SYNTHESIS AND CHARACTERIZATION OF ELECTRODEPOSITED ZINCSULPHIDE (ZnS) THIN FILMS FOR PHOTOVOLTAIC APPLICATION

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ABSTRACT

Zinc sulphide (ZnS) thin films were deposited from inorganic reagents (solution electrolytes) using a two electrodes electrochemical cell. The film's thickness and particle distribution were determined by Surface profiler. The film's particles are continuous but not uniformly distributed across the substrate and the thickness was determined to be 70 nm. X-ray diffraction (XRD) study indicated that the film possesses Zinc blend cubic structure. Crystal size and inter-planar spacing were estimated as 0.36 nm and 0.29 nm respectively. Optical characterization showed that the film has poor absorbance in the visible light region while transmittance is enhanced as wavelength increases. Energy band gap of 3.49 eV was estimated for the film. I-V characteristic of ITO/ZnS/Ag is linear indicating possibility of an ohmic contact between ITO substrate and ZnS film and also between ZnS and Ag. Thus, this study demonstrates that ZnS thin film can be a good recipe for window layer of tin film solar cells.

Keywords: *Electrodeposition, Characterization, Zinc Sulphide, thin films, Photovoltaic*

INTRODUCTION

The window/buffer layer of most thin film solar cells at present are made of cadmium sulphide (CdS) thin films deposited mostly by chemical bath deposition (CBD). CdS contains Cadmium which is very harmful to the environment. More so, the CBD technique is a batch process which produces large amount of waste product which enlarges the amount of Cd waste introduced to the environment. Thus, there are needs to produce Cd free window/buffer layer using deposition technique that introduces less waste to the environment.

Zinc sulphide thin films is II–VI semiconductor with a wide band gap which is suitable for applications in solar cells. It is nontoxic to human body, very cheap and abundant (Kassim et al., 2010). Several deposition techniques such as CBD (Sanap and Pawar, 2011, Liu et al., 2011, Oladeji and Chow, 1999 and Ndukwe, 1996), Chemical vapour deposition (Shibata et al, 1987), Organomettallic chemical vapour deposition (Wright and Cockayne, 1982), electron beam evaporation (Benoit et al, 1988), Atomic layer epitaxy (Hunter and Kitai, 1988), and RF sputtering (Warren et al., 1983) have been used to produce Zinc Sulphide thin films. All these techniques produce good quality films but required highly cost vacuum equipment and/or expensive chemicals. They also waste most of the starting materials since not all ZnS precursors deposit on the substrate. Thus, adding to the cost of production. Electrodeposition technique uses little amount of electrolyte and the electrolyte can be used several round and thus, save cost as well as amount of waste introduce to the environment. This technique has been used by Kassim et al., (2010) and Sanders and Kitai (1990) to prepared ZnS thin but they both used three electrodes which implies the use of reference electrode that may introduce impurity to the thin films. This study therefore aimed at synthesis and characterization of Zinc sulphide thin films using two electrodes electro-deposition technique.

MATERIALS AND METHODS

The Zinc sulphide thin films were deposited using two electrodes electro chemical deposition technique as earlier reported by Taleatu *et al.,* (2011). The substrate employed in this study was Indium tin oxide (ITO) coated soda lime glass and was prepared using cleaning method. The starting materials for preparing the electrolytic bath for deposition of Zinc sulphide (ZnS) thin films were Zinc acetate ($C_4H_6O_4Zn.2H_2O$) as a source of Zinc ion, sodium thio sulphate pental hydrate ($Na_2S_2O_3.5H_2O$) as a source of sulphur ion and tetra-oxo-sulphate six acid (H_2SO_4) to adjust the pH of the bath. They were all of analytical grade from sigma-Aldrich and were used as received. The solvent employed is distilled water from Chemistry laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria.

Zinc acetate (2.20 g) was dissolved in 1000 ml of distilled water to make 0.01M of Zinc acetate. 62.04 g of sodium thio sulphate was dissolved in 1000 ml of distilled water to make 0.25 M of sodium thio sulphate. 25 ml of 0.01 M of Zinc acetate was measured into glass container; 25 ml of 0.25 M of sodium thio sulphate was also measured and added to the content of the container. 5 drops of 0.05 M of H_2SO_4 was added to the entire mixture and already well arranged substrates with cover were inserted. A cathodic voltage of 0.9 V was applied, the starting current was observed to be 0.750 mA and the stopping current was observed to be 0.170 mA. The deposition period was measured to be 21:19 minutes. The thin film was removed, rinsed with distilled water and kept in sample holder for characterization.

