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Studies of chemical bath anti-reflection thin films of ZnNiS

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ABSTRACT

Zinc nickel sulphide (ZnNiS) thin films were produced on glass slides by chemical bath deposition technique (CBD). The structural, composition and optical studies were done. These analyses were obtained using an optical microscope and XRD (MD_{10} version 2.0 X-ray) diffractometer, energy dispersive x-ray fluorescence (EDXRF) and a Janway 6405 UV-VIS spectrophotometer respectively. The effects of variation in the deposition time on the electrical, composition and optical properties of the grown films were discovered. From the XRD results, the films crystal structure was found to be tetragonal..The presence of many peaks indicates that the grown films are polycrystalline. An average grain size (D) of the film was estimated to be 0.003μm. The compositional study shows that as the deposition time increases, the Zn^{2+} decreases. The optical analysis indicates that the grown films can be applied as antireflection films, solar control coating and absorber layer films. These were discovered from their optical properties.

Key words: ZnNiS, Chemical bath deposition technique, structural, composition, and applications.

INTRODUCTION

Energy is the livewire of any country, the standard of living depends on the per capital energy consumption. Most of the energy on the earth is received from the sun [1]. Plants use solar energy for photosynthesis and store carbohydrates, proteins, fats, oil, alcohols, cellulose and lignin. Humans and animals consume plant materials as primary food. Plants and animal remains are converted to petroleum products and coal over millions of years [2]. Solar energy is therefore the world's most abundant source of energy known and used by mankind [3]. This renewable energy resource remains inexhaustible with time. However, the only problem is that the conversion efficiency is still low. Consequently, intensive research has been going on to find the suitable thin films that will minimize the loss of this energy during conversion [4]. ZnNiS thin films are one of the ternary chalcogenide thin films that have been investigated for specific applications in the solar industries, optical and electronic devices. The thin films are also applied in window coatings [5]. Various methods which include thermal evaporation, electrochemical deposition and chemical bath deposition have been employed for the deposition of thin films [6&7]. The chemical bath deposition (CBD) technique has been found to have a low cost and low temperature method that produces quality films for device applications [9]. In this paper, ZnNiS thin films which were fabricated through (CBD) are presented. The structural, optical and compositional studies were also carried out.

MATERIALS AND METHODS

ZnNiS thin films were prepared on glass slides using chemical bath deposition technique. The glass slides were degreased in hydrochloric acid for 24 hours, washed with detergent, rinsed in distilled water and dried in air. The acid treatment caused the oxidation of halide ions in glass slides used as substrate thereby introducing functional groups called nucleation and epitaxial centers on which the thin films were grafted. The degreased cleaned surfaces have the advantage of providing nucleation centers for the growth of film hence yielding highly adhesive and uniformly deposited films. The reaction bath for the deposition of ZnNiS contained 10mls of 1.0M of $ZnCl_2$, 10mls of 1.0M of $SC(NH_2)_2$ and 10mls of 14.0M of Ammonia.50mls of distilled water was added to make up 90mls in a 100ml beaker. Ammonia solution was used for dual purposes as a complexing agent as well as provision of alkaline medium for the growth. The function of the complexing agent is to slow down the reaction in order to eliminate spontaneous precipitation. The equations for the reaction and deposition of ZnNiS are as follows:

$$ZnCl_2 + 3NH_4 \longleftrightarrow [Zn\,(NH_3)_4]^{2+} + 2Cl^-$$
$$[Zn\,(NH_3)_4]^{2+} \longleftrightarrow Zn^{2+} + 3NH_4$$
$$NiCl_2 + 3NH_4 \longleftrightarrow [Ni\,(NH_3)_4]^{2+} + 2Cl^-$$
$$[Ni\,(NH_3)_4]^{2+} \longleftrightarrow Ni^{2+} + 3NH_4$$
$$SC[NH_2)_2 + OH^- \longleftrightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \longleftrightarrow H_2O + S^{2-}$$
$$Zn^{2+} + Ni^{2+} + S^{2-} \longrightarrow ZnNiS$$

