



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(6), 2011 [399-404]

Influence of [S]/[Cd] ratio on the structural, morphological and optical properties of CdS thin films prepared by chemical bath deposition

F.Ouachtari¹, A.Rmili¹, A.Bouaoud¹, A.Louardi¹, B.Elidrissi^{*1}, H.Erguig¹, P.Elies²¹Laboratoire des Hautes Energies, Sciences de l'Ingénierie et Réacteurs (*LHESIR*), Equipe Ingénierie et Matériaux (INMA), Département de Physique, Faculté des Sciences, Kénitra, (MAROC)²Plateforme d'Imagerie et de Mesures en Microscopie 6, av. Le Gorgeu-CS93837 29238 Brest Cedex3, (FRANCE)

E-mail : e.bachir@mailcity.com

Received: 9th May, 2011 ; Accepted: 9th June, 2011

ABSTRACT

Cadmium sulphide (CdS) thin films were deposited by chemical bath deposition method (CBD) on glass substrates at solution temperature of 75°C for 60 min. Anhydrous cadmium chloride (CdCl₂) and thiourea (CS(NH₂)₂) were used as sources of cadmium and sulphur ions respectively. The influence of [S]/[Cd] ratio in the solution on the structural, morphological, chemical composition and optical properties of these films were investigated. X-ray diffraction (XRD) studies revealed that all the deposited films were polycrystalline with hexagonal or cubic structure and exhibited [002] or [111] preferential orientation, respectively. The film deposited with [S]/[Cd] ratio = 2.5 was found relatively well crystallized. It showed large final thickness and its surface morphology was composed of small grains with an approximate size of 12 to 21 nm and grains grouped together to form large clusters. Energy Dispersive X-ray Analysis (EDAX) revealed that this film was nonstoichiometric with a slight sulphur deficiency. This film exhibited also an average transmittance value of about 79 % in the visible and infra red regions.

© 2011 Trade Science Inc. - INDIA

KEYWORDS

Cadmium sulphide;
Chemical bath deposition;
Structure;
Morphology;
Optical properties.

INTRODUCTION

Amongst of the chalcogenide thin films like PbS, CdS, ZnS, MnS, CdS appear as an interesting material for using as n-type window layer for p-CdTe and chalcopyrite-based solar cells such as p-CuInSe₂, and/or p-Cu(In,Ga)Se₂ (CIGS)^[1]. This is because CdS has high transparency, wide and direct band gap transition (2.42 eV), photoconductivity, high electron affinity and

n-type conductivity. CdS can also be used in a lot of applications including electronic^[2] and optoelectronic devices^[3]. Undoped and doped CdS thin films have been reported using different methods viz. Sol-Gel dip coating (S.G)^[4], spray pyrolysis (SP)^[5], chemical bath deposition (CBD)^[6], RF-Sputtering (RFS)^[7], metal organic chemical vapour deposition (MOCVD)^[8], successive ionic layer adsorption and reaction (SILAR)^[9], and pulsed laser ablation (PLA)^[10]. Among

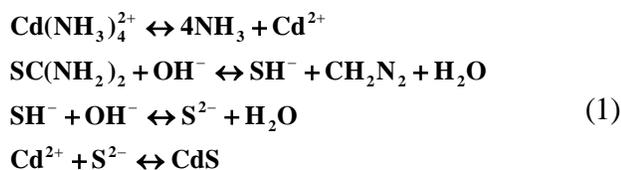
Full Paper

these methods, the CBD technique is relatively simple, low cost compared to other methods requiring vacuum environment and its capable to yield films with good quality at optimum growth conditions.

The aim of this present work is to study the influence of [S]/[Cd] ratio in the solution (thiourea to cadmium chloride concentration) on the crystalline structure, surface morphology, chemical composition and optical properties of CdS thin films prepared by chemical bath deposition.

