Chalcogenide Letters Vol. 7, No. 8, August 2010, p. 501 – 508

VARIATION OF OPTICAL PROPERTIES WITH POST DEPOSITION ANNEALING IN CHEMICALLY DEPOSITED CdZnS THIN FILMS

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Thin films of CdZnS were synthesized on the glass substrates by chemical bath deposition at room temperature. The bath is made up of solution of cadmium chloride ($CdCl_2$), as a source of Cd^{2+}, Zinc sulphate ($ZnSO_4$) as a source of Zn^{2+}, thiourea [$(NH_2)_2CS$] as a source of sulphide ions (S^{2-}) in the presence of ammonia (NH_3) as the complexing agent. In the present paper, some interesting results of optical absorption and transmittance spectral studies of chemically deposited CdZnS films are presented. The parameters like band gap, extinction coefficient and refractive index are calculated using the data obtained by different measurements.

(Received August 5, 2010; accepted August 26, 2010)

Keywords: Chemical bath deposition, CdZnS, Structural and Optical studies

1. Introduction

In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other opto-electronic devices, with much interest shown in the use of CdS as window layer in solar cell architecture [1, 2]. However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of such solar cells [3-5]. For the high performance of solar cell device, it is imperative to use an appropriate window material. Ternary CdZnS thin films often exhibit improved chemical, structural and optical properties and hence are potentially useful as a window layer in solar cells.

CdZnS thin films have been prepared by various techniques, such as electro-deposition [6], successive ionic layer adsorption and reaction (SILAR) [7] chemical bath deposition (CBD) [5, 8] and metalorganic chemical vapour deposition [9]. Of these techniques, chemical bath deposition is simple, reproducible and cost effective technique compared to others. Currently, CBD is being employed for fabrication of high quality compound semiconductor metal halide and chalcogenide thin films on both metallic and non-metallic substrates [10-12]. The method is well studied and produces films that have comparable structural and optoelectronic properties to those produced using other sophisticated thin film deposition techniques [10,13-15]. The technique has been applied in producing emerging materials for solar cells, laminated sheet glass for transport, protective coating, solar thermal controls in buildings and is being adopted by some industries [15-17].

In this report, results of chemical bath deposited ternary semiconductor thin films of CdZnS are presented. The as-deposited films were annealed at high temperature and studied for possible integration in solar cell architecture.

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2. Materials and Method

The bath constituents for deposition of cadmium zinc sulphide (CdZnS) thin films were cadmium chloride ($CdCl_2$) as a source of Cd^{2+}, Zinc sulphate ($ZnSO_4$) as a source of Zn^{2+}, thiourea [$(NH_2)_2CS$] as a source of sulphide ions (S^{2-}) in the presence of ammonia (NH_3) as the complexing agent. In a typical deposition set up, the bath was composed of 3ml of 1M $CdCl_2$, 2ml of 1M $ZnSO_4$, 5ml of 1M thiourea and 35ml of distilled water put in that order into a 50 ml beaker. The solution was made alkaline by addition of NH_3. The mixture was stirred well to form a homogeneous solution. The microlide glass substrates were cleaned using procedure already reported [12] and placed vertically inside the beaker for 5hrs at room temperature. After deposition, the substrates were removed from the bath, rinsed with distilled water and allowed to drip dry in air. Two of the as-grown films were then annealed in the oven for 1hour each and labelled as A2 (unannealed film), A4 (annealed at 200^{o}C) and A6 (annealed at 300^{o}C).

The chemical reaction for the deposition of CdZnS by CBD is given by:

$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
$SC(NH_2)_2 + 3OH^- \leftrightarrow 2NH_3 + CO_3^{2-} + HS^-$
$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$
$Cd^{2+} + 4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$
$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$
$[Cd(NH_3)_4]^{2+} + [Zn(NH_3)_4]^{2+} + S^{2-} \leftrightarrow$ CdZnS + by product

The structural properties of thin films of CdZnS deposited in this work were studied by using Philips PW 1800 XRD. The absorption coefficient (α) together with the band gap was determined using the transmission and absorption measurement carried out with unico UV-2102 PC spectrophotometer.

