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Effects Of Concentration On The Structural, Morphological And Electrical Properties Of Kesterite Cu_2ZnSnS_4 Thin Films.

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Abstract
Kesterite Cu_2ZnSnS_4 thin films were successfully deposited on glass substrates using the chemical bath deposition (CBD) technique at a bath temperature of 343K, for 5 hours. The optical and structural properties of the films were investigated using spectrophotometer and X-ray diffractometer at iThemba Laboratory Research Department, FAURE, South Africa. The morphology was characterized by Scanning Electron Microscopy (SEM) and the electrical properties or energy gaps were determined from the extrapolation of the straight portion of the graph of $(\alpha h\nu)^2$ against $h\nu$ to the horizontal axis. All the film samples were polycrystalline with hexagonal wurtzite crystal structure. The films covered the substrates very well, had no cracks or pores and had uniform distribution of agglomerated particles on the substrates. Increase in Zn concentration to 0.5M resulted to high mechanical stability of the films, more crystallization and increased grain size. The films had direct interband transitions. Between 0.1 – 0.4M of Zn, there was a blue shift in the energy gaps, from 1.32 – 1.25eV. The optoelectronic device applications of the films were enhanced, when Zn concentration was increased to 0.4M.

Keywords: *Kesterite, concentration, structural, morphology and electrical properties.*

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I. Introduction

The advantages of the use of photovoltaic systems in generating electricity cannot be overemphasized when compared with the conventional means such as fossil fuels, coal, hydrogen gas liquids and nuclear energy etc. Photovoltaic systems offer the possibility of a renewable energy resource with few inherent environmental disadvantages (1). The voltage generation from a device (solar cell) which is exposed to sunlight is known as photovoltaic effect. A solar cell is a p – n junction device with no voltage applied directly across the junction (2). The wide applications of nanostructure metal oxide, thin films such as TiO_2, ZnO, CuO and NiO etc, have generated lots of interests over the years (3 – 7). Semiconductor devices that have photovoltaic properties must have band gap energy less than the photon energy. Solar energy conversion is attractive because it is inexhaustible and non-polluting and the applications include: generation of power for remote and rural areas, applications in space vehicles and satellites, water pumping and treatment systems, health care systems, communications, agriculture, transport aids, security systems and corrosion protection systems (2, 8).

Thin film technology is essential to the development of terrestrial solar cells. Thin films are important for; the photoelectrically active layers, contacts, window materials, antireflection coatings, transport conducting coatings and passivating layers (9). There are other thin film solar cells that have got well developed technology and these include; GaAs, CdS, Cu_2S, Cu_2S/CdS, $CuGaS_2$, ZnSe and CdSe etc (10, 11). Thin film solar cells are cells which have been deposited on electrically active or passive substrates such as glass, plastic, ceramic, metal, graphic or metallurgical silicon (12). These thin films have main advantages of using low cost materials and simple inexpensive techniques for their deposition on glass substrates such as spray pyrolysis and chemical bath deposition techniques (7, 13).

Research interests in semiconductor, low cost solar cells with relatively high efficiencies are ever-increasing. Examples of cells in this category are kesterite thin film solar cells such as Cu_2ZnSn ($SxSe_1$-x)

(CZTSSe) which has a high absorption coefficient of ~ 10^4 cm^{-1} (14), and kesterite Cu_2ZnSnS_4 nanoflake thin film that has a direct transition with a band gap energy of 1.50 eV has been synthesized and deposited by successive ionic layer adsorption and reaction (SILAR) technique (15). Kesterite is defined as sulfide mineral with Zn – rich variety while the Zn – poor form is known as ferrokesterite or stannite (16).

