Effect of Precursor pHon Cadmium Doped Manganese Sulphide (CdMnS) Thin Films For Photovoltaic Application

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Abstract

Synthesis of cadmium doped manganese sulphide thin film semiconductor material includes; manganous acetate tetrahydrate ($C_4H_6MnO_44H2O$), cadmium sulphate ($CdSO_4$), Thioacetamide ($SC(NH_2)_2$) and Ammonia (NH_3). CdMnS thin films exhibit the hexagonal structure with reflection peaks observed at (100), (002), (101) and (203) diffraction planes with corresponding angels at 2θ (25.86, 27.97, 32.55 and 34.65) diffraction angels. The spectra showed that as the wavelength of incident radiation increases the absorbance of the electromagnetic radiation decreases. It was also noticed that sample CD0 which represent MnS recorded the lowest absorbance value of 0.732 while sample CD4 which represents CdMnS thin films deposited with a pH of 12.5 recorded the highest absorbance value of 0.899. It was shows in the SEM a random distribution of big nano-grains on the substrate for sample CD0 and small nano-grain for sample CD3 but for sample CD1, CD2 and CD4 the nano-grains were observed to agglomerate due to the presence of large free energy characteristic of small particles. The band gap energy of CdMnS thin films grown at different pH as obtained from the plot is given as 1.25 eV – 1.15 eV.

Keyword: *CdMnS, ECD, SEM, EDX, optical properties*

I. Introduction

Manganese (Mn) is a transition metal having interesting physical and chemical properties [1-2]. It has optoelectronic application and metal-metal sulphides can be deposited on metals, glass and polymer substrates that are immersed in solutions containing metal complex ions and a source of sulphide [3]. CdMnS thin films have attracted considerable interests because of their novel magnetic and magneto-optical properties derived from this hybridization between the Mn 3d and sp-hexagonal CdS. The introduction of large mole fraction moves the intrinsic edge through the visible region and dominates the optical properties [4]. Several authors have syntheses CdMnS thin films via electrodeposition technique [2, 18-21], vacuum thermal evaporation [17], chemical bath deposition [1, 3-6, 10-15], spray pyrolysis, sputtering [9]. Electrochemical deposition technique is used to prepare CdMnS thin film; The various methods electrodeposition technique provides a simple root of synthesizing thin films because of its simplicity, low-cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. CVD techniques, without exceptional, require high vacuum and or temperature because it is necessary to produce gaseous precursor molecules or atoms. Besides the high energy needed for the film processing, emission of gaseous waste materials is another serious problem with these techniques.

In this paper we report effect of precursor pH on cadmium doped manganese sulphide (CdMnS) thin films for photovoltaic application via electrochemical deposition technique

II. Materials and Method

Chemical used for this research were analytical grade purchased from Sigma-Aldrich. The synthesis of CdMnS thin film semiconductor material includes; manganous acetate tetrahydrate ($C_4H_6MnO_44H2O$), cadmium sulphate ($CdSO_4$), Thioacetamide ($SC(NH_2)_2$) and Ammonia (NH_3). Electrochemical deposition technique (ECD) was used in this research which involves the deposition of any substance on an electrode as a result of electrolysis which is the

occurrence of chemical changes owing to the passage of electric current through an electrolyte. This process involves oriented diffusion of charged growth species through a solution when an external field is applied and reduction of charged growth species at the growth or deposition which also serves as an electrode. The electrochemical bath system is composed of a source of cation (i.e$C_4H_6MnO_4$4H2O, CdSO4 for Mn^{2+}, Cd^{2+}), a source of anion (i.e Thioacetamide ($SC(NH_2)_2$) for S^{2-}), deionized water all in 100ml beaker, magnetic stirrer was used to stir the reaction bath. A power supply was used to provide electric field (DC voltage), a conducting glass was used as the cathode while the anode was carbon and fluorine electrode . Finally, uniform deposition of thin films by electrochemical deposition technique was achieved.

