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# Preparation and Optical Characterization of Chemical Bath Deposited $CdCoS_2$ Thin Films

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**Abstract:** Thin film of $CdCoS_2$ was deposited on glass slide from aqueous solutions of $CoCl_2.6H_2O$, $CdCl_2.2½H_2O$ and thiourea in which ammonium solution and TEA were employed as complexing agents. The film was studied for its optical properties using spectrophotometers. The optical characterization show that the band gap range between 2.50 and 2.70 eV which is between the band gap of CoS and CdS but very close to that of CdS which shows that the film is rich in cadmium. The film was found to have an average transmittance of greater than 55% in the VIS-NIR regions and exhibit average reflectance of greater than 11% in the same regions. Other optical parameters such as refractive index, extinction coefficient, real and imaginary dielectric constants and optical conductivities were also estimated. The film exhibits poor transmittance in the UV regions, hence, they could be effective as coatings for poultry houses and as well good materials for solar cell fabrication.

**Key words:** Chemical bath deposition technique, $CdCoS_2$, poultry house coating, solar cells

## INTRODUCTION

The Chemical Bath Deposition (CBD) method has become very popular in recent decades, especially for thin-film deposition, due to its low cost since no expensive and sophisticated vacuum equipments are required, ease of handling and ease of application to many compounds such as sulfides and selenides which include ZnS, CdS, PbS, CdSe, PbSe, $CuS_2$ $Bi_2S_3$ and CoS (Pentia *et al*., 2004; Eze and Okeke, 1997).

The CBD method, being less expensive than other thin-film deposition methods, allows for the manufacture of relatively low cost devices, especially light detectors and light energy conversion cells. Thin alloy film in the non-isoelectronic system has been prepared by reacting thiourea with a mixture of different complexed ions in chemical baths. For two non-interfering, independent complexing agents used for complexing the two cations, the ions dissociates in an aqueous solution to give metal ions according the reactions (Chopra and Das, 1983).

$$M(A)^{2+}_n \rightleftharpoons M^{2+} + nA \quad (1)$$

and

$$M(B)^{2+}_n \rightleftharpoons M^{2+} + nB \quad (2)$$

When one complexing agent is used, only one equation above correctly applies however in this report two non-interfering complexing agents were used.

Since thiourea has a higher dissociation constant, the fraction of $S^{2-}$ ions in the solution is expected to be more than the fraction of the remaining thiourea in the solution. As is the case in an atom-by-atom deposition process, the solubility conditions of multi-components in an ion-by-ion condensation process are relaxed (Chopra and Das, 1983).

Some attempts were made to obtain ternary compounds materials using the CBD method (Pentia *et al*., 2004; Ezema, 2004; Chopra and Das, 1983; Padam and Rao, 1986; Ver ´ onica Estrella *et al*., 2003). The search for new semiconductor materials for efficient solar energy conversion through photo-electrochemical solar cells, has led to the increasing deposition of metal-metal chalcogenides (Chopra and Das, 1983; Padam and Rao, 1986; Ver ´ onica Estrella *et al*., 2003). These materials have been known to be potential candidates for photo-electrochemical solar cells (Pawar *et al*., 1986; Lee *et al*., 2003).

This study reports on the preparation and optical properties of $CdCoS_2$ films, prepared on glass substrates by CBD. The purpose of this study was to try to get ternary compounds with variable gap by the CBD method and investigation of the optical properties of chemical bath deposited cadmium cobalt sulphide thin film, with potential application in areas of solar energy.

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## MATERIALS AND METHODS

The preparation of $CdCoS_2$ thin films on glass slide was carried out using chemical bath deposition technique, the glass substrates were previously degreased in $HNO_3$ for 48 h (Eze and Okeke, 1997), 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 (halide glass) used as substrates, thereby introducing functional groups called nucleation and/or epitaxial centers on which the $CdCoS_2$ thin film is grafted. 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 $CdCoS_2$ contained 0.2M 5 mL cobalt chloride, 0.2M 5 mL cadmium chloride, 14M 2 mL ammonia, 0.01M 2 mL triethanolamine (TEA), 0.1M 10 mL thiourea and 21 mL distilled water, which were added in that order and allowed for 20 h deposition time. The pH after the mixtures were thoroughly stirred with glass stirring rod came to 9. During 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 $NH_3$ and TEA could achieve, then thin solid films of neutral atoms could form on the substrate. The complexing agents used slow down the precipitation action and enables the formation of $CdCoS_2$. The step wise reactions involved in the complex ion formation and film deposition processes for $CdCoS_2$ here are:

