ZnSe BUFFER LAYER DEPOSITION FOR SOLAR CELL APPLICATION.

N. A. OKEREKE*, A. J. EKPUNOBI[a]
Department of Industrial PhysicsAnambra State University, Uli, Nigeria.
[a]Department of Physics and Industrial Physics, Nnamdi Azikiwe University, Awka, Anambra State.

Zinc selenide (ZnSe) buffer have been deposited by a simple and inexpensive chemical bath deposition (CBD) technique. They have been characterized by optical microscope, spectrophotometer and four point probe. The optical band gaps of the films were estimated to be in the range of 2.50–2.70eV. The optical absorption data shows that the films have high absorbance in the ultraviolet range of 0.36–0.45 microns and low absorbance in the visible and infrared regions. Electrical properties show that ZnSe films have high resistance. The thin film would therefore make good buffer layer for solar cells.

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1. Introduction

ZnSe is a technological important optoelectronic semiconducting material with a wide band gap of 2.7eV. It can be substituted for CdS in photovoltaic solar cells (Dona J. M. and Herero J. 1995). It is considered as an important technological material due to their potential applications in various optical and electronic devices and as buffer/ window material for thin film hetero-junction solar cells (Krause et al 1994 and Hariskos et al 2005). The properties of interest in most of these applications are the energy band gap, film thickness and the wavelength of transmission or absorption of the films. Various methods have been employed for the deposition of ZnSe thin films which include thermal evaporation, electrochemical deposition and chemical bath deposition (Kale et al 2006).

The composition of a buffer layer often depends on the deposition method and the preparation conditions. For example, the chemical bath deposition of sulphides and selenides, normally yields films containing hydroxides and/or oxides. The chemical bath deposition technique (Wang et al 1999) has been found to be an inexpensive and simple low temperature method that could be used to produce good quality film for device applications. It is well studied and produces films that have comparable structure and opto-electronic properties to those produced using other sophisticated thin film deposition technique.

Recently, it has been found that CBD methods is most useful for deposition of buffer layers for $CuInS_2$, CuInSe or CuInGaSe based solar cells (Naciri et al, 2007). High efficiency solar cells have been fabricated by using CBD CdS buffer layers. However, since cadmium is a toxic material, serious effort to substitute the CdS buffer layer by other non-toxic low absorbing materials have been made. ZnSe is such an important material with large direct band gap (2.7eV) which allows transmission of higher energy photons than the band gap of CdS (2.4eV). It has a better lattice match with CuInGaSe (CIGS), thin films absorbers. Using the CBD ZnSe buffer, a cell efficiency of 15.7% (Hariskos et al 2007) was achieved. It is an attractive buffer layer for thin film solar cell (TFSC) application (Shimizu et al 2002).

ZnSe film is also a precursor material for the formation of ZnInSe. ZnInSe is Cd free buffer which was successfully tested as an alternative to the CdS buffer (Hariskos et al 2005). The

*Corresponding author: ngozigoddyokereke@hotmail.co.uk

primary function of a buffer layer in a hetero-junction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer, no photo current generation occurs in the window layer (McCandless and Hegedus 1991). The benefit of the buffer layers arises because they essentially remove the contact which has high minority carrier recombination losses from the absorber or base layer. Secondly when these layers are used near the top of a cell, because of reduced absorption and reflection losses, optical enhancement is achieved (Roedern B. Von and Bauer a 1999).

In the present work, we report the chemical bath deposition of ZnSe thin films from an aqueous solution bath containing $Zn(NO_3)_2$ and $SeSO_3$ using $Na_2S_2O_3$ as the complexing agent. The deposition was carried out at room temperature. The ZnSe film characterizations such as morphological, optical and electrical properties have been carried out and results are reported.

2. Materials and methods

The ZnSe layer is grown by chemical bath deposition (CBD) using an aqueous solution containing a zinc trioxonitrate (v) $Zn(NO_3)_2$ and the selenium sulphite ($SeSO_3$) used respectively as the zinc and the selenide ions source, sodium thiosulphate $Na_2S_2O_3$ as the complexing agent and 25% NH_3 which provide the alkaline medium.