EXPERIMENTAL PROCEDURE

CBD is a technique in which thin films are deposited on substrates immersed in dilute alkaline solution containing metal ions and the chalcogenide source. This method of deposition usually uses a complexing agent to control the slow release of metal ions (Cd^{2+}) and sulphur ions (S^{2-}) to produce the controlled homogeneous precipitation of the film on the solid substrate. When the complexing agent is ammonia (NH_3), the possible chemical reactions to form CdS films are as follows^[11]:



In this work, the initial solutions to elaborate CBD-CdS films were prepared from anhydrous cadmium chloride (CdCl_2), thiourea ($(\text{NH}_2)_2\text{CS}$), ammonia (NH_3), ammonium chloride (NH_4Cl). Cadmium chloride of 0.12 M and thiourea of 0.3 M were employed as the cadmium and the sulphur sources, respectively. Ammonia of 10 M was used as a complexing agent. Firstly, 3.75 ml cadmium chloride solution was added to 112.5 ml of de-ionized water. Thereafter, 15 ml ammonia solution was added at the same time with 15 ml ammonium chloride solution of 0.01 to 2 M to adjust the pH at about 10 under the control of a pH meter. Pre-treated commercial microscope slides ($1.5 \times 2.5 \text{ cm}^2$) were inserted vertically into the bath and the solution was heated at appropriate temperature (between 60 and 90°C). Finally, when a desired temperature was obtained, 3.75 ml of thiourea

solution was added under stirring condition to ensure homogeneous distribution of the chemicals. The total volume of solution was 150 ml. After deposition, the substrates were removed from the chemical bath, and cleaned for several times with de-ionized water, then dried in air.

The as deposited films were yellow in colour and found to be uniform, pin holes-free and strongly adherent to the glass substrates. Their thickness was calculated by using gravimetric method and it was found to vary from 400 to 800 nm. The structure, crystallinity and phase of the CdS thin films were determined by the X-ray diffraction (XRD) analysis, using $\text{CuK}\alpha$ radiation with 2θ ranging from 15° to 70°. The surface morphology of the films was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical composition was performed with an EDAX spectrometer attached to the scanning electron microscope. In order to determine the band gap energy of CdS in thin film form, the optical transmission studies were carried out in the wavelength range of 300 to 2500 nm, using a SHIMADZU 3101 PC UV-VIS-NIR spectrophotometer.

RESULTS AND DISCUSSION

Crystal structure determination

Figure 1 shows the X-ray diffraction diagrams of CdS thin films prepared with different [S]/[Cd] ratios at solution temperature of 75°C for 60 min. A single diffraction peak at $2\theta = 26.7^\circ$ is observed for the all the deposited films. The interplanar spacing value corresponding to this diffraction peak ($d_{hkl} = 3.34 \text{ \AA}$) is compared with the ASTM DATA^[12]. This suggest that the obtained films are crystallized in the hexagonal or cubic structure with a preferred orientation along the [002] or [111] direction, respectively. However, M. Karimi et al.^[13], A.

Cortes et al.^[14] and H. Moulkia et al.^[15], using chemical bath deposition and other techniques, have been found a cubic structure of CdS films. In fact, depending on the preparation method, cadmium sulphide can exist in both sphalerite cubic and hexagonal forms, but the latter structure is more stable^[16]. In addition the hexagonal structure of CdS films is preferable to use in

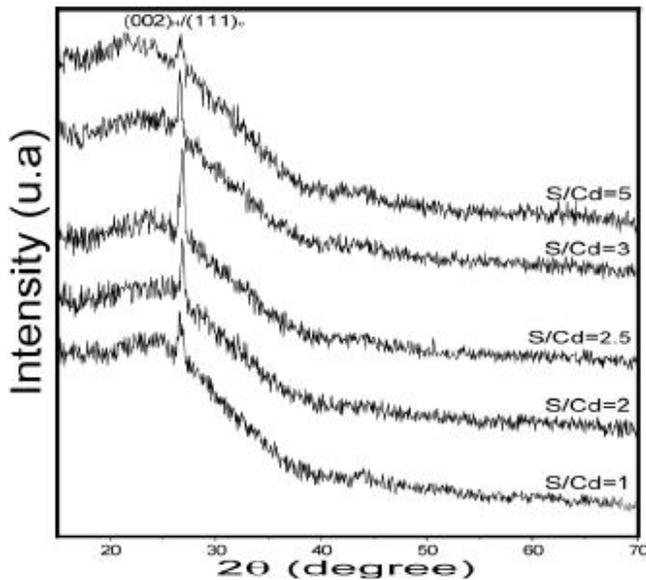


Figure 1 : X-ray diffraction patterns of CdS thin films elaborated with different [S]/[Cd] ratios at 75°C for 60 min : (a) [S]/[Cd] = 1 (b) [S]/[Cd] = 2, (c) [S]/[Cd] = 2.5, (d) [S]/[Cd] = 3 and (e) [S]/[Cd] = 5.

