STRUCTURAL AND OPTICAL PROPERTIES OF CHEMICAL BATH DEPOSITES ZINC NICKEL SULPHIDE (ZnNiS) THIN FILMS

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Abstract

Thin films of zinc nickel sulphide (ZnNiS) were grown on glass substrates using the chemical bath deposition (CBD) technique at room temperature. Effects of ion concentration of $NiCl_2$ on the film's optical and structural properties were investigated. This was achieved by measuring the optical absorbance of the films at normal incident light in a wavelength range of 200–1000 nm with a Janway 6405 UV–VIS spectrophotometer. Other properties, such as transmittance, reflectance, thickness, and energy gap, were calculated from the measured absorbance values. The low reflectance and large band gap properties make the film a good material for anti-reflection coating and absorber layer of solar cells, respectively. The films grown were further characterized using an X-ray diffractometer and an optical microscope to determine the structural properties. From the XRD results, the film crystal structure was found to be cubic. The lattice constant and grain size of the grown films were found to be 5.420 Å and 0.31 μm, respectively.

1. Introduction

Zinc nickel sulphide (ZnNiS) thin film is an important ternary optoelectronic semiconducting material with a direct band gap transition. Depending upon the application and usage, a semiconductor material may be required to have smaller or larger band gap. Although none of the elemental semiconductors show precise gap required for particular device application, efforts are made to grow pairs of elements neither of which needs to be a semiconductor. This leads to the growth of many multinary semiconductors [1-3]. In this study, polycrystalline ZnNiS thin films were prepared by the chemical bath deposition technique at room temperature from an aqueous solution bath containing $ZnCl_2$, $NiCl_2$, and $SC(NH_2)_2$. Chemical bath deposition is an interesting growth technique which yields high quality semiconductor thin films. It is inexpensive, simple and requires low temperature [4–5]. This method produces films that have structural and optoelectronic properties comparable to those produced using other sophisticated deposition techniques [6]. The CBD technique has been applied in producing emerging materials for solar cells, protective coatings, and solar thermal control in buildings and is being adopted by some industries [7–9]. Also, this method is convenient for producing large area device and there is possibility of controlling film thicknesses by adjusting the deposition parameter. The method of chemical bath is based on a controlled precipitation of the desired compound from a reaction solution. The condition is that the ionic product (Zn^{2+}, Ni^{2+} and S^{2-}) must exceed the solubility (ZnNiS) [10].

2. Experimental

The preparation of ZnNiS thin films on glass slides were carried out using the chemical bath deposition technique. The glass slides were previously degreased in hydrochloric acid for 24 h, washed with a detergent, rinsed in distilled water, and dried in the air. The acid treatment caused the oxidation of halide ions in glass slides used as substrates, 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 thin films contained 10 ml of 1.0M of $ZnCl_2$, 10 ml of 1.0M of $SC(NH_2)_2$, 10 ml of various ion conc. of $NiCl_2$ and 10 ml of 14.0M of ammonia. Fifty milliliters of distilled water was added to make up 90 ml in a 100-ml beaker. The amonia solution was used for dual purposes as a complexing agent an as an 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 shown below:

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

The sulphide ions are released by the hydrolysis of thiourea but Zn^{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 heterogeneous nucleation and growth take place by ionic exchange of reactive S^{2-} ions. This process is referred to as ion by ion process, and, in this way, ZnNiS films were deposited on glass slides as uniform and adherent thin films. Five depositions were made with five different ion concentration of $NiCl_2$. 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 let dry in the air. The films grown were characterized for optical absorbance using a Janway 6405 UV–VIS spectrophotometer. From the values of absorbance obtained, other properties, such as film transmittance, reflectance, thickness, and band gap energy were determined through theoretical calculations [12]. These optical properties were obtained in a wavelength range of 280 nm–1000 nm. The structural composition of the grown ZnNiS films was studied with the optical micrograph and an MD_{10} X-ray diffractometer version 2.00.

3. Results and Discussion

3.1 Optical Characterization

The optical properties of the grown thin films were studied in a wavelength range of 0.28 to 1.0 μm of a Janway 6405 UV – VIS model of spectrophotometer. From the results, the following properties and their applications were determined.