$$CoCl_2.6H_2O + TEA \rightleftharpoons [Co(TEA)]^{2+} + 2Cl^-$$
$$[Co(TEA)]^{2+} \rightleftharpoons Co^{2+} + TEA$$
$$CdCl_2.2\tfrac{1}{2}H_2O + NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+} + 2Cl^-$$
$$[Cd(NH_3)_4]^{2+} \rightleftharpoons Cd^{2+} + 4NH_3$$
$$(NH_2)_2CS + OH^- \rightleftharpoons CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \rightleftharpoons H_2O + S^{2-}$$
$$Co^{2+} + Cd^{2+} + 2S^{2-} \rightleftharpoons CdCoS_2$$

Sulphide ions are released by the hydrolysis of thiourea but $Co^{2+}$ and $Cd^{2+}$ ions form cobalt-triethanolamine complex and tetra amine cadmium complex ions by combining with TEA and $NH_3$ respectively in the pH range of 9 and 10. The $[Co(TEA)]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ complexes adsorb on the glass, then a heterogeneous nucleation and growth takes place by ionic exchange of reaction $S^{2-}$ ions. This process is referred to as ion-by-ion process and in this way brownish (reddish) yellow $CdCoS_2$ was deposited on glass slide in form of transparent, uniform and adherent thin film.

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 UV-VIS-NIR regions by means of PYE UNICAM SP8-100 double beam spectrophotometer with uncoated glass slide as reference. The optical properties investigated include the Absorbance (A), Transmittance (T) and Reflectance (R), which were used to calculate the 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 (Pankove, 1971; Ezema and Okeke, 2002; 2003) while the film thicknesses were obtained by optical methods (Theye, 1985).

## RESULTS AND DISCUSSION

Figure 1 shows the combined effect of film - glass system on transmittance of infrared for $CdCoS_2$ when compared with uncoated glass.

This was carried out using a single beam Fourier transform spectrometer. Uncoated glass reduced transmittance from 50.64% at 3527 $cm^{-1}$ then to 48.62% at 2900 $cm^{-1}$ and then finally dropped to only about 2% transmittance at 1896 to 2000 $cm^{-1}$. At about 1999 $cm^{-1}$, no radiation is transmitted through the glass. Coated glass reduces transmittance from 5.43% at 3744 to 2.72% at 3448 $cm^{-1}$, it raised the transmittance slightly from 2.75% at 3331 to 2.79% at 2854 $cm^{-1}$ and then reduced to 0.09% at 2129 $cm^{-1}$ before finally it drops to only about 0.02% transmittance at 1999-2010 $cm^{-1}$. By about 1999 $cm^{-1}$, no radiation is transmitted through the film-glass system.

It is observed that the film-glass system transmit less 1R than the plain glass.

These films are capable of allowing solar radiation (0.3-3.0 μm) to be transmitted into a building but prevent thermal re-radiation out of the building through the glassing system. It is observed that the film-glass system suppresses transmission of IR when compared with the plain glass.

The spectral Absorbance of cadmium cobalt sulphide thin films prepared at 300K is displayed in Fig. 2. Thin film sample absorbs heavily throughout UV-VIS regions but moderately in the NIR regions.

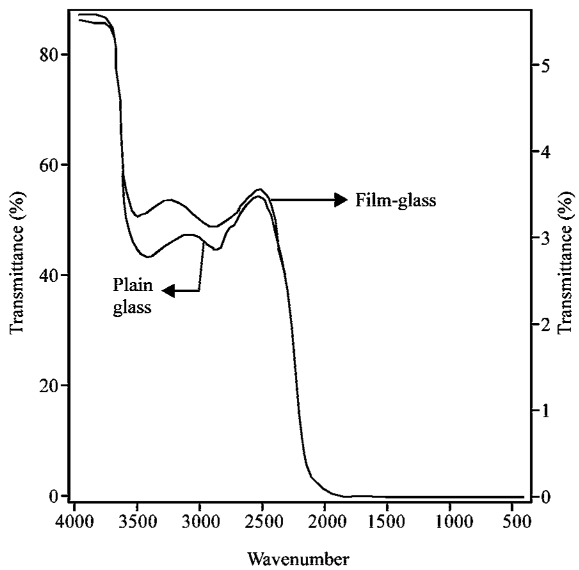


Fig. 1: Spectral infrared transmittance of plain glass/commbined film-glass for $CdCoS_2$ sample

