SYNTHESIS AND CHARACTERIZATION OF Co DOPED CdS THIN FILMS GROWN WITHIN A POLYMER MATRIX BY SOLUTION GROWTH TECHNIQUE

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Thin films of CdS were doped with Co to form CdCoS ternary thin films. The films were deposited on glass substrate using the solution growth technique at room temperature from aqueous solution of $CdCl_2$, thiourea and $CoCl_2$. Optical properties such as absorbance and transmittance were determined using Unico UV-2102 PC Spectrophotometer, at normal incidence of light in the wavelength range of 200-1000nm. From absorbance and transmittance spectra, the band gap energy was determined. The band gap energy was found in the 2.10 to 2.60eV range. The result shows that deposition time influences both the optical properties and band-gap energy of the films.

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1. Introduction

World annual energy consumption is predicted to grow from the current 13 terawatt years (TWyr) to as much as 30 TWyrs by 2050[1]. As we struggle to meet this huge demand, the global energy sector will also face two pressing issues: declining fossil reserves and climate change caused by artificially produced green house gas emissions.

With roughly 125 000TW of solar power striking the earth at any time, solar energy may be the only renewable energy source with the capacity to meet a large fraction of future needs [2]. There are many different approaches for capturing and utilizing solar energy [1, 3, 4]. They include photochemical conversion, photo thermal conversion and photoelectrical conversion. The use of photovoltaic (PV) modulus for electricity generation has come under intensive research in recent time, with a view to increasing the efficiency and reduces investment capital. It has been reported that lowering PV costs to a level competitive with conventional power sources will require significant reduction in manufacturing cost, which may be realized in thin films, and/or new architectures that lead to dramatic improvement in efficiency [5].

Cadmium Sulphide (CdS) is one of the most promising II-VI compound materials because of its wide range of application in various optoelectronic, piezo-electronic and semi conducting devices [6, 7]. Thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cells [8]. Because of its optical properties, CdS is used in CdTe devices as an optical window [8, 9]. However, poor conductivity as low as $10^{-8}(\Omega m)^{-1}$ have been reported [10]. In order to overcome this problem, annealing and doping are used [10 - 12].

In this study, we successfully deposited thin films of CdCoS by using the solution growth technique, at room temperature within the self-organized pores of polyvinyl alcohol (PVA). The deposited films were then characterized and studied for possible application in solar cells.

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2. Materials and method

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following manner. First the PVA solution was prepared by adding 450ml of distilled water to 0.9g of solid PVA $(-C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at 90^{o}C for 1hour. The temperature of the resulting solution was then allowed to drop to room temperature. The chemical reaction for the deposition of CdCoS by CBD is given by

$$CdCl_2 + NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+} + 2Cl^-$$
$$[Cd(NH_3)_4]^{2+} \leftrightarrow Cd^{2+} + 4NH_3$$
$$CoCl_2 + NH_3 \leftrightarrow [Co(NH_3)_4]^{2+} + 2Cl^-$$
$$[Co(NH_3)_4]^{2+} \leftrightarrow Co^{2+} + 4NH_3$$
$$SC(NH_2)_2 + OH^- \leftrightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$
$$Cd^{2+} + Co^{2+} + S^{2-} \leftrightarrow CdCoS$$

When the ionic product of the ions exceeds the solubility product, the precipitation of CdCoS can occur either in solution or on the surface of the substrate. In this case the later process occurred. Five samples were deposited at different dip time: AM(7hrs), BM(71/2hrs), CM(8hrs), DM(81/2hrs) and EM(9hrs).

The structure of the films was studied with optical microscope and Philips PW 1500 XRD. The composition of the films were also determined by using energy dispersive x-ray fluorescence (ED XRF). The band gap of the films was determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm.

3. Results and discussion

3.1 X-ray diffraction study

Typical XRD diffractograms of CBD CdCoS are presented in Fig.1a-b. The pattern for the thin film of CdCoS displayed diffraction peaks at 2θ values of approximately 25^o, 27^o, 30^o and 67^o. The existence of identifiable peaks in the diffractograms suggests that the films are not amorphous but crystalline in nature.

