Printed ISSN 1330–0008
Online ISSN 1333–9125
CD ISSN 1333–8390
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PREPARATION AND OPTICAL PROPERTIES OF CHEMICAL BATH DEPOSITED $MnCdS_2$ THIN FILMS

F. I. EZEMA[a,b] and R. U. OSUJI[a]

[a]*Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria*
E-mail address: fiezema@yahoo.com

[b]*School of General Studies, Natural Science Unit, University of Nigeria, Nsukka, Nigeria*
E-mail address: uzosuji@yahoo.com

Received 30 December 2005; Accepted 5 September 2007
Online 8 February 2008

Thin films of $MnCdS_2$ were deposited on glass slide from aqueous solutions of $MnCl_2{\cdot}4H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ and thiourea. Ammonium solutions and EDTA (or TEA) were employed as complexing agents. The optical characterization yielded band gap values in the range between 2.58 and 2.82 eV. Some of the films were found to have an average transmittance of greater than 60% in the UV-VIS regions while exhibiting high reflectance of greater than 12% in the same regions. Some of the films exhibit poor transmittance in the UV regions while exhibiting high transmittance of greater than 75% in the VIS-NIR regions. Hence, while some of the films could be effective as thermal coatings for cold climates, some could be effective as coatings against intensive sunlight as well good material for fabrication of solar cell.

PACS numbers: 78.66.-w, 68.55.-a UDC 539.23, 538.975

Keywords: chemical bath deposition technique, $MnCdS_2$, sunlight shielding, thermal coating, solar cells

1. Introduction

Large-area thin film semiconductors of metal-metal sulphides and selenides can be deposited on metals, glass and polymer substrates that are immersed in solutions containing metal complex ions and a source of sulphide or selenide ion. The properties of ternary thin films prepared by various techniques such as chemical bath deposition, spray pyrolysis, molecular beam epitaxy, electrodeposition, and chemical vapour deposition have been reported [1 - 3]. The metal-metal chalcogenides are increasingly studied in the search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells. These materials have been known to be potential candidates for photo-electrochemical solar cells [4-5].

The chemical bath deposition (CBD) technique is a relatively simple, inexpensive method to prepare a homogenous film with controlled composition [6]. The optical properties and stoichiometry of the film deposited by this technique differ depending on the deposition conditions such as stirring, deposition time, temperature and pH of the solution. CBD is low cost and relatively simple technique for achieving good quality ternary thin films which can be used for coating surfaces of complex morphology and geometry [7].

This paper reports on an investigation of the optical properties of chemical bath deposited $MnCdS_2$ thin films. The optical properties investigated include the absorbance (A), transmittance (T) and reflectance (R), which were used to calculate other properties such as refractive index (n), extinction coefficient (k), dielectric constant (ϵ), and optical conductivity (σ). These optical properties and the band gap of the films were deduced from equations given in literature [8-15], while the film thicknesses were obtained by optical methods [16].

2. Experimental details

The preparation of $MnCdS_2$ thin films on glass slide was carried out using chemical bath deposition technique. The glass substrates were 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 the halide ions in glass slides used as substrates, thereby introducing functional groups called nucleation and/or epitaxial centers on which the $MnCdS_2$ thin film is grown.The degreased cleaned surface has the advantage of providing nucleation centers for the growth of the films, hence yielding highly adhesive and uniformly deposited films.

The reaction bath for the deposition of $MnCdS_2$ contained $MnCl_2{\cdot}4H_2O$, cadmium chloride, ethylenediaminetetraacetate (EDTA), triethanolamine (TEA), ammonia, thiourea ($(NH_2)_2CS$) and distilled water which were added in that order. The deposition time was 20 hours. Table 1 shows the parameter variations of the reaction bath and the corresponding pH values.

After the mixtures were thoroughly stirred with a glass rod the pH came to between 9 and 12. During the deposition, cations and anions, which are both present in the deposition solution, react with each other and become neutral atoms, which either precipitate 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 TEA, NH_3 and EDTA achieve, then thin solid films of neutral atoms can form on the substrate. The used complexing agents slow down the precipitation action and enable the formation of thin $MnCdS_2$ films.

TABLE 1. Preparation of $MnCdS_2$.

