# Solid State and Optical Properties of Chemical Bath Deposited Copper Nickel Sulphide (CuNiS) Thin Films.

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## ABSTRACT

Thin films of CuNiS were grown on glass substrates by the chemical bath deposition (CBD) technique. Copper chloride, nickel chloride, and thiourea were used as sources for copper, nickel, and sulphur ions, respectively. Effects of deposition time on the film's optical and structural properties were determined. The optical characterization was done by using a Janway UV-VIS spectrophotometer in the wavelength range of 280nm – 1000nm. The optical absorbance of the films was determined directly by the spectrophotometer. Other properties such as transmittance, reflectance and absorption coefficient squared were calculated.

An average band gap energy was also determined to be 3.60eV. From the optical analysis, the films showed low reflectance values in the UV, VIS–NIR regions. This property makes it suitable material for anti reflection coatings in the flat solar collector plates. Other applications such as solar control and warming coatings were discovered. The grown thin films were further characterized using an X-ray diffractometer $MD_{10}$ version 2.00 and an optical micrograph. From the XRD results, the film crystal structure was found to be tetragonal. An average grain size of 0.20μm was obtained. The presence of several peaks in the XRD analysis confirms that the grown thin films are polycrystalline.

(Keywords: chemical bath deposition, CBD, CuNiS, thin films, applications)

## INTRODUCTION

CuNiS is one of the important ternary optoelectronic semiconductor materials. The growth and study of the properties of ternary chalcogenide compounds and their possible applications in solar cells, light emitting diodes and non–linear optical devices has been increasing in recent years [Ortega – Lopez et al. (2003)].

Ternary compounds are found to be promising materials for optoelectronic device applications such as green- emitting devices and are recommended as suitable materials for window layer of solar cells [Woon – Jo and Gye – Choon (2003)]. Some of them have been investigated for specific applications in super ionic conducting materials [Sasaki et al. (2003)]. Interest on ternary compounds is increasingly being studied for efficient solar energy conversion through photo – electrochemical solar cells. [Padam and Rao 1986] and have become potential candidates for such applications [Pawar et al. 1986, Jae – Hyeong et al (2003)].

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 simple chemical bath deposition technique seems to be much better [Padam and Rao (1986)]. Chemical bath deposition is a new and interesting technique which yields high quality semiconductor thin films. It is simple and requires low temperature. The CBD technique produces good quality film [Wang et al (1999)]. This method has been applied in producing emerging materials for solar cells, protective coatings, solar thermal control in buildings and is being adopted by some industries [Chopra et al. (1985), Nnabuchi (2005) and Ezema et al. (2009)] CBD 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. In this paper, the effect of deposition time on the optical and structural properties of the films was studied. The possible applications of the films were discovered from their properties. The optical properties investigated include absorbance (A), transmittance (T) and reflectance (R), which were used to calculate other properties such as refractive index (n), extinction coefficient (K), dielectric constant (ε), optical conductivity (σ), and the band gap energy of the film. These properties were determined based on the equations found in the literature [Pankove (1971), Ezema et al. (2003)].

## EXPERIMENTAL DETAILS

The growth of CuNiS thin films on glass slides was carried out using chemical bath deposition technique. The glass slides used 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 $NiCl_2$, 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 chemical equation of the reaction for the deposition is given below:

$$CuCl_2 + 3NH_4 \longleftrightarrow [Cu(NH_3)_4]^{2+} + 2Cl^-$$
$$[Cu(NH_3)_4]2+ \longleftrightarrow Cu^{2+} + 3NH_4$$
$$NiCl_2 + 3NH_4 \longleftrightarrow [Ni(NH_3)_4]^{2+} + 2Cl^-$$
$$[Ni(NH_3)_4]^{2+} \longleftrightarrow Ni^{2+} + 3NH_4$$
$$SC(NH_2)_2 + OH^- \longleftrightarrow CH_2N_2 + H_2O + HS$$
$$HS^- + OH^- \longleftrightarrow H_2O + S^{2-}$$
$$Cu^{2+} + Ni^{2+} + S^{2-} \longrightarrow CuNiS \downarrow$$

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 CuNiS 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 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 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. The structural properties of the grown CuNiS films were studied with the optical micrograph and X–ray diffractometer $MD_{10}$ version 2.00.

