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Studies of chemically deposited Cd_{x-1} N_xS thin films

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ABSTRACT

Cadmium Nickel sulfide (CdNiS) thin films were grown on glass slides by chemical bath deposited (CBD) technique. The optical and compositional studies of the films were done. These analyses were done using a Janway 6405 UV-VIS spectrophotometers and energy dispersive X-ray fluorescence (EDXRF) respectively. The effects of variations of the concentration of Nickel Chloride ion on the optical and composition of the growing films were revealed. The optical analysis indicated that the grown films can be applied as solar control coating antireflection films and warming coatings. The compositional study indicates that the prepared films are rich in and the S^- is almost constant. It also revealed that as the ion concentration increases, the Cd^{2+} decreases.

Keywords: Chemical bath deposition technique, CdNiS, applications and composition

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INTRODUCTION

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

CdNiS thin film is one of the tenary chalcogenide films. These films have been investigated for specific applications in super ionic conducting materials [1]. 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 [2].Several thin film deposition techniques of advanced technologies have been employed in the preparation of ternary thin films. However, a low cost and less sophisticated chemical bath deposition (CBD) technique seems to be much better [3]. The CBD technique produces good quality films. This method has been applied in producing materials for solar cells, protective coatings, and solar thermal control in buildings and is being adopted by some industries. CBD technique is convenient for producing large area device and there is possibility to control film thickness by adjusting the growth parameter. CdNiS thin films are semiconducting materials with direct band gap transition. This research reports the effects of variation of the concentration of nickel chloride ion on the optical and composition of the grown film.

MATERIALS AND METHODS

The preparation of CdNiS thin films on glass slides was 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 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 CdNiS thin film contained 10mls of 1.0M of $CdCl_2$, 10mls of 1.0M of $SC(NH_2)_2$, 10mls of varied molar concentration 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 chemical equations for the reaction and depositions are given below

$$CdCl_2 + 3NH_4 \leftrightarrow [Cd(NH_3)_4]^{2+} + 2Cl^-$$

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

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

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

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

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

$$Cd^{2+} + Ni^{2+} + S^{2-} \longrightarrow CdNiS\downarrow$$

The sulphide ions are released by the hydrolysis of Thiourea but Cd^{2+} and Ni^{2+} ions are from complexes which the solution of $CdCl_2$ and $NiCl_2$ formed with NH_3. The Cd^{2+}, Ni^{2+} and S^{2-} present in the solution combined to form CdNiS molecules which were adsorbed on the glass rod. Five depositions were made with five different values of molar concentrations of $NiCl_2$ 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 elemental composition of the films was done by energy dispersive x-ray fluorescence (EDXRF)

Table 1: Preparation of CdNiS thin films

Slide No.	Vol. of $CdCl_2$ (mls)	Conc. $CdCl_2$ (M)	Vol. of $NiCl_2$ (mls)	Conc. $NiCl_2$ (M)	Vol. of NH_3 (mls)	Vol. of $SC(NH_2)_2$ (mls)	Conc. $SC(NH_2)_2$ M	Vol. of Distilled H_2O	Dip Time (hrs)
G11	10.0	1.0	10.0	0.10	10.0	10.0	1.0	50.0	12.0
G12	10.0	1.0	10.0	0.25	10.0	10.0	1.0	50.0	12.0
G13	10.0	1.0	10.0	0.50	10.0	10.0	1.0	50.0	12.0
G14	10.0	1.0	10.0	0.75	10.0	10.0	1.0	50.0	12.0
G15	10.0	1.0	10.0	1.00	10.0	10.0	1.0	50.0	12.0

RESULTS AND DISCUSSION

Optical characterization

The optical properties of the grown thin films of CdNiS 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 showed the nature of the properties investigated.

