

Effect of Concentration on the Optical Properties of Manganese Alloyed Cadmium Oxide Thin Films Deposited by Solution Growth Technique

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Abstract:

Manganese alloyed cadmium oxide (CdMnO₂) thin films were deposited on a substrate at room temperature of 303k by solution growth techniques using hydrated cadmium chloride salt as a source of cadmium ion, hydrated manganese chloride as a source of manganese ion and ammonium hydroxide as a pH adjuster. The concentration of manganese ion precursor was varied. The effect of concentration on the properties of the films was studied. The optical absorbance, reflectance, extinction coefficient and refractive index of the films increased with increased in concentration of manganese ion precursors but decreased with increase in wavelength. They are generally high (maximum) in UV region and tends to minimum in NIR region. However, transmittance of the film increased as wavelength increased. It decreased as the concentration of manganese ion precursor tends to maximum. The bandgap of the manganese alloyed cadmium oxide thin films decreased from 2.75 eV to 2.40 eV as the concentration of the manganese ion precursors increased in the range of 0.02 M to 0.10 M. The elemental structure of the film showed that manganese, cadmium and oxygen were all deposited on the substrate. The variation of thickness with concentration of manganese ion precursor showed that the thickness increased with increase in concentration of manganese ions. XRD result showed that the thin films are polycrystalline and crystallized in cubic structure with preferred orientation in (111) plane. The SEM micrograph showed that the films are conglomerate of particles in different shape formations..

Keywords:

Optical Properties, Semiconductor, Bandgap, Polycrystalline, Conglomerate

1. Introduction

Research on metal oxide thin film are growing day by day due to their numerous uses in electronics, plasmonic, optical, thermal and solar energy devices. Special

attention paid on transparent conductivity oxide such as CdO due to its high conductivity and high transparency in the visible region of electromagnetic radiation [1]. Moreover, tremendous effort has given in recent past to CdO thin film due to its important role to both fundamental and breakthrough development of technologies in various areas such as solar cells [2], interlayers for diodes [3], gas sensor [4], phototransistors [5], thin film photovoltaic [6], information storage [7] and many other opto-electronic devices. This is due to fact that cadmium oxide (CdO) is an n-type semiconductor having direct bandgap of 2.20eV [8] with a cubic crystal structure. This work seeks to alloy manganese ion into it with a view to ascertaining the property and possible applications.

CdO thin film have been deposited by various techniques such as spray pyrolysis [9] chemical vapour deposition [10], successive ionic layer adsorption and reaction [11], thermal evaporation [12], sol-gel dip coating [13] and magnetron sputtering [14]. Chemical bath deposition [14]. Among all these techniques, chemical bath deposition is opted for because it does not require complex instrumentation and offers minimum toxicity and occupational hazards.

2. Materials and Method

The precursors for the deposition of thin films of CdMnO₂ at various concentration are hydrated cadmium chloride salt (CdCl₂.2½H₂O), manganese chloride tetrahydrate (MnCl₂.4H₂O) and ammonium hydroxide (NH₄OH). Deposition was made at room temperature of 30 °C (303K).

Absorbance and transmittance of the films were characterized with UV/visible spectrophotometer (Jenway 6405 UV visible). Thickness (t) of the films was calculated using gravimetric method.

The precursors were mixed as shown in Table 1. The effect of concentration variation was studied on the optical properties: Absorbance, Transmittance, reflectance, refractive index, extinction coefficient and bandgap.

Table 1. Concentration Variation of MnCl₂.4H₂O.

