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$\text{Cd}_{1-x}\text{Mn}_x\text{S}$ dilute magnetic semiconductor: application in photoelectrochemical cells

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Abstract

A new class of dilute magnetic semiconductor (DMS, CdMnS) thin film based photoelectrochemical cell is presented. DMS thin films are synthesized on both glass and stainless steel substrates using a chemical growth process. The preparation parameters, such as growth temperature, time, reaction pH, precursor concentrations, etc., were optimized to yield characteristically oriented films. The layer thickness was found to decrease with increase in Mn^{2+} concentration. Composition of the as-grown samples was determined by an EDS technique. The electrochemical cells were then formed out of these series of films as the active photoelectrodes, an electrolyte and a counter electrode. The cells were then characterized through their dark and photosensing properties. The other cell parameters were determined from these studies and the cell performance has been evaluated with a special reference to Mn^{2+} concentration in CdS . A significant enhancement in performance has been observed for a cell with electrode composition of $x = 0.01$.

Key Words: $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ Magnetic semiconductor, DMS, Photoelectrochemical cell, Magnetic properties, fill factor.

1. Introduction

Alloyed ternary materials are attracting a great deal of attention in the scientific community because one can tune in them basic material characteristics such as energy gap, the effective mass and the lattice constants, merely by varying their materials composition. Diluted magnetic semiconductors (DMS's) are potential high performance candidates and are II-VI, IV-VI, II-V and III-V compounds in which a sizable numbers of nonmagnetic ions (e.g. Mn^{2+} , Fe^{2+} , Co^{2+}) offer a variety of cooperative effects (not present in nonmagnetic semiconductors) via spin-spin exchange interaction [1–6]. These materials, especially II-VI and

IV-VI compounds, have the general configuration of type $A_{1-x}^{II}B_xC^{IV}$ [where $A_{1-x}^{II} = \{\text{Cd, Zn, Hg}\}$, $B_x =$ magnetic ions (Mn, Fe, Co) and $C^{IV} = \{\text{S, Se, Te}\}$] and have been extensively studied devoting to the semiconducting magnetic structures of the selenides, and tellurides; sulphides being less investigated [3–5]. Among DMS's studied, Mn-based DMS's can be grown over a wide range of composition than the others and due to their tunable lattice parameters and energy gaps, these Mn-based alloys are excellent candidates for fabrication of quantum wells and super lattices [6, 7–10].

Our aim is to synthesize a series of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ DMS's materials under controlled conditions for application in electrochemical photovoltaic devices illustrating that CdMnS is a potential candidate for optoelectronic device applications, although it has been scantily studied.

2. Experimental procedures

2.1. Materials synthesis

A series of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ thin layers of various x values ($0 \leq x \leq 0.5$) were deposited onto mechanically cleaned glass and stainless steel substrates by a solution growth technique [11–12]. For deposition, hydrolyzed solutions of cadmium sulphate (at 1 M concentration), manganese sulphate (1 M) and thiourea (1 M) in stoichiometric proportions were prepared and placed in a 250 ml glass beaker. Triethanolamine (TEA) and liquid ammonia (NH_3) were added into the reaction container as the complexing agent. For each material series prepared, the film stoichiometry was maintained by adjusting the ion concentration volumes of the basic reactants. The glass and stainless steel substrates were cleaned and mounted on a specially designed substrate holder and were rotated in the reaction mixture by means of a constant speed gear motor. This provides a continuous and uniform mechanical churning of the reaction mixture. To obtain good quality samples, the amount of complexing agent, the deposition time, temperature, pH and speed of the substrate rotation were optimized. The terminal thicknesses of these as-deposited layers were measured using an interference technique. The microscopic features were observed through a scanning electron microscope (CEMECA, SU-30, France). Chemical composition of the films was determined using a Kevex 7000-77 ED spectrometer. The accelerating voltage was 20 kV.

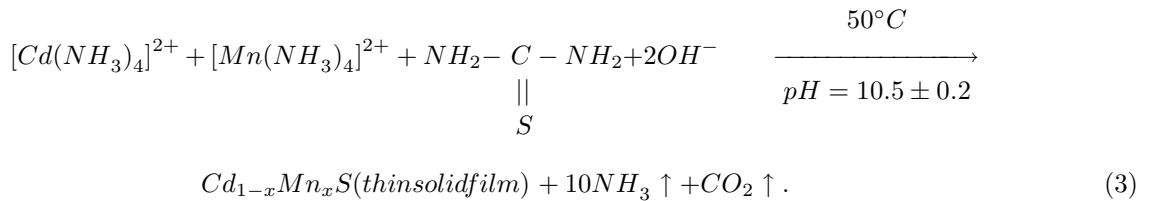
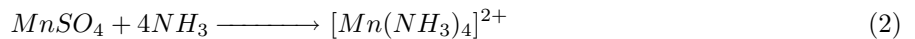
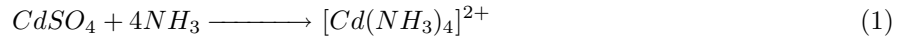
2.2. Fabrication of the photoelectrochemical cell