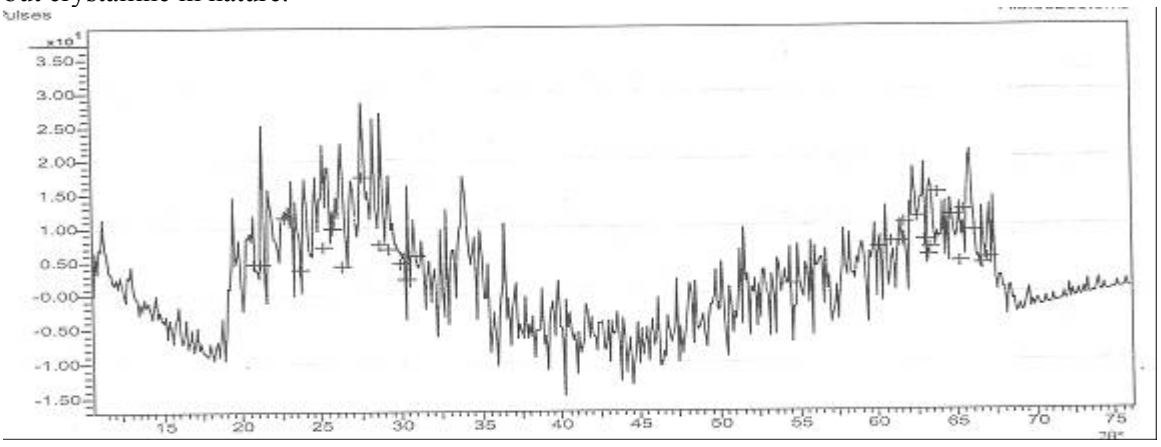

Fig.1a. XRD pattern of CdCoS thin film (deposition time = 7 hrs).

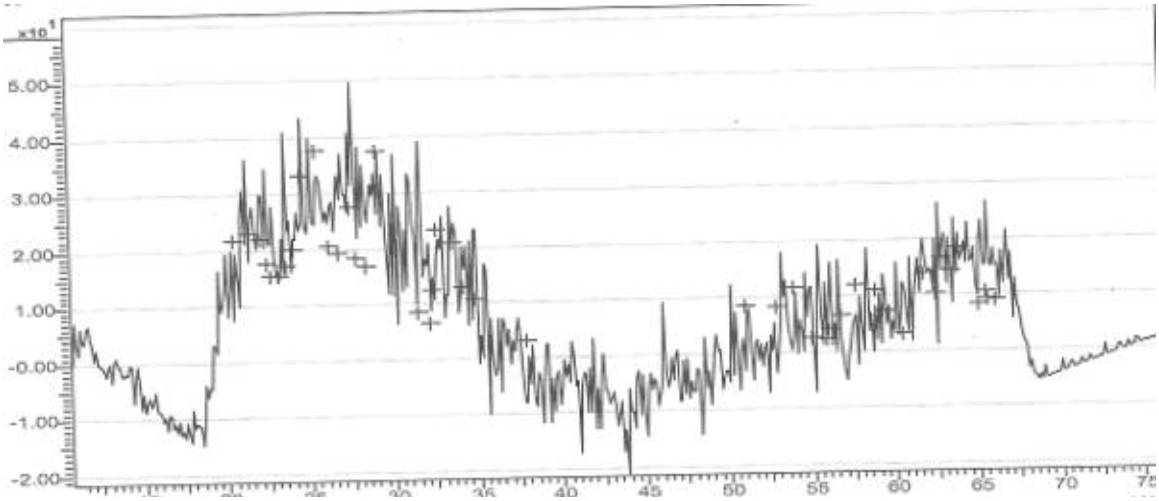

Fig. 1b. XRD pattern of CdCoS thin film (deposition time = 9hrs)

A close examination of the two diffractograms shows an improvement in the crystallinity of the films as deposition time increases. It has been reported that as deposition time increases, the thickness of the film increases as well [13–14]. A comparison between the spectra of the two films in (a) and (b) show that there is more crystallization and more orientation of the crystal growth in the case of the film deposited at 9.0hrs dip time. The lines became more stronger with slight preferential orientation in the H(101) direction.

3.2. Photomicrography study

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M_{35} 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in plates 1-2. A close observation of the optical micrographs of CdCoS thin films show a decrease in grain size as dip time increases. Similar observation has been reported in other work [15-16]. It was suggested that the decrease in grain size as dip time increases is due to the function of the complexing elements during reaction. This accelerates the chemical deposition reaction in such a way that acceleration causes a decrease in the grain size.

