Effect of deposition time on the band-gap and optical properties of chemical bath deposited CdNiS thin films

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Thin films of CdNiS have been grown on glass substrate using the chemical bath deposition (CBD) technique. Cadmium chloride, Nickel chloride and thiourea were taken as the source of cadmium, cobalt and sulphur respectively. Effects of deposition time on the films' optical properties and band gap energy were studied by depositing CdNiS thin films under different dip time. Optical properties such as absorptance and transmittance were determined using Unico UV-2102 PC Spectrophotometer, at normal incidence of light in the wavelength range of 200-1000μm. From the absorbance and transmittance spectra, the band gap energy was determined. The high transmittance of the films in certain range of the solar spectrum and the large band gap make them good material for selective coatings and absorber layer for solar cell, respectively.

1. Introduction

In an ideal defect free semiconductor, electrons are distributed in such away that they occupy energy levels in a completely filled band which is separated from a higher lying empty band. The gap between these two bands is called band gap (E_g). Depending upon the application and usage, a semiconductor material may be required to have smaller or larger band gap. Where none of the elemental semiconductors show the precise gap required for a particular device application, efforts are made to compound pairs of elements, neither of which needs to be a semiconductor. This has lead to the formation of many multinary semiconductors [1 – 5].
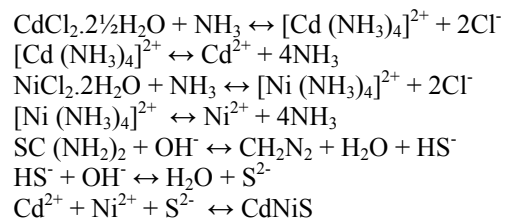
Thin films of CdS have been extensively studied due to the variety of applications in optoelectronic devices. Because of its conducting and optical properties, CdS is used in CdTe devices as an optical window [6, 7]. However, poor conductivity as low as 10^{-8} $(\Omega cm)^{-1}$ have been reported [8]. In order to overcome this problem, annealing and doping are used [8 – 10].

In this study, polycrystalline CdNiS thin films were prepared by chemical bath deposition technique at room temperature. The effects of deposition time on the optical and band gap energy of CdNiS thin films were investigated through the analysis of the absorption-transmittance, the XRD and the RBS spectra.

2. Materials and method

The chemical bath used for the preparation of the thin films of CdNiS in this work was composed of cadmium chloride, Nickel chloride and thiourea. Ammonia solution was employed as the complexing agent. The chemical reaction for the deposition of CdNiS by CBD is given by:

$$CdCl_2.2\tfrac{1}{2}H_2O + NH_3 \leftrightarrow [Cd\,(NH_3)_4]^{2+} + 2Cl^-$$
$$[Cd\,(NH_3)_4]^{2+} \leftrightarrow Cd^{2+} + 4NH_3$$
$$NiCl_2.2H_2O + NH_3 \leftrightarrow [Ni\,(NH_3)_4]^{2+} + 2Cl^-$$
$$[Ni\,(NH_3)_4]^{2+} \leftrightarrow Ni^{2+} + 4NH_3$$
$$SC\,(NH_2)_2 + OH^- \leftrightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$
$$Cd^{2+} + Ni^{2+} + S^{2-} \leftrightarrow CdNiS$$

When the ionic product of the ions exceeds the solubility product, the precipitation of CdNiS can occur on the surface of the substrate. Five samples were deposited at different dip time as shown in Table 1.

Table 1. The preparation of CdNiS for varied dip times at room temperature.

Reaction Bath	Dip Time (hr)	CdCl$_2$		NH$_3$	SC(NH$_2$)2		NiCl$_2$		H$_2$O
		Conc. (M)	Vol (ml)	Vol (ml)	Conc. (M)	Vol (V)	Conc. (M)	Vol (ml)	Vol (ml)
E1	3	1	2	5	1	5	0.1	3	35
E2	3½	1	2	5	1	5	0.1	3	35
E3	4	1	2	5	1	5	0.1	3	35
E4	4½	1	2	5	1	5	0.1	3	35
E5	5	1	2	5	1	5	0.1	3	35

3. Film characterization

The structure of the films was studied with optical microscope and Philips PW 1500 XRD. The composition of the films was determined by Rutherford back scattering (RBS). The absorption coefficient (α) and the band gap of the films were determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000 nm.

