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# Characterization of Manganese Dioxide ($MnO_2$) thin films

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**ABSTRACT**

Good quality manganese oxide thin films have been prepared with a sol-gel dip coating process. The films have been cast onto glass substrates with coatings applied for one and four minutes respectively. XRD patterns reveal that the films are amorphous in nature having only one peak corresponding to diffraction from [220] plane. The thicknesses of the films were determined from the weight difference method. In addition to the structural studies, optical characterization of pure $MnO_2$ thin films were also investigated.

## 1. INTRODUCTION

Of late, Manganese dioxide ($MnO_2$) is arousing interest of material scientists due to its inexpensive, non toxic nature. It mostly finds use as a catalyst, as a remover of dangerous waste materials and in batteries which require recharging. Bernassite and Cryptomelane are two important varieties of Manganese oxides. Manganese oxides can be prepared by a variety of experimental techniques, which require reaction conditions that are not too severe[1-4]. A sol-gel synthesis technique was used to prepare $MnO_2$ thin films [5-9] Thin films based on Manganese oxide sol-gel process has also found applications such as in battery cathodes, capacitors and chemical sensors.

## 2. EXPERIMENTAL METHODOLOGY

A 100 mL beaker was taken and cleaned thoroughly with running water and subsequently with Acetone. Measured amounts of Pure water (38mL), Potassium permanganate ($KMnO_4$) 2.4021g with a molarity of 0.1mol/L and Sodium Thiosulfate ( $Na_2S_2O_3.5H_2O$) having mass 0.754g and molarity of 0.0188mol/L were poured into the beaker. The solution was mixed thoroughly with the help of a stirrer. After preparation of solution, the solution was sonicated for 8 minutes in order to remove the organic impurities present in the solution. Similarly, two glass slides and a petridish were cleaned with running water and subsequently with acetone to remove the organic impurities which might be present on the surface of these slides. The glass slides were marked as Slide 1 and Slide 2. Weight of Slide 1 and Slide 2 were found to be 5.0301g and 4.9303g respectively. The Slide 1 was dipped in the solution for 1 minute while the Slide 2 was dipped in the solution for 4 minutes. Both glass slides were placed in different petri dishes and placed in the microwave oven for 20 minutes at a temperature of 60$^oC$. After deposition of the thin film, the glass slides were weighed again. Weight of the Glass Slide 1

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was found to be 5.0683g while the weight of glass slide 2 was found to be 4.9879g respectively. Applying following formula for calculation of weight difference, film thickness was calculated.

$$t = \frac{w_2 - w_1}{A\rho} \times 10^4 \ \mu m$$

Where $W = W_2 - W_1$. Where $W_2$ is the weight of the glass slide with film deposited on it while $W_1$ is the weight of the glass slide without the deposition of thin film. 'ρ' is the density of $MnO_2$ while A is the area of the thin film deposited which in the present case was found to be 18.96 sq. cm.