The sulphide ions are released by the hydrolysis of thiourea but Mg^{2+} and Ni^{2+} ions are from complexes which the solution of $ZnCl_2$ and $NiCl_2$ formed with NH_3. The Zn^{2+}, Ni^{2+} and S^{2-} present in the solution combined to form ZnNiS molecules which were adsorbed on the glass rod. The growth takes place by ionic exchange of reactive S^{2-} ions. This process is referred to as ion by ion process and ZnNiS films were deposited on glass slides as uniform and adherent thin films. Five depositions were made with five different deposition time as shown in the table below. For each deposition, the glass slide which was mounted on the beaker with the synthetic material was taken out of the beaker, rinsed with distilled water and allowed to dry in air. The structural composition of the grown ZnNiS films was studied with the optical micrograph and X – ray diffractometer MD_{10} version 2.00. The films were further characterized for optical absorbance using Janway 6405 UV – VIS spectrophotometer. From the values of absorbance obtained, other properties such as film transmittance, reflectance, and band gap energy were determined through theoretical calculations [10]. These optical properties were obtained in the wavelength range of 280nm – 1000nm.

Table 1: Preparation of ZnNiS Thin Films

Reaction bath	Vol. $MgCl_2$ (ml)	Conc. $MgCl_2$ (M)	Vol. $NiCl_2$ (ml)	Conc. $NiCl_2$ (M)	Vol. $SC(NH_2)_2$ (ml)	Conc. $SC(NH_2)_2$ (M)	Vol. NH_3 (ml)	Distilled H_2O (ml)	Dip time (hr)
H_1	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	8.0
H_2	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	10.0
H_3	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	12.0
H_4	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	16.0
H_5	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	20.0

RESULTS AND DISCUSSION

Structural Analysis of ZnNiS Thin Films

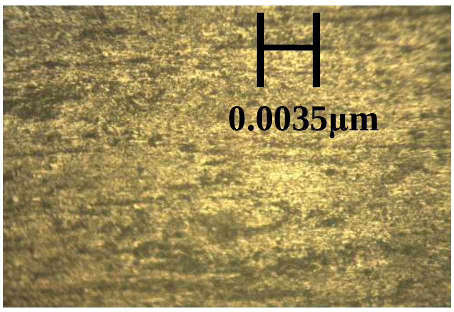

Fig. 1: photo micrograph of ZnNiS (h_2)

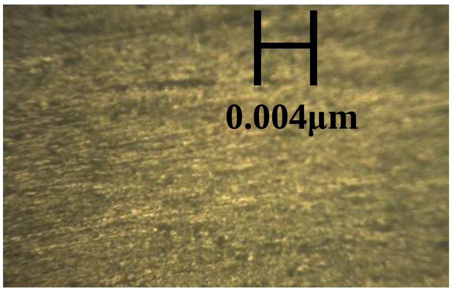

Fig. 2: photo micrograph of ZnNiS (H_4)

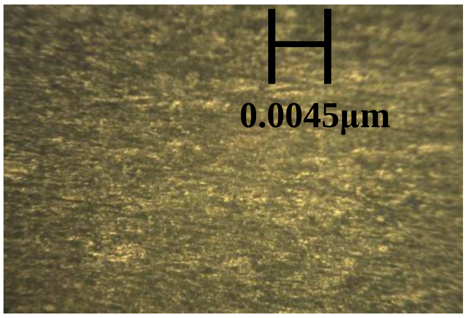

Fig 3: photo micrograph of ZnNiS (H_5)

