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GROWTH AND OPTICAL PROPERTIES OF CHEMICAL BATH DEPOSITED $MgCdS_2$ THIN FILMS

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Abstract
Chemical bath deposited magnesium cadmium sulphide ($MgCdS_2$) thin films on glass slides were studied for its optical properties using spectrophotometers. The optical characterizations show that the band gaps range between 2.30 and 2.60eV which are band gaps close to and higher than the band gaps reported for CdS thin films. The films were found to have average transmittance of greater than 69% in the UV-VIS-NIR regions while exhibiting reflectance of greater than 9% in the same regions. The estimated data using spectrophotometer show maximum values of refractive index n that range between 2.19 and 2.28, the extinction coefficient k range between 1.57 x 10^{-2} and 6.16 x 10^{-2} and that of optical conductivity σ_o between 0.33 x 10^{14} S^{-1} and 0.60 x 10^{14} S^{-1}. Some of the films exhibit poor transmittance in the UV regions; hence, they could be effective as coatings for poultry houses as well as a good material for solar cell fabrication.

Keywords: Chemical bath deposition technique, $MgCdS_2$ thin films, poultry house coatings, solar cells.

INTRODUCTION

Interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in solar cells, light emitting diodes and non-linear optical devices [Ortega-Lopez *et al*. 2003] has been increasing in the recent years. Ternary compounds are found to be promising material for optoelectronic device applications such as green emitting devices and are suggested to be possible material for window layer of solar cells [Woon-Jo and Gye-Choon 2003]. Some of them have been investigated for specific applications to superionic conducting materials [Sasaki *et al*. 2003]. These ternary compounds are increasingly being studied for efficient solar energy conversion through photo-electrochemical solar cells [Padam and Rao 1986, Ver´ onica Estrella *et al.* 2003] and have become potential candidates for such applications [Pawar *et al.* 1986, Jae-Hyeong *et al*. 2003]. Although, the deposition of ternary thin films have been reported using advanced technologies, the low cost and simple chemical bath deposition technique seems to be much better [Padam and Rao 1986].

This paper reports the investigation of optical properties of magnesium cadmium sulphide thin films, which were deposited using chemical bath deposition technique. The optical properties investigated include absorbance (A), transmittance (T) and reflectance (R), which were then used to calculate other parameters such as refractive index (n), extinction coefficient (k), dielectric constant (ε), and optical conductivity (σ_o). The determination of these optical properties and the band gap energy of these films were based upon equations found in the literature [Pankove 1971, Ezema and Okeke 2003].

EXPERIMENTAL DETAILS

The preparation of $MgCdS_2$ thin films on glass slides was carried out using solution growth technique. The glass substrates were previously degreased in HNO_3 for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air. The nitric acid treatment caused the oxidation of halide ions in glass slides (halide glass) used as substrates; thereby introducing functional groups called nucleation and/or epitaxial centers on which the $MgCdS_2$ 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 $MgCdS_2$ contained 5ml of 0.2M $MgSO_4.7H_2O$, 5ml of 0.2M cadmium chloride, 2ml of 14M ammonia, 2ml of 0.01M Ethylenediamine-tetraacetate (EDTA) or triethanolamine (TEA), 10ml of 0.1M thiourea [$(NH_2)_2CS$] and 21ml of distilled water. All these chemicals were added in that order as shown in Table 1 and allowed for 20 hours for the deposition of films. Table 1 also shows various variations of reaction bath and the corresponding pH.

Table 1: The reaction bath for the preparation of $MgCdS_2$ thin films.