The electrodeposited zinc sulphide thin films were characterised using Surface profiler to determine the thickness and study surface roughness, XRD to determine its structure, Uv-visible spectrometer to study its optical properties and four point probes to determine the electrical properties of the films.

RESULTS AND DISCUSSION

Surface Roughness study and measurement of thickness of ZnS thin films

The surface roughness and thickness of the film was studied using surface profiler. Fig, 1 shows the surface profile of the film.

The above figure reveals that, the film is continuously though not uniformly distributed on the substrate surface. The average crystal growth height (film thickness) is given as 0.07 µm which is the same as 70 nm. This is within the optimal film thickness required of ZnS thin films to be used for window layer of thin film solar cells as stated by Liu et al., (2012).

Structural study of ZnS thin films

The structure of the film was studied using XRD. The XRD pattern of the film is as shown in Fig.2

From the pattern, the observed peaks are at angle 2θ equals 30.2°, 35.2°, 43.2° and 50.5°. This gave the evidence of the crystalline nature of the film. On comparing the pattern with JCPDS cards, the compound with the best match was ZnS with Zinc blend cubic structure. The crystallite was determined to be 0.36 nm while the inter planar spacing was 0.29 nm. This implies that the thin film is a nanostructured material. This result is in agreement with Sanders and Kitai, (1990), Kassim, et al, (2010) and Liu et al, (2012) who have found various cubic structures for ZnS thin films.