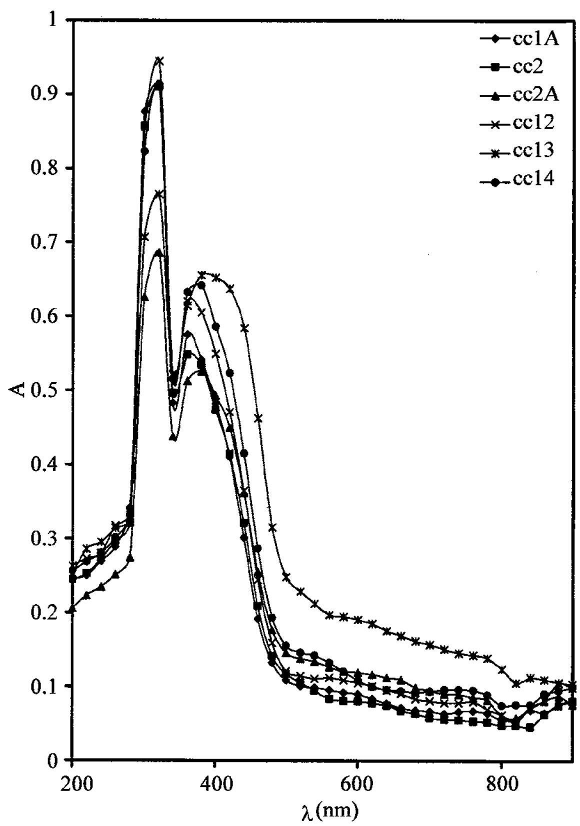


Fig. 2: Spectral absorbance of $CdCoS_2$ thin films

The transmittance and reflectance spectra (Fig. 3) deduced from absorbance spectra showed that all the films show poor transmittance between 12 and 50% in the UV regions and some portions of the VIS regions but moderately (> 50%) in the remaining portions VIS and NIR regions. The film shows high reflectance (>12%) in the VIS-NIR regions.

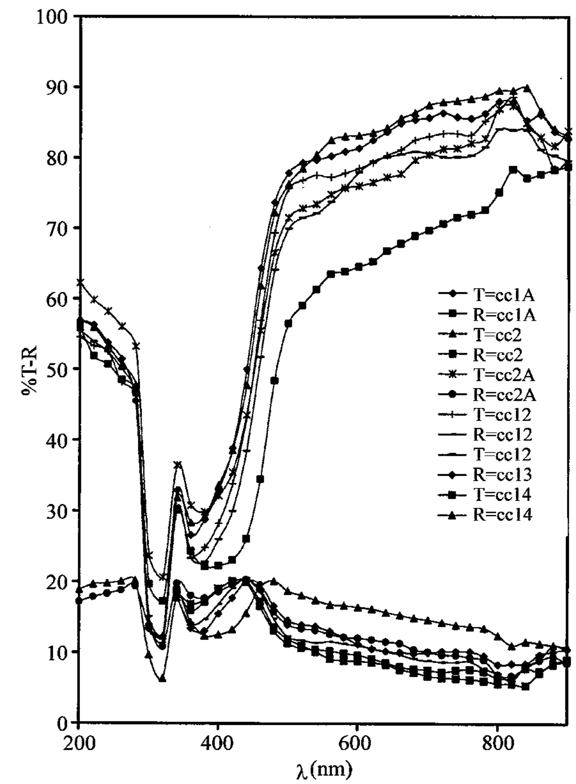


Fig. 3: Spectral transmittance-reflectance for $CdCoS_2$ thin films

The properties of poor transmittance in the UV regions and some portions of the VIS regions but moderately high transmittance in some portions of the VIS regions and NIR regions make the film good materials for screening off UV portion of electromagnetic spectrum which is dangerous to human health and as well harmful to domestic animals. The films can be used for coating eye glasses for protection from sunburn caused by UV radiations. Since they show moderately high VIS-NIR transmittance it can be used for coating of poultry roofs and walls. This will ensure that young chicks which have not developed protective thick feather are protected from UV radiation while the heating of the poultry house is maintained by the heating portion of the electromagnetic spectrum and as well there is admittance of VIS light in the house.