3. Results and discussion

3.1. Structural study

To determine the crystal structure of the films deposited in this work, the X-ray diffraction patterns were studied and are shown in fig.1. The pattern shows that the as-grown film possessed poor crystallinity compared to the annealed films. The recorded data from the XRD measurements were compared with data in the JCPDS data files. The planes (101) [d = 3.13148], (002) [d = 3.3419], (100) [d = 3.56877] exhibited the wurtzite (hexagonal type) structure of CdZnS film (which agrees with the standard JCPDS card no. 80-0006). The low intensity peaks observed in the XRD pattern of the sample under study shows that the films are coarsely fine crystallites or nanocrystalline. The broad hump (noise) in the displayed pattern is due to the amorphous glass substrate and also possibly due to some amorphous phase present in the CdZnS thin films.

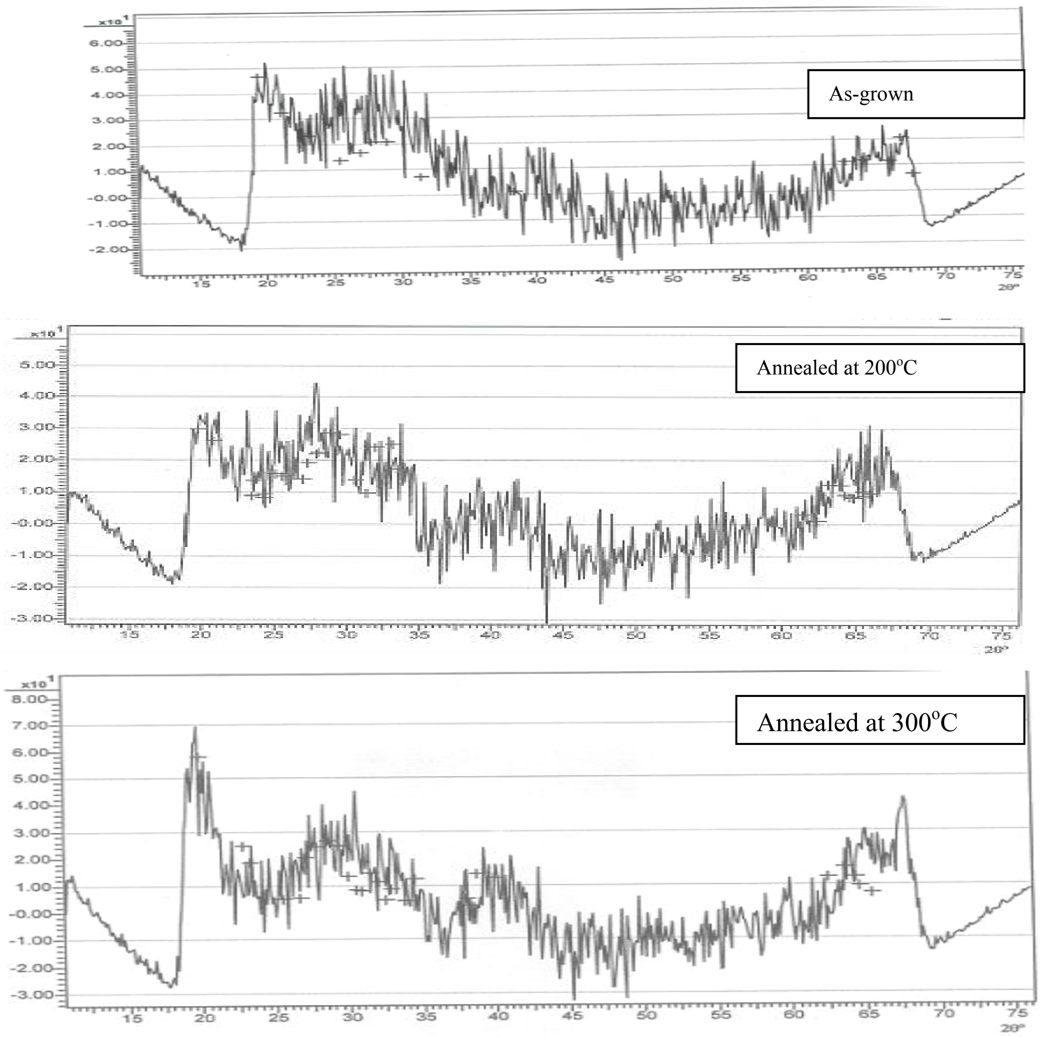

Fig.1. XRD spectra of CdZnS thin films

The average crystallite size of the films was calculated from the recorded XRD patterns using Scherrer formula: $D = 0.89\lambda/\beta\cos\theta$, where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The average crystallite size for the thin film of CdZnS was found to be 60.39nm

3.2 Surface microstructure

The surface microstructure of the films were obtained by taking photomicrographs of the films coated on the transparent glass slides with a wide KPL-W10x/18 Zeiss Standard 14 photomicroscope with M_{35} 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in fig. 2a-b.