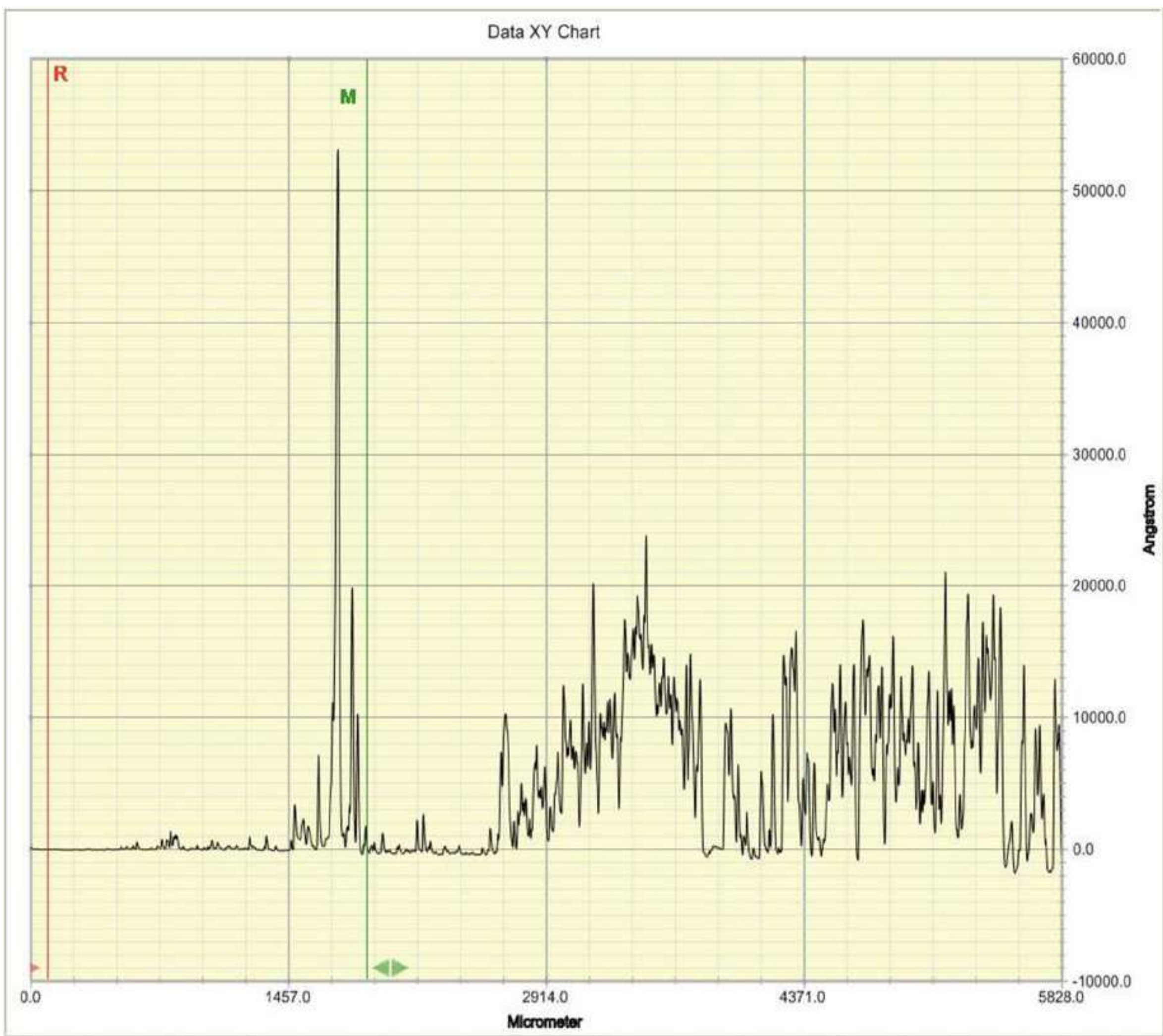

Fig.1 SURFACE PROFILE IMAGE OF THE ZnS THIN FILMS

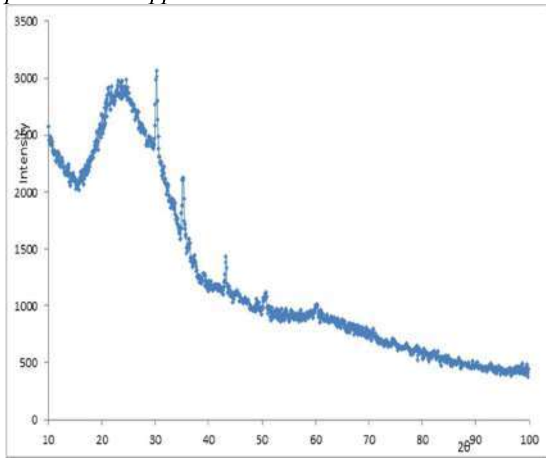

Fig.2 XRD PATTERN OF ZnS THIN FILMS ON ITO COATED GLASS

Optical study of ZnS thin films.

The optical properties of ZnS thin films were studied using Uv-visible spectrometer. The data obtained from Uv-visible spectrometer were analysed using the following formulae:

$R = 1 - (A + T)$, where A= Absorbance, T=Transmittance, R=Reflectance,

$\alpha = \frac{1}{t} ln\left(\frac{1}{T}\right)$, α = absorption coefficient, t=thickness, T=Transmittance,

$E(eV) = \frac{hc}{\lambda}$, h = Planck's constant, c=speed of light and λ=wavelength and

$\alpha h\upsilon = A(h\upsilon - E_g)^{\frac{n}{2}}$, n =1 for direct and 4 for indirect band gap.

Thus, the Transmittance, Reflectance and Absorbance spectrum of the film were plot in the visible region and they are as shown in Figs.3, 4 and 5:

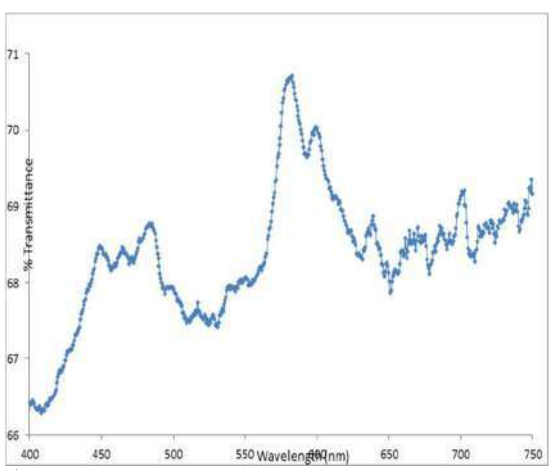

Fig.3 GRAPH OF %TRANSMITTANCE VERSUS WAVELENGTH

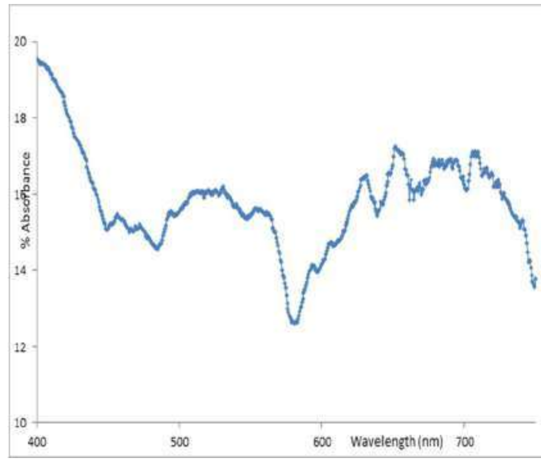

Fig.4 GRAPH OF %ABSORBANCE VERSUS WAVELENGTH (nm)

