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Effects of nickel ion concentration on the optical and compositional studies of Cu_{x-1} N_xS thin films

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ABSTRACT

Thin films of CuNiS were growm on glass substrates by solution growth deposition(SGT) technique. Copper chloride, Nickel chloride and thiourea were used as sources for Copper, Nickel and Sulphur ions respectively. The effects of nickel ion concentration on optical and compositional properties were determined. The optical and solid state properties of the deposited films were investigated by measuring the optical absorbance of the films at the normal incident of light in the range of 200 – 1000nm. This was done with the aid of a Janway 6405 UV–VIS spectrophotometer. From the absorbance values, other properties such as transmittance, reflectance, thickness and energy gap were calculated. The high transmittance and high absorbance of the film at various values of the growth parameter make the film good materials for coating in cold and temperate regions respectively. The compositional analysis was dome by Energy dispersive x-ray fluorescence (EDXRF) technique.

Keywords: Thin films, solution growth, CuNiS, composition, applications.

INTRODUCTION

The energy needs of most countries have been met the non-renewable energy resources such as petroleum. Recently, there is an increase in cost of these non-renewable energy resources. As a result, emphasis is shifted to the renewable energy. The major problem with the renewable energy is that the conversion efficiency has been so low. Scientists are growing thin films to find which among them can help increase this conversion efficiency.

CuNiS thin film is one of the tenary chalcogenide films. These films have been investigated for specific applications in super ionic conducting materials [Ezugwu *et al* 2009]. Interests on ternary alloy compounds are increasingly being studied for efficient solar energy conversion through photo – electrochemical solar cell and have become potential candidates for such applications [Okoli *et a*l]. A number of thin film deposition techniques of advanced technologies have been employed in the preparation of ternary thin films. However, a low cost and less sophisticated solution growth technique seems to be much better [Ottih *et al* 2010]. The SGT technique produces good quality films . This method 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 . SGT technique is convenient for producing large area device and there is possibility to control film thickness by adjusting the growth parameter . Polycrystalline grown CuNiS thin films are semiconducting materials with direct band gap transition. This research reports the effects of varied volumes of the complexing agent on the optical properties of the grown films. The possible applications of the films were discovered from their properties. The optical properties investigated include absorbance (A), transmittance (T) reflectance (R), thickness (T) and the band gap energy of the films. These properties were determined based on the equations found in the literature.

MATERIALS AND METHODS

The preparation of CuNiS thin films on glass slides were carried out using chemical bath deposition technique. The glass slides were previously 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 CuNiS contained 10mls of 1.0M of $CuCl_2$, 10mls of 1.0M of $SC(NH_2)_2$, 10mls of 1.0M of $NiCl_2$ 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 CuNiS are as follows:

$$CuCl_2 + 3NH_4 \leftrightarrow [Cu\,(NH_3)_4]^{2+} + 2Cl^-$$

$$[Cu\,(NH_3)_4]^{2+} \leftrightarrow Cu^{2+} + 3NH_4$$

$$NiCl_2 + 3NH_4 \leftrightarrow [Ni\,(NH_3)_4]^{2+} + 2Cl^-$$

$$[Ni\,(NH_3)_4]^{2+} \leftrightarrow Ni^{2+} + 3NH_4$$

$$SC(NH_2)_2 + OH^- \leftrightarrow CH_2N_2 + H_2O + HS$$

$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$

$$Cu^{2+} + Ni^{2+} + S^{2-} \longrightarrow CuNiS \downarrow$$

The sulphide ions are released by the hydrolysis of Thiourea but Cu^{2+} and Ni^{2+} ions are from complexes which the solution of $CuCl_2$ and $NiCl_2$ formed with NH_3. The Cu^{2+}, Ni^{2+} and S^{2-} present in the solution combined to form MgNiS 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, CuNiS films were deposited on glass slides as uniform and adherent thin films. Five depositions were made with five different values of $NiCl_2$ ion concentration as shown in the table 1 below and labeled as $F_{11} – F_{15}$. 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 films grown were characterized for optical absorbance using 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. These optical properties were obtained in the wavelength range of 280nm – 1000nm.

