

## **Effects of deposition time on the electrical and composition of chemically deposited $Mg_{x-1}N_xS$ thin films**

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### **ABSTRACT**

*Magnesium nickel sulphide ( $MgNiS$ ) thin films were prepared on glass slides by chemical bath deposition technique (CBD). The electrical, composition and optical studies were done. These analyses were obtained using a four point probe technique, 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. The electrical analysis shows that the grown films are P-type semiconductors. This is because their electrical conductivities are greater than the intrinsic conductivities. The compositional study shows that as the deposition time increases, the  $Mg^{2+}$  decreases. The optical analysis indicates that the grown films can be used as antireflection films, solar control coating and absorber layer films. These were discovered from their optical properties.*

**Key words:**  $MgNiS$ , Chemical bath deposition technique, composition, electrical and applications.

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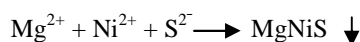
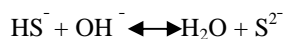
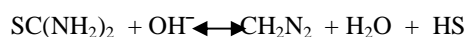
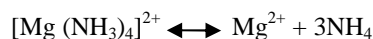
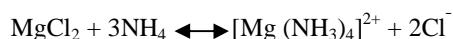
### **INTRODUCTION**

For many decades, the energy needs of many countries have been met by the nonrenewable resources like oil and petroleum products [1]. Recently, there is an increase in the cost of these resources. Consequently, research is shifted to the renewable energy [2]. The renewable resource such as the sun has the problem of low conversion efficiency. Consequently, scientific researchers are carrying out intensive research to see how this problem can be reduced by using suitable semiconductor thin films can boast the energy efficiency [3]. Compound semiconductors have attracted much attention of the researchers during the past years because of their application in solar cell and optoelectronics [4]. Interest in ternary alloy compounds is increasingly being studied because of its specific applications in solar energy industries. [5]. This is of great importance because most binary thin films are of poor conductivity and their usefulness resides in the ability to dope them with impurities so as to achieve their desired properties and make them multifunctional [6]. A number of thin film deposition methods have been used in the preparation of ternary films. A low temperature and less sophisticated chemical bath deposition (CBD) technique produces good quality films. This method has been applied in producing materials for solar cells, solar thermal control in buildings and protective coatings [7]. This research reports the effect of deposition time on the electrical, composition and optical properties of  $MgNiS$  thin film

### **MATERIALS AND METHODS**

The preparation of  $MgNiS$  thin films on glass slides were carried out 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. This 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 adhesive and uniformly deposited films.[8]. The reaction bath for the deposition of MgNiS contained 10mls of 1.0M of  $MgCl_2$ , 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 MgNiS are as follows:



The sulphide ions are released by the hydrolysis of thiourea but  $Mg^{2+}$  and  $Ni^{2+}$  ions are from complexes which the solution of  $MgCl_2$  and  $NiCl_2$  formed with  $NH_3$ . The  $Mg^{2+}$ ,  $Ni^{2+}$  and  $S^{2-}$  present in the solution combined to form MgNiS molecules which were adsorbed on the glass rod. The 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, MgNiS 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 electrical, compositional and optical properties. From the values of absorbance obtained, other properties such as film transmittance, reflectance, and band gap energy were calculated

Table 1: Preparation of MgNiS 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)
E <sub>1</sub>	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	8.0
E <sub>2</sub>	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	9.0
E <sub>3</sub>	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	10.0
E <sub>4</sub>	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	12.0
E <sub>5</sub>	10.0	1.0	10.0	1.0	10.0	1.0	10.0	50.0	24.0

## RESULTS AND DISCUSSION

### Electrical Characterization:

The electrical properties of the grown films were investigated using a four point probe technique. The purpose of the four point probe is to measure the resistivity of the semiconductor thin films grown. The four point probe consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurement. A high impedance current source is used to supply current through the outer two probes, a voltmeter measures the voltage across the inner two probes. The relationship of the current and the voltage values is dependent on the sheet resistivity and the thickness of the films under test. Hence the resistivity is given as

$$\rho_s = \frac{\pi V}{\ln 2I}$$

or

$$\rho_s = \frac{\pi t V}{\ln 2 I}$$

Where  $\frac{\pi}{\ln 2} = 4.523$  and  $t$  = thickness of the film.