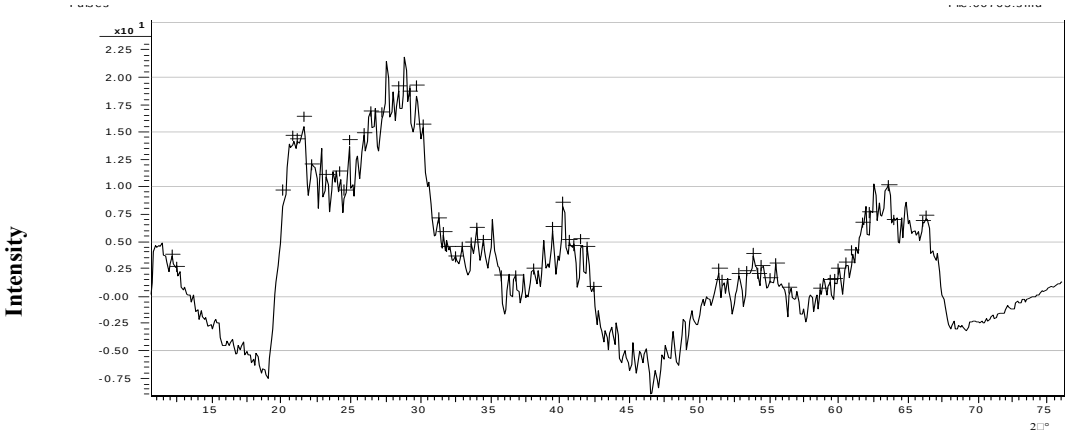
The baths for the deposition of ZnSe layer were constituted with 0.5M solution of zinc trioxonitrate (v) $Zn(N0_3)_2$. 0.1M solution of selenium sulphite, 25% ammonia (aq as supplied) and 0.1M solution of sodium thiosulphate ($Na_2S_2O_3$) used as complexing agent. The films were deposited on commercial glass slides (76mm x 26mm x 1mm) degreased in Aqua Regia solution, washed in detergent and rinsed in distilled water. At the end of the deposition period (15 – 20 hours), the films were rinsed in distilled water and dried in air. The deposition was done at temperature of 300k.

Measurements for the analysis of the optical properties of the films were made using Janway 6405 UV–VIS model of spectrophotometer. The morphological analysis was done using an Olympus optical microscope. Four point Probe was used for the measurement of the electrical resistivity of the films.

3. Results and discussion

3.1 Structural and optical investigations of CBD ZnSe thin films.

ZnSe can exist in two crystalline structures: the cubic phase and the hexagonal phase. The as deposited ZnSe films on various substrates are found to exhibit cubic structure. The x-ray diffraction spectrums of ZnSe films grown showed that the films have highly oriented crystallites with a preferred orientation along the (111) plane.



In the case of the film shown in Fig. 1 the (111) diffraction line localized at approximately 27.2^{o} and the weak other ones at approximately 45.5^{o} and 53.6^{o} match with the (220) and (311) diffraction lines of cubic phase ZnSe films which is in good agreement with the reported ones by several authors (Muralli et al 2009 and Mahalingam et al 2007).