Table 1: Preparation of CuNiS thin films with varied NiCl ion concentration

Slide No	Vol. of $CuCl_2$ (mls)	Conc. $CuCl_2$ (M)	Vol. $NiCl_2$ (mls)	Conc. $NiCl_2$ (M)	Vol. of NH_3 Solution (mls)	Vol. of $SC(NH_2)_2$ (mls)	Conc. $SC(NH_2)_2$ (M)	Vol. of Distilled H_2O (mls)	Dip. Time (Hrs)
F_{11}	10.0	1.0	10.0	0.10	10.00	10.0	1.0	50.0	12.0
F_{12}	10.0	1.0	10.0	0.25	10.00	10.0	1.0	50.0	12.0
F_{13}	10.0	1.0	10.0	0.50	10.00	10.0	1.0	50.0	12.0
F_{14}	10.0	1.0	10.0	0.75	10.00	10.0	1.0	50.0	12.0
F_{15}	10.0	1.0	10.0	1.00	10.00	10.0	1.0	50.0	12.0

RESULTS AND DISCUSSION

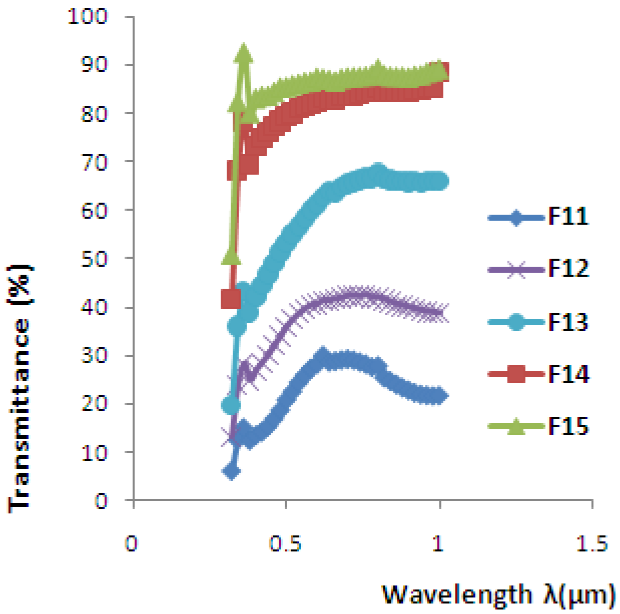

Fig.1 Spectral transmittance of CuNiS thin film (Slide F_{11}-F_{15})

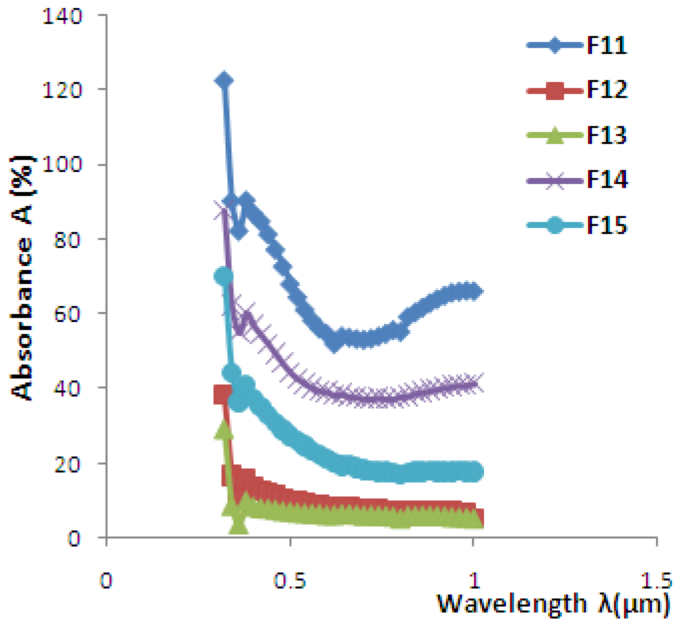

Fig. 2: Spectral absorbance of CuNiS thin film (Slide F_{11}-F_{15})