Sample No.	$MgSO_4.7H_2O$		$CdCl_2.2½H_2O$		7.4M TEA	14M NH_3	0.01M EDTA	0.1M $(NH_2)_2CS$	pH
	M	Vol. (ml)	M	Vol. (ml)	Vol. (ml)	Vol. (ml)	Vol. (ml)	Vol. (ml)	
mc1	0.01	10	0.1	10	2	1	-	10	11
mc2	0.02	05	0.2	05	2	1	-	10	10
mc4	0.01	10	0.1	10	drops	drops	-	10	12
mc5	0.10	10	0.1	10	-	drops	2	08	09

The mixtures were thoroughly stirred with glass stirring rod and the pH values observed after stirring were in the range between 9 and 12. During deposition cations and anions, which are both present in the deposition solutions, react with each other and become neutral atoms by precipitating either spontaneously or very slowly in the bath. Fast precipitation implies that a thin film cannot form on the substrate immersed in the solution. However, if the reaction is slow, which the additives like NH_3 and EDTA or TEA could achieve, thin solid films of neutral atoms could form on the substrate. The complexing agents slow down the precipitation process and enable the formation of $MgCdS_2$. The step wise reactions involved in the complex ion formation and film deposition processes for $MgCdS_2$ are as follows:

$$Mg\,SO_4.7H_2O + TEA \rightleftharpoons [Mg\,(TEA)]^{2+} + SO_4^{2-}$$

$$[Mg\,(TEA)]^{2+} \rightleftharpoons Mg^{2+} + TEA$$

$$CdCl_2.2\tfrac{1}{2}H_2O + NH_3 \rightleftharpoons [Cd\,(NH_3)_4]^{2+} + 2Cl^-$$

$$[Cd\,(NH_3)_4]^{2+} \rightleftharpoons Cd^{2+} + 4NH_3$$

$$(NH_2)_2CS + OH^- \rightleftharpoons CH_2N_2 + H_2O + HS^-$$

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

$$Mg^{2+} + Cd^{2+} + 2S^{2-} \rightleftharpoons MgCdS_2$$

Sulphide ions are released by the hydrolysis of thiourea but Mg^{2+} and Cd^{2+} ions form Mg-TEA complex and tetra amine cadmium complex ions by combining with TEA and NH_3 respectively in the pH range between 9 and 12. The $[Mg\,(TEA)]^{2+}$ and $[Cd\,(NH_3)_4]^{2+}$ complexes adsorb on the glass and then a heterogeneous nucleation and growth takes place by ionic exchange of reactive S^{2-} ions. This process is referred to as ion-by-ion process and in this way $MgCdS_2$ films were deposited on glass slides as transparent, uniform and adherent thin films.
These deposited films were then characterized using UNICAM SP8-100 double beam UV spectrophotometer and Fourier transform single beam infrared spectrometer. The A-T-R spectra of films were obtained in the UV-VIS-NIR regions using PYE UNICAM SP8-100 double beam spectrophotometer with uncoated glass slide as reference.

RESULTS AND DISCUSSION

Fig. 1 shows infrared transmittance (using a single beam Fourier transform spectrometer) of $MgCdS_2$ thin film + glass system as compared with uncoated glass. It is clear from Fig. 1 that the infrared transmittance of uncoated glass first reduced to 50.64% at 3527cm^{-1} then to 48.62% at 2900cm^{-1} and finally to only about 2% at 1896cm^{-1} to 2000cm^{-1}. By about 2001 cm^{-1}, no radiation at all is transmitted through the glass. Whereas for coated glass infrared transmittance reduced 4% more at 3525cm^{-1} and 4.01% more at 2866cm^{-1} as compared to uncoated glass and finally dropped to only about 0.2% transmittance of uncoated glass at 1896 –2000cm^{-1}. By about 1999cm^{-1}, no radiation at all is transmitted through the film-glass system. These films are capable of allowing solar radiation (0.3 – 3.0μm) to be transmitted into a building but prevent thermal re-radiation out of the building through the glass system. It is observed that the film+glass system suppresses transmission of IR when compared with the plain/uncoated glass.
The spectral absorbance of magnesium cadmium sulphide films prepared at 300K is displayed in Fig. 2, which shows that some films absorb heavily in the UV and partly in the VIS regions but poorly in the remaining VIS and NIR regions.