An electrochemical photovoltaic cell was devised out of these films as photoelectrodes, an electrolyte consisting of polysulfide redox couple (pH = 12.2) and a graphite counter electrode in a H-shaped corning glass cuvette. The counter electrode was sensitized in a CoS solution and placed behind the film electrode at a distance of about 3 mm. The exposed area (1 cm^2) of the active electrode was defined by an epoxy resin. The cell was then sealed by means of a rubber cork and contacts were drawn. The second arm of the cell was used for placement of saturated calomel electrode (SCE). The whole assembly was covered by means of a copper pot. The cell was illuminated through an electrolyte solution using a simple tungsten halogen lamp. The various cell properties such as I-V characteristics in dark, barrier height, photovoltaic output (under 20 mW/cm^2) characteristic and photoresponse were studied as a function of an electrode composition x .

3. Results and discussion

3.1. Growth and physical observations

Co-deposition of Cd^{+2} , Mn^{2+} and S^{2-} ions to form $Cd_{1-x}Mn_xS$ thin layers was carried out in an aqueous alkaline medium ($pH = 10.5 \pm 0.2$), with $0 \leq x \leq 0.5$. Deposition targets were glass and stainless steel substrates in a reaction container with varying solutions of cadmium, manganese, thiourea, aqueous ammonia and TEA. A series of reactions can be proposed as follows:



The deposition rate is controlled by both the pH of the reacting solution and deposition temperature. We varied the deposition temperature from 30 to 70 °C. It has been found that at and a few degrees above room temperature, no film formation was evidenced at our experimental conditions; the reason being that, at such low temperatures, almost all the ions are in a bound complex states [10–12]. The temperature of the reaction container was therefore raised from 30–70 °C and the terminal layer thickness was measured. It is observed that the terminal layer thickness increased almost linearly with increase in the deposition temperature, maximizes at around 50 °C and then decreased for higher deposition temperatures [10–12]. The variation of layer thickness with temperature is shown in Figure 1. The time of deposition was also optimized at our experimental conditions. A deposition time of approximately 4 hours is found to be suitable [10–12]. It has been seen that the film growth is time-dependent and is initially linear, then saturates. The film growth was also examined for other crucial parameters, namely speed of the substrate rotation and pH of the reaction mixture. A moderate speed of the substrate rotation (70 ± 2 rpm) was selected to obtain a sufficient layer thickness. A pH value of 10.5 ± 2 was selected for growth of the films [10–12].

The various preparative parameters and deposition conditions that were optimized and are [10–12]:

- a) Deposition temperature = 50 ° C;
- b) Substrate rotation speed = 70 ± 2 rpm;
- c) Deposition time = 240 min;
- d) Reaction mixture pH = 10.5 ± 2 ;
- e) Quantity of the TEA = 4 ml, and ammonia = 16 ml.

The as-grown CdS ($x = 0$) samples are reddish orange red in color, whereas the color of the other composites changed gradually from reddish orange to reddish brown as x increased from 0 to 0.5. The change in color with the increased Mn-concentration in CdS indicates that Mn^{2+} forms an alloy with CdS under certain controlled experimental conditions. The films were then analyzed compositionally by an energy dispersive spectroscopy technique. It has been seen that Mn^{2+} replaces Cd^{2+} rather than S^{2-} [10–12].

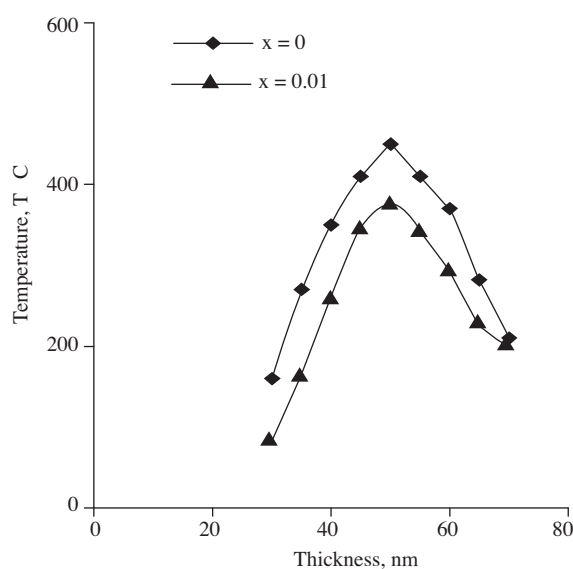


Figure 1. Variation in CdMnS layer thickness with deposition temperature, at 240 minutes, for $x = 0$ and $x = 0.01$.