4. Results and discussion

4.1. X-ray diffraction study

Typical XRD diffractograms of CBD Ni dopped CdS are presented in Fig. 1. The samples were grounded to below 100 mesh in an agate mortar and then loaded into a 2.5 cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. CuKα was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15. Phase identification was then made from an analysis of peak intensity versus 2θ.

The XRD pattern displayed in Fig. 1 show several peaks at 2θ values of around 24.45^0, 25.45^0, 26.75^0, 30.33^0 and 67.16^0. The 2θ value of 26.75^0 (d = 3.33201 Å) and 30.33^0 (d = 2.94699 Å) correspond to the diffraction lines produced by (002) and (200) planes respectively [16]. Intensity of the peaks increased with increase in dip time. The grain sizes is estimated using Scherrer relation, $D = K\lambda/ \beta\cos\theta$, where K is a constant taken to be 0.94, λ the wavelength of X-ray used ($\lambda = 1.54$Å). The calculated grain size of the film is about 2.59 nm.
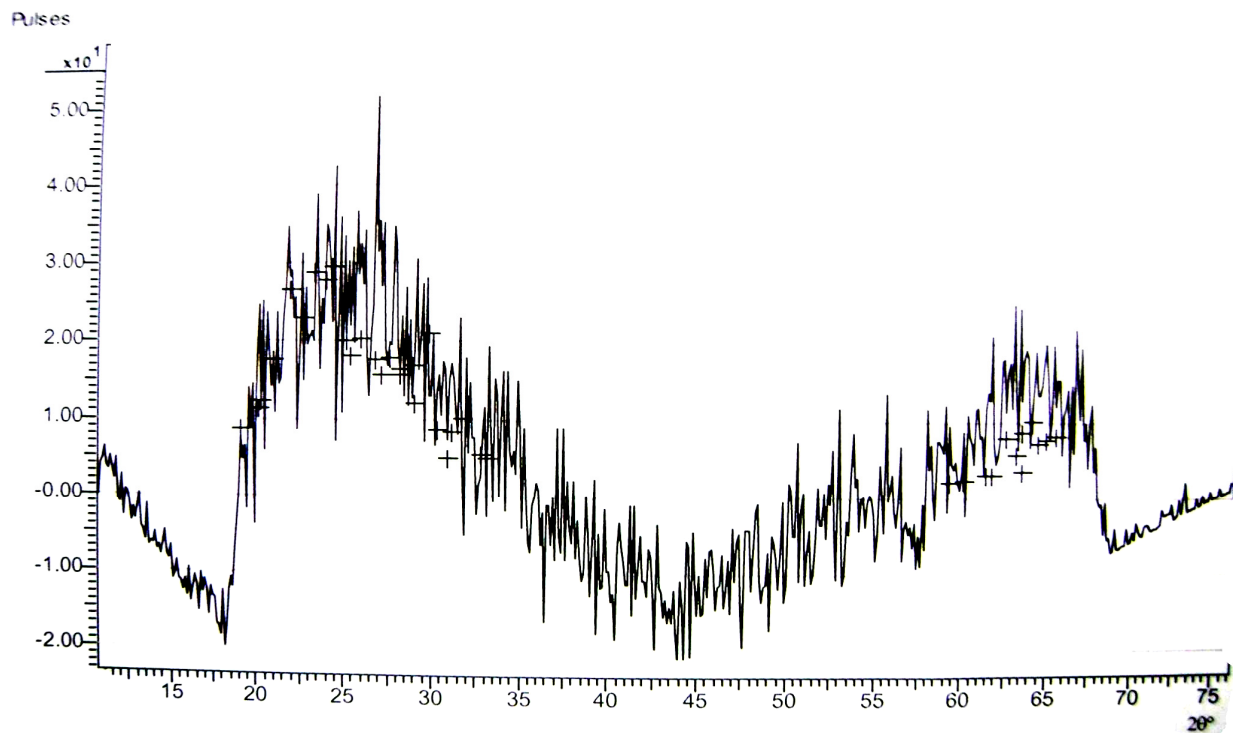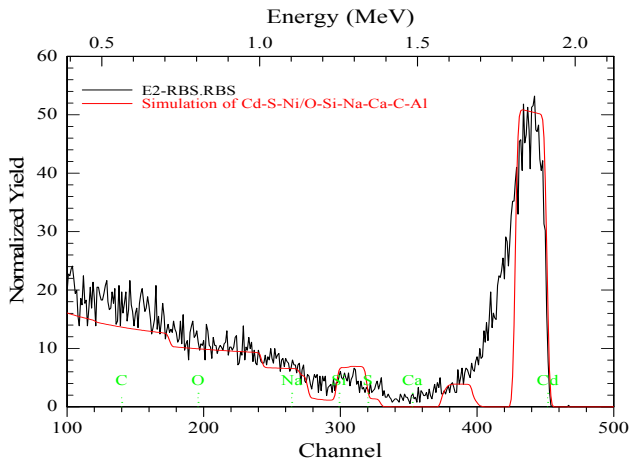