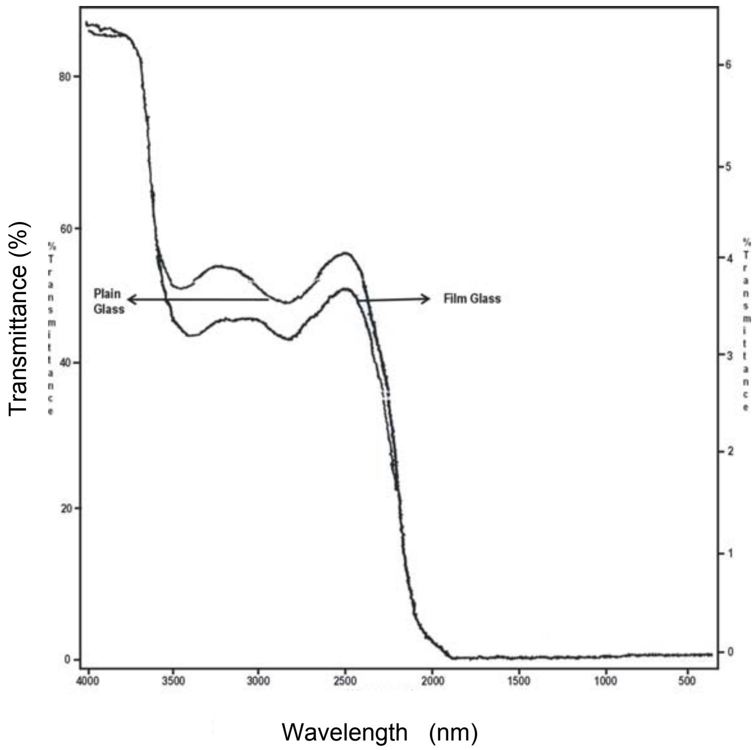

Fig. 1: Spectral Infrared Transmittance of uncoated and $MgCdS_2$ coated glass.

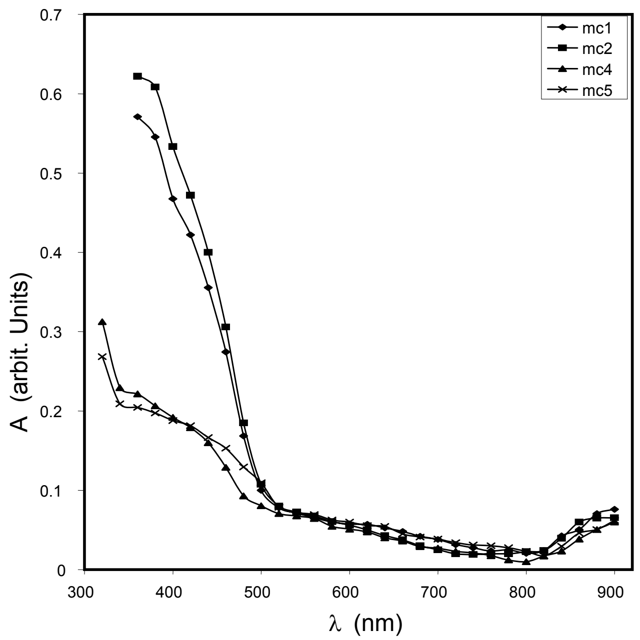

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Fig. 2: Spectral Absorbance (A) of $MgCdS_2$ thin films as a function of wavelength (λ).

The absorbance of thin films was observed to decrease with wavelength through UV-VIS regions but a rise in the NIR regions.
The transmittance and reflectance spectra (Fig. 3), deduced from absorbance spectra, indicate that all the films show 24% to 98% transmittance in the UV-VIS-NIR regions. Furthermore, transmittance increased with wavelength from the UV to the VIS regions but decreased with wavelength in the NIR region. Whereas films show decrease in reflectance with wavelength in the UV-VIS regions but increase with wavelength in the NIR regions (Fig. 3). Samples mc1 and mc2 show weak transmittance (between 24% and 30%) in the UV region and partly in the VIS regions (between 30% and 49%) but strong transmittance in the remaining VIS and NIR regions (between 53% and 98%). Samples mc4 and mc5 show strong transmittance throughout UV-VIS-NIR regions.