This implies that  $\rho_s = 4.523 \frac{V}{I} = 4.523R$

From table 2, it is observed that as the deposition time increases, the electrical resistance decreases but the electrical conductivity increases.

The table also reveals that the electrical conductivities of the grown films are greater than the intrinsic conductivity of the semiconductor film. This implies that the thin films of MgNiS grown are of p-type semiconductors [9].

**Table 2. Electrical properties of MgNiS films with variation in dip. Time**

Slide No	Dip. Time(hr)	Resistivity $\rho$ ( $\Omega m$ )	Conductivity $\sigma$ ( $\Omega m$ )
E2	9.0	$2.48 \times 10^2$	$4.03 \times 10^{-3}$
E4	12.0	$2.14 \times 10^2$	$4.067 \times 10^{-3}$
E5	24.0	$1.82 \times 10^2$	$5.50 \times 10^{-3}$

#### Composition of the Films:

The determination of the composition of thin films is very necessary particularly for films deposited by CBD growth techniques and electro chemical deposition methods. There are several methods for determining thin film composition. 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 E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>, E<sub>4</sub>, and E<sub>5</sub>, were selected for this analysis.  $Cd^{109}$  source was used to analyze the quantities of Mg, while  $^{55}Fe$  was used for the determination of the quantity of sulphur. The contents of  $Mg^{2+}$ ,  $Ni^{2+}$  and  $S^{2-}$  for the grown films are shown in table 3.0.

**Table 3.0 Compositional analysis of Mg<sub>1-x</sub> Ni<sub>x</sub>S thin films**

Slide No	Composition (x)	Mg content Wt%	Ni content Wt%	S content Wt%	Impurity Cl <sub>2</sub> Wt%
E <sub>1</sub>	0.000	55.45	-	44.55	-
E <sub>2</sub>	0.010	53.16	0.45	43.81	1.00
E <sub>3</sub>	0.075	52.19	1.37	45.44	-
E <sub>4</sub>	0.100	52.17	1.81	45.00	1.00
E <sub>5</sub>	0.150	51.19	3.98	44.83	-

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

#### Optical Characterization:

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

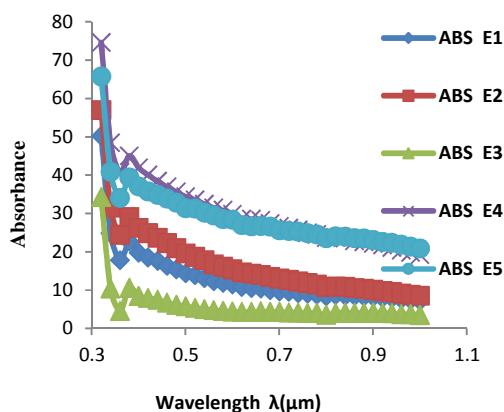


Fig1: Spectral Absorbance of MgNiS thin film (Slide E<sub>1</sub>-E<sub>5</sub>)

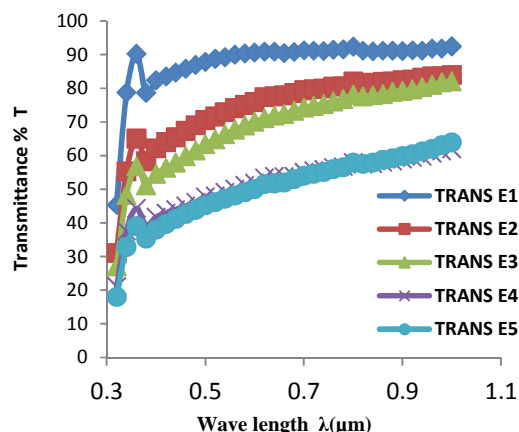


Fig.2 Spectral Transmittance of MgNiS thin films (Slide E<sub>1</sub>-E<sub>5</sub>)