3.2. Compositional analysis

The films were analyzed compositionally by an energy dispersive spectroscopy technique. As-grown CdS films appeared more or less stoichiometric. Addition of Mn^{2+} in CdS substitutes Cd^{2+} , whereas S^{2-} content remained practically constant. The chemical compositional analysis of the $Cd_{1-x}Mn_xS$ thin films, i.e. contents of Cd^{2+} , Mn^{2+} , and S^{2-} for various film structures are listed in Table 1.

Table 1. Chemical compositional analysis of the $Cd_{1-x}Mn_xS$ thin composites.

Composition, x	Mn (L A), at%	Cd (L A), at%	S (L A), at%
0.00	—	50.08	49.92
0.01	0.16	49.89	49.95
0.025	0.30	49.68	50.02
0.05	1.75	48.26	49.99
0.10	2.72	47.34	49.94
0.20	3.68	46.29	50.03
0.30	5.33	44.74	49.93
0.50	8.27	41.82	49.91

3.3. Photonic studies

When a semiconductor photoelectrode, dipped in an electrolyte, is illuminated by a light of suitable wavelength, excess charge carriers are generated, at the cost of light absorption, and separated at the space charge region. For an n-type material, the electrons move deep into the bulk, while holes move to the surface of the semiconductor causing a redox reaction to occur [13–15]. The charge separation process results in a counter field which is maximum at open-circuit conditions called the open-circuit photovoltage, which acts as a

driving force for the electrons to move from the semiconductor to the counter electrode; whereas the electrolyte captures the holes [14–15].

The current voltage relation for these cells devised with a $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ photoelectrode of varying composition and sulfide/polysulfide electrolyte were therefore studied. When dipped into an electrolyte solution, the cell developed a dark voltage V_D , and a dark current I_D , presumably due to the difference in two half cell potentials of the $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ and counter electrode [13, 16–18]. In an electrode-electrolyte system, the nature of the charge transfer reaction is governed solely by the Butler-Volmer relation [13–18], and the magnitude of the symmetry factor decides the nature of the junction formed at the interface. The junctions formed are of the rectifying type [13–18] and are analogous to the Schottky barrier junction. The junction ideality factor n_d , which is a measure of the quality of the junction, has been determined from the variation of short-circuit current, as $\log I_{sc}$, as a function of short-circuit voltage V_{sc} for all cells. It has been seen that the recombination mechanism is dominant at the electrode/electrolyte interface [14].

The junction barrier heights ϕ_B of the various cells were also determined from the temperature dependence of the reverse saturation current. At higher temperature saturation current obeys non linear behavior and could be attributed to the Pool-Frenkel type conduction mechanism [13, 14, 17]. The barrier heights are cited in the Table 2.

Table 2. Showing electrochemical performance of the cells formed out of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ electrodes ($0 \leq x \leq 0.5$) and electrolyte.

Sr. no.	Electrode Comp., x	V_{oc} , mV	I_{sc} , $\mu\text{A}/\text{cm}$	R_s , $\text{k}\Omega$	R_{sh} , $\text{k}\Omega$	η , %	ff, %	n_d , mV	Φ_B , eV
1	0.000	386	178	0.755	5.00	0.13	37.2	2.52	0.83
2	0.005	427	195	0.100	5.33	0.16	39.1	2.23	1.08
3	0.0075	465	205	0.640	5.71	0.21	42.7	2.18	1.15
3	0.010	510	223	0.620	6.50	0.25	44.9	1.95	1.18
4	0.050	480	189	0.790	4.70	0.20	42.8	2.13	0.79
5	0.075	390	148	0.850	4.44	0.15	40.1	2.23	0.64
6	0.100	305	139	0.910	4.21	0.11	39.0	2.40	0.60
7	0.200	268	121	0.940	3.83	0.08	37.3	2.61	0.65
8	0.300	235	103	0.975	3.63	0.06	36.2	2.85	0.50
9	0.500	208	089	1.050	3.47	0.03	35.3	3.14	0.46

The power output curves were obtained for various cell configurations. The cell parameters namely, short-circuit current I_{sc} , open circuit voltage V_{oc} , efficiency (η) and fill factor (ff), were determined. It is seen that the short-circuit current, and open circuit voltage V_{oc} enhanced significantly as x increased from 0 to .01, then decreased for higher values of x . The enhancement in I_{sc} and V_{oc} at $x = 0.01$ can be correlated to the improved grain structure of the electrode material and observed decrease in series resistance of a cell [13–15, 19, 20].