Samp. no.	$MnCl_2{\cdot}4H_2O$		$CdCl_2 \cdot 2\frac{1}{2}H_2O$		7.4 M TEA	14 M NH_3	0.01 M EDTA	1 M $(NH_2)_2CS$	pH
	M	Vol. (ml)	M	Vol. (ml)	Vol. (ml)	Vol. (ml)	Vol. (ml)	Vol. (ml)	
Mnc1	0.1	10	0.1	10	drops	1	–	10	9
Mnc2	0.2	5	0.2	5	2	1	–	10	12
Mnc3	0.6	5	0.6	5	2	1	–	10	10
Mnc4	0.1	10	0.1	10	–	drops	2	10	11

The step-wise reactions involved in the complex ion formation and film deposition processes are given below.

$$
\begin{aligned}
MnCl_2{\cdot}4H_2O + TEA &\rightleftharpoons [Mn(TEA)]^{2+} + 2Cl^- \\
[Mn(TEA)]^{2+} &\rightleftharpoons Mn^{2+} + TEA \\
CdCl_2 \cdot 2\tfrac{1}{2}H_2O + NH_3 &\rightleftharpoons [Cd(NH_3)_4]^{2+} + 2Cl^- \\
[Cd(NH_3)_4]^{2+} &\rightleftharpoons Cd^{2+} + 4NH_3 \\
(NH_2)_2CS + OH^- &\rightleftharpoons CH_2N_2 + H_2O + HS^- \\
HS^- + OH^- &\rightleftharpoons H_2O + S^{2-} \\
Mn^{2+} + Cd^{2+} + 2S^{2-} &\rightleftharpoons MnCdS_2
\end{aligned}
$$

Sulphide ions are released by the hydrolysis of thiourea, but Mn^{2+} and Cd^{2+} ions form Mn-triethanolamine or Mn-ethylenediamine tetraacetic complex and tetraamine cadmium complex ions by combining with TEA or EDTA and NH_3, respectively, in the pH range of 9 to 12. The $[Mn(TEA)]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ complexes adsorb on the glass and then a heterogeneous nucleation and growth process takes place by ionic exchange reaction of S^{2-} ions. This process is referred to as ion-by-ion process. The bluish yellow $MnCdS_2$ was deposited on glass slides in the form of transparent, uniform and adherent thin films.

After the films were deposited, they were characterized using UNICAM SP8-100 double-beam UV spectrophotometer and Fourier transform single-beam infrared spectrometer.

The A-T-R spectra of the films were obtained in the UV-VIS-NIR regions by means of PYE UNICAM SP8-100 double-beam spectrophotometer with uncoated glass slide as reference.

3. Results and discussion

Figure 1 show the combined effect of film–glass system on transmittance of infrared radiation for $MnCdS_2$ in comparison with uncoated glass. This was carried out using a single-beam Fourier transform spectrometer. The uncoated glass reduced transmittance to 50.64% at 3527 cm^{-1}, to 48.62% at 2900 cm^{-1} and to only about 2% transmittance at 2000 cm^{-1}. At about 1896 cm^{-1}, no radiation could be detected through the glass. Coated glass reduced transmittance to 2.28% at 3491 cm^{-1}, to 2.21% at 2879 cm^{-1} and to only about 0.2% transmittance at 2000 cm^{-1}. At about 1999 cm^{-1}, no radiation could be detected through the film–glass system. The transmittance of the films in the mid infrared regions ranges between 46.41 and 48.36%. These films allow transmission of solar radiation (0.3 - 3.0 μm) into a building, but prevent thermal re-radiation out of the building through the film.

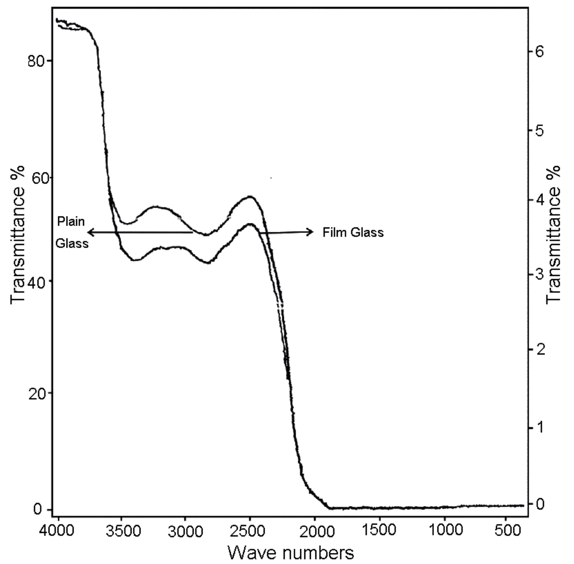
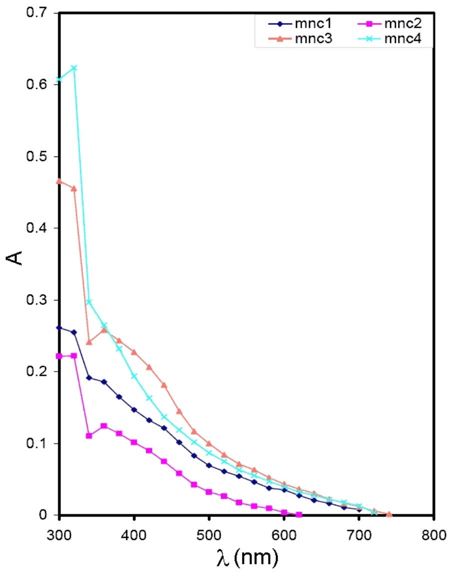