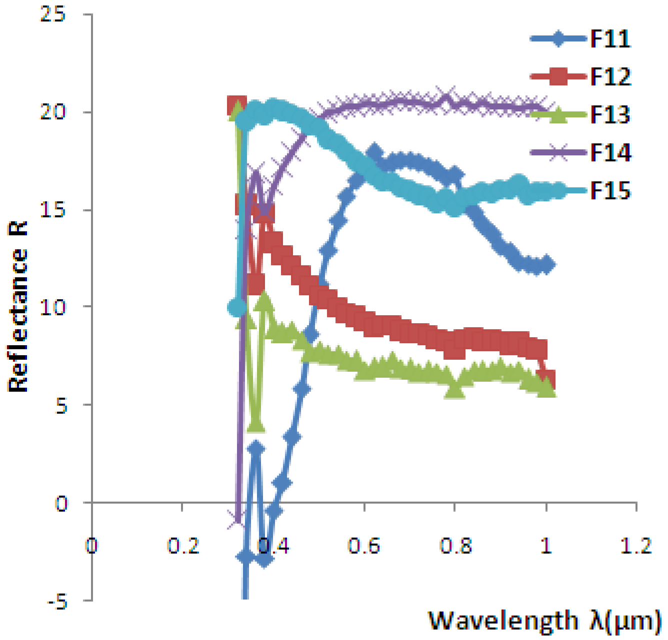

Fig. 3 Spectral reflectance of CuNiS thin film (Slide F_{11}-F_{15})

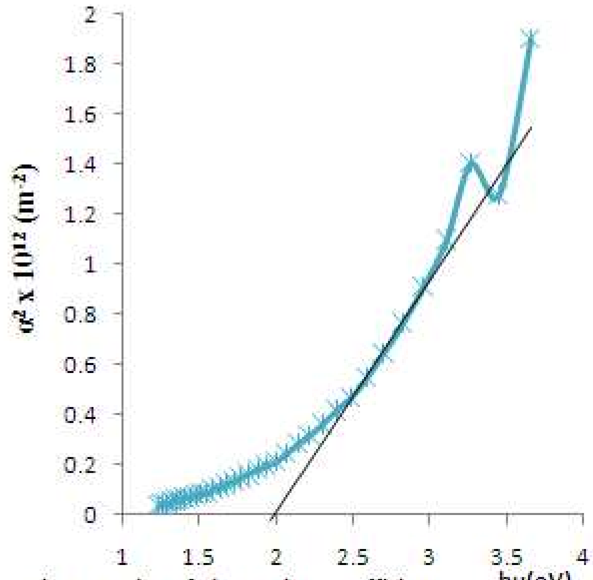

Fig. 4: A plot of absorption coefficient squared versus photon energy of MgNiS for E_6 - E_{10}

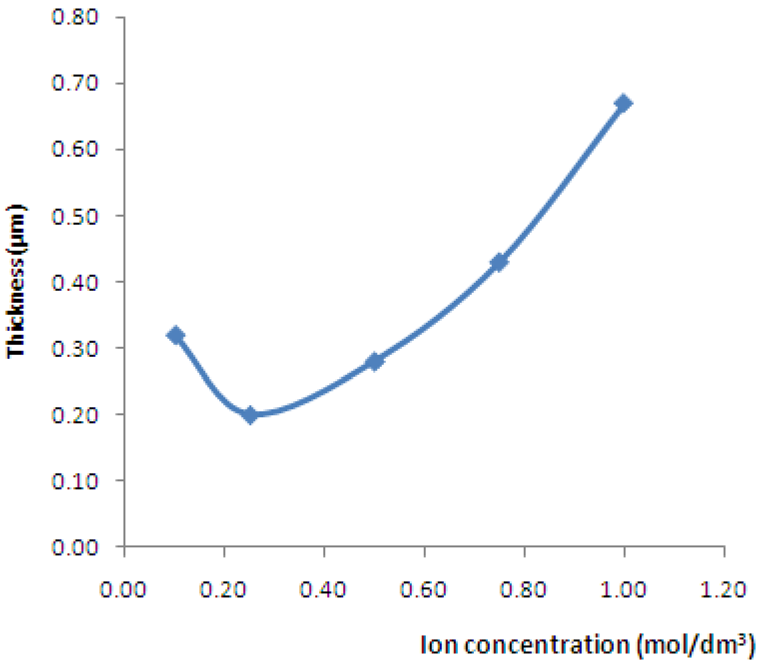

Fig. 5 Variation of thickness with $NiCl_2$ ion concentration for CuNiS thin film (slide F_{11} - F_{15})

Analysis of Optical Properties of CuNiS Thin Films

The transmittance spectra of copper nickel sulphide thin films grown in this work at a room temperature is shown in figure 1. A close observation of the plots reveals that the transmittance of CuNiS is high across the UV, VIS and NIR regions. Thin films of high transmittance values are used for photosynthetic coatings. This is because such films exhibit selective transmittance of photosynthetic active radiation which is useful in the process of photosynthesis.