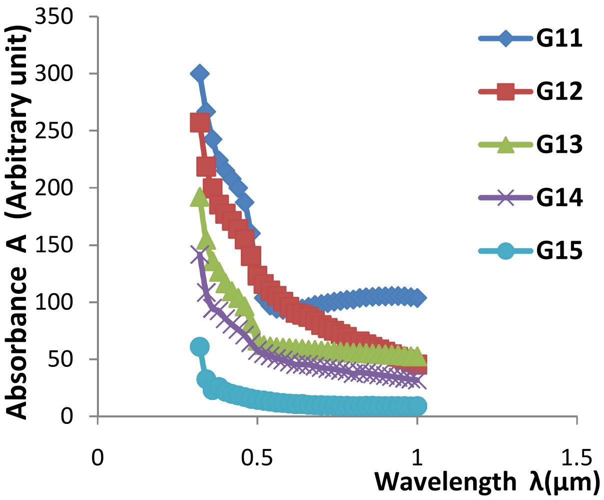

Fig. 4.35c: Spectral absorbance of CdNiS thin film (Slide G_{11}-G_{15})

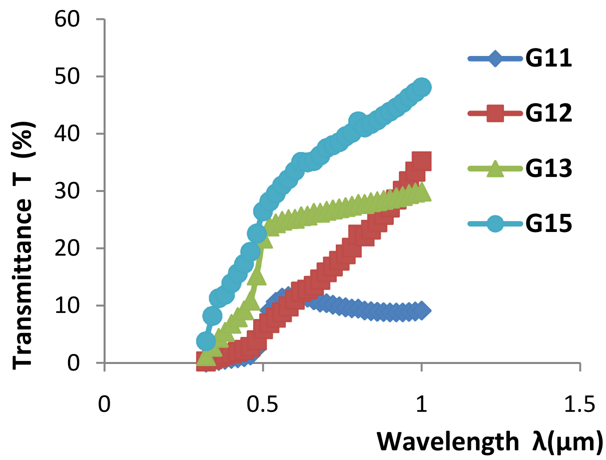

Fig. 4.34c: Spectral transmittance of CdNiS thin film (Slide G_{11}, G_{12}, G_{13}, G_{15})

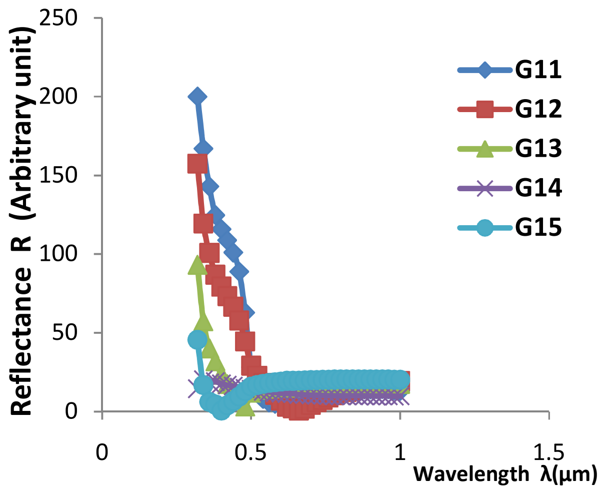

Fig. 4.36c: Spectral reflectance of CdNiS thin film slide (G_{11}-G_{15})

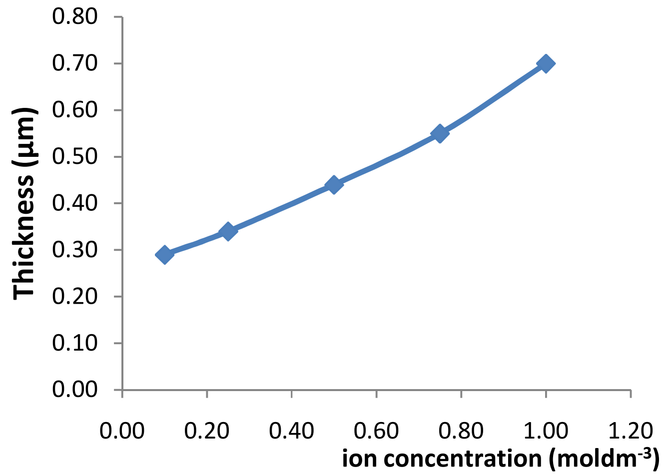

Fig. 4.37c: Variation of thickness with $NiCl_2$ ion concentration of CdNiS thin film (Slide G_{11} - G_{15}))