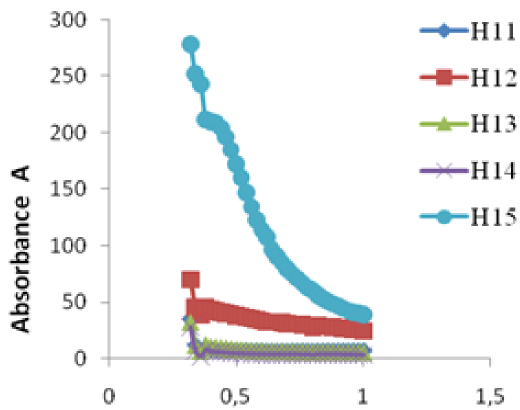

Fig. 1. Spectral Absorbance of ZnNiS thin film (Slide $H_{11} - H_{15}$)

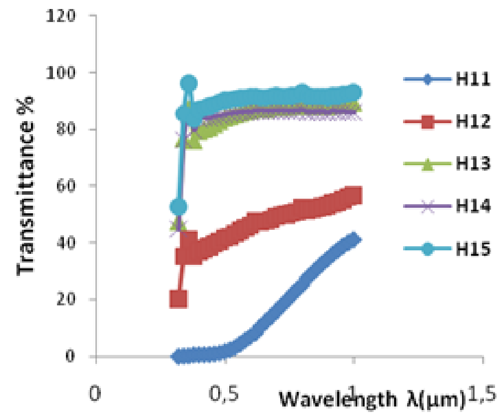

Fig. 1. Spectral Transmittance of ZnNiS thin film (Slide $H_{11} - H_{15}$)

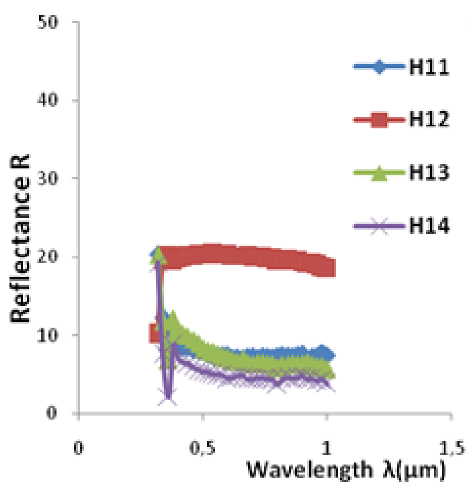

Fig. 3. Spectral Reflectance of ZnNiS thin film (Slide $H_{11} - H_{14}$)

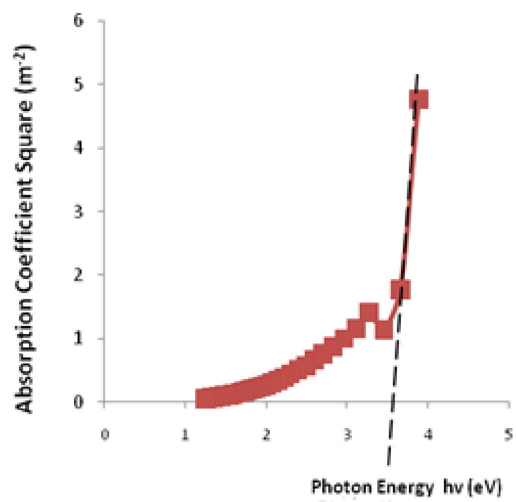

Fig. 4. A Plot of Average Value of Absorption Coefficient Squared Versus Photon Energy for ZnNiS thin film (Slide $H_{11} - H_{15}$)

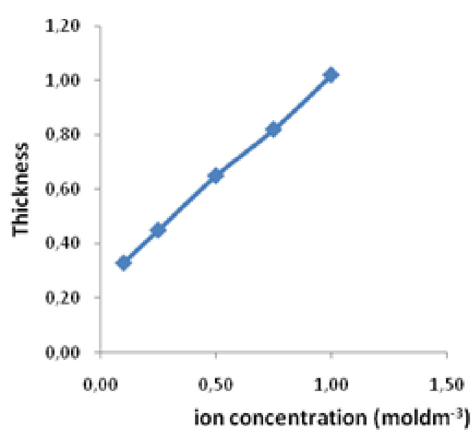

Fig. 5. A plot of thickness as a function of $NiCl_2$ ion concentration for ZnNiS thin film (Slide $H_{11} - H_{15}$)

Figure 1 shows the spectral absorbance of ZnNiS thin films. A close observation of the plot reveals that the ZnNiS film with the highest value of absorbance in the UV region was produced when 1.0 M of the $NiCl_2$ solution was used during deposition. This is illustrated by the film on slide H_{15}. The implication of this is that thin ZnNiS films of high absorbance in the UV region can be obtained when the ion concentration of the $NiCl_2$ solution used in the preparation is high.

The figure also reveals that zinc nickel sulphide film of low absorbance in UV region was produced when a small value of the nickel chloride ion concentration is used.

The film of high absorbance value in the UV region and moderate absorbance in the visible region is used as a thin film for window coating in temperate regions to control solar radiation. This is possible because the harmful UV radiation will be screened off or absorbed leaving the inside cool. This film acts as the convectional air-conditioner. However, films of absorbance, such as the film on slide H_{11} used in the VIS-UV regions, are useful in coating windscreens and driving mirrors. This is because it prevents the effect of dazzling light into the driver's eyes and also helps to protect the skin around eyes from sunburn.