The variations of n with hν for sample of $CdCoS_2$ are shown in Fig. 4. The average values of n ranged between 1.97 and 2.27 with maximum values that ranged between 2.63 and 2.64.

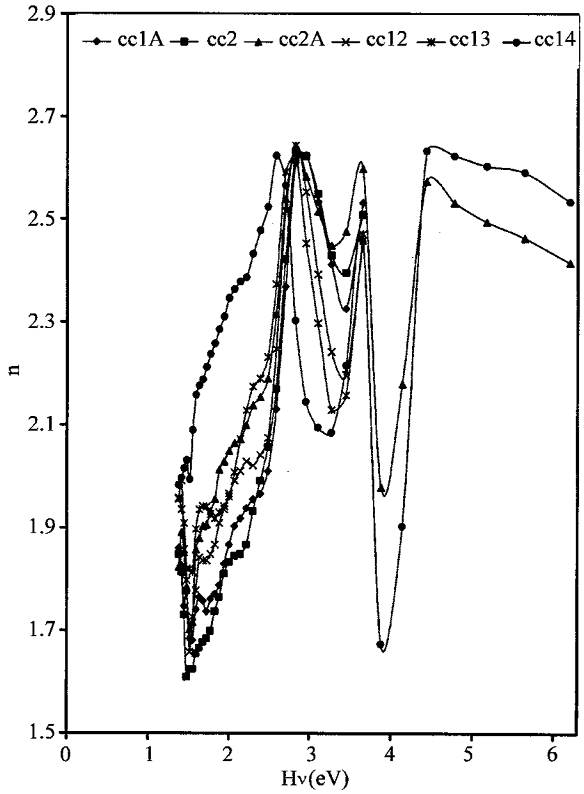


Fig. 4: Plot of n against hν for $CdCoS_2$ thin films

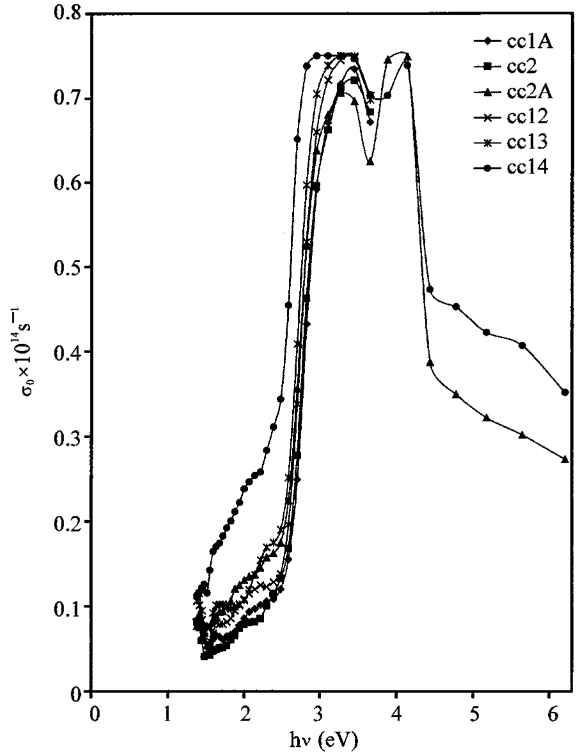


Fig. 6: Plot of $\sigma_o$ against hν for $CdCoS_2$ thin films

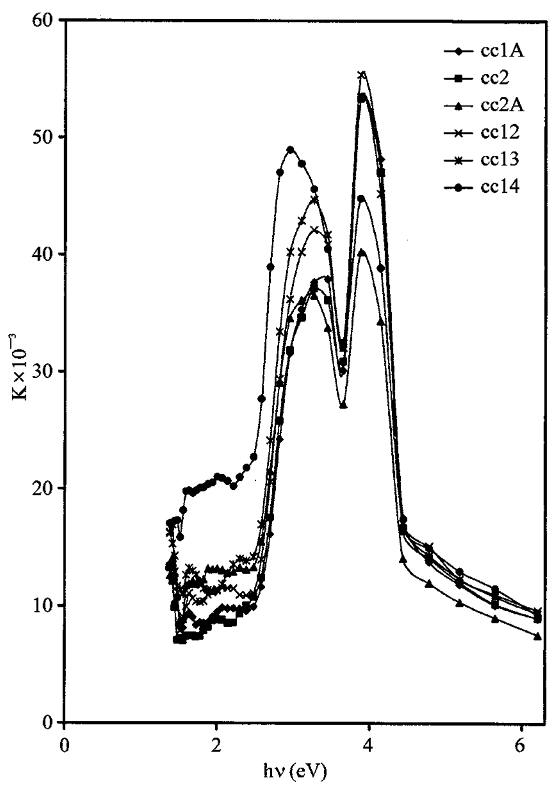


Fig. 5: Plot of k against hν for $CdCoS_2$ thin films

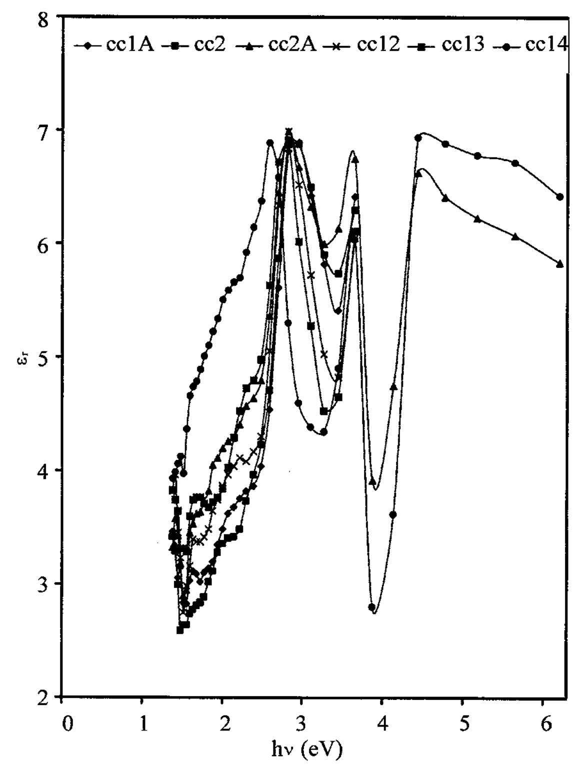


Fig. 7: Plot of $\varepsilon_r$ against hν for $CdCoS_2$ thin films

The variations of k with hν for samples of $CdCoS_2$ are shown in Fig. 5. The average values of k ranged between $1.59\times10^{-2}$ and $2.47\times10^{-2}$ with maximum values that ranged between $4.02\times10^{-2}$ and $5.54\times10^{-2}$.