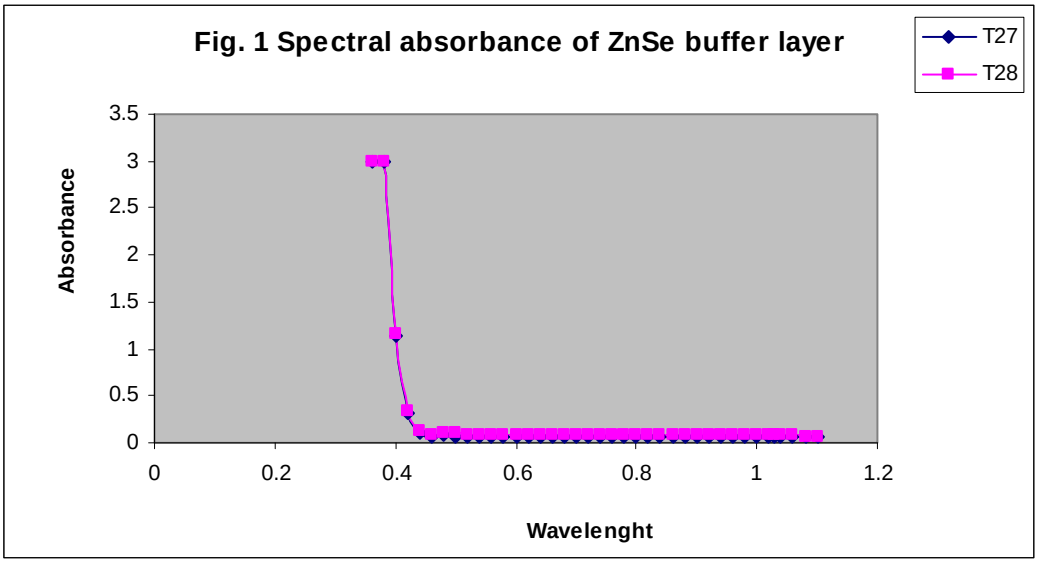
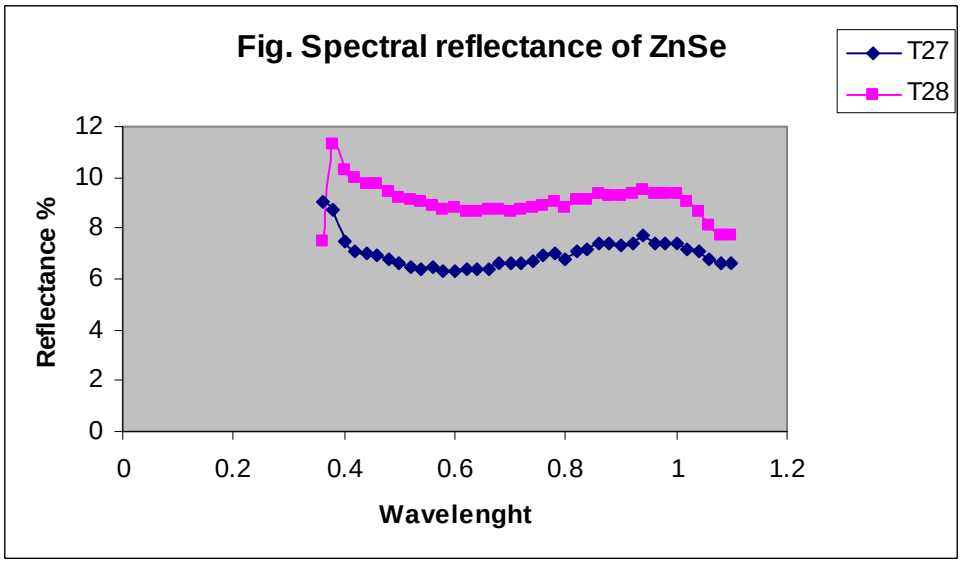
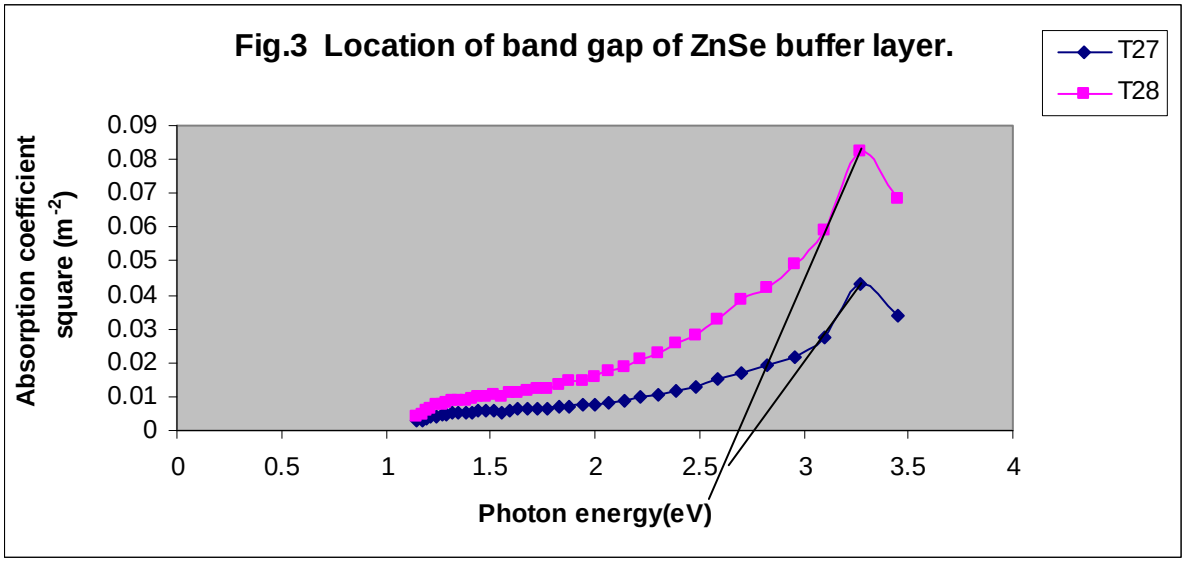