Fig 1. XRD pattern of CdNiS thin film.

4. 2. Composition study

The elemental composition and chemical states of sample E2 was analyzed using Rutherford Backscattering (RSB). The RBS analysis was carried out using 2.20 MeV 4He+ ions and 1.20 μC at 2.34 nA. The results are presented in Fig. 2.

From the film composition presented in Fig. 2, we can deduce that sample E2 comprises of Cd, Ni and S with Ni appearing in trace quantity. This implies that Ni acts as an impurity in the as-deposited CdNiS thin film.

Film   Composition (CM2):
Film   Cd 0.450   S 0.450   Ni 0.100
Glass   O 0.250   Si 0.150   Na 0.150   Ca 0.020
C 0.050   Al 0.050

Fig. 2. RBS spectrum for CdNiS thin film.

4. 3. Optical studies

4. 3. 1. Variation of the absorbance and transmittance of the films with wavelength

Figs. 3 and 4 are plots of absorbance vs. wavelength and transmittance vs. wavelength for CdNiS thin films deposited in this work. From the absorption spectra of CdNiS, we observe that the absorption edge of the films shift towards shorter wavelength (blue shift) with increasing dip time. The optical studies reveal that the films absorb strongly in the VIS domain and are highly transmitting in the NIR region.

Table 2 gives the summary of the effect of dip time on the transmittance of thin films of CdNiS as the wavelength increases.

Table 2. Variation of optical transmittance (%) with wavelength (nm) for CdNiS thin films.

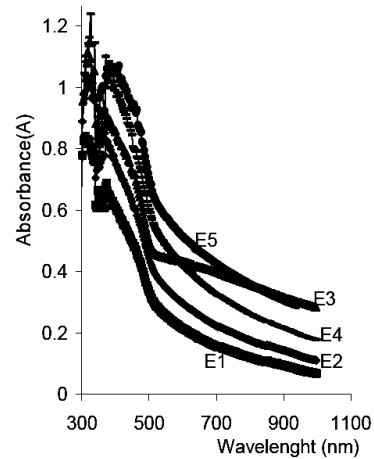| Wavelength (nm)	E1 (3hrs)	E2 (31/2 hrs)	E3 (4hrs)	E4 (41/2 hrs)	E5 (5hrs)
400	24.71	17.82	13.87	10.73	9.88
500	46.12	36.09	31.65	24.93	19.82
600	61.17	50.14	36.87	36.87	30.68
700	70.13	59.85	40.12	47.60	37.39
800	75.95	66.70	44.04	54.82	44.04

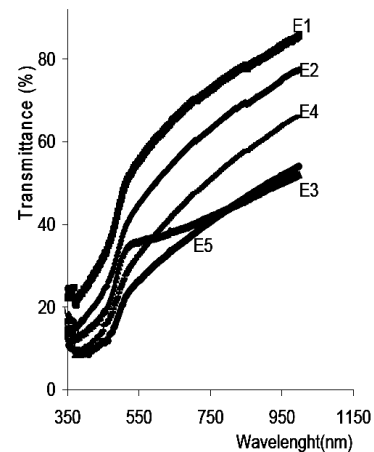*Fig. 3. Absorbance vs wavelength for CdNiS thin films.*

Fig. 4.Ttransmittance vs wavelength for CdNiS thin films.