**Table 1:** Preparation of CuNiS Thin Films

| Slide No | Vol. $CuCl_2$ (ml) | Conc. (M) $CuCl_2$ | Vol. $NiCl_2$ (ml) | Conc. (M) $NiCl_2$ | Vol. $SC(NH_2)_2$ (ml) | Conc. (M) $Sc(NH_2)_2$ | Vol. $NH_3$ (ml) | Vol. Distilled $H_2O$ (ml) | Dip. Time (hr) |
|---|---|---|---|---|---|---|---|---|---|
| F1 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 50.0 | 8.0 |
| F2 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 50.0 | 9.0 |
| F3 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 50.0 | 10.0 |
| F4 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 50.0 | 12.0 |
| F5 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 1.0 | 10.0 | 50.0 | 24.0 |

## RESULTS AND DISCUSSIONS

### Optical Properties

The optical properties of the grown thin films of CuNiS were investigated using a Janway 6405 UV–VIS model of spectrophotometer in the 280nm – 1000nm wavelength range. The effect of deposition time on each property and their applications were determined. The figures below show the nature of the properties.

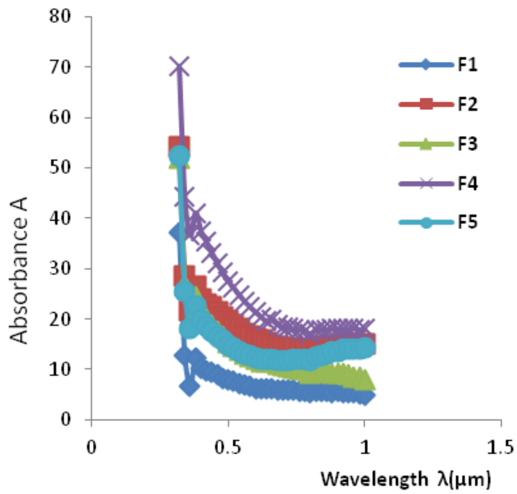



Fig. 1: Spectral Absorbance of CuNiS thin filmS (Slide $F_1$-$F_5$)

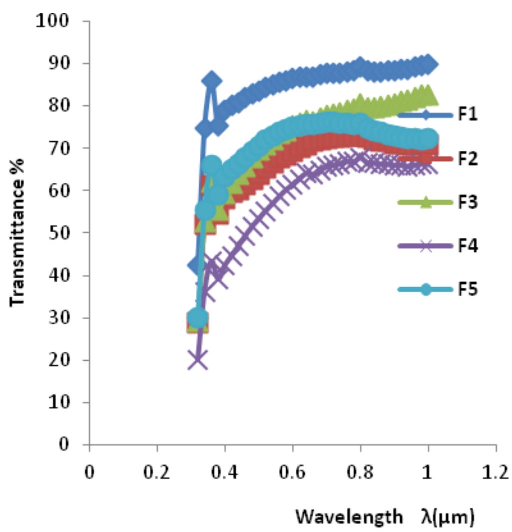



Fig. 2: Spectral Transmittance for CuNiS thin filmS (Slide $F_1$-$F_5$)

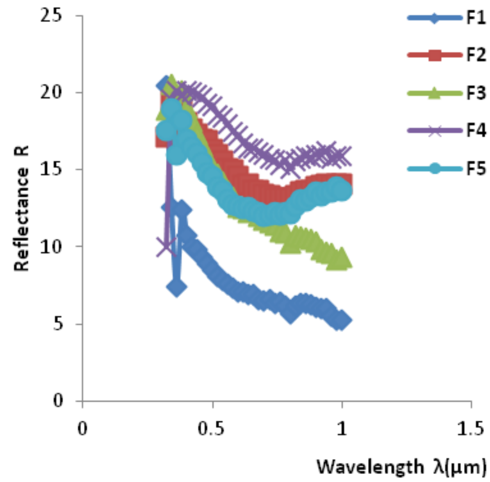



Fig. 3: Spectral Reflectance of CuNiS thin filmS (Slide $F_1$-$F_5$)

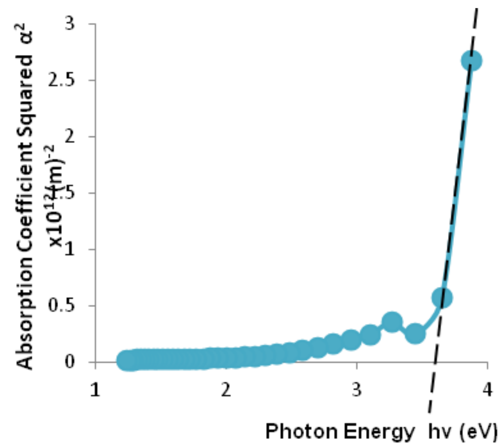



Fig. 4: A plot of Average Values of Absorption Coefficient Squared Versus Photon Energy for CuNiS thin film (Slide $F_1$-$F_5$)