In this study, we present a report on the deposition of kesterite Cu_2ZnSnS_4 thin film solar cells by chemical bath deposition (CBD) technique, with particular interests on the effects of concentration of zinc (Zn) on the structural, morphological and electrical properties of the deposited thin films. The choice of using CBD technique in this study was based on its obvious advantages over other methods/techniques. These include the following: it is highly specific, inexpensive, simple, convenient and easily adapted to large area processing; it can be used in depositing both conducting and non-conducting thin films by electrochemical processes without the presence of an externally applied field; thin films can be deposited on the substrates at low temperature using this method; bath parameters and deposition times can be readily used to control thicknesses of the films and the method has been applied in producing some emerging materials (thin films) for solar cell applications (17 – 20).

II. Experimental Details

Substrates were properly prepared before the deposition of the thin films. They were cleaned with detergent, followed by cleaning with deionised water, then ammonia acid and finally rinsed with acetone. The substrate preparation was to ensure uniform coating and also to break the bond between the substrates and contaminants. The effects of the contaminants on the properties of the thin films such as nucleation and morphology were thus removed (21). Chemical bath deposition technique was used in the deposition of kesterite Cu_2ZnSnS_4 thin film solar cells on glass substrates. In the synthesis of the thin films, zinc (Zn) concentrations were varied from 0.1 – 0.5 M in steps of 0.1 M. The bath temperature was 343K. The chemicals used include: copper sulphate ($SnSO_4$), zin sulphate ($ZnSO_4.7H_2O$), thioacetemide ($SuSO_4.5H_2O$), tin sulphate ($C_2H_2N_2S$) and ammonia (NH_3) as a complexing agent.

III. Thin Film Characterization

Spectrophotometer analysis was done at Centre for Energy and Research Development (CERD), Obafemi Awolowo University (OAU) Ile-Ife, Osun State, Nigeria. Scanning Electron Microscopy (SEM) analysis was done at iThemba Laboratory Research Department, FAURE, South Africa. The structural properties of the deposited thin films were studied using Rigak D/ma x 2100 diffractometer with a Cukα $(\lambda = 1.5406\ \text{Å})$ and the optical absorption theory was used to determine the energy gaps or electrical properties of the thin films, from the extrapolation of the straight portion of the graph of $(\alpha\lambda)^2$ against $\lambda\nu$ to the horizontal axis. Characterization was done within 300 nm to 1000 nm (i.e), within the UV , visible and NIR regions of electromagnetic spectrum.

IV. Results And Discussion

Structural properties

The XRD patterns of the kesterite Cu_2ZnSnS_4 thin films doped with 0.1 M, 0.3 M and 0.5 M of Zn are shown in Figure 1.

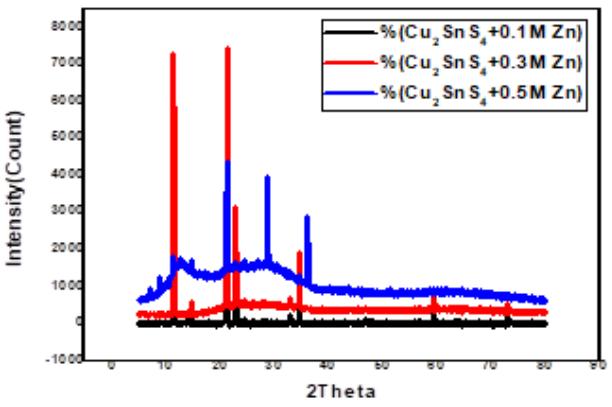

Figure 1: XRD of the thin films with 0.1M, 0.3M and).5M of Zn

In Figure 1, it was noted that all the thin film samples were polycrystalline with hexagonal wurtzite crystal structure. The major XRD peak reflection for the sample with 0.1M of Zn concentration had low scattering intensities observed at 21º (022), 23º (017) and 35º (201). The XRD peak reflections for the sample with 0.3M of Zn concentration had highest intensities observed at 11º (101), 21º (022) and 35º (201) while the sample with 0.5M of Zn concentration had intensities observed at 21º (022), 28º (122) and 36º (132). The peak reflections were not explicit functions of Zn concentrations. The average crystalline sizes were calculated using the well known Debye – Scherer formula giving in equation (1).

$$D = \frac{0.9\lambda}{\beta \, Cos\theta} \qquad (1)$$

where β is the observed angular line width at half maximum intensity in radians, θ is the Bragg's angle and λ is the wavelength used (1.5406Å). The values of D calculated using equation (1) for the thin film samples with 0.1M, 0.3M and 0.5M of Zn are 77.5nm, 79.2nm and 113.5nm respectively. These values were close to the ones obtained by other scholars for the thin films deposited using spray pyrolysis technique (7).