Fig. 1. Spectral infrared transmittance of plain glass and combined film-glass system of a $MgCdS_2$ *sample.*

The spectral absorbance of $MnCdS_2$ films prepared at 300 K is displayed in Fig. 2. The film samples mnc1 and mnc2 absorb poorly throughout the UV-VIS-NIR regions while mnc3 and mnc4 absorb strongly in the UV regions, moderately in the VIS regions but poorly in the NIR regions of the electromagnetic spectrum.

The transmittance and reflectance spectra (Fig. 3) deduced from the absorbance spectra show that mnc1 and mnc2 have high transmittance in the UV–VIS regions (between 55 and 100%), while mnc3 and mnc4 show moderate transmittance (between 24 and 64%) in the UV regions but high transmittance (between 64 and 100%) in the VIS-NIR. The films show that reflectance decreases from a maximum of between 20 and 18% in the UV-VIS regions to a minimum of between 2 and 0.07% throughout the UV-VIS-NIR regions of the electromagnetic spectrum. The pH value of the deposition bath affects the transmittance/absorbance of the film more than the dip time. This may be due to the fact the pH of the deposition bath depends on the concentration of the starting solutions.

The low transmittance in the UV but high transmittance in the VIS-NIR make mnc3 and mnc4 good materials for screening off the UV portion of the electro-



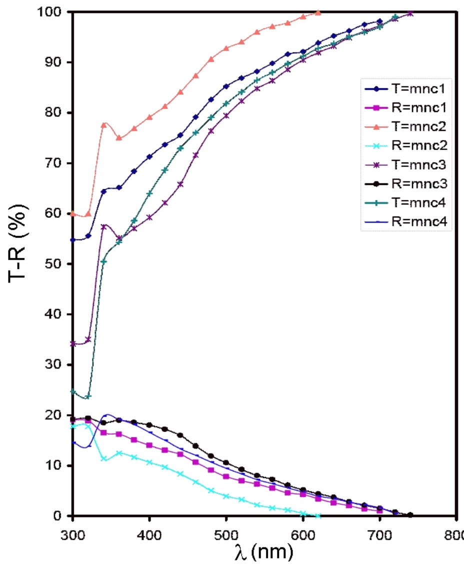


Fig. 2 (left). Spectral absorbance of $MgCdS_2$ *films.*

Fig. 3. Spectral transmittance-reflectance of $MgCdS_2$ *films.*

magnetic spectrum which is dangerous to human health and harmful to domestic animals. The film can be used for coating eye glasses for protection from sunburns caused by UV radiations. They can be used for coating of poultry roofs and walls as young chicks are sensitive the UV radiation, while the visible light and heating is maintained by the VIS-NIR portion of the electromagnetic spectrum. The property of high transmittance [10] throughout UV-VIS-NIR regions exhibited by mnc1 and mnc2 make them a suitable material for thermal coatings in cold climates.