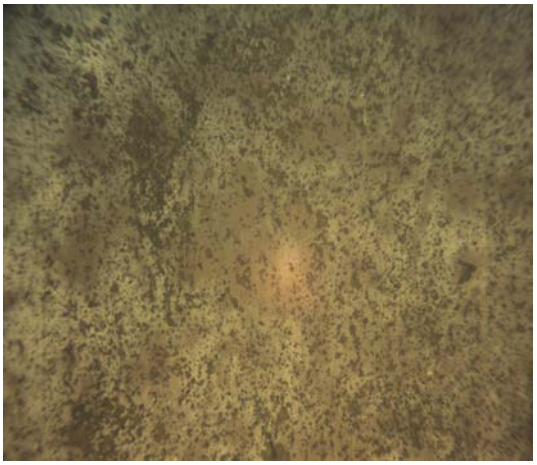

Plate1: Optical micrograph of CdCoS thin film at 7.0hrs dip time

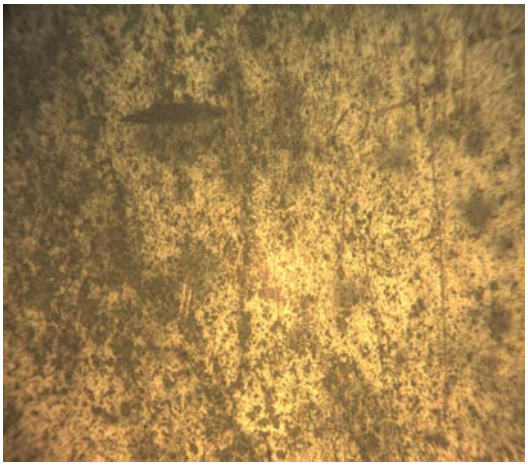

Plate2: Optical micrograph of CdCoS thin film at 9.0hrs dip time

3.3 Optical studies

Fig 2 & 3 are plots of absorbance vs. wavelength and transmittance vs. wavelength for CdCoS grown in this work. From the absorption spectra of the films displayed in fig2, we observe that the absorption edge of the films sift towards shorter wavelength (blue shift) with increasing dip time.

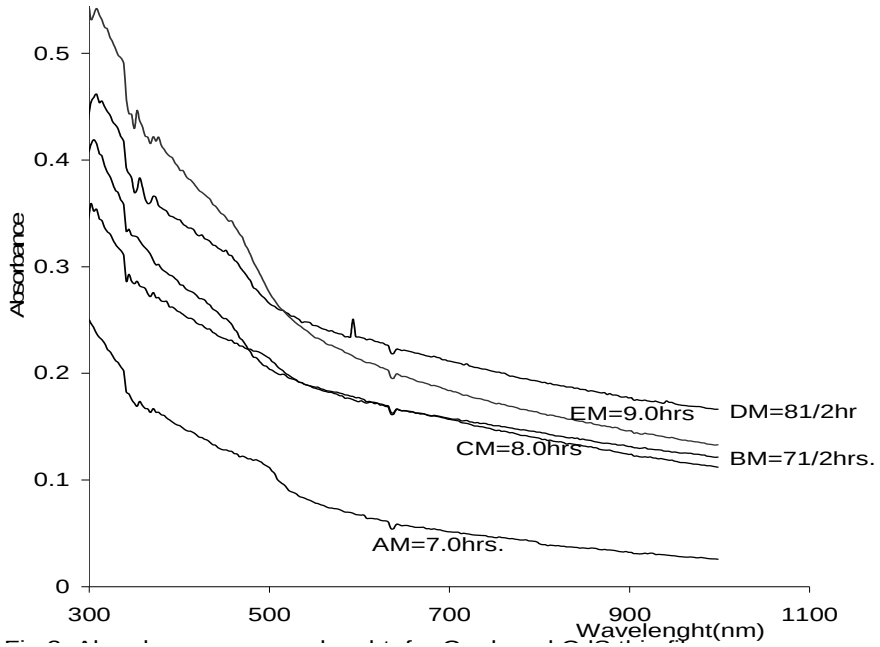

Fig. 2. Absorbance vs. wavelength for Co doped CdS thin films.