The transmittance spectral of ZnNiS thin films are shown in Fig. 2. The plots reveal that the transmittance of zinc nickel sulphide in the visible and NIR regions increases as the ion concentration of the $NiCl_2$ solution increases. This is shown by the film on slide H_{15} which has almost 100% transmittance in the infrared region. This film is used for window coating in cold parts of the world and in materials used for the construction of poultry houses. This is because much IR radiation which heats the inside will be transmitted.

Figure 3 shows the reflectance spectral of ZnNiS thin film prepared in this work. A close observation reveals that the reflectance of the thin film is generally low across the UV, visible, and near IR regions. This thin film can be used as an anti-reflection thin film used for coating in solar energy collector plates. This implies that all the thin films grown with this parameter can be used as anti-reflection films.

The plot of average absorption coefficient squared versus the energy of the photon is shown in Fig. 4. From the graph, the optical band gap of the thin film was determined to be 3.6 eV. This is obtained by extrapolating the straight portion of the graph to a point where α^2 is equal to zero. The value of the photon energy at this point is the band gap of the film. The ZnNiS thin film has a high band gap and can be used as a thin film in the absorber layer of a solar cell.

The plot of the thin film thickness as a function of $NiCl_2$ ion within the concentration considered is displayed in Fig. 5. The graph indicates a linear relationship which implies that, as the ion concentration increases, the thickness increases too. A peak value of 1.02 μm was obtained when 1.0 M of the $NiCl_2$ solution was used.

3.2 Structural Characterization

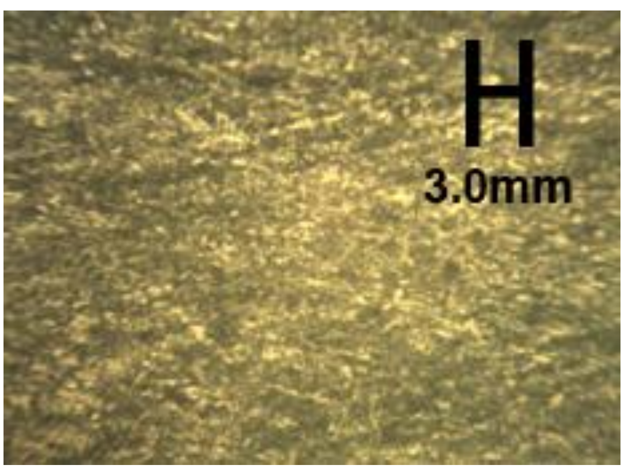

Fig. 6 a) Photo micrograph of ZnNiS (H_{11})

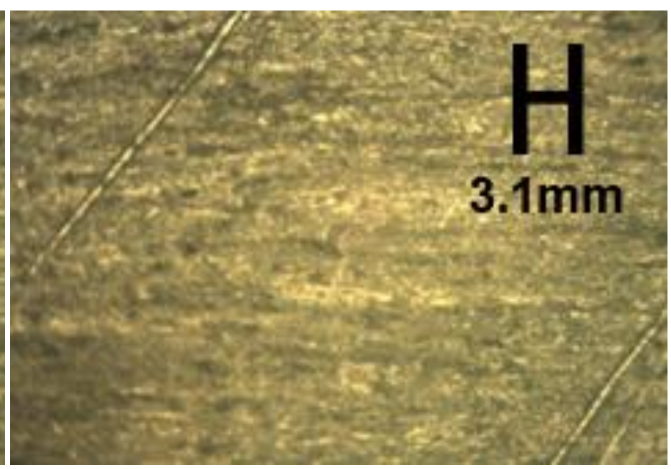

Fig. 6 b) Photo micrograph of ZnNiS (H_{14})

Fig. 6 c) Photo micrograph of ZnNiS (H_{15})

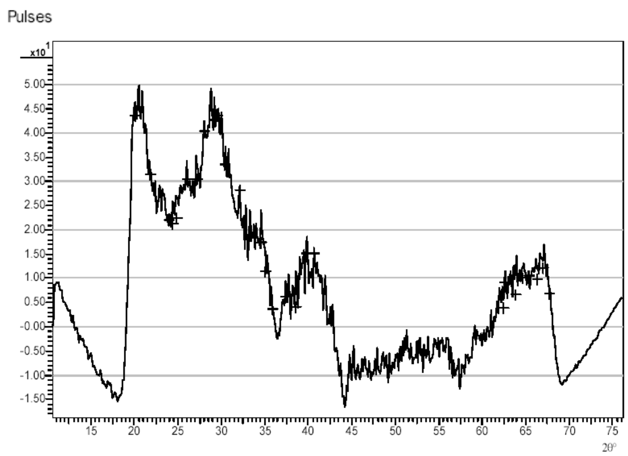

Fig. 7 a) X-ray diffraction Spectra for ZnNiS Thin Film (Slide H_{12}).