Figure 2 shows the absorbance spectra of CuNiS prepared in this work. A close look at the plot reveals that the films have low absorbance values in visible and near ir regions. This is in agreement with what Wang *et al* (1998) and Chopra *et al* (1995) who reported on the optical properties of Ni doped CuS. Thin films of high absorbance in UV region are used as solar or thermal heat control which absorbs the greater part of the harmful UV radiation and keeps the inside surface cool . This thin film acts as the convectional air- conditioners which are used in the hot regions of the world like Nigeria.

The reflectance spectral of CuNiS thin films is displayed in figure 3 . A close look at the plot reveals that the reflectance of the film is generally low across the region of the UV, VIS and NIR regions of electromagnetic spectrum. This is in agreement with what Ottih and Ekpunobi (2011) reported on CuNiS thin films. This implies that the growth parameter does not change the reflectance pathern of CuNiS. Films of low reflectance are used as anti-reflection thin films which are used to coat the flat plates of solar cell collectors in solar energy production. This film is very important because it prevents reflection of the incident solar radiation in solar collector plates.

The optical band gap of CuNiS thin films is displayed in figure 4.The band gap value was determined through the plots of absorption coefficient squared α^2 versus the photon energy hυ. A band gap value of 2.0eV was obtained from the graph. This is done by extrapolating the straight portion of the graphs to a value of $\alpha^2 = 0$. The value of the photon energy becomes the energy gap. It is noted that the band gap of CuNiS thin film obtained above is 2.0eVand is less than the band gap of CuS (2.9eV) as reported by Ottih and Ekpunobi (2003) . This is in agreement with what Subramanian (1997) reported on the effect of transition metal doping on II-VI semiconductors. The band gap of the film is high and can be used in the absorber layer of a solar cell.

Figures 5 is plot of thickness versus varied values of $NiCl_2$ ion concentration. The figure shows that thickness first decreases as the ion increases. But when 0.5M was used, thickness suddenly increases until a terminal thickness of 0.72µm was obtained when 1.0M was used .

Compositional Characterization

The compositional analysis was dome by Energy dispersive x-ray fluorescence (EDXRF) technique. This was done for a period of 3000 seconds after which the spectrum was saved for quantitative analysis. In this work, samples F_{11}, F_{13} and F_{15} were selected for this analysis. Cd^{109} source was used to analyze the quantity of Cu while ^{55}Fe was used for the determination of the quantity of sulphide. The contents of Cu^{2+}, Ni^{2+} and S^{2-} for various films are shown in table 2 below.

Table 2 Compositional analysis of Cu_{1-x} Ni_x S thin films

Slide No	Composition (x)	Cu content Wt%	Ni content Wt%	S content Wt%	ImpurityCl_2 Wt%
F_{11}	0.100	52.17	1.81	45.00	1.00
F_{13}	0.150	51.19	3.98	44.83	-
F_{15}	0.300	50.77	4.14	44.09	1.00

From the composition studies, the grown films are slightly rich in Cu^{2+} whereas S^{2-} is practically constant. The above table shows that the content of Cu^{2+} decreases with increasing nickel content.

CONCLUSION

CuNiS thin films have been successfully deposited on glass slides using chemical bath deposition techniques. 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. With these thin films,the loss of incident radiation due to reflection on the solar collector plates is reduced. Also, CuNiS films were found to have high absorbance in the UV region. This property makes the film a good material for solar control coatings. The thickness of the film was found to be of the range 0.2µm – 7.50µm. The film band gap energy was determined to be 2.2eV. From this large band gap value, the film is good material to be used in the absorber layer of solar cell.

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