Reaction bath	CdCl ₂ .2½H ₂ O		MnCl ₂ .4H ₂ O		H ₂ O	NH ₄ OH	
	Conc. (mol/dm ³)	Vol (ml)	Conc. (mol/dm ³)	Vol (ml)	Vol (ml)	Vol (ml)	pH
CdMnO _{0.02}	0.10	20.00	0.02	5.00	50.00	5.00	10.10
CdMnO _{0.04}	0.10	20.00	0.04	5.00	50.00	5.00	10.10
CdMnO _{0.06}	0.10	20.00	0.06	5.00	50.00	5.00	10.10
CdMnO _{0.08}	0.10	20.00	0.08	5.00	50.00	5.00	10.10
CdMnO _{0.10}	0.10	20.00	0.10	5.00	50.00	5.00	10.10

3. Theory

The following mathematical tools were used in the analysis of the following optical properties.

Reflectance (R)

The reflectance of the films were calculated using equation (1) as given by [15]

$$R = T - (A+T) \quad (1)$$

Refractive Index (n)

The refractive index of the films were calculated using equation (2) as given by [15]

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (2)$$

Extinction Coefficient (K)

Extinction coefficient of the films were calculated using equation (3) as given by [15]

$$K = \frac{\alpha\lambda}{4\pi} \quad (3)$$

where α is absorption coefficient and λ is wavelength

Bandgap (E_g)

Bandgap of the films were calculated using equation (5) as given by [15]

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (4)$$

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5)$$

Crystallite size (D)

The crystallite size of the films were calculated using equation (6) as given by [16]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (6)$$

Dislocation density (δ)

The dislocation density of the films were calculated using equation (7) as given by [16]

$$\delta = \frac{1}{D^2} \quad (7)$$

Microstrain (ϵ)

The microstrain of the films were calculated using equation (8) as given by [16]

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (8)$$

Thickness (t)

The thickness was calculated using equation (9) given by [16]

$$t = \frac{\Delta M}{\rho A} \quad (9)$$

Where ΔM is change in mass of the substrate before and after deposition, ρ is the density of cadmium oxide (CdO) and A is the area of substrate covered by the film.

4. Results

The result showed that the absorbance increased with increased in concentration. It decreased with increased in wavelength. The film has maximum absorbance in the UV region and has a minimum absorbance in NIR region. The absorbance of the manganese ion precursor is generally low with 0.10M manganese ion precursor having an absorbance of 34% in UV region and 5.5% in NIR region. 0.02M concentration of manganese ion precursor has an absorbance of 5% in the UV region and tends to 0% in NIR region. From the results obtained, it shows that the absorbance of the film is generally low.

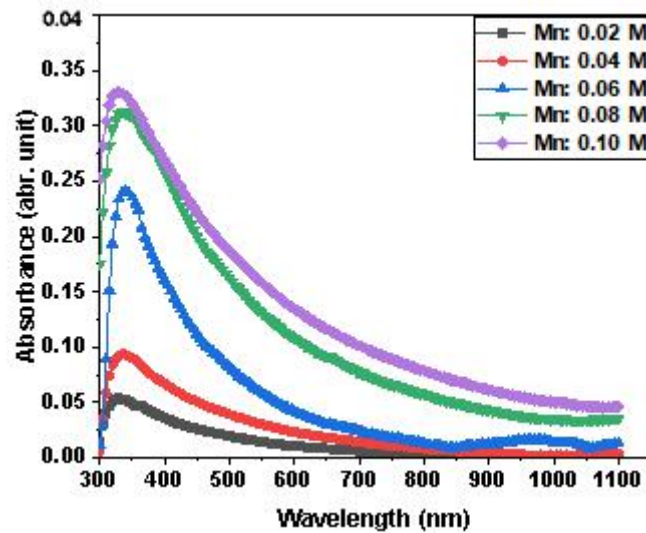


Figure 1. Graph of absorbance plotted against wavelength for CdMnO₂ deposited at different concentration of manganese ion precursor.

Figure 2 is the graph of transmittance plotted against wavelength for CdMnO₂ thin films deposited at different concentration of manganese ion precursor. The result showed that the transmittance of the films decreased with increased in concentration of manganese ion precursor. It increased with increased in wavelength. Transmittance is minimum in UV region and tends to maximum in NIR region. The transmittance of 0.10M concentration of manganese ion precursor is 48% in UV region and 56% in NIR region. 0.02M concentration of manganese ion precursor has a transmittance of 88% in UV region and 95% in NIR region. The film has a high transmittance.