Figure 2 shows the dependence of the conversion efficiency (η , %) and fill factor (ff, %) on electrode composition parameter x . The efficiency increases up to $x = 0.01$ and thereafter decreased. We attribute the observed improvement to the increased I_{sc} and V_{oc} of the cells. The increase in short circuit current can be correlated to the decreased series resistance of the cell whereas increase in V_{oc} can be attributed to the improved

grain structure of the electrode material. These results are analogous to those reported by Mahapatra and Roy [21] and Deshmukh et al [14, 15, 20] for mixed alloyed materials.

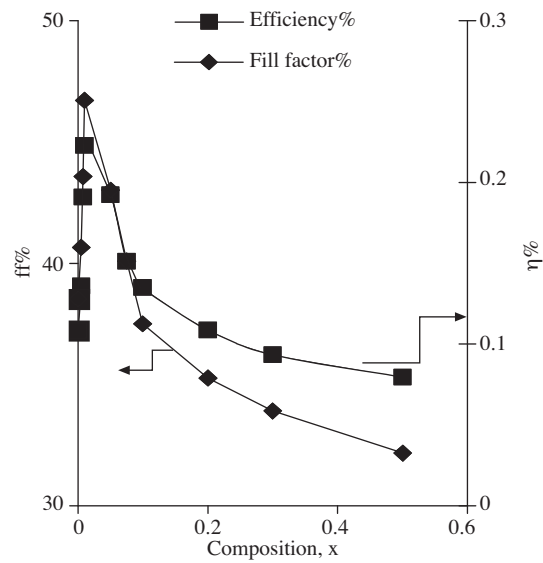


Figure 2. Variation of efficiency (η , %), and fill factor (ff, %), with composition.

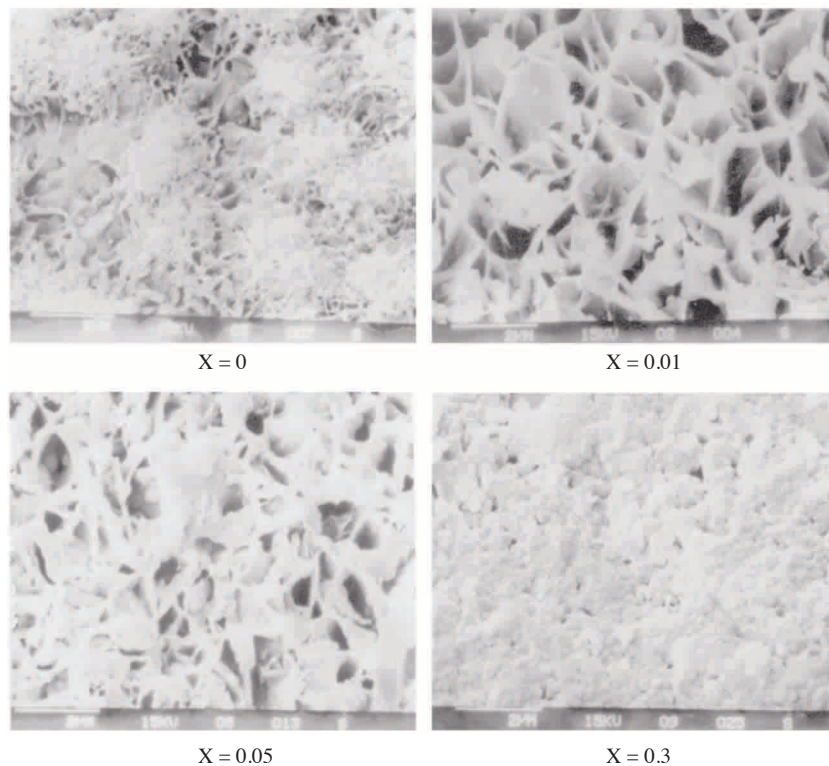


Figure 3. SEM micrographs of few of the CdMnS thin film electrodes.

The surface morphologies of the as-deposited films were examined via scanning electron microscope.

Figure 3 shows the SEM micrographs of four typical electrode compositions. The micrographs show a considerable improvement in grain structure at $x = 0.01$ which is reflected in the electrochemical performance of this material.

4. Conclusions

Highly oriented $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ ($0 \leq x \leq 0.5$) thin films can be synthesized using a simple and non expensive chemical deposition technique. The film structures can be employed in photoelectrochemical cells for the conversion of light into electrical energy. The materials properties can be engineered to cope with the maximum span of the solar spectrum.

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