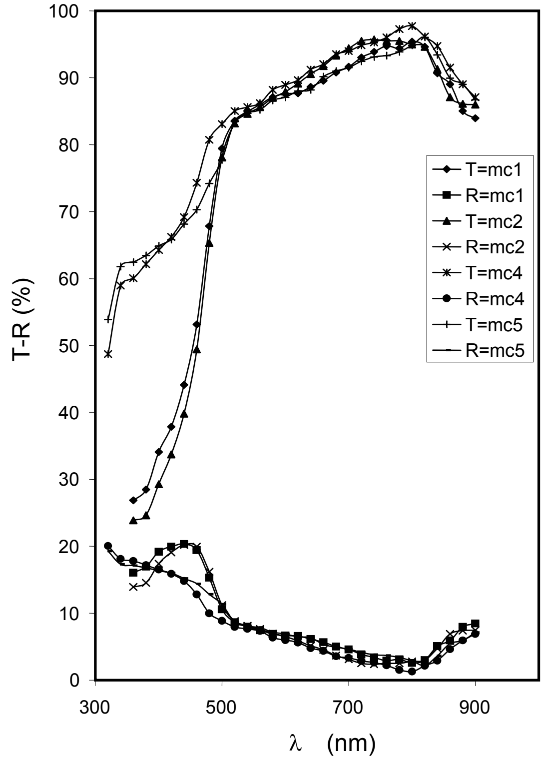

Fig. 3: Spectral Transmittance (T)-Reflectance (R) of $MgCdS_2$ thin films as a function of wavelength (λ).

The properties of weak transmittance in the UV-VIS but moderately high transmittance in the VIS-NIR make mc1 and mc2 good materials for screening off UV portion of electromagnetic spectrum which is dangerous to human health as well as harmful to domestic animals. These films can be used for coating eye glasses for protection from sunburn caused by UV radiations. As they show moderately high VIS-NIR transmittance, so can be used for coating of poultry roofs and walls. This will ensure that young chicks that have not developed protective thick feathers are protected from UV radiation while the heating of

poultry house is maintained by the heating part of the electromagnetic spectrum as well as there is an admittance of VIS light in the house.
It is observed from Fig. 4 that the absorption coefficients (α) of all the samples decrease with decreasing photon energies throughout the UV-VIS regions but increase slightly with decreasing photon energies in the NIR region.

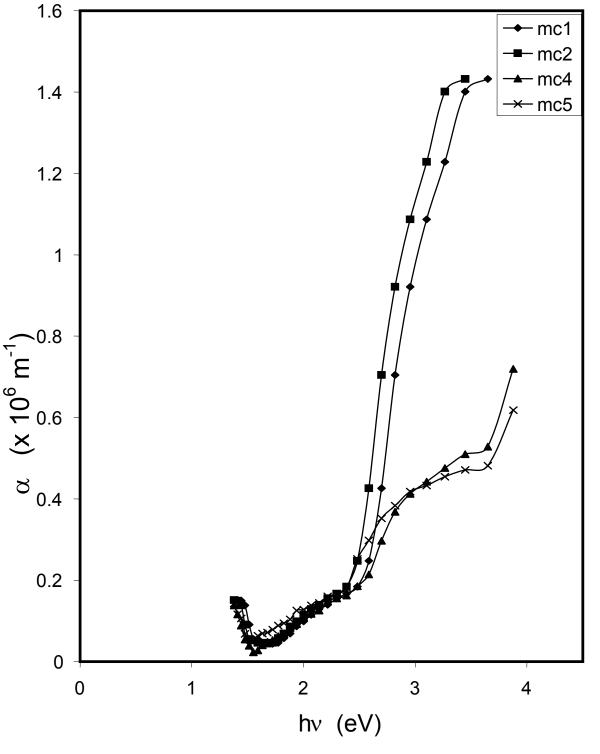

Fig. 4: Plots of Absorption coefficient (α) for $MgCdS_2$ thin films versus photon energy ($h\nu$).