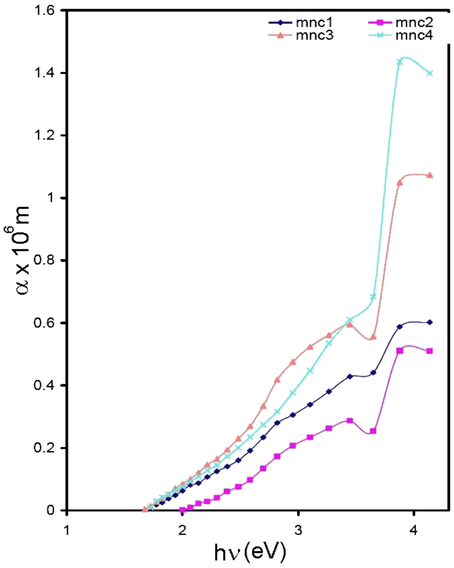
Table 2 shows optical properties and thickness of $MnCdS_2$ thin films prepared under several conditions at 300 K. The maximum absorption coefficient occurred at pH 11, what implies that as the pH increases up to 11, the refractive index, ex-

TABLE 2. Optical properties and thickness of $MnCdS_2$ *thin films prepared under different conditions at 300* K.

Samp. no.	pH	Maximum $\alpha \times 10^6$ (m^{-1})	Maximum refractive index (n)	Maximum $k \times 10^{-2}$	Maximum $\sigma_0 \times 10^{14}$ (s^{-1})	t (μm)
Mnc1	9	0.60	2.55	1.50	0.37	0.090
Mnc2	12	0.51	2.46	1.30	0.30	0.065
Mnc3	10	1.07	2.58	2.67	0.66	0.138
Mnc4	11	1.44	2.61	3.65	0.75	0.154

tinction coefficient and optical conductivity, as well as the thickness, also increased. It is observed from Fig. 4 that the absorption coefficient of all samples increases at decreasing photon energies throughout the UV-VIS regions.

Figure 5 shows that the refractive index of the films increases with increasing photon energy in the UV-VIS region. The maximum refractive index of the films is in the range of 2.46 and 2.61 but at different photon energies. For the mnc1 mnc2 mnc3 mnc4 films, it occurs at about 4.14 eV (300nm), 3.88 eV (320 nm), 3.88 eV (320 nm) and 3.65 eV (360 nm), respectively. It is also observed that the films with a larger refractive index show smaller transmission.



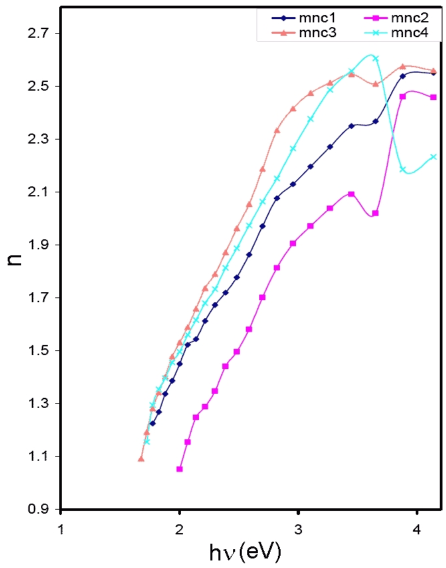


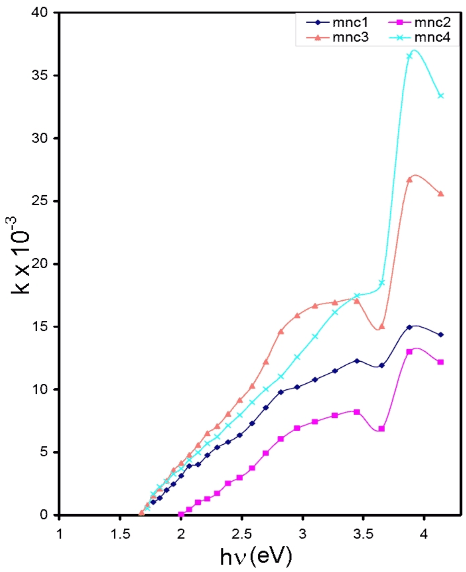
Fig. 4 (left). Plots of α against $h\nu$ for $MgCdS_2$ *films.*

Fig. 5. Plots of n against $h\nu$ for $MgCdS_2$ *films.*

The variation of the extinction coefficient with photon energy for $MnCdS_2$ is shown in Fig. 6. It is observed that all samples had their minimum extinction coefficient at the end of the VIS regions. For the mnc1 mnc2 mnc3 mnc4 films, the values are 1.03×10^{-3} at 1.77 eV (700 nm), 0.06×10^{-3} at 2.00 eV (620 nm), 0.20×10^{-3} at 1.68 eV (720 nm) and 0.53×10^{-3} at 1.72 eV (720 nm), respectively. It is observed that the pH value affects the value of the extinction coefficient. It appears that the optimum pH for the deposition is 11.

