INFLUENCE OF DEPOSITION TIME ON THE OPTICAL AND STRUCTURAL PROPERTIES OF CHEMICAL BATH DEPOSITED MAGNESIUM NICKEL SULPHIDE (MGNIS) THIN FILMS

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Abstract

Thin films of magnesium nickel sulphide (MgNiS) were grown on glass substrates using the chemical bath deposition (CBD) techniques at room temperature. Effects of deposition time on the optical and structural properties of the films were studied via depositing MgNiS thin films for different dip time. The optical properties of the deposited films were investigated by measuring the optical absorbance of the films at the normal incident of light in a range of 200–1000 nm with a Janway 6405 UV–VIS spectrophotometer. From the absorbance values, other properties such as transmittance, reflectance, thickness, and energy gap, were calculated. The low reflectance and large band gap make the film good materials for antireflection coatings and absorber layers of solar cells, respectively. The films grown were further characterized using an MD10 version 2.0 X–ray diffractometer and an Olumpus optical microscope to determine the structural properties of the films. From the XRD results, the film crystal structure was found to be rhombohedral. The lattice constant and an average grain size of the grown films were found to be 5.32 Å and 0.45 μm, respectively. The presence of large peak indicates that the MgNiS film is polycrystalline.

1. Introduction

Thin films of II–VI Semiconductor chalcogenides, especially sulphide and selenides, have been extensively investigated owing to their interesting optoelectronic properties. Magnesium sulphide (MgS) with a direct band gaps of 3.90 eV at room temperature (RT) is a useful candidate for solar cells, green lasers, window coatings, and light emitting diodes [1]. Transmission metal (TM) doped semiconductors, which are known as diluted magnetic semiconductors (DMSs), have attracted widespread scientific attention due to their prospective applications [2]. The usefulness of MgS resides in the ability to dope it with impurities so as to achieve the desired properties and to make them multifunctional. It was reported that TM doping, with Fe and Ni in particular, diminishes the quantum size yields in the visible and near band gap region by acting as quenching or killer centers for fluorescence and photoconduction and results in short carrier life times useful in fast optoelectronic devices [3, 4].

Recently, many scientists are looking for new chalcogenide materials for solar, architectural, and industrial applications other than silicon-based thin films. This is because silicon-based films, which are dominant products in the market, are expensive, and scientists hope to replace them with cheaper chalcogenide materials. The more so, most binary thin films are of poor conductivity as reported by Mane R.S. 2000. In order to overcome this problem, doping and annealing are used [6, 7].
Magnesium nickel sulphide (MgNiS) is a technological important 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 [8-10]. In this study, polycrystalline MgNiS thin films were prepared by the chemical bath deposition (CDB) technique at room temperature from an aqueous solution bath containing MgCl₂, NiCl₂ and SC(NH₂)₂. CBD is an interesting growth technique which yields high quality semiconductor thin films. It is inexpensive, simple and requires low temperature [11–12]. This method produces films that have comparable structural and optoelectronic properties to those produced using other sophisticated deposition techniques [13]. The CBD technique was applied in producing emerging materials for solar cells, protective coatings, and solar thermal control in buildings and is being adopted by some industries [14–16]. In addition, this method is convenient for producing large-area devices, and there is the possibility of controlling the film thicknesses by adjusting the deposition parameter. The method of chemical bath is based on the controlled precipitation of a desired compound from a reaction solution. The condition is that the ionic product (Mg²⁺, Ni²⁺ and S²⁻) must exceed the solubility (MgNiS) [17].

2. Experimental

The preparation of MgNiS thin films on glass slides were carried out using the CBD technique. The glass slides were previously degreased in hydrochloric acid for 24 hs, washed with detergent, rinsed in distilled water, and dried in the air. The acid treatment caused the oxidation of halide ions in glass slides used as substrate thereby introducing functional groups, which are 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 MgNiS contained 10ml of 1.0 M MgCl₂, 10 ml of 1.0M of SC(NH₂)₂, and 10ml of 14.0 M ammonia. Fifty milliliters of distilled water was added to make up 90 ml in a 100-ml beaker. Ammonia solution was used for dual purposes: as a complexing agent and 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 MgNiS are as follows:

\[
\begin{align*}
\text{MgCl}_2 + 3\text{NH}_4 & \rightleftharpoons [\text{Mg} (\text{NH}_3)_4]^{2+} + 2\text{Cl}^- \\
[\text{Mg} (\text{NH}_3)_4]^{2+} & \rightleftharpoons \text{Mg}^{2+} + 3\text{NH}_4 \\
\text{NiCl}_2 + 3\text{NH}_4 & \rightleftharpoons [\text{Ni} (\text{NH}_3)_4]^{2+} + 2\text{Cl}^- \\
[\text{Ni} (\text{NH}_3)_4]^{2+} & \rightleftharpoons \text{Ni}^{2+} + 3\text{NH}_4 \\
\text{SC(NH}_2)_2 + \text{OH}^- & \rightleftharpoons \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{HS}^- \\
\text{HS}^- + \text{OH}^- & \rightleftharpoons \text{H}_2\text{O} + \text{S}^2^- \\
\text{Mg}^{2+} + \text{Ni}^{2+} + \text{S}^2^- & \rightarrow \text{MgNiS} \\
\end{align*}
\]

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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\(_3\), Mg\(^{2+}\), Ni\(^{2+}\), and S\(^2-\) present in the solution associate to form MgNiS molecules which were adsorbed on the glass rod. The heterogeneous nucleation and growth take place through ionic exchange of reactive S\(^2-\) ions. This process is referred to as ion by ion process; in this way, MgNiS films were deposited on glass slides as uniform and adherent thin films. Five depositions were made for five different deposition times as shown in the table below. For each deposition, the glass slide, which was mounted on a beaker with the synthetic material, was taken out of the beaker, rinsed with distilled water, and allowed drying in the air. The grown films 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 280–1000 nm. The structural composition of the grown MgNiS films was studied with an optical micrograph an MD\(_{10}\) version 2.00 X-ray diffractometer.