The variation of refractive index n with photon energy $h\nu$ for $MgCdS_2$ thin films is shown in Fig. 5. The peaks/maxima of refractive indices for samples mc1 and mc2 occurred within the range 2.01 and 2.27 but at different photon energies. For instance for mc1, maxima occurred at 4.43eV with n = 2.25, at 3.65eV with n = 2.02 and at 2.82eV with n = 2.27 while for mc2 maxima observed at 4.43eV with n = 2.27, at 3.65eV with n = 2.01 and at 2.82eV with n = 2.27. Sample mc1 showed three minima at photon energies of 3.88eV, 3.45eV and 1.55eV with n = 0.79, 1.91 and 1.11, respectively. Whereas sample mc2 showed three minima at photon energies of 3.88eV, 3.45eV and 1.55eV with n = 0.57, 1.75 and 1.12, respectively. The peak values of n for mc4 (n=2.28) and mc5 (n=2.19) occurred at the same photon energy i.e. 4.13eV. It is further noted that mc1 and mc2 show minima at 3.88eV, while mc4 and mc5 show peak values (maxima) at 4.13eV, which are nearly opposite to the former.
The variation of the extinction coefficient k with photon energy $h\nu$ for $MgCdS_2$ thin films is shown in Fig. 6. It is obvious from Fig. 6 that the spectral curves for mc1 and mc2 closely resemble that of mc4 and mc5 but mc4 and mc5 show

higher values of k as compared to those of mc1 and mc2 in the range between 6.21 eV and 2.59 eV. The k-maxima lie in the range between 61.6 x 10^{-3} and 15.7 x 10^{-3} while k-minima range between 14.7 x 10^{-3} and 32.7 x 10^{-3}.

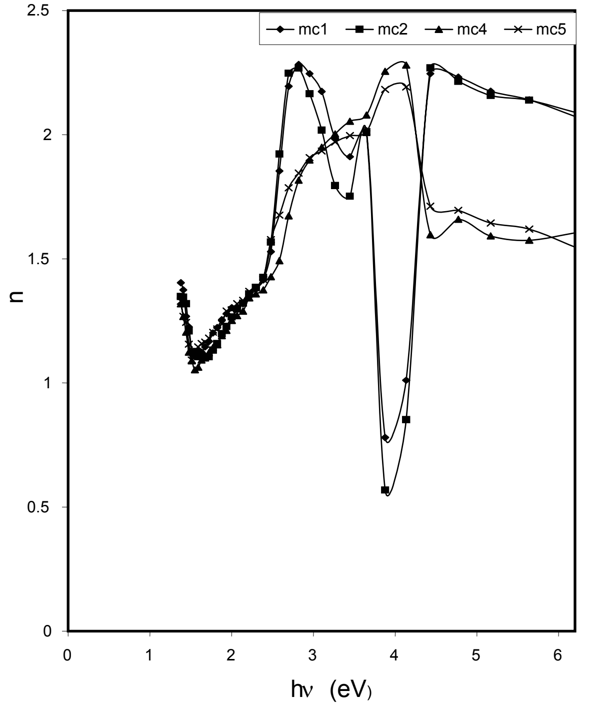

Fig. 5: Plots of Refractive Index (n) for $MgCdS_2$ thin films versus photon energy (hν).

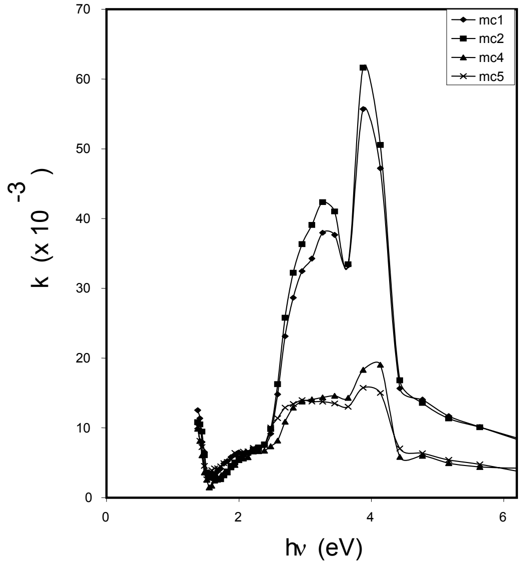

Fig. 6: Plots of Extinction coefficient (k) for $MgCdS_2$ thin films versus photon energy (hν).