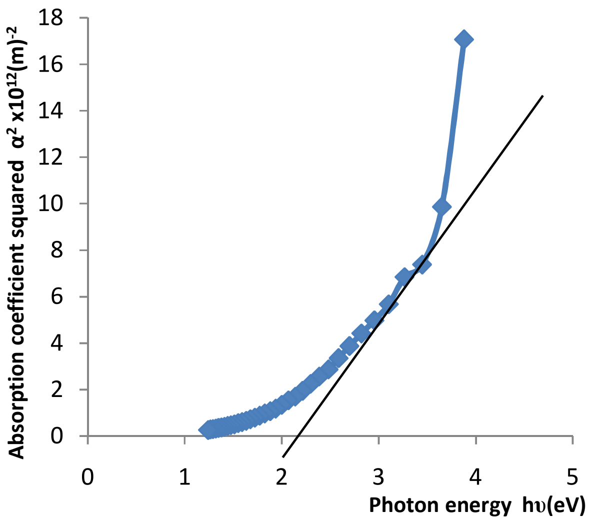

Fig. 4.38c: A plot of absorption coefficient squared versus photon energy for (G11-G15)

The spectral absorbance of CdNiS is shown in figure 1. The figure indicates that the film with the lowest concentration has the highest absorbance in the UV region. This is shown by film on slide G_{11} which is grown with only 0.1M of $NiCl_2$. Film grown with higher value of $NiCl_2$ ion concentration has the least absorbance value, this implies that the lower the ion concentration of $Nicl_2$ solution the lesser the absorbance value for CdNiS thin films. These films prepared are good materials for coating windows in the temperate regions of the world, this is because, and the films are capable of absorbing the harmful ultraviolet radiations thereby keeping the inside cool.

Figure 2 is the spectral transmittance of CdNiS thin film grown in this work at a room temperature. A close observation of the plot reveals that CdNiS thin film has a high transmittance value in the near infrared region (NIR) region. The figure shows that the value of transmittance for CdNiS thin film increases as the molar concentration increases. Film on slide G_{15} which was grown with 1,0M of $NiCl_2$ has a high transmittance value almost 0% at UV region. This film can be used in the construction of poultry farms because it allows much infrared radiation to warm the chicks.

Figure 3 is spectral reflectance of CdNiS thin film grown in this work. A close observation of the plots reveals that the reflectance of the thin film is low in UV, visible and near infrared regions. The figure indicates that the thin film of CdNiS grown with 1.0M of $NiCl_2$ has the lowest value of reflectance. Film of low reflectance value is used as antireflection film.

Figure 4 shows the plot of thickness as a function of nickel chloride ion concentration for CdNiS thin film grown in this work at room temperature. The figure reveals that thickness increases linearly with increase in ion concentration of nickel chloride solution. A terminal thickness of 0.7μm was obtained when 1.0M of $NiCl_2$ was used.

The plot of the value of absorption coefficient squared (α^2) versus photon energy for CdNiS thin films grown in this work are displayed in figure 5. From the plot, the band gap energy value was obtained as 2.20eV. This is obtained by extrapolating the straight part of the graph to a point where α^2 =0. The above band gap values for CdNiS compared well with what [4, 5] obtained for the same film. CdNiS grown in this work are of direct and high band gap values. Films of high band gap values are used in the absorber layer of a solar cell because absorption of the photon energy only when the energy gap of the absorber layer is higher than the energy gap of the photon.

Composition Studies of the Thin Films

The compositional analysis was done 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 G_{11}, G_{13} and G_{15} were selected for this analysis. Cd^{109} source was used to analyze the quantity of Cd while ^{55}Fe was used for the determination of the quantity of sulphide. The contents of Cd^{2+}, Ni^{2+} and S^{2-} for various films are shown in table 2 below.

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

Slide No	Composition (x)	Cd content Wt%	Ni content Wt%	S content Wt%	Impurity Cl_2 Wt%
G_{11}	0.000	54.55	-	45.45	-
G_{13}	0.025	51.15	0.91	46.94	1.00
G_{15}	0.100	50.81	1.17	47.00	1.00

From the composition studies, the grown films are slightly rich in Cd^{2+}, whereas S^{2-} is practically constant. It appears from the tables that the content of Cd^{2+} decreases with increasing nickel content.

CONCLUSION

CdNiS thin films have been successfully deposited on glass slides using chemical bath deposition techniques. The optical studies showed that the films have high absorbance and can be used for coating windows in temperate regions of the world. This implies that the films can be used as substitute for the conventional air conditioner. Also, the thin films grown have low reflectance values in the UV, VIS – NIR regions. This makes the films 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. Again, CuNiS films were found to have high absorbance in the UV region. This property makes the films good materials for solar control coatings. 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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