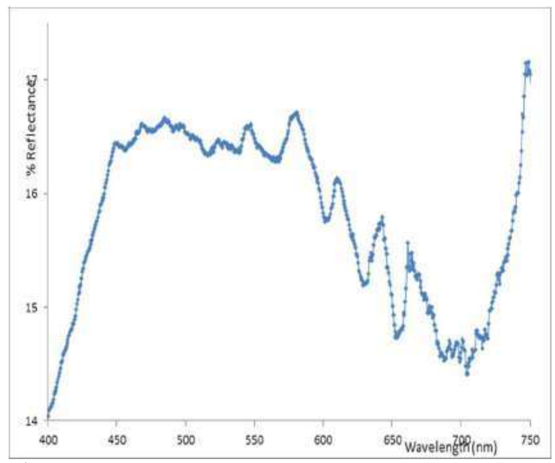

Fig.5 GRAPH OF % REFLECTANCE VERSUS WAVELENGTH (nm)

From the Figs. 3, 4 and 5, it can be deduced that, ZnS thin films transmittance in the visible region varies from 66 % to 71 %. The absorbance varies from 12 % to 19 % and reflectance varies from 14 % to17 %. Thus, the film is a good transmittance but a poor absorbance and reflectance of light in the visible region. These results agreed very well with the work of Sander and Kitai (1990), Ndukwe (1996) and Liu et al., (2012) that have found out that ZnS thin film is a good transmittance but a poor reflector and absorber of visible light.

The energy band gap of ZnS thin films was determined by extrapolating to the horizontal axis, the graph of α^2 versus energy as shown in Fig.6. From the graph, the direct band gap energy of ZnS thin films was estimated to be 3.49 eV. This compared well with the results of Lange, (1973), Sze, (1985), Sanders and Kitai, (1990), Ndukwe, (1996) and Liu et al., (2012) who have reported energy band gap ranging between 3.6 eV and 3.85 eV for ZnS thin films.

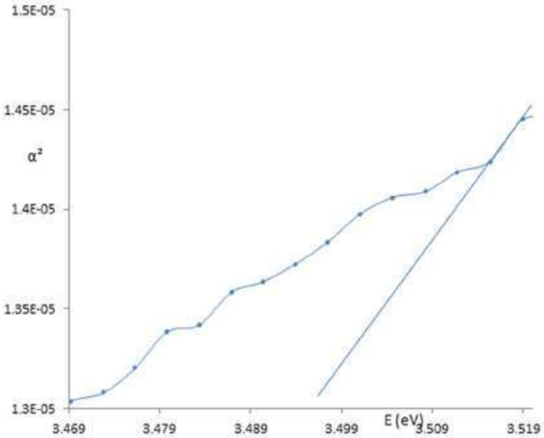

Fig. 6: GRAPH OF α² VERSUS ENERGY (eV)

Electrical study of ZnS thin films

The electrical properties of ZnS thin film were studied using four points probe with Keithley source metre and laboratory tracer software in collinear array mode to study their resistivity. The I-V characteristics of the ITO/ZnS/Ag structure were studied using Keithley source metre with interactive characterization software.

The sheet resistivity of the film was given to be 49.89 Ω/cm and resistivity was calculated to be 4.984 x 10^{-4} Ωcm. The conductivity of the film was calculated to be 2.01 x 10^{3} $\Omega^{-1}cm^{-1}$. This implies that ZnS thin film is a good conductor of electricity. The I-V characteristics curve of ITO/ZnS/Ag structure is given in Fig.7. The linear curve obtained implies that, the ITO/ZnS and ZnS/Ag junction are ohmic.

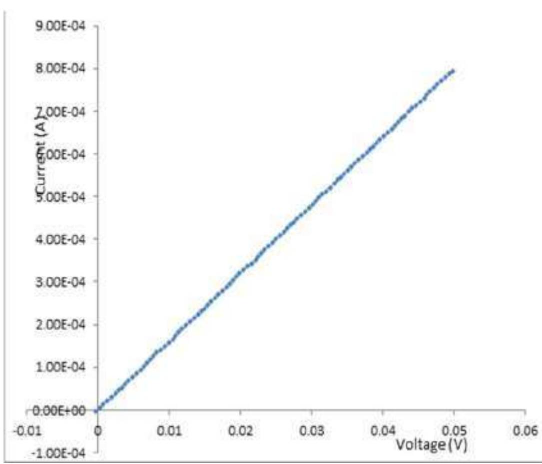

Fig. 7: I-V CHARACTERISTICS OF ITO/ZnS/Ag STRUCTURE

Conclusion

The results from various characterization reveals that electrodeposited ZnS thin films are nanostructured material which are continuously distributed with high percentage transmittance of visible light and wide band gap energy coupled with good conductivity is a suitable material for window layer of hetero-junction thin film solar cells. Thus, the study conclude that Zinc sulphide thin films are suitable for window/buffer layer of hetero junction thin film solar cells and can be fabricated using simple two electrodes electrochemical deposition technique.

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