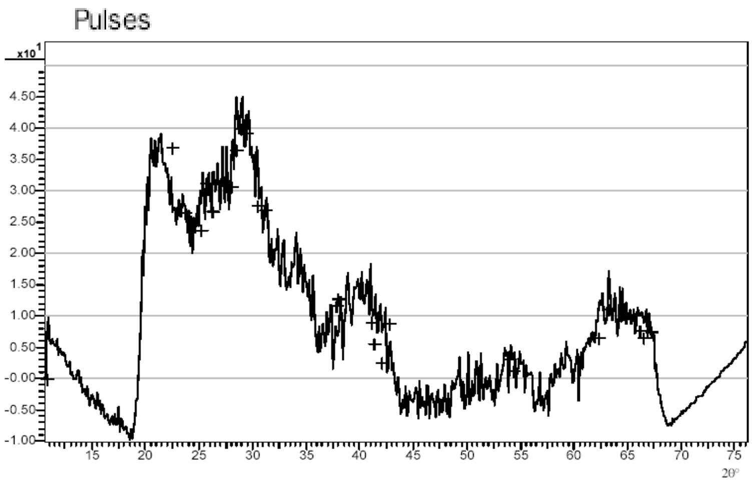

Fig. 4:X-ray Diffraction Spectra for ZnNiS Thin Film (Slide H_5)

MD-10. 4/26/10
Exposure Time: 1200/1200sec. Radiation: CuKa, avg Sample:H_5
Operator: EMDI Akure
File:ottih_H_5.smd

The structural characterization of the grown thin films was studied with the aid of optical micrograph and XRD spectrophotometer.

The structural parameter of the above thin films shows that the grain size of the grown thin films decreases as the dip time increases. This may be attributed to the increase in imperfections of the films with increasing deposition time. It also indicates a uniform surface coverage and an average size of 0.004µm. The grain crystallite size D was calculated using the Scherer's formula [11].

$$D = \frac{K\lambda}{B\cos\theta}$$

Where λ is the wavelength of X- ray, β is FWHM (Full width half maximum) given by the re Further confirmation of the structure of the grown thin films was done using XRD analysis. This helps to analyze various crystalline aspects. According to Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta_{hkl}$$

The direction of scattered beams (θ_{hkl}) is related to the interplanar distance (d_{hkl}) in the lattice (hkl) which represents the property of the material [12]. The XRD pattern for ZnNiS thin films indicates that there is a prominent peak in 2θ. The presence of large peaks indicates that the film is polycrystalline [13]. The outstanding of crystallites perpendicular to (111) plane gives rise to the tetragonal structure.

Compositional Analysis

The determination of the composition of thin films is very important especially for films deposited by CBD growth techniques deposition method. The method adopted in this research is the energy dispersive X-ray fluorescence (EDXRF).

The radioisotope x-ray machine has a Silicon-lithium detector (model SL 12170) with Beryllium window. When a sample was placed on an x-ray excitation source Cd^{109}, the sample was excited and subsequently characteristic x-rays were given out and detected by the Si-li detector. A preamplifier attached to the detector amplified the signal. This was sent to the spectroscopy amplifier for further amplification. With the help of the computer system, the spectrum was displayed. This was done for a period of 3000 seconds after which the spectrum was saved for quantitative analysis. In this work, samples H_1, H_2, H_3, H_4, and H_5, were selected for this analysis. Cd^{109} source was used to analyze the quantities of Zn, while ^{55}Fe was used for the determination of the quantity of sulphur. The contents of Zn^{2+}, Ni^{2+} and S^{2-} for the grown films are shown in table 3.0.

Optical Properties

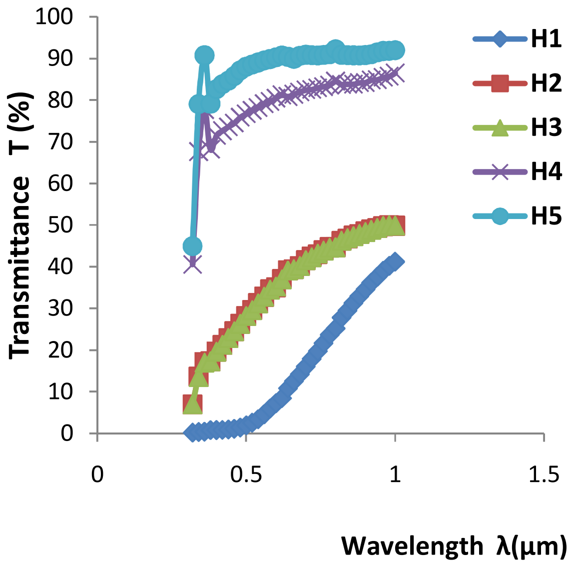

Fig. 5: Spectral transmittance of ZnNiS thin film (Slide H_1-H_5)