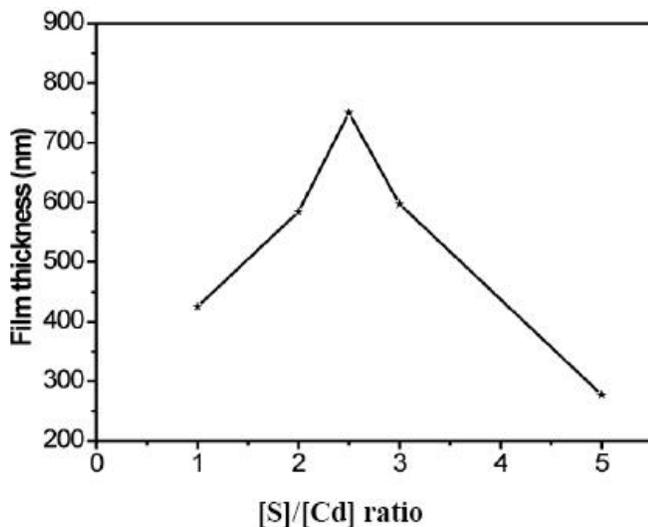


Figure 2 : Variation of CdS film thickness with [S]/[Cd] ratio. solar cell applications because the lattice parameter mismatch with CuInSe₂ (1.2%) compared to that of cubic CdS (0.7%). Furthermore, Figure 1 shows that the whole X-ray diffraction diagrams exhibit a broad hump near the (002)/(111) peak at $2\theta = 26.7^\circ$, which is due to the glass substrates. It is also observed that the intensity of the (002)/(111) peak increases and its full width at half maximum (FWHM) decreases when [S]/[Cd] ratio increases up to 2.5, indicating an improvement of the crystallinity. In contrary, films prepared with [S]/[Cd] ratio greater than 2.5 show a decrease of the (002)/(111) peak intensity and an increase of its

FWHM, indicating a degradation of the crystallinity. Figure 2 depicts the variation of CdS film thickness with [S]/[Cd] ratio. It shows that the films thickness increases when [S]/[Cd] ratio increases up to 2.5 and then decreases afterwards. The increase of the film thickness with [S]/[Cd] ratio is probably due to the decomposition of reactants and production of ions which are necessary for films formation, while the decrease one is explained by the dissolution of the preformed CdS films and the desorption phenomenon. The same behaviour is also observed for other chalcogenide materials prepared by CBD method such as ZnS^[17] and MnS^[18]. The lattice parameters a_H and c_H or a_C are calculated from the peak at $2\theta = 26.7^\circ$ using the formula of hexagonal (Equation 2) or cubic (Equation 3) system, respectively. The values are found to be $a_H = 4.13 \text{ \AA}$, $c_H = 6.70 \text{ \AA}$ with $c_H/a_H = 1.63$ and $a_C = 5.78 \text{ \AA}$, which are close to the values published in the literature^[19].

$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + k^2 + hk)}{3a_H^2} + \frac{l^2}{c_H^2} \quad (2)$$

$$d_{hkl} = \frac{a_C}{\sqrt{(h^2 + k^2 + l^2)}} \quad (3)$$

The average crystallite size (D_{hkl}) of CdS films are estimated from the X-ray diffraction patterns using the Scherrer formula^[20]:

$$D = 0.9 \frac{\lambda}{\beta_{hkl} \cos(\theta_{hkl})} \quad (4)$$

Where λ is the wavelength of incident radiation ($\lambda = 1.544 \text{ \AA}$), β_{hkl} is the full-width at half maximum (FWHM) of the respective diffraction peak and θ_{hkl} is the Bragg diffraction angle. The calculated values are reported in TABLE 1. As it can be seen the values are found in the nanometer region (10–21 nm), indicating that the polycrystalline CdS films are made up of nanocrystal particles.

TABLE 1 : Average crystallite size (D_{hkl}), band gap (E_g) and average transmittance values (% T) of CdS thin films with varying ratios of [S]/[Cd].