The variation of the optical conductivity of $MnCdS_2$ thin films with photon energy is shown in Fig. 7. It is observed that the optical conductivity decreases with decreasing photon energy in the UV-VIS regions.

Table 3 shows the solid state properties and thickness of $MnCdS_2$ thin films prepared under different conditions at 300 K. The results in the table show that there is no correlation between thickness and the band gap. However, as the thick-



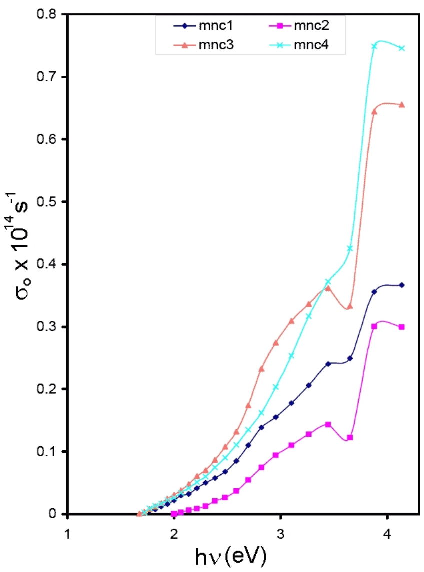


Fig. 6 (left). Plots of k against $h\nu$ for $MgCdS_2$ *films.*

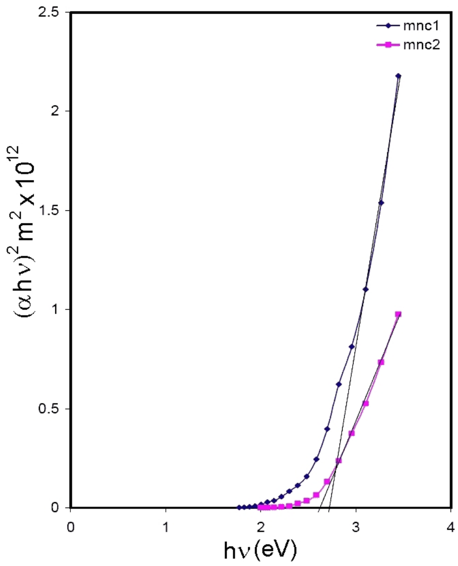
Fig. 7. Plots of σ_0 against $h\nu$ for $MgCdS_2$ *films.*

TABLE 3. Dielectric properties, thickness and energy gap of $MnCdS_2$ *thin films prepared under different conditions at 300* K.

Sample no.	pH	Maximum ϵ_r	Maximum $\epsilon_i \times 10^{-1}$	t (μm)	E_g (eV)
Mnc1	9	6.51	0.76	0.090	2.70
Mnc2	12	6.06	0.64	0.065	2.60
Mnc3	10	6.63	1.38	0.138	2.58
Mnc4	11	6.79	1.60	0.154	2.82

ness increased, the dielectric constants also increased but optimum thickness was observed at pH 11 which corresponds to the maximum band gap.

Figures 8 and 9 show the variation of $(\alpha h\nu)^2$ with photon energy. From the curves, the band gaps of the samples were deduced and are given in Table 3. The band gaps have been found to be higher than the band gaps reported for the CdS thin films (2.37 eV [6], 2.38 - 2.45 eV [7] and 2.40 eV [4]) but lower than the band gaps reported for the MnS thin films (3.88 eV [13], 3.16 - 3.23 eV [14] and 3.23 eV [15]). Since the band gaps of the $MnCdS_2$ are intermediate between those of the CdS and MnS thin films, it makes them a good material for the fabrication of solar cells.