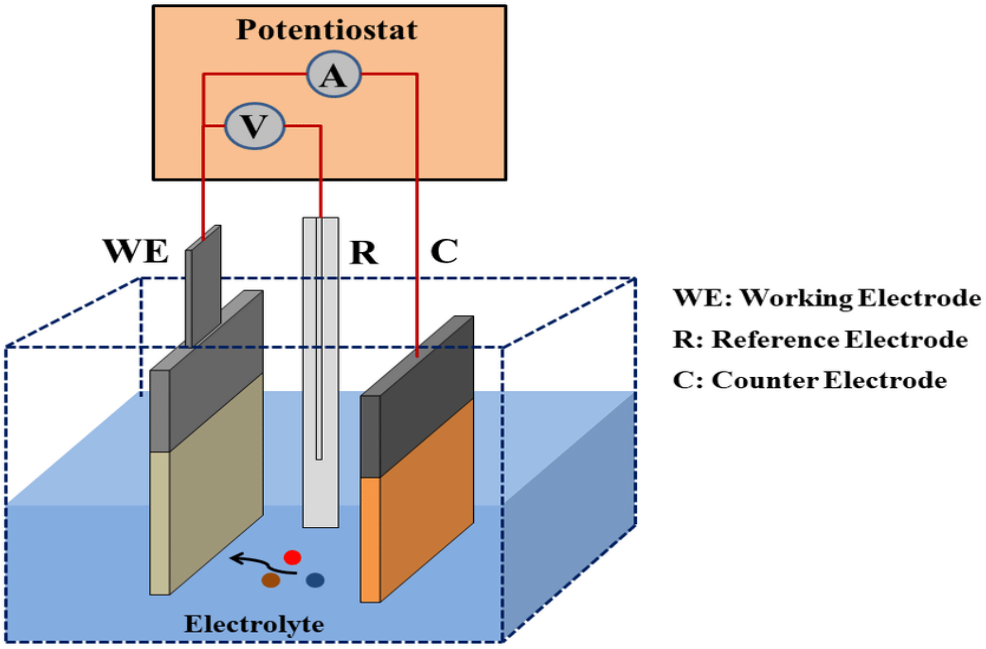

Figure 1: Schematic diagram of electrochemical deposition technique

A. Substrate Fluorine Doped Tin Oxide (FTO)

The glass substrates were coated only on one side and theconducting side of the glass was detected by the use of a digital multimeter which gave reading as the non-conducting side does not give any reading for the deposition of thin films materials. Hand gloves were used to handle the substrates to avoid contamination. The substrates were dipped in acetone, methanol, rinsed with distilled water and later ultrasonicated for 30min in acetone solution after which they were rinsed in distilled water and kept in an oven to dry. All the prepared substrates were kept in air-tight container.

B. The growth of CdMnS thin films

The growth of CdMnS thin filmsmaterials was carried out using aqueous solution of 0.1 mol solution of $C_4H_6MnO_4$4H_2O, $CdSO_4$while the anionic precursor was 0.1 mol solution of Thioacetamide ($SC(NH_2)_2$) and ammonia was used to varies the pH of the precursor. The electrochemical bath system is composed of a source of cation (i.e$C_4H_6MnO_4$4H2O, CdSO4 for Mn^{2+}, Cd^{2+}), a source of anion (i.e Thioacetamide ($SC(NH_2)_2$) for S^{2-}), deionized water all in 100ml beaker, magnetic stirrer was used to stir the reaction bath. A power supply was used to provide electric field (DC voltage), a Fluorine doped tin oxide (FTO) was used as the cathode while the anode was carbon and fluorine electrode.

Table 1: **Variations of growth parameters**

Sample	$CdSO_4$ (ml)	$C_4H_6MnO_4 4H_2O$ (ml)	$(SC(NH_2)_2)$ (ml)	pH	Time (Sec)	Voltage (V)
CD0	10	20	20	Normal	10	10
CD1	10	20	20	9.5	10	10
CD2	10	20	20	10.5	10	10
CD3	10	20	20	11.5	10	10
CD4	10	20	20	12.5	10	10