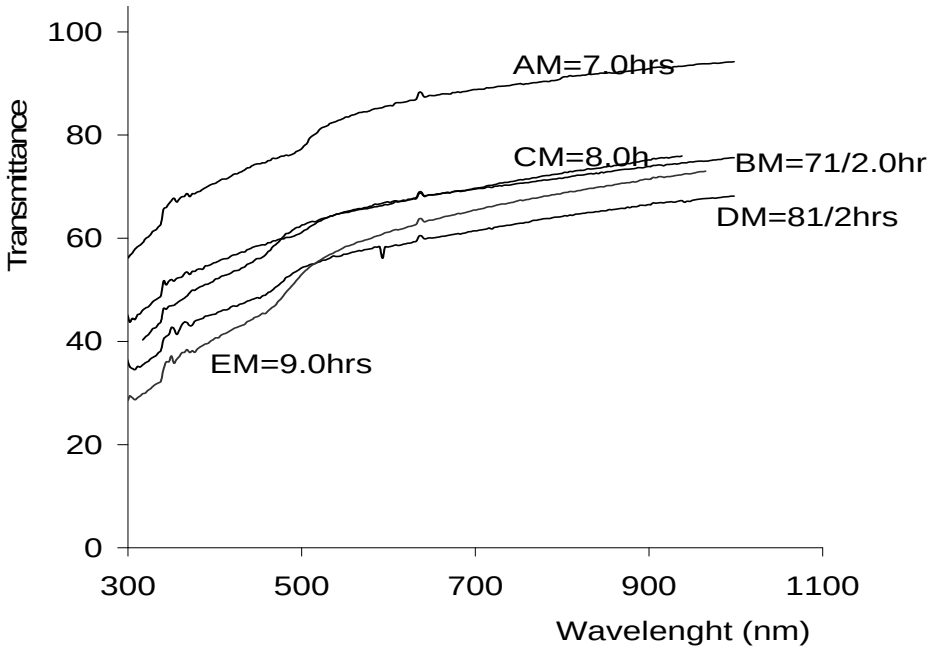

Fig. 3. Transmittance vs. wavelength for Co doped CdS.

The optical studies reveal that the films' absorbance is less than 50% and 20% in the VIS and NIR domain of solar radiation respectively. However the films show strong transmittance (T)

in the NIR spectrum. Table 2 gives the summary of the effect of dip time on the transmittance of the films as the wavelength increases.

A close observation of table 2 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 [15, 16]. Hence, the observed differences in transmission are only due to difference in thickness but also to fundamental differences in film absorption. This observation is similar to the result reported by other authors [15, 16].

Table 2: Variation of optical transmittance (%) with wavelength (nm) for CdCoS thin films

Wavelength(nm)	AM (7hrs)	BM (71/2 hrs)	CM (8hrs)	DM (81/2 hrs)	EM (9hrs)
400	70.67	55.31	52.12	45.32	40.72
500	77.35	62.53	62.53	54.29	53.00
600	85.65	66.95	66.64	58.32	61.29
700	88.83	70.01	69.72	61.45	65.46
800	91.14	72.98	72.59	64.36	68.75

The property of high transmittance in the NIR exhibited by the films therefore makes them good materials for the construction of poultry roofs and walls. This will allow maximum infrared radiation to warm the chicks during the day thereby reducing the high cost on energy required in poultry houses.

Fig. 4 shows typical curves of the energy versus the squared absorption coefficient for thin films of CdCoS. 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 ($h\nu$) can be written as [17]: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$ 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 $h\nu$ plot as shown in figure 4.

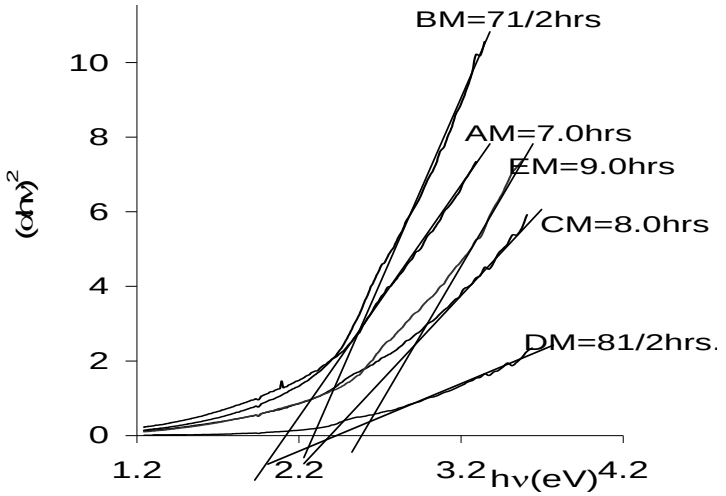

Fig. 4. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for Co doped CdS

The values obtained for the thin films lie in the range of 2.1 – 2.6eV. We can deduce from figure 4 that as dip time increase, the thickness of the films increases as well and this leads to decrease in band edge sharpness and an increase in energy gap. This is in agreement with the report [8] that optical band gap depends on film thickness, deposition and annealing temperature. For CdCoS, the maximum of the values obtained here are higher than the values reported for the CdS thin films (2.37 eV [19], 2.38 – 2.45eV [20], 2.40eV [21] and 1.9 – 2.45eV [22]). However, the values are in close agreement with the values reported by other authors for doped CdS thin films (2.46 – 2.62eV [23], 2.58 – 2.82eV [24]).

4. Conclusions

CdS has been successfully doped with elemental Co to form CdCoS thin films. The optical studies reveal that the films showed very good transmittance in both VIS and the NIR portion of the solar spectrum. This thus suggests that CdCoS thin films are suitable as solar energy collector and could also be employed in the fabrication of solar brooder.

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 application, 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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