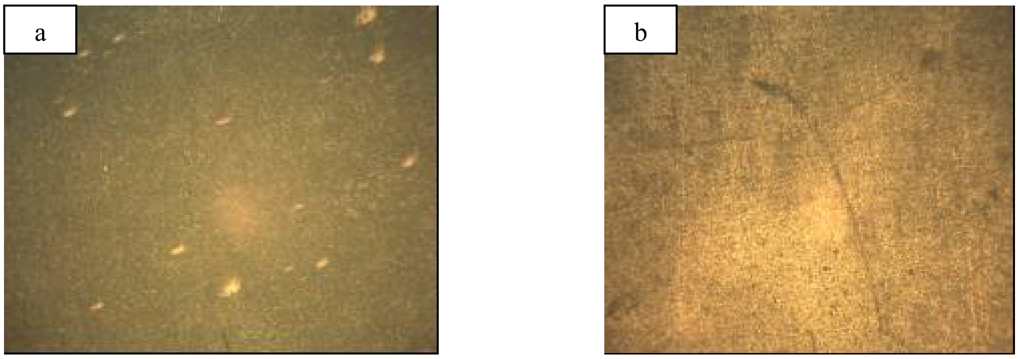

Fig.2. Photomicrograph of CdZnS thin films (a) as-grown and (b) annealed at 300°C.

A close observation of the optical micrographs of CdZnS thin films shows that the film annealed at 300°C covers the substrate well, the grains are well distributed throughout the surface while the as-grown film looks darker. The over growth noticed in fig. 2a disappeared after annealing at 300°C (fig. 2b).

3.3. Optical and solid-state properties

The optical absorption spectra of CdZnS thin films annealed at different temperatures and the as-grown are shown in fig 3. It is found that with increasing annealing temperature, the optical edge shifts towards the lesser value of wavelength. The observed blue shift in the absorption edge is a reflection of increase in band gap, resulting from better quantum confinement effect with the annealing temperature.