C. Characterization of The Films.

The growth films were characterized for their optical, structural, scanning electron microscope and the elemental composition of the deposited material. The structural characterization of the films was carried out using Bruker D8 Advance X-ray diffractometer with Cu Kα line (λ= 1.54056Å) in 2θ range from 10° - 90° the instrument helped in determining the type of lattice crystal and intensities of diffraction peaks, with the help of data base software supplied by the international center of diffraction data. The quantitative analysis of the films were carried out using Energy Dispersive X-ray Analysis (EDX) for the thin films to study the stoichiometry of the film. This unit is attached to the Zeiss scanning electron microscope (SEM). When a beam of electrons strikes the specimen, some of the incident electrons excite the atom of the specimen which emits X-ray on returning to the ground state. The energy of the X-ray is related to the atomic number of the excited element. Lithium drifted Si-diode, held at liquid nitrogen temperature is used as a detector of the X-rays. JEOL-JSM 7600F Japan was employed in the present investigation. The absorbance spectral of the films was obtained in UV- visible NIR using UV-1800 visible spectrophotometer. UV-visible spectrophotometer uses the principle that when a beam of electromagnetic radiation of initial flux I is incident on a transparent object, it is transmitted. Some part of the incident flux could be absorbed for an absorbing medium while some part could be reflected.

III. Results and Discussion

A. XRD Analysis of CdMnS Thin Films

Thin films of CdMnS deposited on FTO substrates at different temperature were characterize using Bruker D8 Advance X-ray diffractometer with Cu Kα line (λ= 1.54056Å) in 2θ range from 10° - 90° see fig. 6, CdMnS thin films exhibit the hexagonal structure with reflection peaks observed at (100), (002), (101) and (203) diffraction planes with corresponding angels at 2θ (25.86, 27.97, 32.55 and 34.65) diffraction angels respectively with [JCPDS card no. 77-2306 of CdS and 76-2049 for MnS] reported by [15-17, 5-14]. The un-indexed peaks could have possibly resulted from the FTO substrates used for deposition. The lattice constant a = 5.991Å

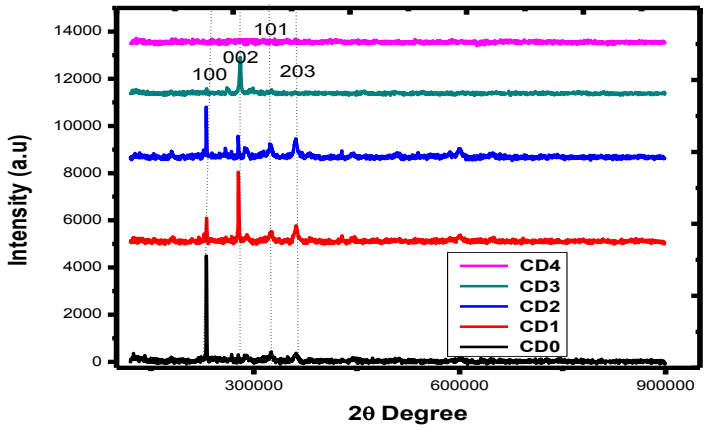

Figure 6: XRD Plot of CdMnS Thin Films

B. Surface Morphology of CdMnS thin Films

CdMnS thin film grown on fluorine doped tin oxide (FTO) substrates at different precursor pH were characterize using Zeiss scanning electron microscope (SEM). It shows random distribution of big nano-grains on the substrate for sample CD0 and small nano-grain for sample CD3 but for sample CD1, CD2 and CD4 the nano-grains were observed to agglomerate due to the presence of large free energy characteristic of small particles. Sample CM1 and CM4 the nano grain become more densely packed (see figure 7) and homogenous without cracks on the surface which shows uniform deposition of CdMnS thin films semiconductor reported by [15-17, 5-14].