Surface morphology

The photomicrographs of the thin films with 0.1M, 0.3M and 0.5M concentrations of Zn obtained from SEM images are shown in Figures 2 – 4 respectively.

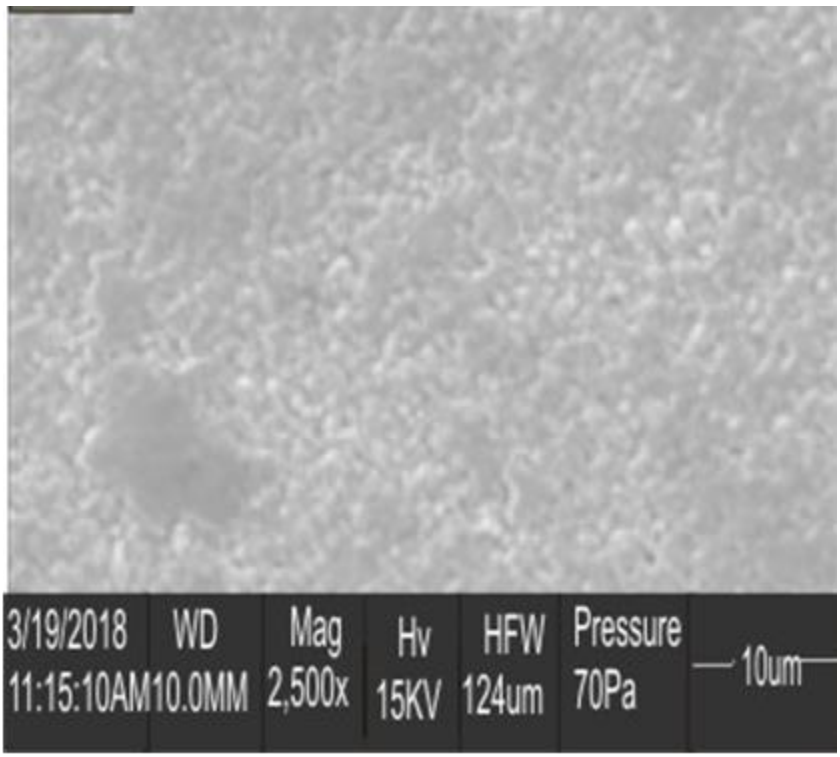

Figure 2: SEM image of thin film with 0.1M of Zn

In Figure 2, it can be seen from the SEM image that the deposited kesterite Cu_2ZnSnS_4 with 0.1M of Zn, covered the substrate very well, dense, had no pores or cracks nor any pin hole and on the whole had even and uniform distribution of agglomerated particles on the substrates, without well-defined boundaries. This result disagreed with the one obtained for Cu_2ZnSnS_4 thin films deposited using successive ionic layer adsorption and reaction (SILAR) technique, which had non-uniform distribution of particles and well-defined boundaries (15).