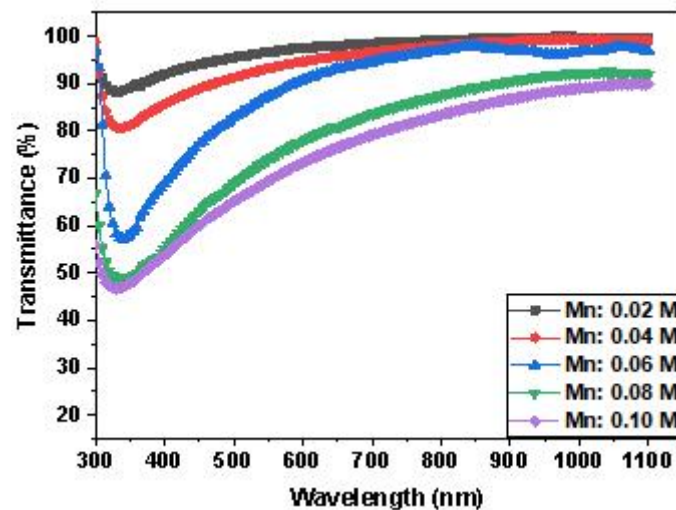


Figure 2. Graph of transmittance plotted against wavelength for CdMnO₂ deposited at different concentration of manganese ion precursor.

Figure 3 is the graph of reflectance plotted against wavelength for CdMnO₂ thin film deposited at different concentration of manganese ion precursors. From the graph, the reflectance of the films increased with increased in concentration of manganese ion precursors. It decreases with increased wavelength. 0.10M concentration reflectance of 20% in UV region and a minimum reflectance of 7% in NIR region. 0.02M concentration of manganese ion precursors has a reflectance of 6% in UV region and tends to zero percent in NIR region. Generally, the film has a low reflectance.

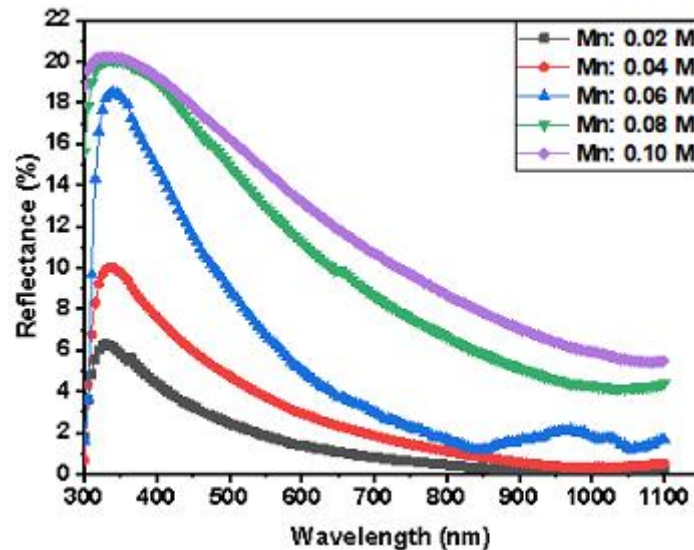


Figure 3. Graph of reflectance plotted against wavelength for CdMnO_2 deposited at different concentration of manganese ion precursor.

Figure 4 is the graph of extinction coefficient plotted against wavelength for CdMnO_2 thin films deposited at different concentration of manganese ion precursor. The extinction coefficient of the film decreased with increased wavelength. It is maximum in UV region and tends to minimum in NIR region. It increased with increase in concentration of the manganese ion precursor except for 0.08M and 0.06M concentration which deviated from the trend.