A plot of optical conductivity σ_o against photon energy hν is shown in Fig. 7. All the samples show a peak at 4.13 eV with σ_o = 0.48 x 10^{14} S^{-1}, 0.43 x 10^{14} S^{-1}, 0.43 x 10^{14} S^{-1} and 0.33 x 10^{14} S^{-1} for mc1, mc2, mc4 and mc5, respectively. Furthermore, the maximum values of σ_o range between 0.60 x 10^{14} S^{-1} and 0.33 x 10^{14} S^{-1} for all the samples while minimum values range between 0.006 x 10^{14} S^{-1} and 0.012 x 10^{14} S^{-1}.

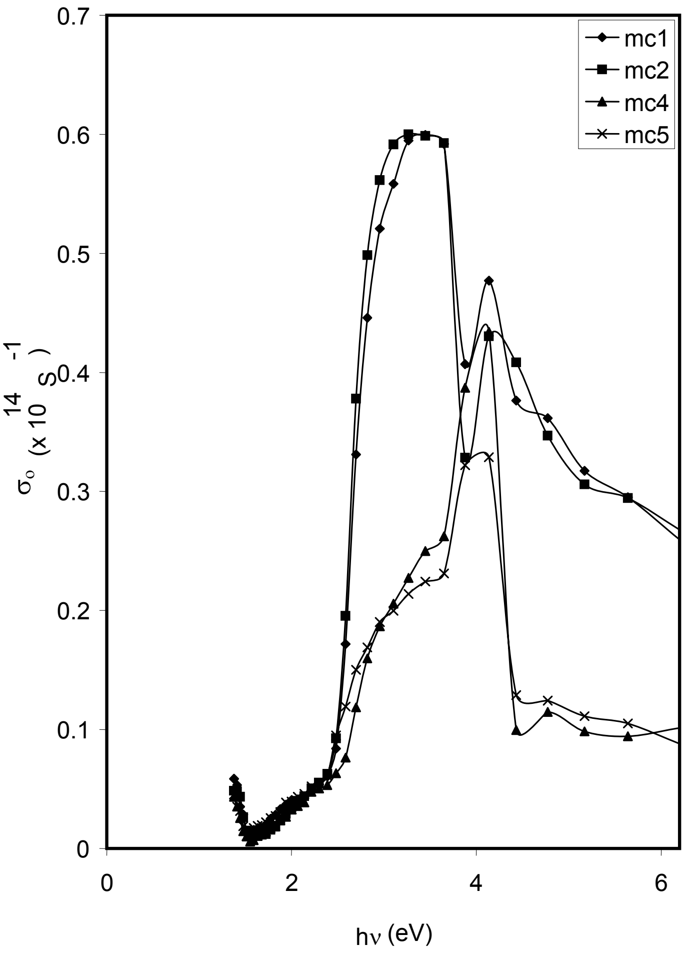

Fig. 7: Plots of Optical Conductivity (σ_o) for $MgCdS_2$ thin films versus photon energy (hν).

The plots of ε_r (real part of the dielectric constant) against photon energy hν are displayed in Fig. 8. It is seen from these plots that the maximum values of ε_r for all the samples range between 4.80 and 5.21 while the minimum values range between 0.32 and 1.19. The plots of ε_i (imaginary part of the dielectric constant) against photon energy hν are depicted in Fig. 9, which show that ε_i has minimum values in the range between 3.08 x 10^{-3} and 6.65 x 10^{-3} whereas maximum values in the range between 69 x 10^{-3} and 158 x 10^{-3}.