Fig. 2 shows the optical absorbance spectrum for wavelengths of 0.30 – 1.10µm for ZnSe films deposited under the deposition conditions with different thickness. The spectra show a high absorbance in ultra violet region and very low absorbance in visible and infrared regions. Because of the very high absorbance that the films have shown in the UV region, they will transmit only negligible amount of UV thereby saving the cell more from over heating resulting from lattice vibrations.



The optical transmittance spectra in figure 3 indicate that an average transmission of above 80% was obtained in the visible range. These characteristics make the film a good buffer layer for solar cell application.



The energy gaps of the films fall within the range 2.4 – 2.8eV, the typical range for good solar cell buffer layers. They will transmit all solar radiation of wavelength greater than its absorption edge wavelength (0.4μm) and this includes substantial part of the visible radiation and simultaneously absorbing all solar radiation of energy greater than 2.7eV.

3.2 Electrical properties

The electrical properties of the films were investigated using a standard collinear four point probe technique. The arrangement was made in such a way that the voltage across the transverse distance of the films and the corresponding values of the current were measured using silver paste to ensure good ohmic contact to the film. The sheet resistivities ρ_s of the films at room temperature were calculated using the expression.

$$\rho_s = (\pi \mathrm{In}2)\ V/I = 4.53R$$

where V = the potential difference (voltage) across the transverse distance of the film.
I = current
R = resistanc

The results are shown in the table below:

Reaction Bath	**Film thickness, t (μm)**	**Resistivity, ρ (Ωm^{-1})**	**Conductivity, σ $(\Omega m)^{-1}$**
K_4	1.502	3.15×10^{8}	3.0×10^{-9}
T_{27}	1.644	4.46×10^{8}	2.0×10^{-9}

The results are comparable with the reported value by Sankpal et al (1999) whose value of resistivity of ZnSe is of the order of $10^4 – 10^{12}$ Ωm^{-1}. The results clearly show that ZnSe films have high resistivity. The high resistivity makes ZnSe suitable as buffer layer in thin film technology. It is a semiconductor that has large potential applications in thin films like photo luminescence and electroluminescent devices (Panthan and Lokande 2004).

4. Conclusions

We used the chemical bath deposition process, CBD for growing uniform and reproducible ZnSe buffer layer. XRD spectra confirm the cubic structure with the preferred orientation along (111) planes. The films have region of the electromagnetic spectrum and high rate of adsorption in the UV region. The high transmittance makes the films potential for use in manufacture of optical components, windows, mirrors, lenses etc for high power IR laser. Also, the electrical characterization reveal that the ZnSe thin films presented here have high resistivity and are well suited for use as buffer layer in thin film solar cell.

References

[1] Karause, E., H. Hartmann, J. Menninger,A. Hotffmann, R. Fricke, B. Heitz, B. Hummer, V. Kutzer, I. Broser, J.Cryst. Growth **138**, 75 (1994). http://ieeexplore ieee.org/ie15/23/5485051/0

[2] Kale, R.B., S.D. Sartale, V. Ganessan, C.D. Lokhande, V.F. Lin, S.Y. Lu, Applied Surface Sci., **253**: 930 (2006) 10.1016/j.apsusc.2006.01.050 http://adsabs.harvard.edu/abs/2006ApSS..253..930K

[3] Wang, C., X.F. Qian, W.X. Zhang, X.M. Zhang, Y. Xie and Y.T. Qian,. Mater. Res. Bull., **34**, 1637 (1999). 10.1016/S0025-5408(99)00187 http://www.ingentaconnect.com/content/els/00255408/1999/00000034/00000010/art00187

[4] Mahalingan, Soonilee, M. Sunghvan and D.K. Yong,. Studies of Electrosynthesized Zinc Selenide Thin Films. Journal of New Materials for Electrochemical Systems **10**,15 (2007). www.newmaterial.polymtl.com