[S]/[Cd]	E_g (eV)	Average transmittance (%)	Average crystallite size (nm)
1	2.37	69	12 ± 3
2	2.39	71	17 ± 4
2.5	2.44	79	21 ± 5
3	2.42	75	19 ± 4
5	2.36	66	10 ± 2

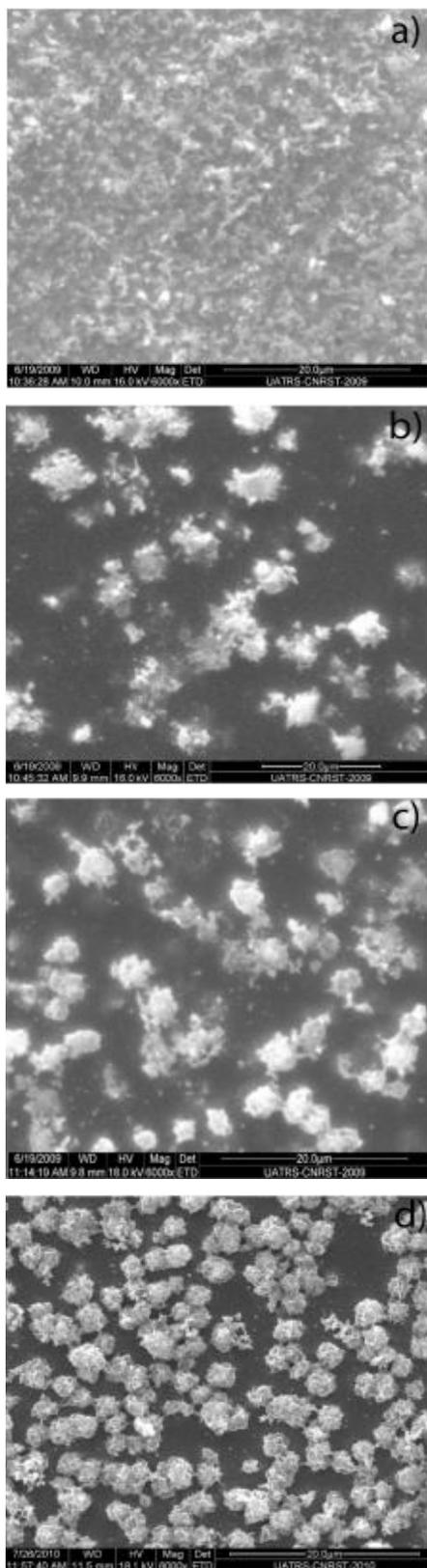


Figure 3 : S.E.M micrographs of CdS thin films deposited with different [S]/[Cd] ratios: (a) [S]/[Cd] = 1, (b) [S]/[Cd] = 2, (c) [S]/[Cd] = 2.5, (d) [S]/[Cd] = 3 and (e) [S]/[Cd] = 5.

Surface morphology

SEM micrographs of the surface morphology of CdS films prepared with different [S]/[Cd] ratios in the solution (1, 2, 2.5, 3 and 5) are shown in Figure 3. These micrographs show that the obtained films have good adherence on the substrates without pinholes or cracks. In addition, the films are covered by spherical grains, whose their size and density increase noticeably when [S]/[Cd] ratio increases from 1 to 3 and then decrease afterwards. It is also observed from the micrographs (Figure 3(b), (c) and (d)) that a small particles are grouped to form larger clusters discreetly distributed in the films. This indicates that the mechanism film formation is may be due to cluster-by-cluster deposition (homogeneous mechanism). The average crystallite size of these films varies between 500 and 1000 nm while that estimated by Scherrer's equation varies between 12 to 21 nm. These values are much less than those obtained from SEM analysis. This is can be explained by agglomeration of small particles of CdS to form large clusters. To have more details on the surface morphology of CdS films, Atomic Force Microscopy (AFM) analysis is used. Figure 4 presents 3D AFM images obtained by scanning an area of $20\mu\text{m} \times 20\mu\text{m}$ of the surface of CdS films deposited with [S]/[Cd] ratio = 2.5. It shows that the surface is composed of small grains with an approximate size of 15 to 30 nm and grains grouped together to form large clusters like a cauliflower with a mean size of 200 to 500 nm, confirming the results obtained by X-ray diffraction and SEM analysis, respectively.