Plots of optical conductivity $\sigma_o$ against hν are shown in Fig. 6. It has maximum values that ranged between $0.72\times10^{14}S^{-1}$ and $0.76\times10^{14}S^{-1}$ with average values that ranged between $0.20\times10^{14}S^{-1}$ and $0.37\times10^{14}S^{-1}$.

Table 1 below shows the optical properties and thickness, while Table 2 shows the solid state properties and thickness of $CdCoS_2$ thin films prepared under varying conditions at 300 K.

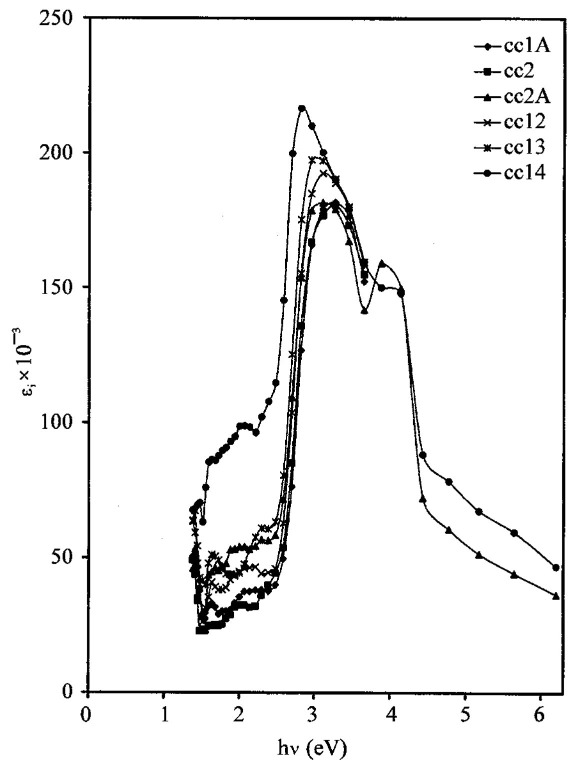


Fig. 8: Plot of $\varepsilon_i$ against hν for $CdCoS_2$ thin films

The plots of $\varepsilon_r$ against hν are displayed in Fig. 7. $\varepsilon_r$ has maximum values that ranged between 6.91 and 6.99 with average values that ranged between 3.97 and 5.23.