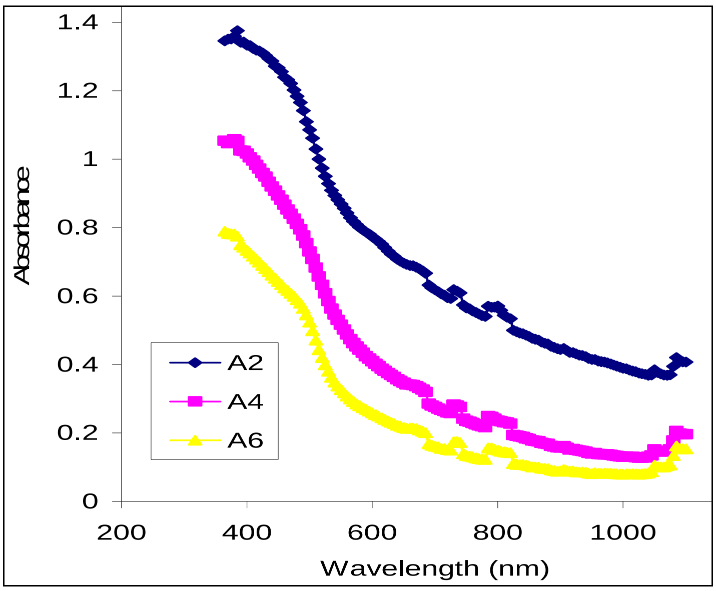

Fig.3: Plot of absorbance against wavelength for CdZnS thin films

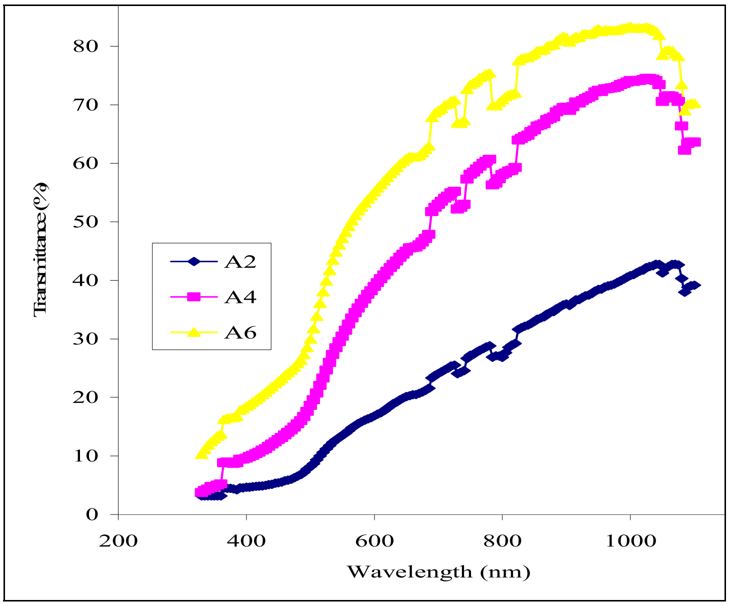

Fig. 4. Plot of transmittance against wavelength for CdZnS thin films.

The spectral dependence of the transmittance for the CdZnS thin films annealed at different temperature and the as-grown film is shown in fig. 4 while that of reflectance is shown in fig.5. The transmittance of the films increases steadily with wavelength and with the annealing temperature to maximum values in the NIR region of the solar spectrum. The film annealed at 300^{o}C exhibited the highest transmittance of 69% at a wavelength of 700nm. Table 1 gives the summary of the average values of the transmittance, reflectance and other solid-state properties investigated in this work.

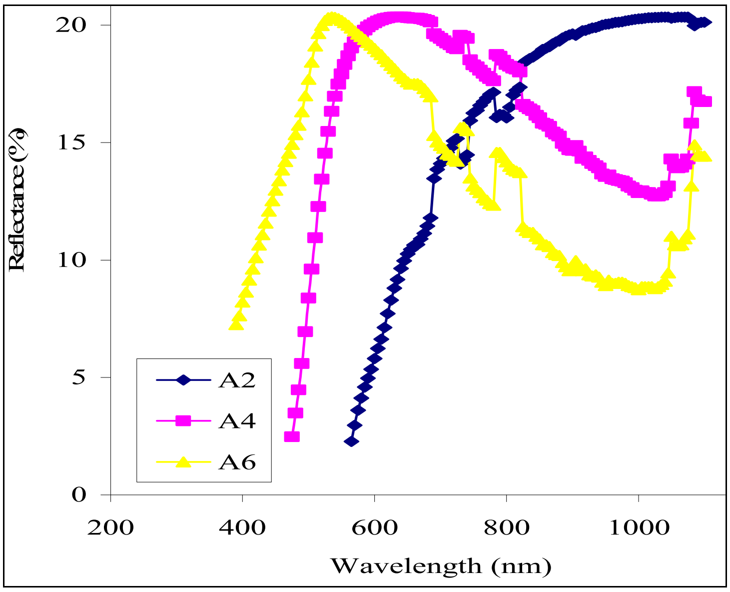

Fig.5: Plot of absorbance against wavelength for CdZnS thin films

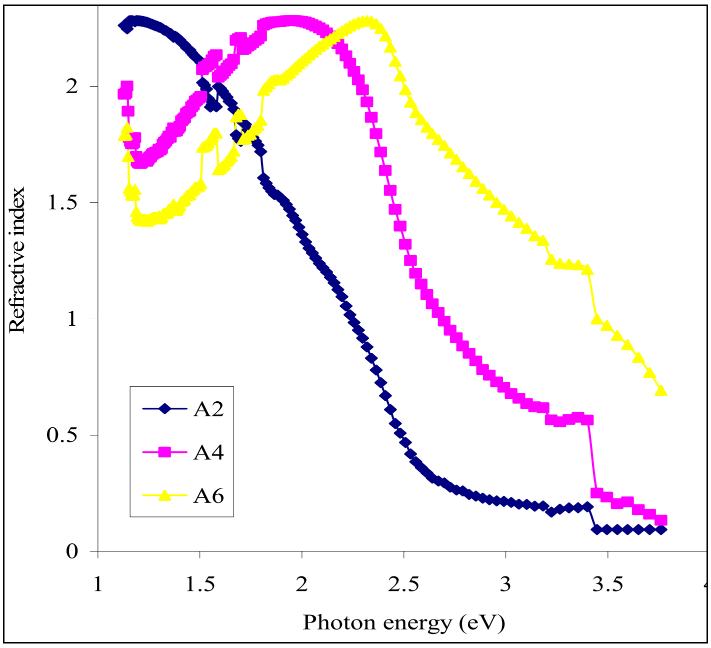

Fig.6: Variation of refractive index with photon energy for CdZnS thin films

Table 1: Average optical and solid-state properties of CdZnS thin films.