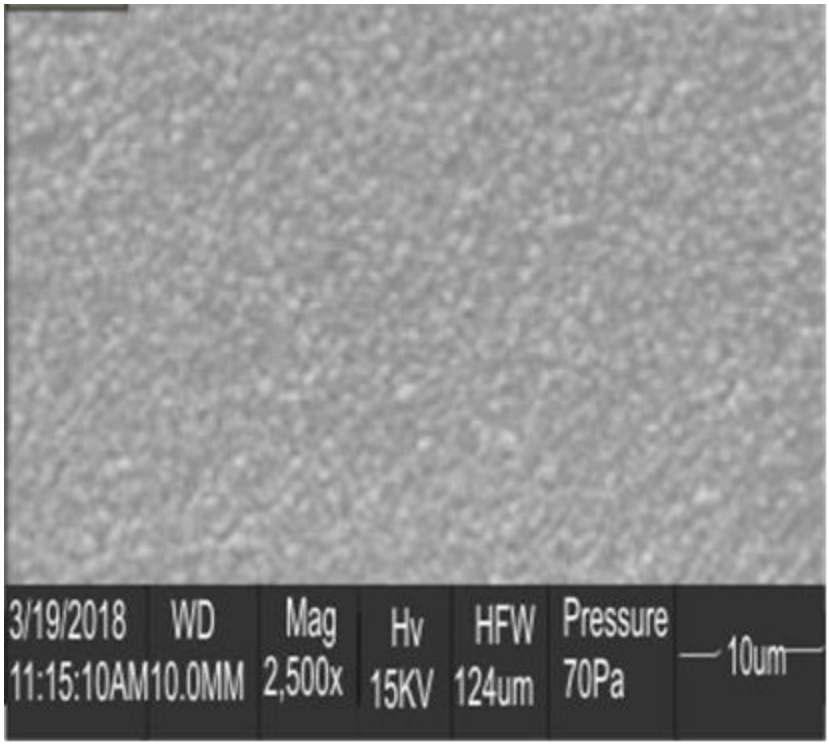

Figure 3: SEM image of thin film with 0.3M of Zn

A close visual observation of Figure 3, showed that the kesterite Cu_2ZnSnS_4 thin film sample with 0.3M of Zn, is more or less smooth, reflective and bright. It also had strong adherence with the substrate and covered it very well. There was no significant difference in the SEM images of the two thin film samples in Figures 2 and 3. Small grains with fine structures and also good surface coverage of the substrate were observed in the two Figures. However, much significant differences were observed in the SEM image of the thin film sample with 0.5M of Zn, as can be observed in Figure 4.

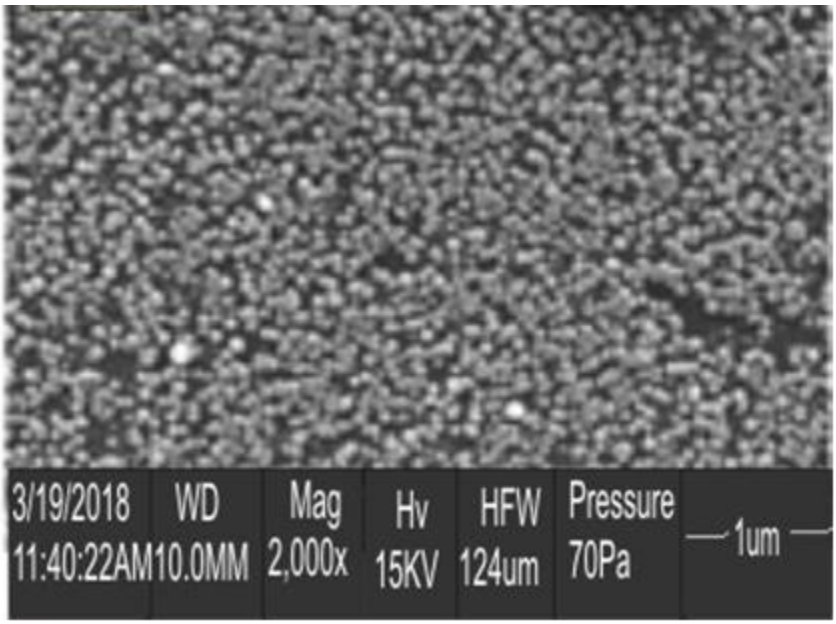

Figure 4: SEM image of thin film with 0.5M of Zn

In Figure 4, more noticeable structures were observed as the Zn concentration increased to 0.5M. This might be as a result of high mechanical stability of the films and more crystallization of the grains leading to subsequent increase in grain size, with increase in the concentration of Zn (22).