The plots of $\varepsilon_i$ against hν are displayed in Fig. 8. $\varepsilon_i$ has maximum values that ranged between $1.80\times10^{-1}$ and $2.17\times10^{-1}$ with average values that ranged between $6.15\times10^{-2}$ and $1.11\times10^{-1}$.

A plots of $(ah\nu)^2$ against hν for $CdCoS_2$ films are shown in Fig. 9. It shows band gaps that ranged between

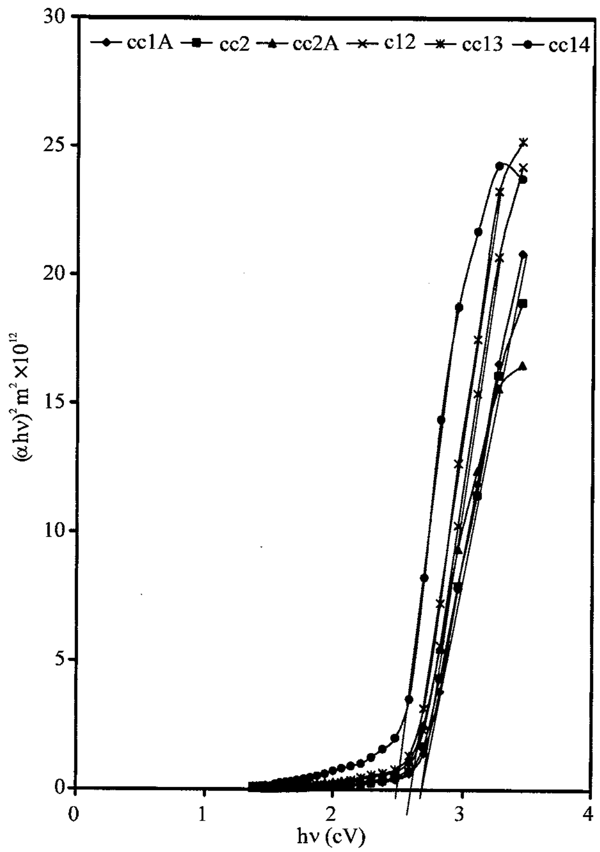


Fig. 9: Plot of $(\alpha h\nu)^2$ against hν for $CdCoS_2$ thin films

Table 1: Optical properties and thickness of $CdCoS_2$ thin films prepared at 300 K

| Samp. No. | Maximum $\alpha\times10^6$ ($m^{-1}$) | Maximum refractive index (n) | Maximum $k\times10^{-2}$ | Maximum $\sigma_o\times10^{14}$ $s^{-1}$ | t(μm) |
|---|---|---|---|---|---|
| cc1A | 2.10 | 2.64 | 5.35 | 0.74 | 0.238 |
| cc2 | 2.09 | 2.63 | 5.33 | 0.72 | 0.244 |
| cc2A | 1.58 | 2.64 | 4.02 | 0.75 | 0.224 |
| cc12 | 2.17 | 2.64 | 5.54 | 0.76 | 0.255 |
| cc13 | 2.10 | 2.64 | 5.35 | 0.75 | 0.264 |
| cc14 | 1.76 | 2.64 | 4.90 | 0.75 | 0.330 |

Table 2: Solid state properties and thickness of $CdCoS_2$ Thin Films at 300 K

| Samp. No. | Maximum $\varepsilon_r$ | Maximum $\varepsilon_i\times10^{-1}$ | $\sigma_c\times10^2$ $W^{-1}m^{-1}$ | t (μm) | Eg(eV) |
|---|---|---|---|---|---|
| cc1A | 6.97 | 1.82 | 6.50 | 0.238 | 2.70 |
| cc2 | 6.91 | 1.80 | 6.39 | 0.244 | 2.70 |
| cc2A | 6.99 | 1.81 | 6.63 | 0.224 | 2.60 |
| cc12 | 6.99 | 1.93 | 6.62 | 0.255 | 2.60 |
| cc13 | 6.95 | 1.97 | 6.64 | 0.264 | 2.60 |
| cc14 | 6.93 | 2.17 | 6.64 | 0.330 | 2.50 |