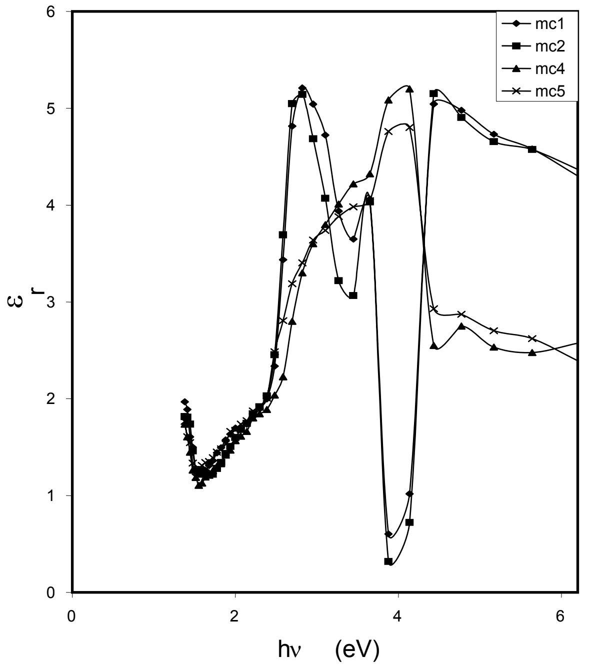

Fig. 8: Plots of Dielectric Constant (ε_r) for $MgCdS_2$ thin films versus photon energy (hν).

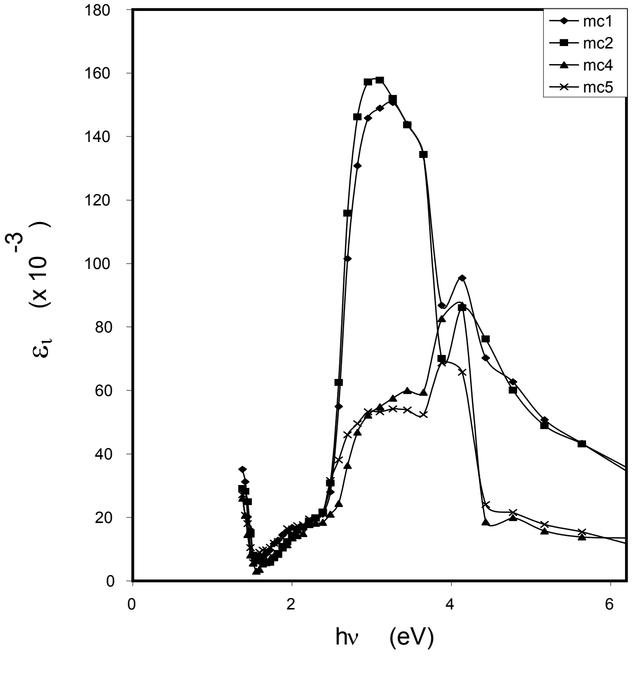

Fig. 9: Plots of Dielectric Constant (ε_i) for $MgCdS_2$ thin films versus photon energy (hν).

In order to determine the band gap energy of $MgCdS_2$ thin films, plots of $(\alpha h\nu)^2$ are drawn against photon energy $h\nu$ as shown in Figs. 10 and 11. These plots reveal band gaps of 2.30eV and 2.62eV. The band gaps for mc1 and mc2 (2.62eV) were found to be higher than the band gaps of 2.40eV [Pawar *et al*. 1986], 2.37eV [Choi *et al*. 1998], 2.38-2.45eV [Metin and Esen 2003] and 2.30-2.50 eV [Rusu *et al*. 2004] reported for CdS thin films. Whereas the band gaps for mc4 (2.30eV) and mc5 (2.50eV) is in good agreement with the reported range (2.30-2.50eV) for CdS thin films. The close match in the band gaps of $MgCdS_2$ thin films (2.30eV and 2.50eV) and that of the CdS show that deposited films (mc4 and mc5) are rich in cadmium. These band gaps of $MgCdS_2$ films make them good material for fabrication of solar cell.