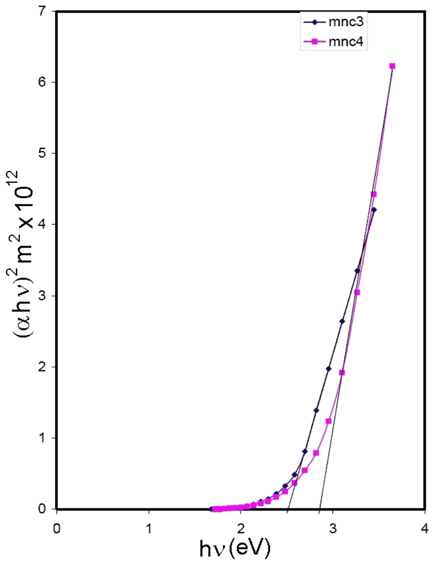
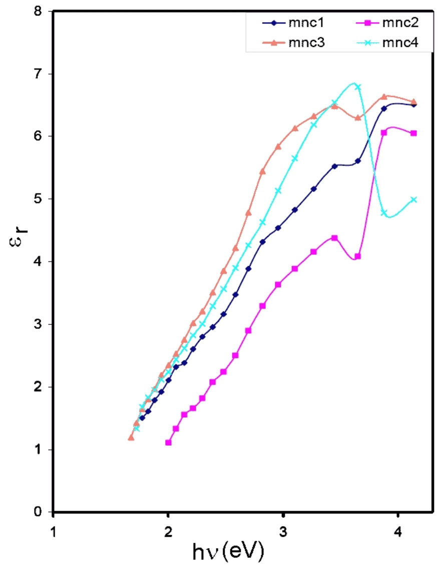


Fig. 8. Plots of $(\alpha h\nu)^2$ *against* $h\nu$ *for* $\mathrm{MgCdS_2}$ *films.*

Fig. 9. Plots of $(\alpha h\nu)^2$ *against* $h\nu$ *for* $\mathrm{MgCdS_2}$ *films.*



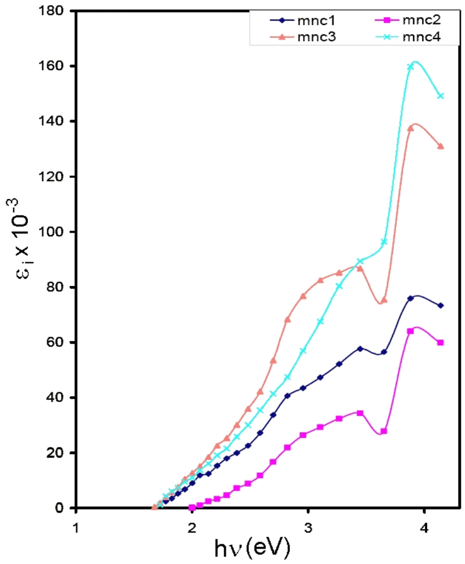


Fig. 10. Plots of ϵ_r *against* $h\nu$ *for* $\mathrm{MgCdS_2}$ *films.*

Fig. 11. Plots of ϵ_i *against* $h\nu$ *for* $\mathrm{MgCdS_2}$ *films.*

The variation of the real dielectric constant with photon energy is shown in Fig. 10. The values of ϵ_r increase with increasing photon energy and the maximum is observed near the VIS-UV region of the electromagnetic spectrum. The variation of the imaginary dielectric constant with photon energy (Fig. 11) follows almost the same pattern as the real dielectric constant.

4. Conclusion

$MnCdS_2$ thin films of thickness in the range between 0.065 and 0.154 μm, with energy band gaps between 2.58 eV and 2.82 eV, have been successfully deposited using chemical bath deposition technique. These band gaps are higher than those in CdS thin films but lower than those in MnS thin films.

The FTIR spectroscopy showed that the transmittance ranged between 46 and 48% in the mid infrared regions. Some of the films were found to have high transmittance of greater than 60% in the UV-VIS regions while exhibiting high reflectance of greater than 12% in the same regions. These films could be effective as thermal coatings for cold climates.

Other films exhibit a poor transmittance in the UV regions while exhibiting high transmittance in the VIS and IR regions of electromagnetic spectrum. These films could be effective for shielding off UV radiation in buildings as well a good material for fabrication of solar cells.

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IZRADA I OPTIČKA SVOJSTVA TANKIH SLOJEVA $MnCdS_2$ TALOŽENIH U KEMIJSKOJ KUPKI

Proizveli smo tanke slojeve $MnCdS_2$ na staklenim pločicama taloženjem iz vodenih otopina $MnCl_2 \cdot 4H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ i tiouree. Primijenili smo otopine amonijaka i EDTA (ili TEA) za kompleksiranje. Optička mjerenja dala su za procijepe vrpci vrijednosti između 2.58 i 2.82 eV. Za neke smo slojeve našli prosječnu propusnost veću od 60% u UV-VIS području, dok im je u tom području odraznost veća od 12%. Drugi slojevi pokazuju malu propusnost u UV području, a veliku propusnost u VIS-NIR području. Stoga se neki slojevi mogu rabiti kao toplinska izolacija u hladnim područjima, a drugi za zaštitu of UV zračenja i u proizvodnji solarnih ćelija.