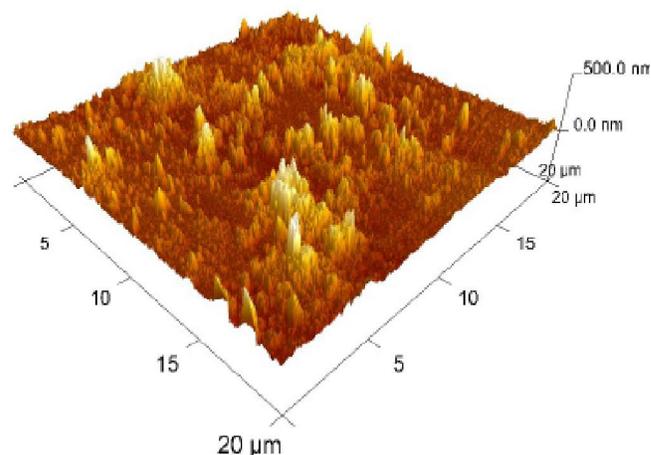


Figure 4 : 3D AFM micrograph of CdS thin film deposited with [S]/[Cd] = 2.5.

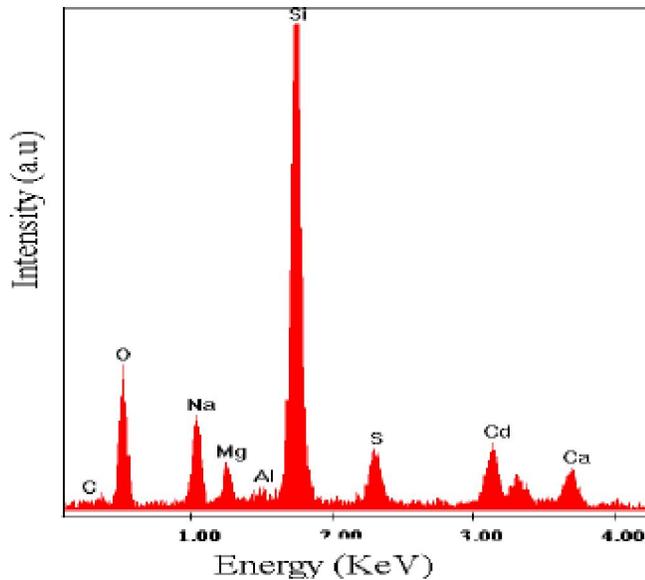


Figure 5 : EDAX spectrum of CdS thin film deposited with $[S]/[Cd] = 2.5$.

TABLE 2 : EDAX analysis of CdS thin film deposited with $[S]/[Cd] = 2.5$.

Element	Cd	S	O	$[S]/[Cd]$
Percentage	7,6 at. %	7,2 at. %	37,7 at. %	0,94

Composition analysis

Figure 5 presents the EDAX spectrum of CdS thin films prepared with $[S]/[Cd]$ ratio equal to 2.5. It shows peaks of Cd, S and some impurities like, Si, Ca, Na and O which are originated probably from the glass substrates and deionised water, respectively. The atomic concentrations from EDAX analysis and the calculated atomic ratio are presented in TABLE 2. As it can be seen, the $[S]/[Cd]$ atomic ratio is 0.94 suggesting the presence of sulphur vacancies (excess of cadmium) in the deposited films, which act as donors, leading to n-type

Optical properties

The optical properties such as transmittance, absorption coefficient and band gap energy of CdS thin films are determined from the variation of the optical transmission with wavelength (λ) in the range of 300 to 1500 nm. Figure 6 shows the optical transmittance spectra of the CdS films elaborated with different $[S]/[Cd]$ ratios. As it can be seen, the films elaborated with $[S]/[Cd]$ ratio equals to 2.5 exhibit a high transmission of about 80% in the visible and near infra-red regions. This can be explained by a relatively better crystallinity

and good stoichiometry of these films as it is shown by X-ray analysis and EDAX analysis.