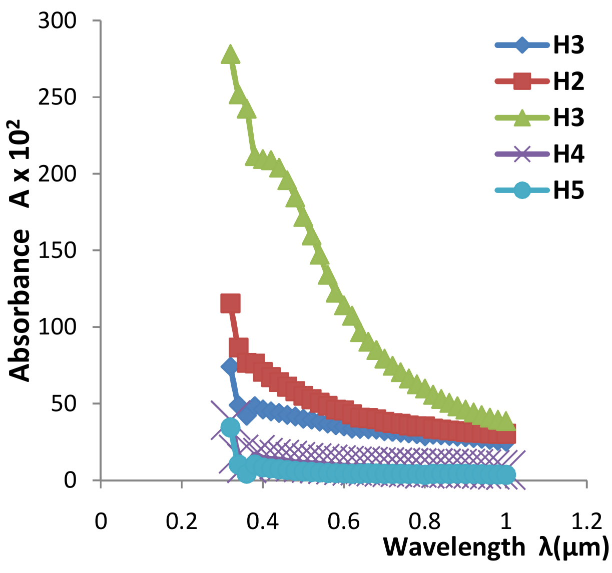

Fig. 6: Spectral absorbance of ZnNiS thin film (Slide H_1-H_5)

Table 3.0 Compositional analysis of Zn_{1-x} Ni_x S thin films

Slide No	Composition (x)	Mg content Wt%	Ni content Wt%	S content Wt%	ImpurityCl_2 Wt%
H_1	0.000	55.45	-	44.55	-
H_2	0.010	53.16	0.45	43.81	1.00
H_3	0.075	52.19	1.37	45.44	-
H_4	0.100	52.17	1.81	45.00	1.00
H_5	0.150	51.19	3.98	44.83	-

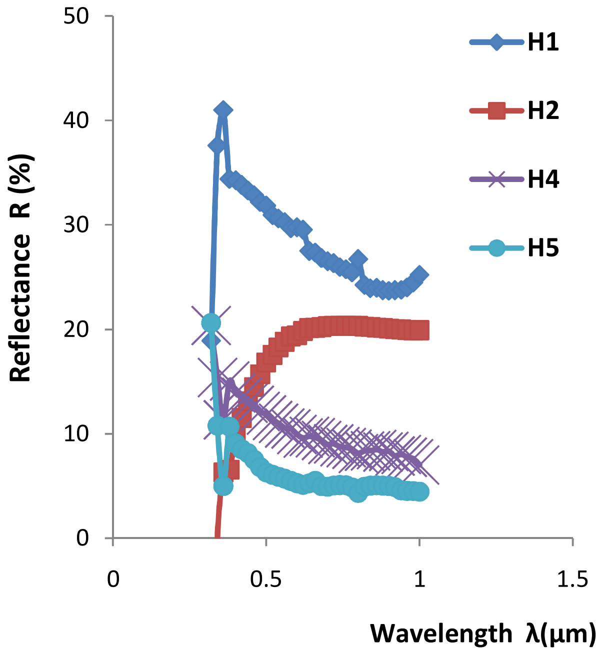

Fig. 7: Spectral reflectance of ZnNiS thin film (Slide H_1, H_2, H_4, H_5)