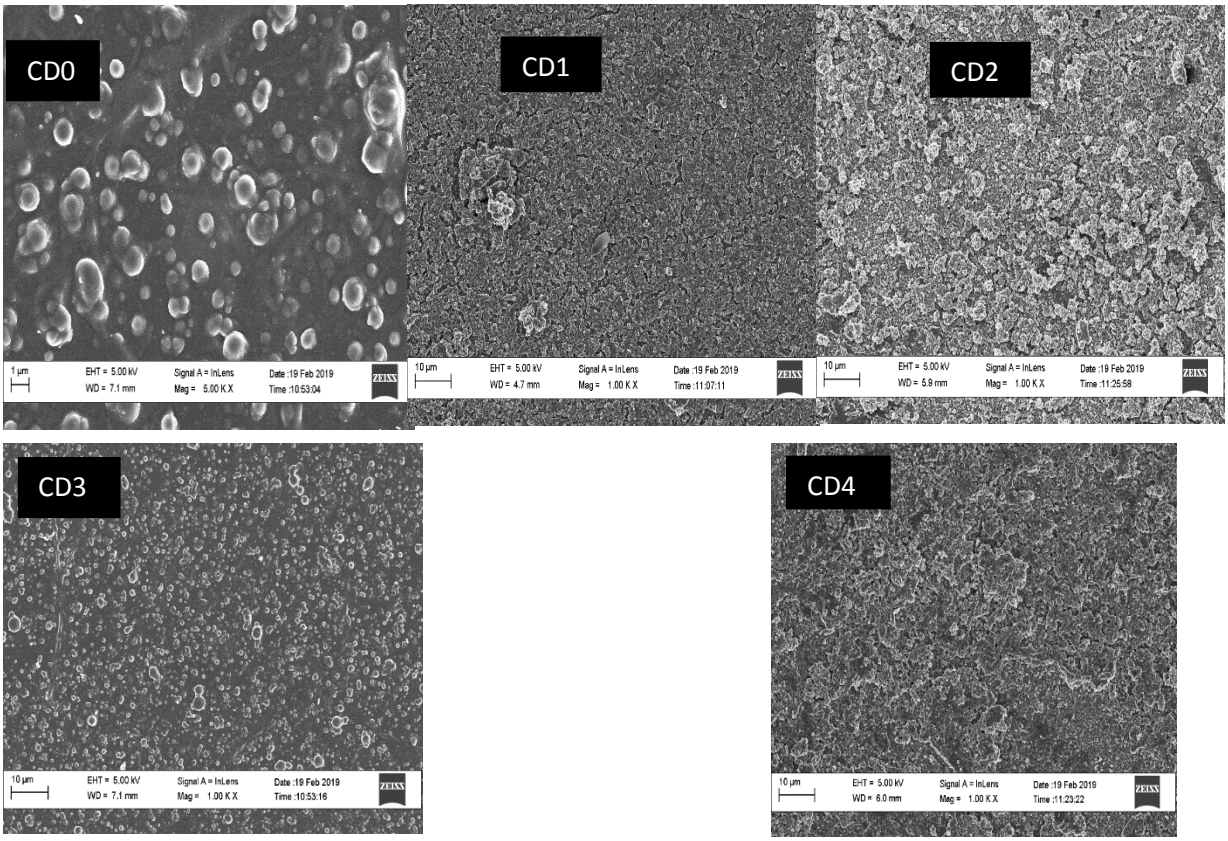

Figure 7: Microgram of CdMnS Thin Films

C. Elemental Composition Analysis of CdMnS Thin Films

EDX was use to study the chemical composition of the deposited films. This unit is attached to the Scanning Electron Microscopy (SEM). JEOL-JSM 7600F Japan was employed in the present investigation. It is clearly observed see figure 8the formation of CdMnS in the EDX spectra analysis and the others element present is due to the elemental composition of the (FTO) substrate used for the deposition of the films

