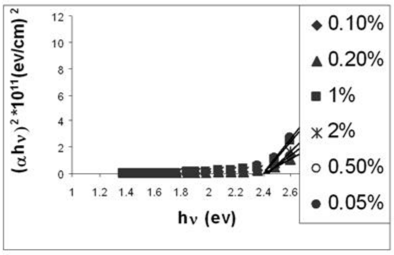


Figure 4. A plots of $(h\upsilon)$ verses $(\alpha h\upsilon)^2$ of CdS thin films for different doping concentration.

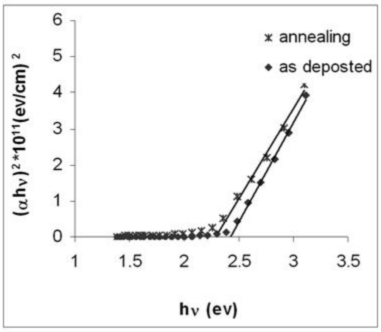


Figure 5. A plot of $(\alpha h\upsilon)^2$ verses $(h\upsilon)$ for as deposited films and for annealing films.

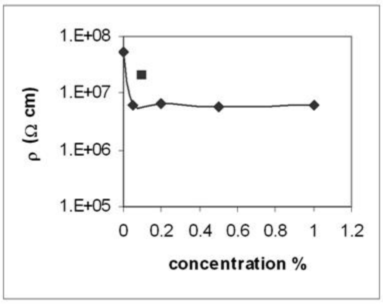


Figure 6. Variation in resistivity as function of doping concentration.

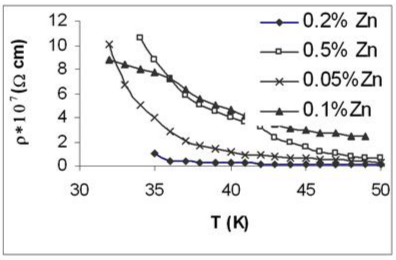


Figure7.The relationship between resistivity and temperature for CdS : Zn films.

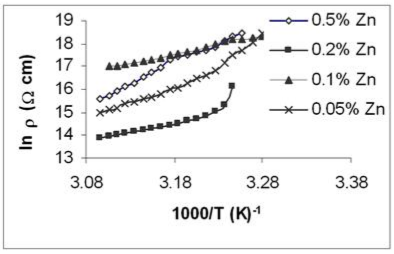


Figure 8. The relationship between ln ρ and 1000/T for CdS : Mn fi

References

1. Pavaskar, N.R.; Menezes ,C.A.; and Sinha , A.P.B.;(1977). Photoconductive CdS film by a chemical bath deposition process, Journal of Electrochem.Soc.,124 (5):743–748.
2. Pisarkiewicz,T.;Schabowska,E.;and Kusio,E.;(2001).cadmium sulfide thin films manufactured by chemical bath deposition method, Journal of Wide Band Gap Materials,9(9):127 – 132.
3. Danaher,W.J.;Lyons,L.E.;andMorris,G.C.;(1985).Some properties of thin films of chemically deposited cadmium sulphide, Solar Energy Materials, 12: 137 – 148.
4. Ezema,F.I.; and Ugwuoke,P.E.; (2003). Investigation of optical properties of barium oxide (BaO) thin films deposited by chemical bath technique , The Pacific J. of Science and Technology,5(1):33–38.
5. Kau,I.;Pandya,D.K.; and Chopra, K.L; (1980).Growth kinetics & polymorphism of chemically deposited CdS films,J.Elc-ochem.Soc.,127(4):943-948.
6. Padam,G.K.; Malhotra G.L.; and Rao, S.U.M.; (1988).Sudies on solution grown thin films of ZnxCd1-xS, J. Appl. Phys., 63 (3): 770 – 774.
7. Rakhani,A.E.;andAzab,A.S.A.;(2001).Appl.Phys.,structure and morphology of chemical bath deposited CdS films and clusters,A 73: 631 – 636.
8. Hodes,G.;(2003)."Chemical solution dep- osition of semiconductor films", Marcel Dekker,.
9. George,P.J.; Sanchez, A.;Nair, P.K.;and Nair, M.T.S.;(1995). doping of chemically deposited intrinsic CdS thin films to n-type by thermal diffusion of indium, Appl.Phys.Lett.66(26):3624–3626.
10. Archbold, M.D.;Halliday, D.P.;Durose, K.;Hase,T.P.A.;Boyle,D.S. and Govender, K.; (2005). Conference Record of the Thirty –First IEEE Photovoltaic Specia-listsConference,Coronado Springs Resort Lake Buena Vista,FL,January3 – 7.
11. Deshmukh,L.P.;Palwe,A.B.; and Sawant, V.S.;(1990).deposition &

characterization of CdS and CdS:As thin films,Solar Energy Materials,20:341– 348.

12. Danaher,W.J.;Lyons,L.E.;and Morris,G.C ;(1985).some properties of thin films of chemically deposited cadmium sulphide, Solar Energy Materials, 12: 148 – 158.
13. Ramaiah,K.S.;Pilkington,R.D.;Hill, A.E.;Tomlinson,R.D.;andBhatnagar,A.K.;(2001). structural and optical investigations on CdS thin films grown by chemical bath technique,Materials Chemistry and Phy- sics,68:22–30.

دراسة أغشية CdS:Zn المرسبة بطريقة النمو بالمحلول المستخدم في تطبيقات الفوتولتائية

سلمى محمد حسين*

* الجامعة التكنولوجية/ بغداد/ العراق

الخلاصة:

درست الخصائص التركيبية والبصرية والكهربائية للاغشية الرقيقة CdS : Zn المحضرة بتقنية النمو بالمحلول كدالة لتركيز شوائب الزنك. اذ توثر اغشية ال CdS المستخدمة كنافذة للخلايا الشمسية CIS على الاستجابية الفوتوفولتائية. حيث غيرت تراكيز شوائب الزنك من 0.05 الى 0.5% , اذ عملت شوائب الزنك على زيادة فجوة الطاقة مع تقليل المقاومية الكهربائية, مع الحفاظ على نفاذية عالية للاغشية الرقيقة المرسبة بتقنية النمو بالمحلول اللازمة لاستخدام غشاء CdS كنافذة للتركيب الهجيني المستخدم في النبائط الالكترونية – البصرية. كذلك اجري تلدين للاغشية الرقيقة بدرجة حرارة 400 درجة مئوية ولمدة ساعة ، الذي ادى الى تغير التركيب البلوري والخصائص البصرية والكهربائية لاغشية CdS:Zn .