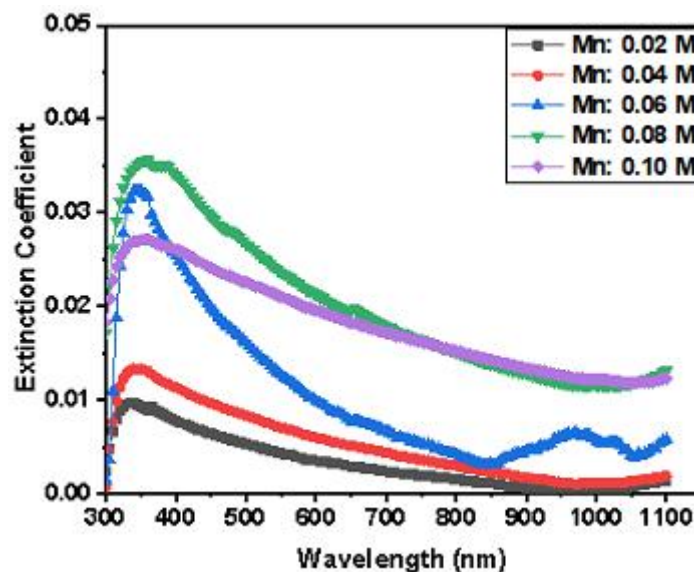


Figure 4. Graph of extinction coefficient plotted against wavelength for CdMnO_2 deposited at different concentration of manganese ion precursor.

Figure 5(a) to 5(e) is the plot of $(\alpha h\nu)^2$ against photon energy for CdMnO_2 thin film deposited at different concentration of manganese ion precursors. The bandgap range from 2.75eV – 2.40eV. From the plot, it is shown that the bandgap decreased as the concentration of manganese ion precursor increased. 0.02M concentration of manganese ion precursor has a bandgap of 2.75eV while 0.10M concentration of manganese ion precursor has a bandgap of 2.40eV.