	2A		**4A**		**6A**	
	VIS	NIR	VIS	NIR	VIS	NIR
T (%)	13.00	34.73	29.33	66.10	43.09	77.58
R (%)	8.42	18.66	16.82	15.67	16.60	11.29
n	0.91	2.14	1.72	1.89	1.97	1.58
$k \times 10^{-2}$	0.92	0.76	0.56	0.29	0.38	0.18
$\alpha \times 10^{6} (m^{-1})$	2.18	1.07	1.36	0.42	0.93	0.26

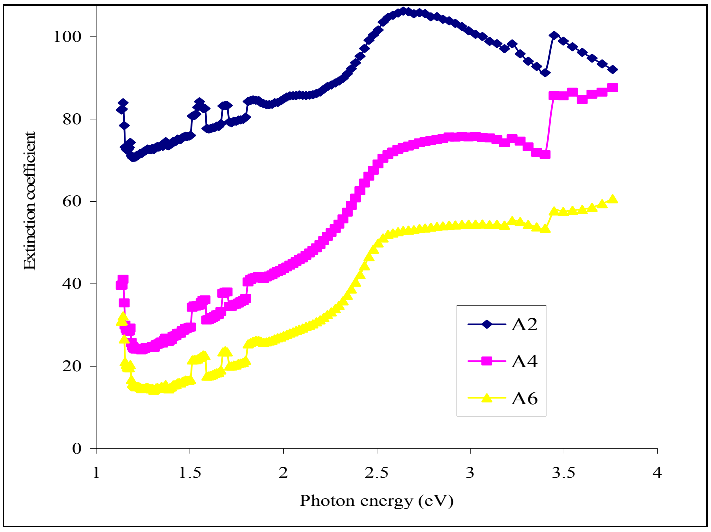

Fig.7: Plot of extinction coefficient against photon energy for CdZnS thin films.

Table 1 shows that the average reflectance of CdZnS thin films increased with the annealing temperature in the visible portion of solar spectrum and reduces in the NIR region. The average refractive index of the film also showed similar trend. The variation of coefficient of absorption (α) with photon energy for CdZnS thin films is shown in fig.8. The magnitude of the coefficient of absorption is within the range for semiconductor thin films suitable for polycrystalline thin film solar cell [18].

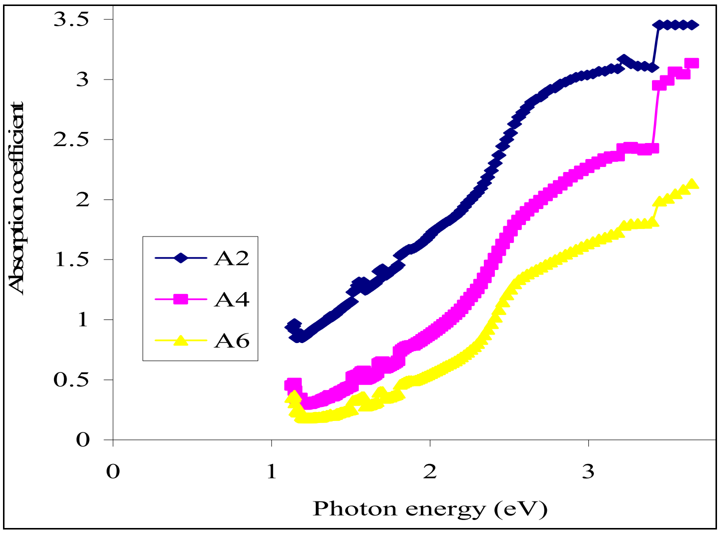

Fig.8: Variation of the coefficient of absorption with photon energy for CdZnS thin films.

The coefficient of absorption method was employed in determining the band gap of CdZnS this films under investigation. The plot is shown in fig.9. Values of the band gap for the deposited CdZnS thin films varies from 2.10 to 2.30 ± 0.05 eV. These values are low compared with the values 2.42 – 2.59 eV [5].