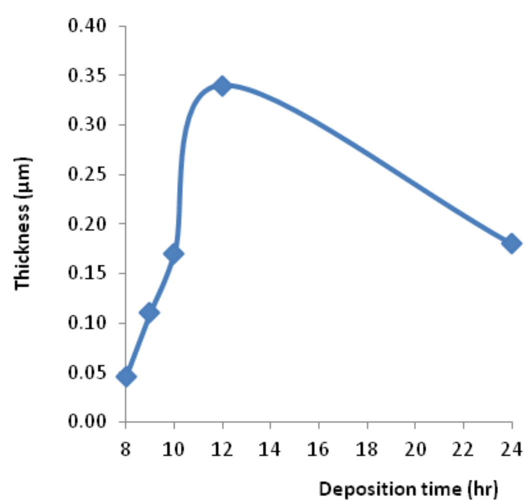



Fig. 5 : A plot of average values of thickness as a function of deposition time for CuNiS thin film (Slide $F_1$-$F_5$)

Figure 1 shows the spectra absorbance of the CuNiS thin film (slide F1–F5). A close observation reveals that CuNiS thin film grown for longer dip-time of 24 hours (slide F5) has the highest absorbance in UV region. Films grown for shorter deposition time such as film on slide $F_1$ has the least absorbance in the UV region.

The implication of this is that the higher the deposition time, the higher the absorbance time at UV region. Films of high absorbance such as films on slide F5 are used as solar control which absorbs the greater part of the harmful UV radiation and keep the inside cool. This thin film acts as the conventional air-conditioner which is used in temperate regions of the world like Nigeria.

Figure 2 shows the spectra transmittance of CuNiS thin film (slide $F_1$ – $F_5$). The plot indicates that film of high transmittance value (85%) in NIR was obtained when deposition was made for 8 hours as shown by film on slide $F_1$. The plot also reveals that CuNiS thin film of least transmittance value (50%) was obtained when deposition was made for 24 hours as shown by film on slide $F_5$. The implication of this is that the higher the deposition time, the lower the transmittance value for CuNiS thin film. Thin films of high transmittance in the infrared region such as film on slide $F_5$ is used for window coating for the people living in the cold part of the world. Also such films are used in materials for the construction of poultry houses. This is because the film allows much infrared heat to penetrate and warm the inside.

Figure 3 indicates the spectra reflectance of the CuNiS thin film (slide $F_1$ – $F_5$). A close look at the graphs indicates that the reflectance of the films is low in UV, visible and NIR regions with a range of 6 – 20. This implies that CuNiS films have low reflectance values irrespective of the length of the deposition. Such films of low reflectance are used as anti-reflection thin films which are suitable for coating in the flat plates of solar collectors. This film is very important because it prevents reflection of the incident solar radiation in solar collector plates and enhances the efficiency of the solar cell made with it.

The plot of absorption coefficient squared against the photon energy is displayed in Figure 4. From the graph, the band gap energy of the film was determined. Its value is 3.6 eV. This is done by extrapolating the straight part of the graph to a point where $\alpha^2 = 0$. The value of the photon energy at that point is the energy gap of the thin film. This implies that CuNiS has high band gap energy and can be used as an absorber layer of a solar cell.

Figure 5 displays the variation of film thickness with deposition time. The graph reveals that the thickness increases as the dip-time increases until it reaches a terminal thickness of 0.33µm when dip-time was 12 hours. Further increase in dip-time decreases the film thickness.