Electrical properties (Energy gaps)

The electrical properties of interest in this study are the energy gaps (E_g). The optical absorption theory in equation (2) was used in the determination of the energy gaps or the electrical properties of interest of the thin films.

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad (2)$$

where A is a constant of different values for different transitions, n has values of $^1/_2$, 2 and $^3/_2$ for direct transition, indirect transition and direct forbidden transitions respectively, α is absorption coefficient and $h\nu$ is photon energy (13, 23). The graph of $(\alpha h\nu)^2$ against $h\nu$ for the thin films at 0.1 – 0.5M of Zn is shown in Figure 5.

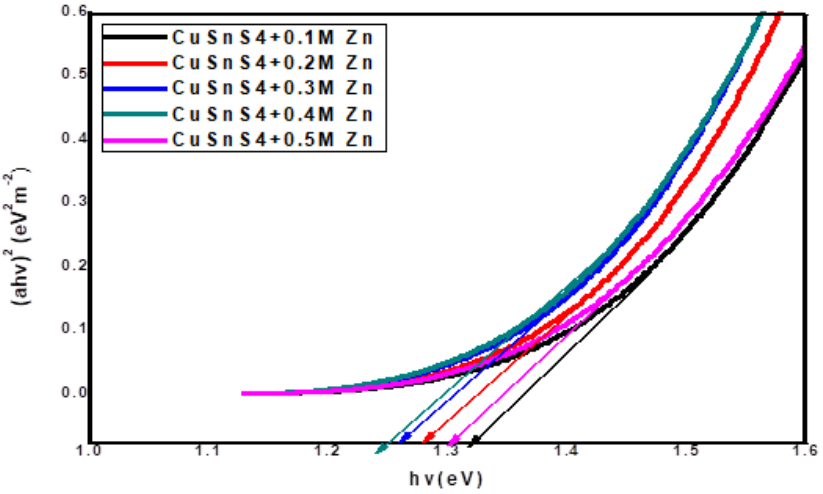

Figure 5: graph of $(\alpha h\nu)^2$ against $h\nu$ for 0.1 - 0.5M of Zn

In Figure 5, the extrapolation of the straight – line portion to the horizontal axis was used in the determination of the band gaps of the thin film samples. The graphs in Figure 5 clearly give a direct interband transition. From Figure 5, the energy gaps of the film samples with 0.1 – 0.5M of Zn were determined as: 1.32eV, 1.28eV, 1.26eV, 1.25eV and 1.3eV respectively. Thus between 0.1 – 0.4M of Zn, there was a blue shift in the energy gaps (0.07eV) of the thin films, whereas a red shift in energy gaps (0.04eV) was obtained when the Zn concentration increased from 0.4M to 0.5M. The range in the energy gap values from 1.25 – 3.2eV was lower than the range in values of band gap 1.4 – 1.5eV and 1.0 – 1.5eV obtained for Cu_2ZnSnS_4 kesterite thin film solar cells obtained by other scholar who used different deposition techniques (15).

V. Conclusion

The deposition of kesterite Cu_2ZnSnS_4 thin film solar cells was successfully done using the chemical bath deposition technique at a bath temperature of 343K for 5 hours. The films were polycrystalline with hexagonal wurtzite crystal structure. The photomicrographs of the thin films showed uniform distribution of agglomerated particles on the substrates without any defined boundaries. The thin films had high mechanical stability and more crystallization of the grains and subsequent increase in grain size with increased concentrations of Zn. The optimized Zinc concentration for the most effective optoelectronic device applications of Cu_2ZnSnS_4 is 0.4M. Between 0.1 – 0.4M of Zn, there was a blue shift of 0.07eV in energy gaps of the thin films whereas a red shift of 0.04eV was determined when Zn concentration increased from 0.4 - 0.5M.

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