MD-10. 4/27/10
Exposure Time:1200/1200sec.
Radiation:CuKa, avg Sample:H_{12}
Operator:EMDI Akure

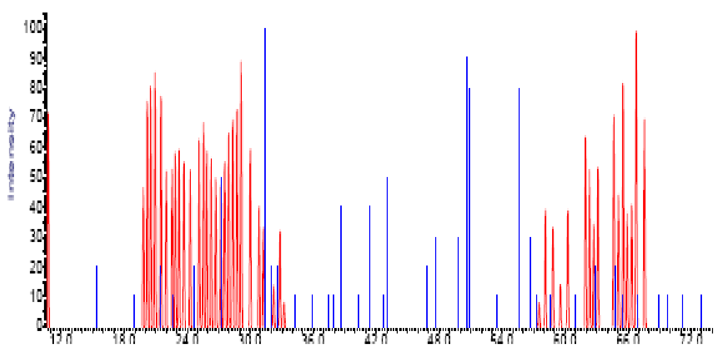

Fig. 7 b) Card # 22-1193 –Zinc Nickel Sulfide; Godlevskite. Formula: Zn Ni S.

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

The structural parameter of the above thin films shows that the grain size of the grown thin films decreases as the ion concentration increases. This may be attributed to the increase in imperfections of the films with increasing ion concentration. It also indicates a uniform surface coverage and an average size of 0.31 μm. The grain crystallite size D was calculated using the Scherer's formula [13]:

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

where λ is the X-ray wavelength, β is the FWHM (Full width half maximum) given by the diffractometer in radians, θ is the diffraction angle, and K is usually 0.9 for crystallite shape. Further confirmation of the structure of the grown thin films was done using XRD analysis. This helps to analyze various crystalline aspects. According to the 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 with respect to the lattice constant and indices [14]. The XRD pattern for ZnNiS thin films indicates that there is a prominent peak in 2θ values which corresponds to the (111) plane and other peaks at different 2θ values which correspond to the (211) and (221) planes, respectively. The presence of large peaks indicates that the film is polycrystalline [15]. The outstanding of crystallites perpendicular to the (111) plane gives rise to the cubic structure with lattice constant a = 5.420Å as indicated in the XRD analysis.

4. Conclusions

Thin films of ZnNiS have been successfully prepared using the chemical bath deposition technique (CBD). The optical studies showed that the films have low reflectance value in the UV and VIS-NIR regions. This makes the films suitable for coating as anti-reflection thin films. In addition, the ZnNiS thin film has a low transmittance in the UV region and moderate in the VIS-NIR regions. This property makes the films materials for warming coating, since much IR heat is allowed transmitting inside the surface. This is important for those living in the cold parts of the world. The film thickness was found to be in a range of 0.25-1.15μm. The band gap energy was determined to be 3.60 eV. This high band gap property of the film makes it a good material for the absorber layer of a solar cell. An XRD analysis showed that the film had a cubic structure and an average grain size of 0.31 μm.

References

[1] Y. Rodriguez–Lazcano, M. T. S. Nair, and P. K. Nair, J. Crystal Growth 223, 399, (2001).
[2] F. I. Ezema and R. U. Osuji, J. Appl. Sci., (2006).
[3] S. Jana, R. Thapa, R. Maity, and K. Chattopadyyay, Physica E doi: 10. 1016/ j. physics 04, 015, (2008).
[4] K.L. Chopra, and I. Kaur, Thin film Device Applications Plenum press, New York, 1993, 385 p.
[5] K.L. Chopr and S.R. Das, Thin Solar Cells, Plenum Press, New York., 1983, 410 p.
[6] R.U. Osuji, Nigerian Journal of Solar energy, 14, 90, (2003).
[7] K.L. Chopra and L.K. Malhotra, Thin Film Technology and Applications, Tata McGraw Hill, New Delhi, 3, 237, (1985).
[8] M.N. Nnabuchi, Thin Films. Pacific Journal of Sciences & Tech. 6, (2) 105, (2005).
[9] F.I. Ezema, Optoelectronics and Advanced Material Rapid Communications 3, (2) 141, (2009).
[10] R. B. Barnes and M. Czeeny, Phys. Rev. 38, 323, (1931).

[11] J.J. Pankove, Optical Processes in Semiconductor, Prentice-Hall, New York., 1971, 475 p.
[12] T.S. Robinson, Thin Films Processes, Soc. Pub., London.,1952, 910 p.
[13] D. Padiyam, P.A. Marikani, and K.R. Murali, Cryst. Res. Technol. 35, 949, (2000).
[14] H. Zisham, M.A. Khan, and K. Majeed, Current Appl. Physics 5,561, (2005).
[15] V. Damodara, S. Das, and B. K. Seetharma, Phys. Rev. 30, 7696, (1989).