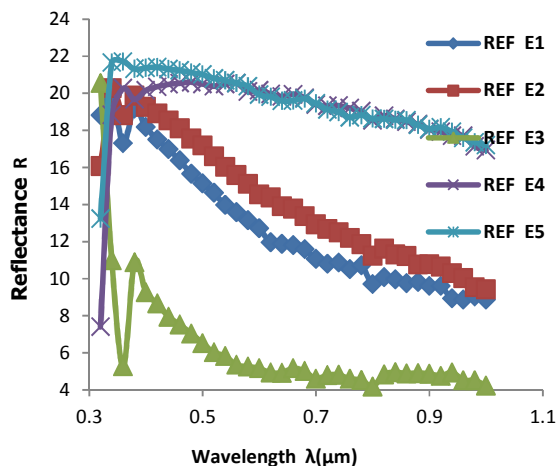


Fig.3: Spectral Reflectance of Magnesium Sulphide (MgNiS) thin film (Slide E<sub>1</sub>-E<sub>5</sub>)

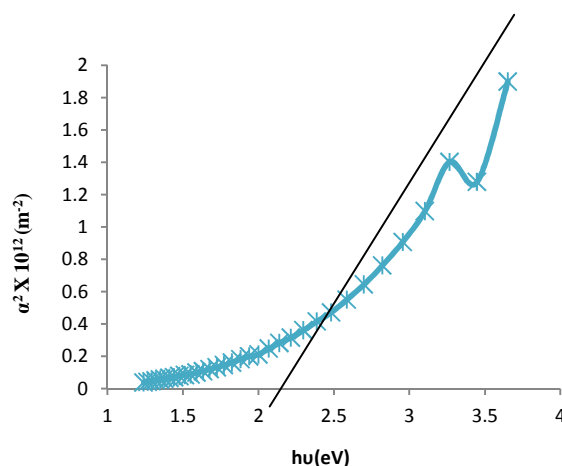


Fig 4: A plot of absorption coefficient squared versus photon energy of MgNiS for E<sub>1</sub> - E<sub>5</sub>

Figure 1 is the absorbance spectra of MgNiS thin films. A close observation indicates that the films grown for a higher deposition time of 24 hours have the highest absorbance value in the UV region. It further reveals that films grown with a shorter deposition time such as film on slide E<sub>1</sub> have the least absorbance value. The implication of this is that the higher the deposition time, the higher the absorbance in the UV region. Such films of high absorbance in the UV region are used as thin films for coatings in temperate regions of the world like Nigeria [10]. This is possible because the films have the ability to absorb a great percentage of the harmful ultra violet radiations and keep the inner surface cool. However, films of low absorbance such as films on slide E<sub>1</sub> in the VIS and UV regions are useful in coating windscreens and driving mirrors. This is because it prevents the effects of dazzling light from entering the drivers' eyes from oncoming vehicles. It could also be used in coating eyeglasses. This helps to protect the skin around the eye from sunburning, which is usually caused by the concentration of the UV radiation.

Figure 2 shows the transmittance spectra of MgNiS thin films. A close look at the plots reveals that the thin films prepared when the deposition time is 24 hours have the least value of transmittance (20 – 35%) in the UV, VIS – NIR regions of the electromagnetic spectrum. Also, thin films prepared when the deposition time is small (8 hours) have the highest transmittance values. The implication of this is that thin films of high transmittance can be obtained when deposition is made for a shorter period of time. Films of high transmittance value such as films on slide E<sub>1</sub> can be used

for warming coatings since it allows greater percentage of solar radiation to pass through. This type of thin film is used in the arctic regions of the world and for materials used in poultry.

Figure 3 shows reflectance spectra of MgNiS thin film grown. The plot indicates that the reflectance values of the thin films grown are generally low irrespective of the length of the deposition time for growth. 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.

Figure 4 is the plot of average values of absorption coefficient squared ( $\alpha^2$ ) versus the photon energy for MgNiS films. From this plot, the band gap energy of the film was determined. This was done by extrapolating the straight portion of the graph to the point where ( $\alpha^2$ ) equals zero. The value of the photon energy at this point is equal to the band gap energy of the MgNiS thin film. A band gap value of 2.1eV for MgNiS was obtained from the graph

### CONCLUSION

MgNiS thin films have been successfully deposited onto glass slides using chemical bath deposition techniques. The electrical analysis shows that the grown films are P-type semiconductors. This is because their electrical conductivities are greater than the intrinsic conductivities. The compositional study reveals that as the deposition time increases, the  $Mg^{2+}$  decreases. 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, MgNiS films were found to have high absorbance in the UV region. This property makes the film candidate for solar control coatings. The film band gap energy was determined to be 2.1eV. From this large band gap value, the film is therefore suitable to be used in the absorber layer of solar cell. .

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