By using the Tauc relationship which is given by the formula^[21]:

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (5)$$

In which $(h\nu)$ is the photon energy, (E_g) is the optical band gap of the semiconductor, A is a

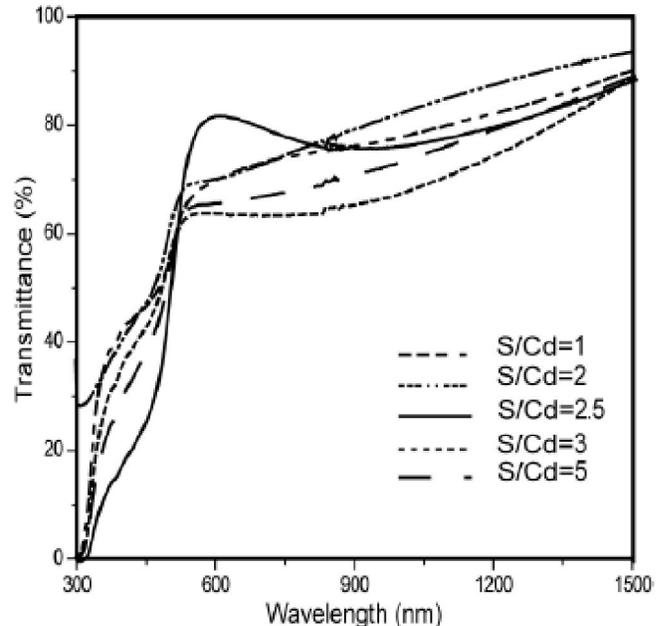


Figure 6 : Optical transmission spectra of CdS thin films prepared with different $[S]/[Cd]$ ratios.

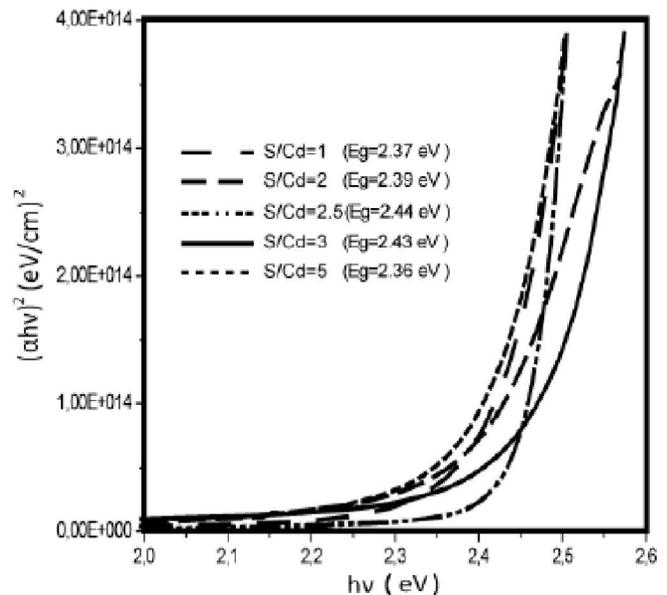


Figure 7 : Variation of $(\alpha h\nu)^2$ with photon energy with photon energy $(h\nu)$ for CdS thin films elaborated with different $[S]/[Cd]$ ratios

Full Paper

conductivity constant and $n = 1/2$ for direct band gap semiconductor such as CdS, the optical band gap value of the CdS thin films is estimated by extrapolation of the straight line of the plot of $(ah\nu)^2$ versus photon energy as it is shown in Figure 7. We found that the value of (E_g) for the films prepared with different [S]/[Cd] ratios varies from 2.36 to 2.44 eV, which is in agreement with the value reported by other authors^[22, 23].

CONCLUSION

CdS thin films were deposited by CBD method on glass substrates at 75°C for 60 min. Anhydrous cadmium chloride (CdCl_2) and thiourea ($\text{CS}(\text{NH}_2)_2$) were used as sources of cadmium and sulphur ions respectively. The optimal [S]/[Cd] ratio was found to be 2.5. The film prepared with this ratio was relatively well crystallized and had hexagonal or cubic structure with a preferential orientation along the [002] or [111] direction, respectively. It has showed also large final thickness and its surface morphology was consisted of small grains with an approximate size of 15 to 25 nm and grains grouped together to form large clusters like a cauliflower. The composition study showed that this film was nonstoichiometric with a slight sulphur deficiency leading to n type conductivity. This film exhibited also a good transmittance of about 79 % in visible and near infra-red regions of the electromagnetic spectrum so it is possible to us it as a window layer in high efficiency thin film solar cells based on CdTe and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS).