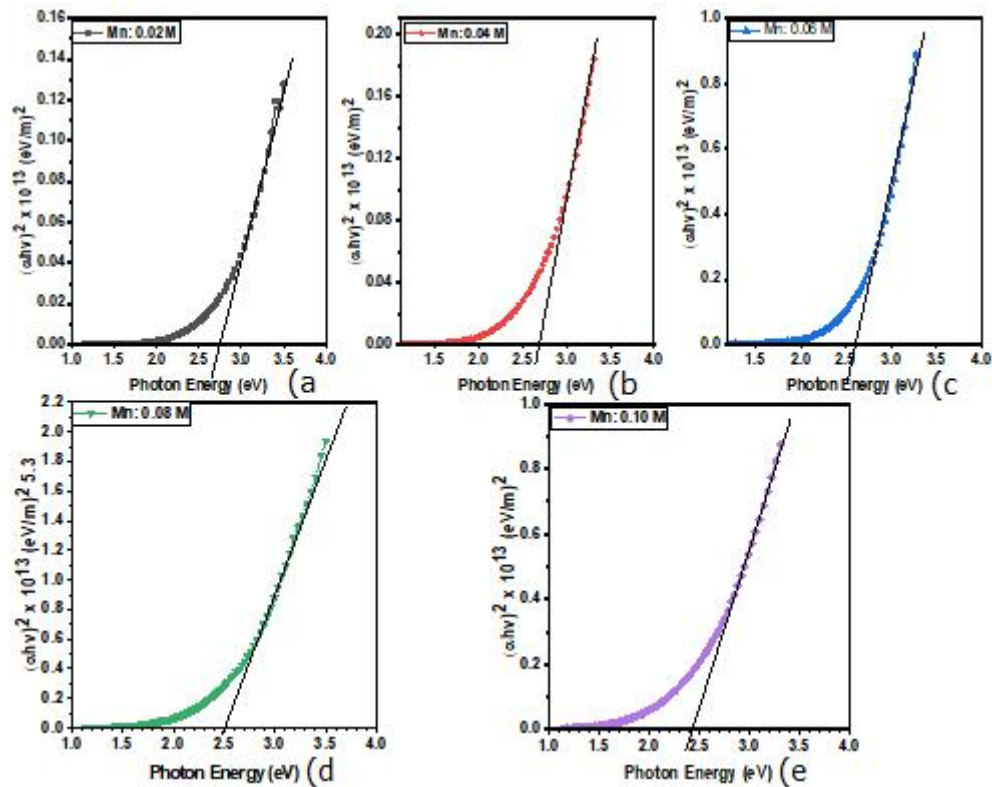


Figure 5. Plot of $(\alpha h\nu)^2$ against photon energy for CdMnO_2 thin film deposited at different concentration of manganese ion precursor.

Structural analysis of deposited CdMnO_2 thin films

Table 2. Analysis of films for various concentration of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

	$2\theta(^{\circ})$	d – spacing (nm)	FWHM ($^{\circ}$)	D (nm)	$\delta \times 10^{15}$ line/m ²	Microstrain $\times 10^{-3}$
Mn: 0.02 M	33.031	0.271	0.349	24.798	1.626	1.46
	38.344	0.235	0.345	25.44	1.545	1.423
	55.209	0.166	0.439	21.338	2.196	1.697
Average				23.859	1.789	1.527
Mn: 0.06 M	33.122	0.27	0.345	25.077	1.590	1.444
	38.327	0.235	0.328	26.805	1.392	1.351
	55.318	0.166	0.431	21.73	2.118	1.666
Average				24.537	1.700	1.487
Mn: 0.10 M	33.101	0.27	0.341	25.362	1.555	1.428
	38.353	0.235	0.351	25.027	1.597	1.447
	55.344	0.166	0.35	26.768	1.396	1.352
Average				25.719	1.516	1.409

Figure 6 is the structural analysis of the deposited CdMnO_2 thin films deposited are different concentration of manganese ion precursor. The XRD result shows that the films are polycrystalline in nature due to their different crystallite sizes. It has a cubic structure and preferred orientation in the (111) plane. It has a lattice constant of $a = b = c = 4.695\text{\AA}$. The average grain size is observed as 23.857 nm for 0.02M concentration of manganese ion precursor, 24.537 nm for 0.06M concentration and 25.719 for 0.10M concentration. The average microstrain for 0.02M concentration of

manganese ion precursor 1.527 lines/m², 1.487 lines/m² for 0.06M concentration and 1.409 lines/m² for 0.10M concentration of manganese ion precursor.

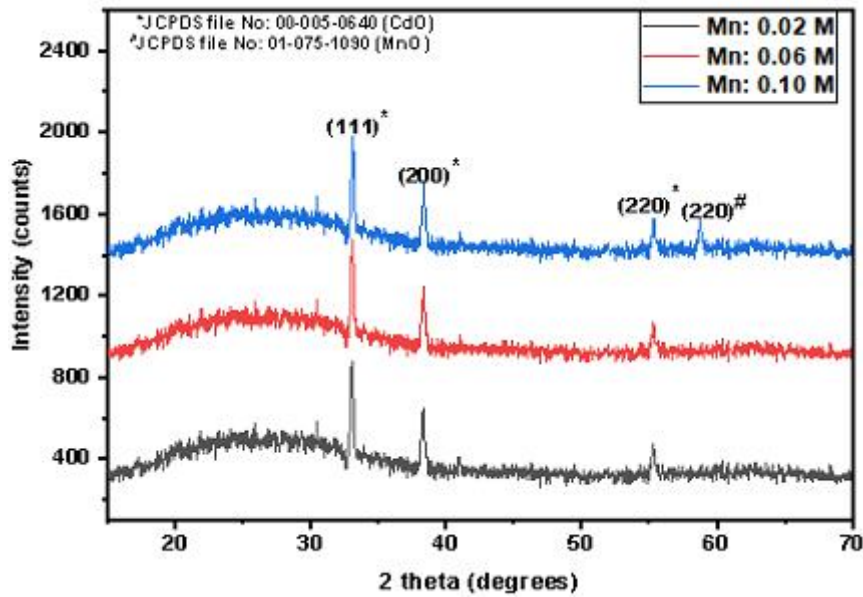


Figure 6. XRD pattern of the CdMnO₂ thin film.