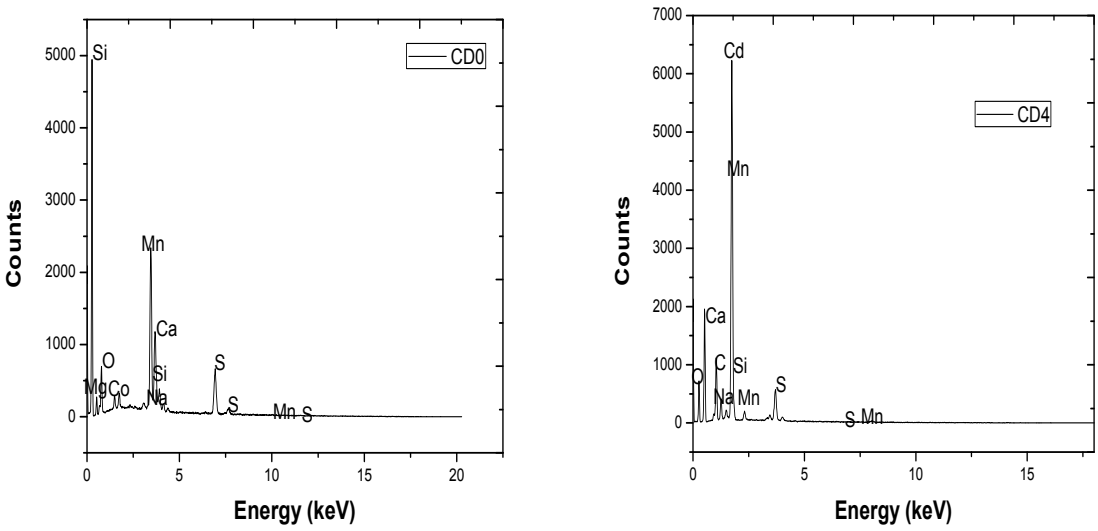

Figure 8: EDX Spectra of CdMnS Thin Films

figure 2). From the spectra it was observed that as the wavelength of incident radiation increases the absorbance of the electromagnetic radiation decreases. It was noticed that sample CD0 which represent MnS absorbance value of 0.899 which indication that doping MnS with Cd and varying the pH with ammonia enhances the absorbance of the deposited material for solar cell fabrication and photovoltaic applications.

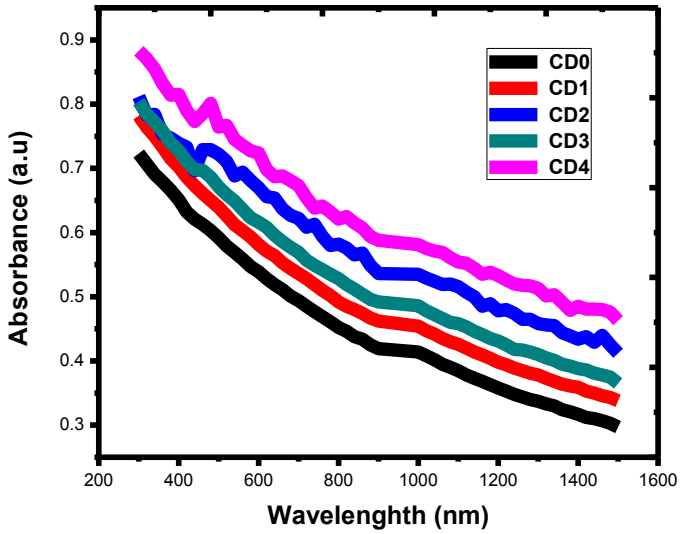

Figure 2: Absorbance versus Wavelength

The transmittance spectral of CdMnS thin films as a function of wavelength (see figure 3). From the spectra it was observed that as the wavelength of incident radiation increases the transmittance of the electromagnetic radiation increases. It was noticed that sample CD0 which represent MnS recorded the highest transmittance value of 0.52% while sample CD4 which represents CdMnS thin films deposited with a pH of 12.5 recorded the lowest transmittance of 0.42%. All the deposited samples transmit above 40% which shows that doping MnS with Cd will be a good material for solar cell fabrication and photovoltaic application.

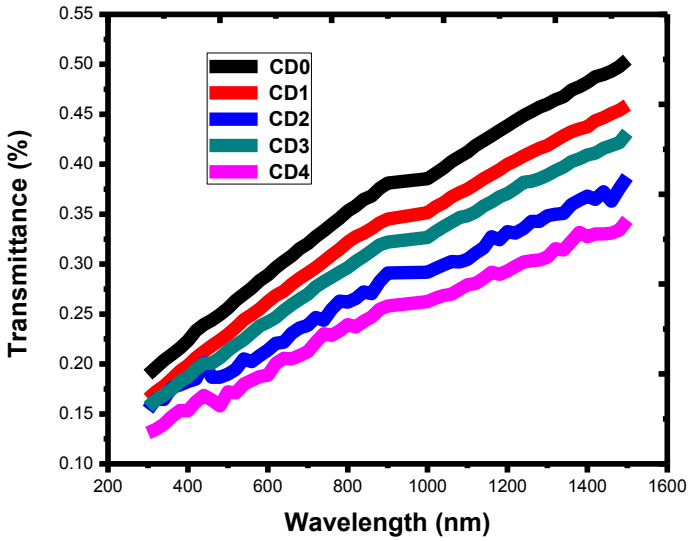

Figure 3: Transmittance versus Wavelength

The reflectance spectral of CdMnS thin films as a function of wavelength (see figure 4). From the spectra it was observed that as the wavelength of incident radiation increases the reflectance of the electromagnetic radiation increases except for sample CD3 which represent CdMnS deposited with a pH of 11.5 decreases as the wavelength of the electromagnetic radiations increases. All the deposited sample shown a very low reflectance which is due to the very absorbance parameters; Hence, the material as deposited are good material for solar cell fabrication and photovoltaic application.