A close observation shows that transmittance generally increases with wavelength and decreases with dip time. This implies that the transmittance is higher if the dip time is low. It has been observed that the thickness of thin solid films in which the film formation and kinetics takes place ion by ion condensation has a linear relationship with deposition time [11, 12]. Hence, the observed differences in transmission are only due to difference in thickness. The property of high transmittance in the IR exhibited by this films therefore make them good materials for the construction of poultry roofs and walls.

This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation. The strong absorbance of CdNiS thin films in the visible region also suggests that the films could be used for the fabrication of solar cells.

4. 3. 2. Study of band gap as a function of photon energy

The fundamental absorption which corresponds to the electron excitation from the valence band to the

conduction band can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as [13]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \qquad (1)$$

where A is a constant, E_g is the band gap of the material and the exponent n depends on the type of transition. The values of n for direct allowed, indirect allowed and direct forbidden transition are n = ½, 2, 3/2 respectively. The direct band gap of the films were obtained from the linear portion of $(\alpha h\nu)^2$ versus hν plot as shown in Figure 5. The values obtain for CdNiS lie in the range of 2.2 – 2.6eV. Different values of band gap energy have been reported for CdS and doped CdS thin films: 1.9 – 2.45eV [14] 2.46 – 2.62eV [15], 2.58 – 2.82eV [3].
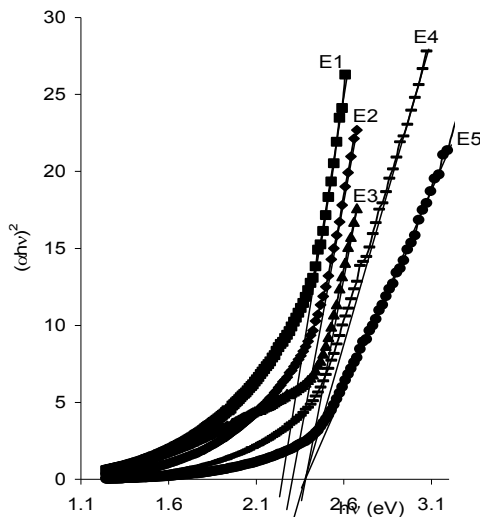

Fig. 5. Plot $(\alpha h\nu)^2$ vs hν for CdNiS thin films.

We can also deduce from Fig. 5 that as dip time increases, the thickness of the films increase as well and this leads to decrease in band edge sharpness and an increase in energy gap. At critical deposition time, the band gap value remains constant irrespective of the increase in the dip time.

5. Conclusions

CdNiS thin films have been successfully deposited onto glass slide using chemical bath deposition technique. The optical studies showed that most of the films have high absorbance in the VIS region of the solar spectrum and high transmittance in the NIR region and therefore can be used as solar control device or selective absorber surface device. The films could also be applied in fabrication of solar cell and in anti-dazzling coatings in car wind screen and driving mirrors to reduce the dazzling effect of light at night. This application has been reported [39]. Again, thin films with high transmittance in the NIR

are employed in construction of poultry houses to allow enough infrared to warm the very young chicks during the day. Some of the films grown in this work could therefore be applied in the construction of poultry roofs and wall. This helps to reduce the cost of energy consumption through stoves, heaters, electric bulbs and the hazards associated with them while at the same time protecting the chicks from UV radiation.

There are two basic sources of energy loss in the photovoltaic conversion process: (1) Non- absorption of photon with energy $E_{ph} < E_g$, and (2) dissipation of excess energy ($E_{ph} - E_g$) of the absorbed photons. The former loss increases with E_g while the latter decreases with E_g. Clearly, there must be an optimal band gap, E_g where the energy conversion efficiency will be maximum. A lowered band-gap would reduce the photon energy threshold for absorption. From the varied bad-gap values reported in this work, some of the films could be selected for solar cell application. In all such applications, the optimal band gap value is dictated by the trade-off between photocurrent (limited by absorption) and photovoltage (set by the magnitude of the built-in potential)

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