## Structural Properties

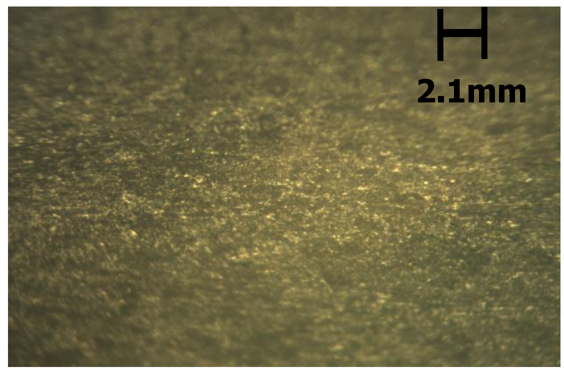



**Figure 6a:** Optical Micrograph of CuNiS (Slide $F_2$).

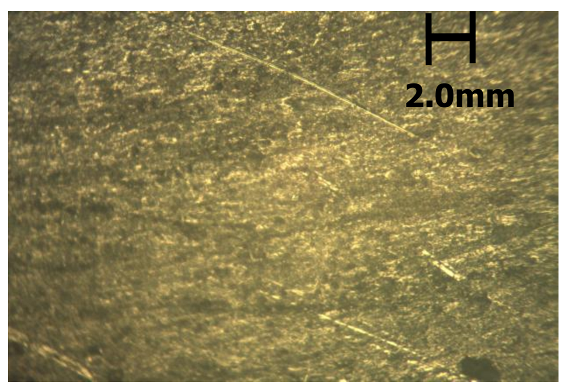



**Figure 6b:** Optical Micrograph of CuNiS (Slide $F_3$).

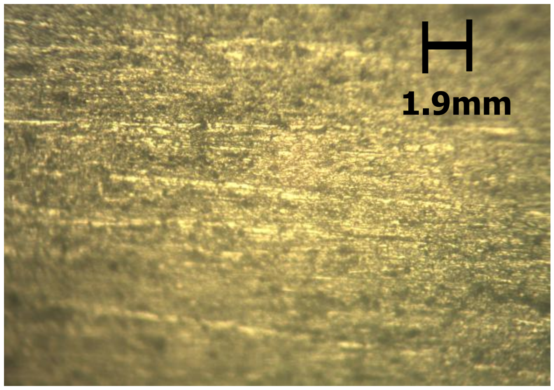
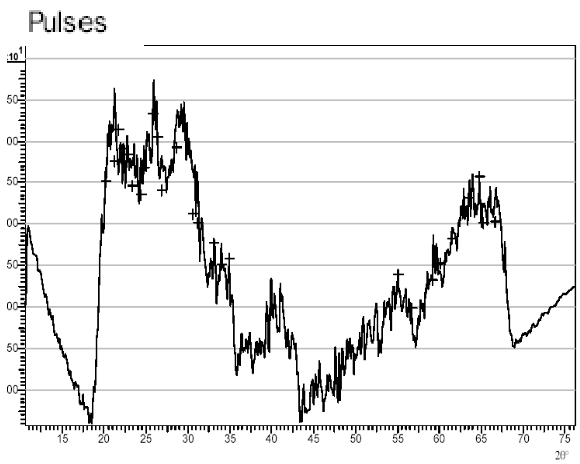



**Fig. 6c:** Optical Micrograph of CuNiS (Slide $F_5$).




*MD-10. 4/20/10*
*Exposure Time:1200/1200sec. Radiation:CuKa, avg*
*Sample:$F_5$*
*Operator:EMDI Akure*
*File:Ottih_$F_5$.smd*

**Figure 7:** X-ray diffraction Spectra for CuNiS Thin Film (Slide $F_5$).

Figures 6 and 7 are the optical micrograph and the x-ray diffraction spectra of CuNiS thin film respectively. From the optical micrograph, an average grain size of CuNiS was found to be 0.20μm. 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 imperfection of the films with increasing deposition time. It also indicates a uniform surface coverage. The grain crystallite size D was calculated using the Scherer's formula [Padiyam et al (2000)].

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

Where λ is the wavelength of X- ray, β is 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 Bragg's law:

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

The direction of scattered beams ($\theta_{hkl}$) 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 [Zisham et al. (2005)]. The XRD pattern for CuNiS thin films indicates that there is a prominent peak in 2θ values which corresponds to (101) plane and other peaks at different 2θ values which correspond to (111) and (121) plane, respectively.

The presence of large peaks indicates that the film is polycrystalline [Damodara et al. (1989)]. From the XRD results, the grown CuNiS thin film has a tetragonal structure. The lattice constant (a) of 3.202Å was obtained.

## CONCLUSIONS

CuNiS thin films have been successfully deposited unto glass slides using chemical bath deposition technique. The optical studies showed that the films have low reflectance values in the UV, VIS-NIR regions. This makes the films suitable for coating in solar collector plates. Again, CuNiS thin film has a low transmittance at UV region and moderate at VIS-NIR regions. This property makes the film candidate for warming coatings since much IR heat is allowed to transmit inside the surface. This is important for those living in the cold parts of the world. The film thickness was found to be of range 0.05μm–0.73μm. The average band gap energy was determined to be 3.60eV. This high band gap property of the film makes it suitable for use as absorber layer thin film. An average grain size of 0.20μm was determined for the film.

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