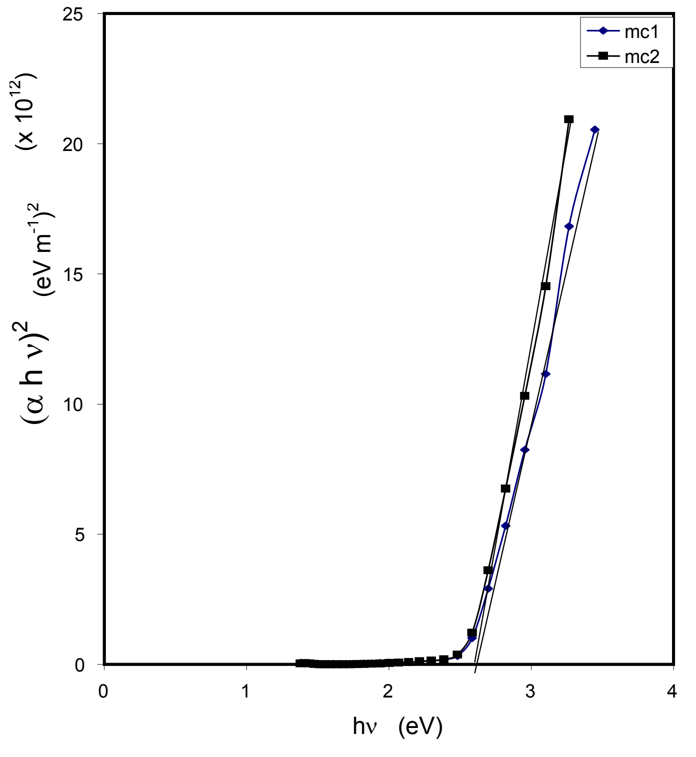

Fig. 10: Plots of $(\alpha h\nu)^2$ for $MgCdS_2$ thin films versus photon energy ($h\nu$).

CONCLUSIONS

$MgCdS_2$ thin films with energy band gaps between 2.30eV and 2.62eV (band gaps are close to and higher than that of CdS) have been successfully deposited using chemical bath deposition technique. The FTIR spectroscopy showed the percentage transmittance ranged between 1.8% and 47% in the far infrared region. The estimated spectrophotometric data shows maximum values of n ranging between 2.19 and 2.28, k between 1.57×10^{-2} and 6.16×10^{-2} and σ_o between $0.33 \times 10^{14} S^{-1}$ and $0.60 \times 10^{14} S^{-1}$. The films were found to have average transmittance > 69% and average reflectance > 9% in the UV-VIS-NIR regions.

Some of the films exhibit poor transmittance in the UV regions; consequently, they could be effective as coatings for poultry houses as well as good materials for solar cell fabrication.

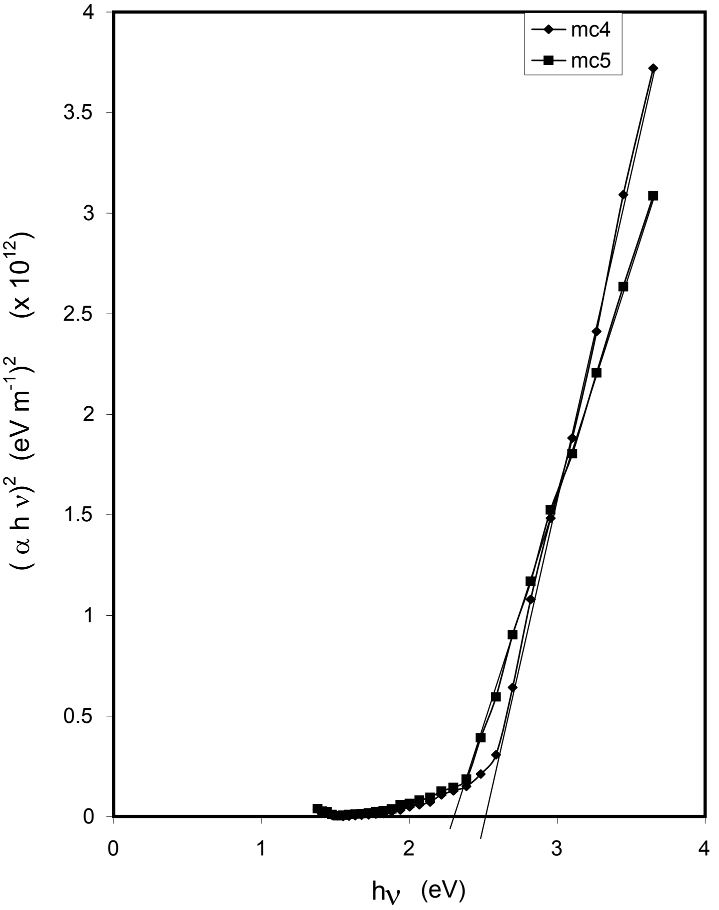

Fig. 11: Plots of $(\alpha h\nu)^2$ for $MgCdS_2$ thin films versus photon energy (hν).

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