2.50 and 2.70 eV. The band gap for CoS has been reported to be 3.20 eV (Ndukwe, 1992) while the band gap for CdS was reported to be 2.37 eV (Choi *et al*., 1998; Osuji, 1994) and 2.40 eV (Pawar *et al*., 1986). When the band gaps 2.37 and 2.40 eV for CdS and 3.20 eV for CoS were compared with that of $CdCoS_2$ thin films, the band gap of $CdCoS_2$ thin films are observed to be between that of CdS and CoS. This band gap lies between the band gap of CoS of 3.20 eV (Ndukwe, 1992) and the band gap of 2.37 eV of CdS (Choi *et al*., 1998; Osuji, 1994) and 2.40 eV (Pawar *et al*., 1986). The difference between the band gap of $CdCoS_2$ and CoS and that of CdS shows the deposited films are rich in cadmium. This band gap of the $CdCoS_2$ film makes it a good material for solar cell fabrication.

## CONCLUSIONS

$CdCoS_2$ thin films with thickness of 0.461 μm and energy band gaps between 2.50 and 2.70 eV which are band gaps between that of CoS and CdS has been successfully deposited using chemical bath deposition technique. The FTIR spectroscopy showed the percentage transmittance that ranged between 7 and 46% in the far infrared regions. The films were found to have average transmittance of greater than 50% in the VIS-NIR regions and exhibit high reflectance of greater than 12% in the same regions. The film exhibits poor transmittance in the UV regions, hence, they could be effective as coatings for poultry houses and as well good materials for solar cell fabrication.

## REFERENCES

Choi, J.Y., K.J. Kim, J.B. Yoo and D. Kim, 1998. Properties of cadmium sulphide films deposited by chemical bath deposition with ultrasonication. Solar Energy, 64: 41-47.

Chopra, K.L. and S.R. Das, 1983. Thin Film Solar Cells. Plenium Press, New York.

Eze, F.C. and C.E. Okeke, 1997. Chemical bath deposited cobalt sulphide films; Preparation effects. Mater. Chem. Phys., 47: 31-36.

Ezema, F.I. and C.E. Okeke, 2002. Preparation and characterization of bismuth bromide oxide film preparation by solution growth technique. Nig. J. Phys., 14: 48-54.

Ezema, F.I. and C.E. Okeke, 2003. Chemical bath deposition of bismuth oxide ($Bi_2O_3$) thin film and its application. Greenwich J. Sci. Technol., 3: 90-109.

Ezema, F.I., 2004. Optical properties of chemical bath deposited $FeCdS_3$ thin films, Academic Open Internet Journal http://www.acadjournal.com/ 2004 /v11/part2/p1/index.htm

Lee, J.H., W.C. Song, J.S. Yi and Y.S. Yoo, 2003. Characteristics of the CdZnS thin film doped by thermal diffusion of vacuum evaporated indium films. Solar Energy Materials and Solar Cells, 75: 227-234.

Ndukwe, I.C., 1992. The growth and characterization of thin films by solution growth technique and their applications, Ph. D Thesis, University of Nigeria Nsukka.

Osuji, R.U., 1994. Growth and characterization of thin films and their possible applications in solar cells. Ph.D Thesis, University of Nigeria, Nsukka.

Padam, G.K. and S.U.M. Rao, 1986. Preparation and characterization of chemically deposited $cuins_2$ thin films. Sol. Ener. Mater., 13: 297-305.

Pankove, J.I., 1971. Optical Processes in Semiconductors. Prentice-Hall, New York.

Pawar, S.H., S.P. Tamhankar and C.D. Lokhande, 1986. Studies on Electrochemical Photovoltaic Cells formed with thin Film $Bi_2CdS_4$ Photoelectrodes, Sol. Ener. Mater., 14: 71-77.

Pentia, E., V. Draghici, G. Sarau, B. Mereu, L. Pintilie, F. Sava and M. Popescu, 2004. Structural, electrical and photoelectrical properties of $Cd_xPb_{1-x}S$ thin films prepared by chemical bath deposition. J. Electrochem. Soc., 151: G729-G733.

Theye, M., 1985. In Optical Properties of Thin Films. K.L. Chopra and L.K. Malhota, (Eds.). Thin Film Technology and Applications, Tata McGraw-Hill, New Delhi.

Ver ´ onica Estrella, M.T.S. Nair and P.K. Nair, 2003. Semiconducting $Cu_3BiS_3$ thin films formed by the solid-state reaction of CuS and bismuth thin films, Semicond. Sci. Technol., 18: 190-194.