Figure 7 is the micrograph image of CdMnO₂ thin films for manganese ion precursor. From the structure, it showed that the film is conglomerate of particles.

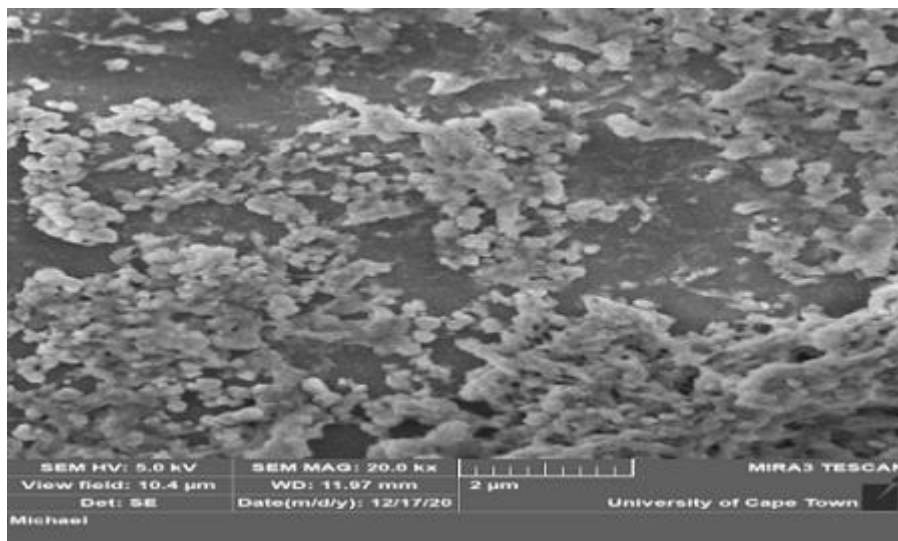


Figure 7. Micrograph image of manganese ion precursor.

Table 3. Compositional analysis.

Compositional elements	C	O	Na	Mg	SI	Ca	Mn	Cd	Total
Spectrum 5	13.05	40.8	4.72	1.33	14.24	1.63	2.48	35.75	100

Figure 8 is the variation of the thickness (nm) against the concentration of manganese ion precursor. It was observed that as thickness increased, the concentration of manganese ion precursor increased. The thickness of the film increased from 314.720nm to 758.899nm.

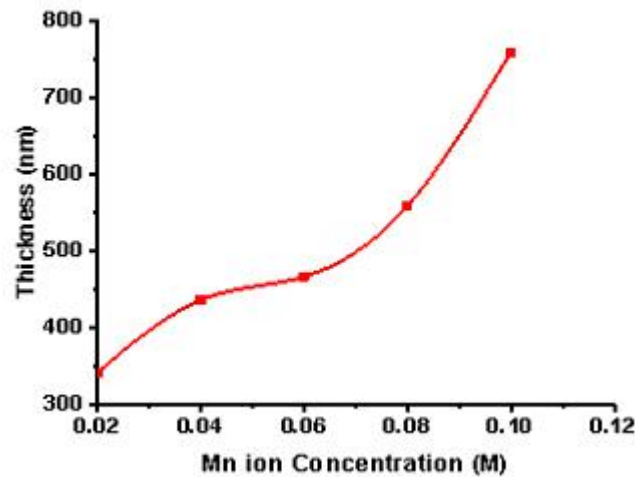


Figure 8. Variation of the thickness of the films with concentration of manganese ion precursor.