Table. Preparation of MgNiS Thin Films

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3. Results and discussion

3.1 Optical Properties

The optical properties of the grown thin films were studied in a wavelength range of 0.28 to 1.0 μm a Janway 6405 UV–VIS model of spectrophotometer. From the results, the following properties and their applications were determined.
Figure 1 shows the absorption spectra of the MgNiS thin films. A close observation indicates that the films grown for a higher deposition time of 24 h have the highest absorbance in the UV region. It further reveals that the films grown for a shorter deposition time, such as the film on slide E1, ve the lowest absorbance. The implication of this is that the higher the deposition time, the higher the absorbance in the UV region. These films with high absorbance in the UV region are used as thin films for coatings in the temperate regions of the world like Nigeria. This is possible because the films have the ability of absorbing a great percentage of the harmful ultra violet radiations and keeping the inner surface cool. However, films with low absorbance, such as films on slide E1, in the VIS and UV regions, are useful in coatings for windscreens and driving mirrors. This is because it prevents the effects of dazzling light into the drivers’ eyes from the oncoming vehicles. It could also be used in coatings of eyeglasses. This helps to protect the skin around the eye from sun burning, which is usually caused by the concentration of the UV radiation.

Figure 2 shows the transmission spectra of the MgNiS thin films. A close look at the plots reveals that the thin films prepared for the deposition time of 24 h have the lowest transmittance (20–35%) in the UV, VIS, and NIR regions of electromagnetic spectrum. In addition, the thin films prepared for the short deposition time (8 h) have the highest transmittance. The implication of this is that thin films of high transmittance can be obtained when deposition occurs for the shorter period of time. Films of high transmittance, such as films on slide E1, can be used for warming coatings, since they allow 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 reflection spectra of the grown MgNiS thin film. It is evident from the plot that the reflectance of the grown thin films is generally low, irrespective of the deposition time for growth. Thin films of low reflectance are used for coatings in the solar collector plates. These films help to reduce the loss of incident solar radiation due to reflection. This enhances the efficiency of the solar collector plates.

The plot of the thickness as a function of deposition time is shown in Fig. 4. The plot indicates that the thickness increases as the deposition time increases and later remains constant. The final thickness of 0.5 μm was obtained when the deposition time was 12 h.

Figure 5 is the plot of average values of absorption coefficient squared (α²) versus the photon energy for the 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 (α²) is 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 3.15 eV for MgNiS was obtained from the graph. This result shows that the band gap of MgS was reduced by doping with TM nickel. This is in accordance with the report of Nnabuchi 2005, who found that MgS grown by CBD has a band gap of 3.9 eV.

### 3.2 Structural Properties

![Fig. 6a. Photo micrograph of MgNiS (E₂).](image)

![Fig. 6b. Photo micrograph of MgNiS (E₄).](image)

![Fig. 6c. Photo micrograph of MgNiS (E₅).](image)

The structural properties of the grown thin films were studied with the aid of an optical micrograph and an XRD spectrophotometer. Figure 6 shows the optical micrograph of the grown films. The figures indicate that the films have uniform surface coverage. From the XRD analysis, the crystallite size D was calculated using the Scherer’s formula [19]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the X-ray wavelength, \(\beta\) is the FWHM (Full width half maximum) given by the diffractometer in radians, \(\theta\) is the diffraction angle, and \(K\) is usually 0.9 for crystallite shape. The surface microstructure of the thin films shows that the grain size of the grown thin films increases as the dip time increases. This may be attributed to the decrease in imperfections of the films with increasing deposition time. It also indicates that an average size of 0.45 μm was obtained for the film. Various crystalline aspects were analyzed 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 [20]. The XRD pattern for MgNiS thin films indicates that there is a pronounced peak in $2\theta$ values which corresponds to the (111) plane and other peaks at different $2\theta$ values which correspond to the (211) and (221) planes, respectively. The presence of large peaks indicates that the film is polycrystalline [21]. The orientation of crystallites perpendicular to the (111) plane gives rise to the rhombohedral structure with lattice constant $a = 5.320 \, \text{Å}$ as indicated in the XRD analysis.

3. Conclusions

MgNiS thin films were successfully deposited onto glass slides using the CBD techniques. The optical studies showed that the films have low reflectance in the UV, VIS, and NIR regions. This makes the film suitable for coatings in solar collector plates as antireflection films. In addition, MgNiS films were found to have high absorbance in the UV region. This property makes the film a candidate for solar control coatings. The thickness of the film was found to be in a range of 0.05–0.85 μm. The film band gap energy was determined to be 3.18 eV. Owing to this large band gap value, the film is suitable to be used in the absorber layer of solar cells. The XRD analysis showed that the film has a rhombohedral structure, and an average grain size of 0.45 μm.
was determined. The presence of large peaks indicates that the MgNiS thin film is polycrystalline with the preferred orientation of the crystallites along the (111) plane.

References