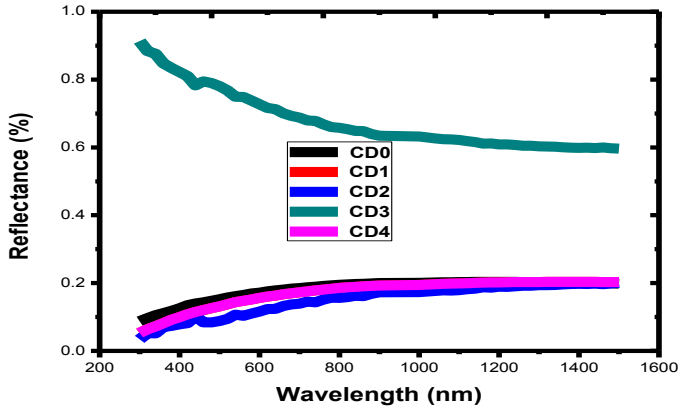

Figure 4: Reflectance versus Wavelength

The optical band gap energy was calculated using the following equation;

$$\alpha h\nu = A(h\nu - E_g)^n$$

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a parameter that depends on the transition probability, h is Planck's constant, and the exponent n depends on the transition during the absorption process. The value of n is 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transition respectively. The band gap energy of CdMnS thin films grown at different pH as obtained from the plot is given as 1.25 eV – 1.15 eV respectively (See figure 5) which was reported by [15-17, 5-14].

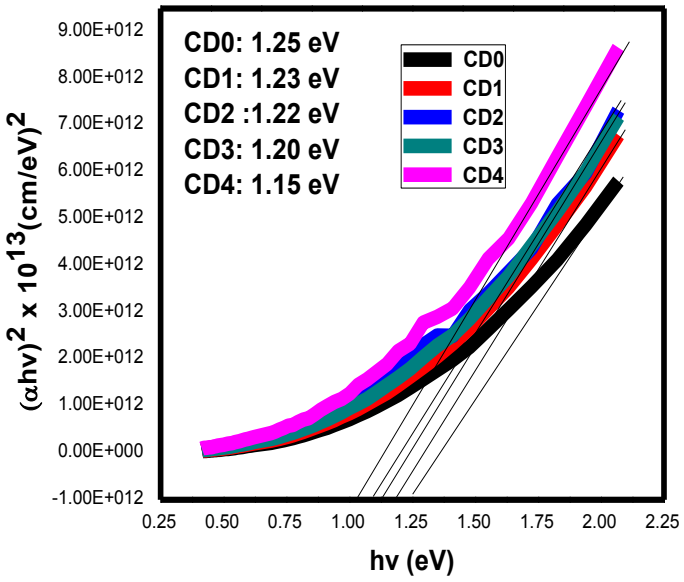

Figure 5: $(\alpha h\nu)^2$ x10^{13} $(cm/eV)^2$ versus hv (eV)

IV. Conclusions

Electrochemical deposition technique have successfully used to carried out the synthesis of CdMnS thin film semiconductor material. CdMnS thin films exhibit the hexagonal structure with reflection peaks observed at (100), (002), (101) and (203) diffraction planes with corresponding angels at 2θ (25.86, 27.97, 32.55 and 34.65) diffraction angels. The spectra showed that as the wavelength of incident radiation increases the absorbance of the electromagnetic radiation decreases. It was also noticed that sample CD0 which represent MnS recorded the lowest absorbance value of 0.732 while sample CD4 which represents CdMnS thin films deposited with a pH of 12.5 recorded the highest absorbance value of 0.899 and It was noticed that sample CD0 which represent MnS recorded the highest transmittance value of 0.52% while sample CD4 which represents CdMnS thin films deposited with a pH of 12.5 recorded the lowest transmittance of 0.42%. It was shows in the SEM a random distribution of big nano-grains on the substrate for sample CD0 and small nano-grain for sample CD3 but for sample CD1, CD2 and CD4 the nano-grains were observed to agglomerate due to the presence of large free energy characteristic of small particles. Sample CM1 and CM4 the nano grain become more densely packed. The band gap energy of CdMnS thin films grown at temperature as obtained from the plot is given as 1.25 eV – 1.15 eV

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