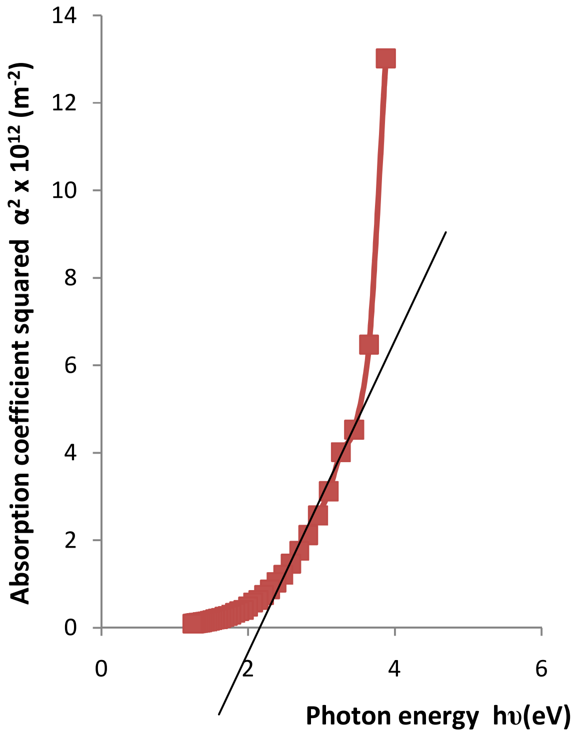

Fig. 8: A plot of absorption coefficient squared versus photon energy for (Slide H_1-H_5)

From the composition studies, the grown films are slightly rich in Zn^{2+}, whereas S^{2-} is practically constant. The table also indicates that the content of Zn^{2+}, decreases with increasing deposition time..

Figure5 is the transmittance spectrum of ZnNiS thin films grown in this work at a room temperature. A close look reveals that the transmittance of ZnNiS thin films increases as the length of deposition increases .The grown when the dip time is highest has the highest value at ultra violent (UV) region. Thin films of this property are used for photosynthetic coatings. This is because they are likely to exhibit selective transmittance of photosynthetic active radiation (PAR). This radiation is useful in the process of photosynthesis for green plants [14].

The plot of spectral absorbance of ZnNiS thin films is displayed in figure 6. The figure indicates that the absorbance of ZnNiS thin films decreases as the length of deposition increases. The highest absorbance was observed in the film labeled H_3. This type of thin film is used for window coating in the hot regions of the world since it is capable of absorbing the harmful UV radiations and leaving the inside surface cool. It acts as convectional air-conditioner.

Figure 7 shows reflectance spectra of ZnNiS thin film grown. From the plot, it is indicated that the reflectance values of the thin films grown is low especially with the films grown when the length of deposition is longer than 8 hours. Thin films of low reflectance values are used for coatings in the solar collector plates. Such films help to reduce the loss of incident solar radiation due to reflection. This enhances the efficiency of the solar cell collector plates. In solar energy collection, the aim is to maximize the absorption of incident radiation and reduce losses arising from processes such as conduction, convection, radiation and reflection. These are bound to occur because of the two different media (air and solar collector plates).This is disadvantageous since part of the incident radiation is lost, it has been found that the films grown in the work reflectance values across the UV, visible and near IR regions and hence suitable for anti-reflection thin films which when used, improves the efficiency of the solar collector plates.

The plot of the average values of absorption coefficient squared versus the photon energy for ZnNiS thin film is displayed on figures 8. From the graph, the band gap energy was found. The plot shows that the band gap energy of ZnNiS thin film is 2.2eV. This was obtained by extrapolating the straight portion of the graphs to a point where $\alpha^2=0$. The value of the photon energy at that point is the band gap was obtained from the graphs.

ZnNiS has a high band gap and can be considered as material for absorber layer of a solar cell.

CONCLUSION

ZnNiS thin films have been successfully fabricated onto glass slides using chemical bath deposition techniques. The structural, optical and composition were performed. The optical studies showed that the films have low reflectance values in the UV, VIS – NIR regions. This makes the film suitable for coating in solar collector plates as anti reflection films. Also, ZnNiS films were found to have high absorbance in the UV region. This property makes the film candidate for solar control coatings. The structural analysis indicates that the grown film has an average grain size of 0.004μm .The film band gap energy was determined to be 2.12eV. From this large band gap value, the film is therefore suitable to be used in the absorber layer of solar cell. An XRD showed that the film has a tetragonal crystalline structure

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