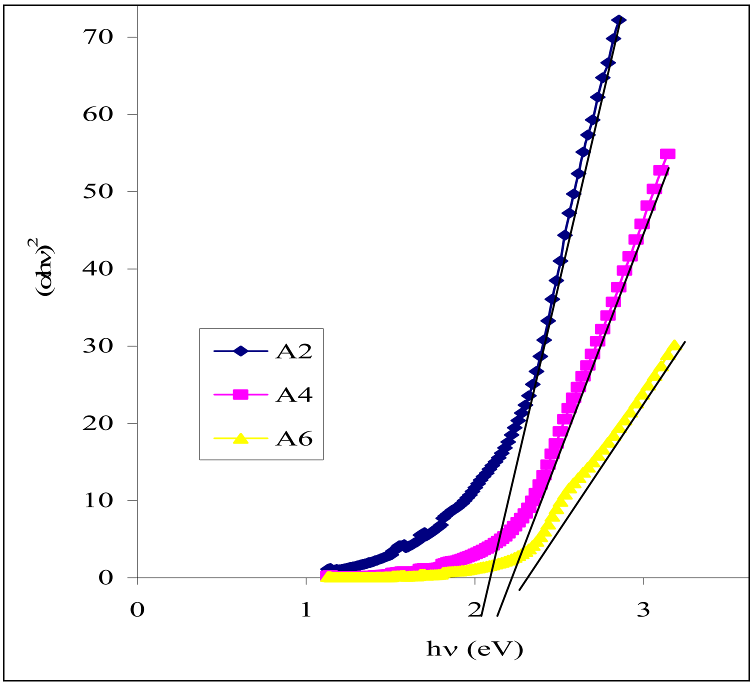

Fig.9: Direct band gap plot for CdZnS thin films

4. Conclusions

Ternary thin films of CdZnS have been successfully deposited on microscope glass slide by chemical bath deposition technique. XRD analysis reveals that thin films of CdZnS deposited and annealed in the oven have preferred orientation along (101) and (002) planes. From the absorption spectra, the band gap energy for CdZnS thin films were found to lie within the range of 2.10 – 2.30eV. Therefore, the films could be applied as window layer in the fabrication of solar cell.

Reference

[1] J.R. Tuttle, J.S. Ward, A.Dude, T.A. Berens, M.A. Contreras, K.R. Rumanathan, A.L. Tenant, J. Keane, E.D. Cole, K. Emergy, R. Noufi, Spring MRS Meeting, San Francisco, (1997) pp 12

[2] T. Ohashi, K. Inakoshi, Y. Hashimoto, K. Ito, Sol. Energy Mater. Sol. Cells, **50**, 37 (1998)

[3] J. Zhou, X. Wu, G. Teeter, B. To, Y. Yan, R.G. Dhere, T.A. Gessert, Phys. Stat. Sol. (b) **241**, 775 (2004).

[4] S.D. Chavhan, R.P. Sharma, J. Phys. Chem. Solids, **66**, 1721 (2005)

[5] S.D. Chavhan, S. Senthilarasu, S. H. Lee, Appl. Surf. Sci. **254**, 4539 (2008)

[6] A.A. Al bassan, Solar Energy Mater. Sol. Cells **57**, 329 (1999)

[7] G. Laukaitish, S. Lindroos, S. Tamulevicius, M. Leskela, M. Rackaitis, Appl. Surf. Sci. **161**, 396 (2000)

[8] T. Yamaguchi, Y. Yamamoto, T. Tanaka, A. Demizu, A. Yoshida, Thin Solid Films **281/282**, 375 (1996)

[9] T.L. Chu, S.S. Chu, J. Britt, C. Ferekids, C.Q. Wu, J. Appl. Phys. **70**, 2688 (1991)

[10] S. Chandra, R.K. Pandy, R.C. Agrawal, J. Phys. D. Appl. Phys. **13**(9), 1957 (1980)

[11] K.L. Chopra, S.R. Das, Thin Film Solar Cells, Plenum Press, New York, 1983, Chapters 2 and 5

[12] F.I. Ezema, S.C. Ezugwu, R.U. Osuji, P.U. Asogwa, B.A. Ezekoye, A.B.C. Ekwealor, M.P. Ogbu, J. Non-Oxide Glasses, **1**(1), 45 (2010)

[13] H.V. Campe, G.H. Pewig, W. Hoffman, Solar Energy Material **52**, 159 (1981)

[14] C.U. Okujagu, C.E. Okeke, Nig. J. Renewable Energy **5**(1,2), 125 (1997)

[15] R.U. Osuji, Nig. J. Solar Energy, **14**, 90 (2003)

[16] F.I. Ezema, C.E. Okeke, Nig. J. Solar Energy, **14**, 66 (2003)

[17] S.C. Ezugwu, F.I. Ezema, P.U. Asogwa, Chalcogenide Letters, **7**(5), 341S (2010)

[18] J.D. Meakin, Workshop on Materials Science and Physics of Non Conventional Energy Sources (World Scientific, Singapore, 1989).