ACKNOWLEDGEMENTS

The authors are gratefully to “Plateforme d’Imagerie et de Mesures en Microscopie de l’université de Brest, France” for assistance in AFM measurements.

REFERENCES

- [1] M.Rusu, A.Rumberg, S.Schuler, S.Nishiwaki, R.Würz, S.M.Babu, M.Dziedzina, C.Kelch; *J.Phys.and Chem. of Solids*, **64**, 1849 (2003).
- [2] N.B.Chaure, S.Bordas, A.P.Samantilleke, S.N.Chaure, J.Haigh, I.M.Dharmadasa; *Thin Solid Films*, **437**, 10 (2003).
- [3] O.Vigil-Galan, A.Morales-Acevedo, F.Cruz-Gandarilla, M.G.Jimenez-Escamilla, J.Aguilar-Hernandez, G.Contreras-Puente, J.Sastre-Hernandez, E.Sanchez-Meza, M.L.Ramon-Garcia; *Thin Solid Films*, **515**, 6085 (2007).
- [4] M.Thambidurai, S.Agilan, N.Muthukumarasamy, N.Murugan, R.Balasundaraprabhu; *International Journal of Nanotechnology and Applications*, **3**, 29 (2009).
- [5] A.Aschour; *Turk Journal Phys.*, **27**, 551 (2003).
- [6] H.Khalaf, O.Oladeji, G.Chai, L.Chow; *Thin Solid Films*, **516**, 7306 (2008).
- [7] H.Hernandez-Contreras, C.Mejia - Garcia, G. Contreras-Puente; *Thin Solid Films*, **451**, 203 (2004).
- [8] S.H.Yoon, S.S.Lee, K.W.Seo, I.W.Shim; *Bulletin of the Korean Chemical Society*, **27**, 2071 (2006).
- [9] M.Sasagawa, Y.Nosaka; *J.Electroanalytical Chemistry*, **536**, 141 (2002).
- [10] O.Vigil-Galan, J.Vida-Larramendi, A.Escamilla-Esquivel, G.Contreras-Puente, F.Cruz-Gandarilla, G.Arriaga-Mejia, M.Chavarria-Castaneda, M.Tufino-Valasquez; *Physica Status Solidi (A) Applications and Materials*, **203**, 2018 (2006).
- [11] I.O.Oladeji, L.Chow; *J.Electrochem.Soc.*, **144**, 2342 (1997).
- [12] ASTM DATA (6-0314).
- [13] M.Karimi, M.Rabiee, F.Moztarzadeh, M.Tahriri, M.Bodaghi; *Current Applied Physics*, **9**, 1263 (2009).
- [14] A.Cortes, H.Gomez, R.E.Marotti, G.Reviros, E.A.Dalchiele; *Solar Energy Materials and Solar Cells*, **82**, 21 (2004).
- [15] H.Moualkia, S.Hareich, M.S.Aida; *Materials Science Forum*, **609**, 243 (2009).
- [16] F.Liu, Y.Lai, J.Liu, B.Wang, S.Kuang, Z.Zhang, J.Li, Y.Liu; *Journal of Alloys and Compounds*, **493**, 305 (2010).
- [17] A.Antony, K.V.Murali, R.Manoj, M.K.Javaraj; *Materials Chemistry and Physics*, **90**, 106 (2005).
- [18] D.Fan, H.Wang, Y.Zhang, J.Cheng. B.Wong. H.Yan; *Materials Chemistry and Physics*, **80**, 44 (2003).
- [19] L.D.Kadam, P.S.Patil; *Mater.Chem.Phys.*, **68**, 225 (2001).
- [20] B.D.Cullity, S.R.Stock; *Elements of X-ray Diffraction*, (Prentice-Hall, Pearson), (2001).
- [21] J.Tauc; Edited by J.Tauc (Plenum Press, NewYork), (1974).
- [22] J.Hiie, T.Dedova, V.Valdna, K.Muska; *Thin Solid Films*, **511**, 443 (2006).
- [23] A.Ates, M.A.Yildirim, M.Kundakci, M.Yildirim; *Chinese Journal of Physics*, **45**, 135 (2007).