Figure 9 is the compositional analysis of the CdMnO₂ thin films deposited at the concentration of manganese ion precursor. It was observed that the component elements of oxygen (40.8%) manganese (2.48%) and cadmium (35.75%) were all deposited on the substrate. Other elements carbon, sodium, silicon and calcium could be impurities from the substrate.

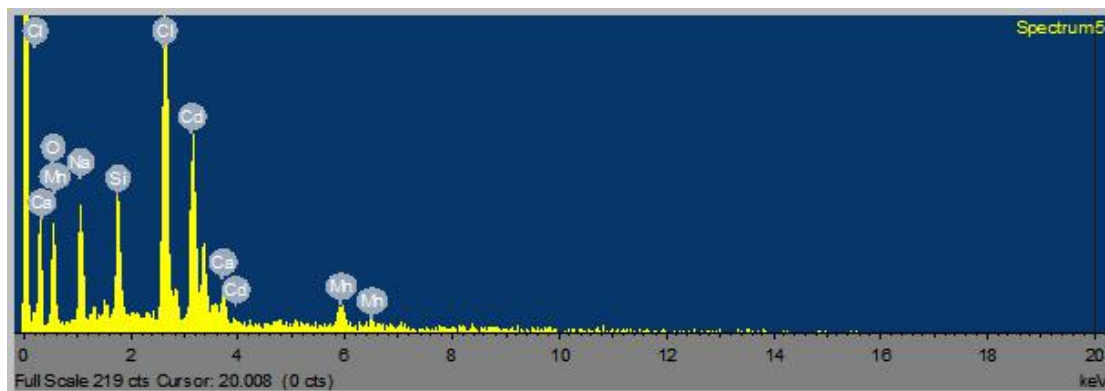


Figure 9. Compositional structure of CdMnO₂ thin films.

5. Conclusions

Manganese alloyed cadmium oxide (CdMnO₂) were carefully deposited on a substrate by solution growth technique. The optical characteristic of the CdMnO₂ thin film showed that the absorbance, reflectance extinction coefficient, real and imaginary dielectric constant, refractive index and optical conductivity respectively generally increased with increased wavelength. They increased with increase in concentration of manganese ion precursor. They are generally maximum in UV region and tends to minimum in NIR region. The transmittance of the thin film increased as wavelength increased.

The film decreased as the concentration of manganese ion precursor increased. It is minimum in UV region and maximum in NIR region. The bandgap of the films decreased as the concentration of manganese ion precursor increased. It ranges from 2.75eV – 2.40eV. The bandgap values were found to be 2.75eV, 2.70eV, 2.60eV, 2.50eV and 2.40eV respectively for 0.02M, 0.04M, 0.05M, 0.08M and 0.1M concentration of manganese ion precursor. The XRD pattern of CdMnO₂ thin films deposited at various concentration of manganese ion precursor showed that they are

polycrystalline in nature due to their grain sizes. It has a preferred orientation in the (111) plane. The SEM image of CdMnO₂ thin film for manganese ion precursor showed that the film has a cubic structure. The variation of thickness with concentration of manganese ion precursor showed that the thickness increased with increased concentration. The compositional structure of the CdMnO₂ thin films showed that manganese, cadmium and oxygen were deposited on the substrate.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Author Contributions

Conceptualization: A.K.A., U.N.S., O.I.E.; Methodology: A.K.A., U.N.S., O.I.E.; Software: A.K.A.; Validation: U.N.S., O.I.E.; Formal analysis: A.K.A., U.N.S.; Investigation: A.K.A.; Resources: A.K.A.; Data Curation: A.K.A.; Writing – original draft preparation: A.K.A.; Writing – review and editing: U.N.S., O.I.E.; Visualization: A.K.A., U.N.S., O.I.E.; Supervision: U.N.S., O.I.E.; Project administration: U.N.S., O.I.E.; Funding acquisition: A.K.A.

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