[5] Nair, M.T.S and P.K. Nair,. Chemical bath deposition of Cu_xS thin films and their prospective large area applications. Semicond. Sci. Technol., **4,** 191-199 (1989). 10.1088/0268-1242/4/3/009, http://iopscience.iop.org/0268-1242/4/3/009

[6] Nair , M.T.S., P.K. Nair, Near Ideal solar control characteristics of Cu_xS thin films. Semicond Sci. Technol., **4**, 599-602 (1989). 10.1088/0268-1242/4/7/020, http://iopscience.iop.org/0268-1242/4/7/020

[7] Okujiagu, C.U.,. Ph.D. Thesis, Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria. 1992

[8] Okujiagu, C.U. and C.E. Okeke,. Photovoltaic potentials of some transparent/translucent thin films. Nig. J. Renewable Energy, **8**, 90-98 (2000).

[9] Okujiagu, C.U., C.E. Okeke,.. Nig. J. Renewable Energy, **8**, 24-23 (2000).

[10] Theye, M., 1985. In Optical properties of Thin films, K.L. Chopra and L.K. Malhota, eds, thin film technology and Applications. Tata McGraw – Hill, New Delli 163.

[11] Murali, K.R. and R.J. Xavier,. Chalcogenide Lett., **6,** 683 (2009). http://www.chalcogen.infim.ro/683_Murali-dec3.pdf

[12] Yamaga, S., A. Yoshikawa and H. Kasai, J. Cryst. Growth **86**, 252 (1998).

[13] Lokande, C., P. Patit, A. Enniwi and Tributch, Chemical Bath ZnSe thin films: deposition and characterization .Appl. Surface Sci. **123-124**,294-297 (1998).

[14] Devyatykh, G. G Koshunov, I. A, and Gavrishahuk, E. M,. Deviation from Socio-metric Composition in Polycrystalline ZnSe Produced by CBD from Gas Phase. Doklady A.N SSSR Khinmiya Russia **T28** (1), 56 (1993).

[15] Chaisitsak S, Tokita Y, Miyazaki H, Mikami R, Yamada A and Kongai M, 2001. Proceedings 17th European Photovoltaic Solar Energy Conference Munich Germany. 1011.

[16] Gutowski J, Michler P, Ruckmann H, Brunig H, Rowe M, Sebald K and Voss T,. Excitons in wide-gap semiconductor, coherence,dynamics and lasing. Phys. Stat. Sol. B **234**, 70 (2000). Onlinelibrary.wiley.com/1521-3951(200211)23

[17] Hariskos D, Spiering S, and Powalla M,. Buffer Layers in Cu(InGa)Se_2 Solar Cells and Modules. Thin Solid Films. **480-481,** 99 (2005). www.sciencedirect.com

[18] McCandless B. E and Hegedus S. S, 1991. Influence of CdS Window Layer on Thin Film CdS/CdTe Solar Cell Performance. Proceedings of the 22nd IEEE Photovoltaic Specialists Conference. 967-972.

[19] Naciri R, Bihri H, MZerd A, Rahioui A, Abd- Lefdil M and Messaoudi C.. The role of CdS buffer layer in the $CuInS_2$ Thin Film Solar Cell. Revue des Energies Reneouvelables CER **07** Oujda. 165-168 (2007). www.cder.dy/download/cer07-pdf

[20] Osuji R. U.. Analysis of chemically Deposited CdSe and CdS Thin Films. Nig. Journ. Of Solar Energy **14**, 90 (2003).

[21] Roedern B. Von and Bauer G. H.. Material Requirements for Buffer Layers Used to Obtain Solar Cells with High Open Circuit Voltages. National Renewable Energy Laboratory/CP-**520**, 263 (1999). http://www.doe.gov/bridge/home.html

[22] Shimizu A, Chaisitsak S, Sugiyama T, Yamada A, and Kongai M,. Zinc-based buffer layer in the $Cu(InGa)Se_2$ thin film solar cells. Thin Solid Films, **361-362**: 193-197 (2002). www.elsezier.com/locate/issn 00406090 2002: 193-197.

[23] Yamada A. Chaisitsak S, Othake Y and Konagai M. 1998. Proceedings 2nd World Conference of Photovoltaic Energy Conversion, Vienna Austria: 1177.