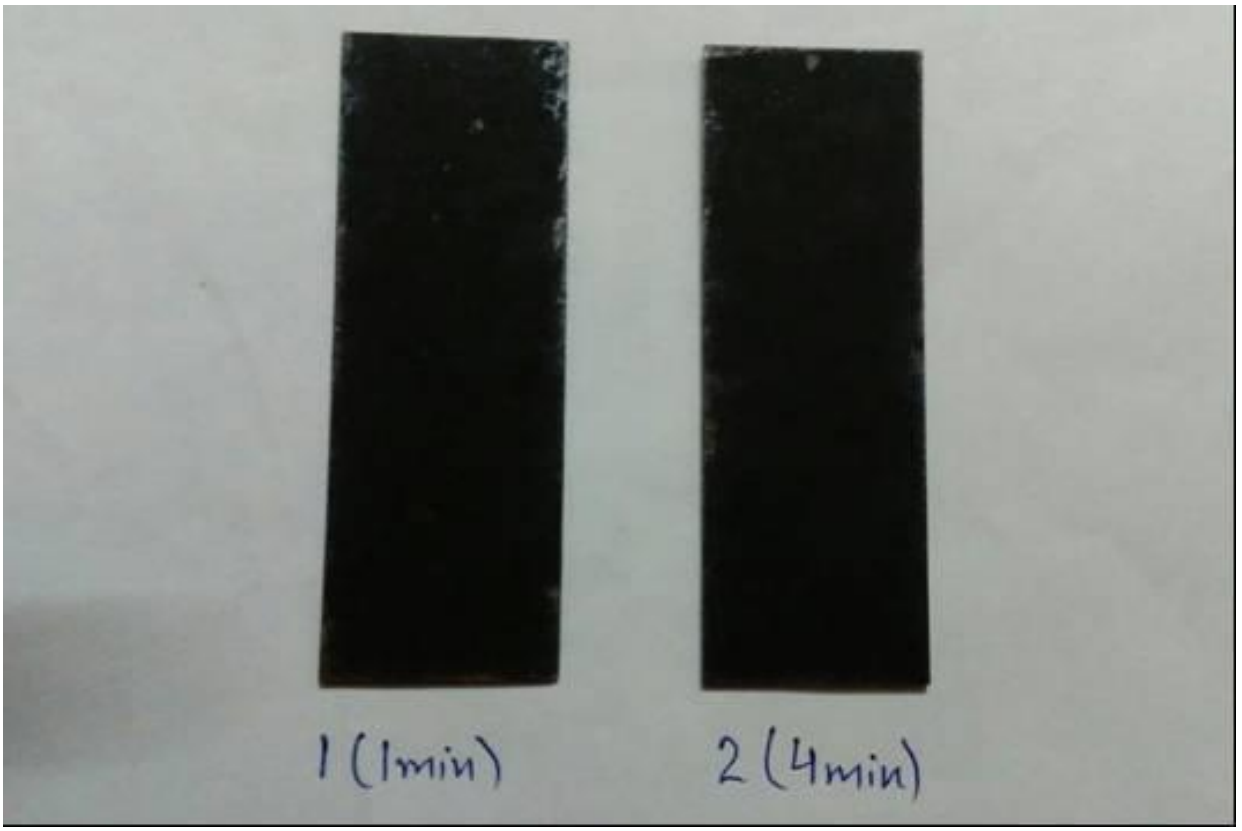


Fig. 1 Films deposited for different deposition times(Sample 1, 1 minute, Sample 2, 4 minutes)
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## 3. RESULTS AND DISCUSSION

The spectrometer used for measuring absorbance of thin film of Manganese dioxide at different wavelength is shown in the given diagram. Optical absorbance spectra of Manganese dioxide thin films were recorded on UV 1601, SHIMADZU make.

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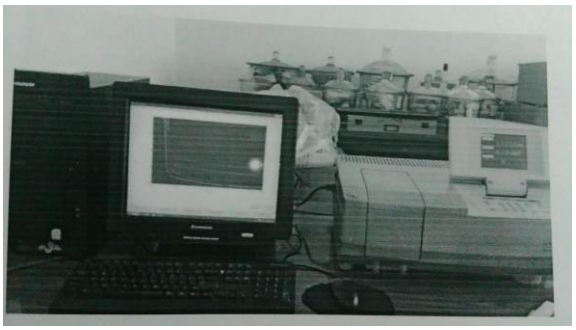

Fig.1 UV Spectrometer used for recording spectrographs.

Fig.2 Two probe set up for resistivity measurement

Band gap was calculated from UV-Visible spectrographs using Tauc's relation

$$\alpha h\nu = K(h\nu - Eg)^{n}$$

'n' can take values as 2 for direct band gap while ½ for indirect band gap.

$E_g$ = band gap while K = constant . The absorption coefficient

α is given by

$\alpha = 2.303A/t$

where, A is absorbance and t is thickness of the thin film samples.

From the graphs, mean energy gap for the thin film samples was found to be 2.45eV which is almost comparable to as reported in the literature (2.33eV).

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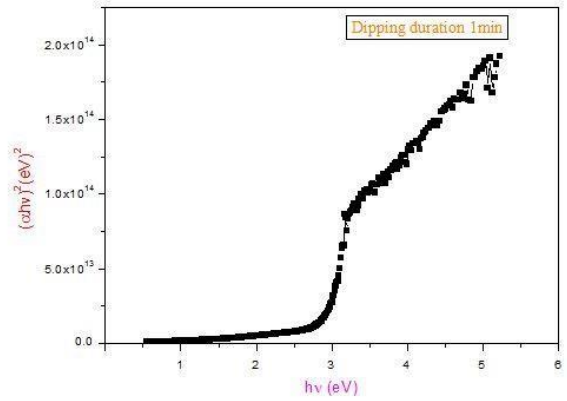


Fig. 3 Direct band gap for the 1st sample (dipping time 1 Minute)

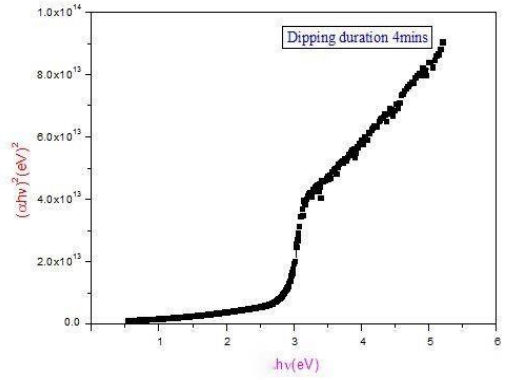


Fig. 4 Direct band gap of 2nd sample (dipping time 4 minutes)

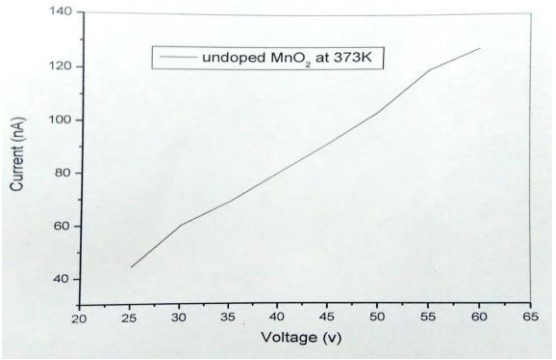


Fig.5 Voltage current graph at 100$^{o}$C

Voltage current of the films were recorded using a two probe set up and a pico-ammeter which was of Keithley Make. Thin copper wires were bonded on to the thin films samples with Silver Paste supplied by BPB Technologies, Mumbai. The V-I Characteristics were recorded at 100$^{O}$C . The characteristics showed an almost linear behaviour which confirmed that the metal contacts were ohmic in nature. This behaviour may be attributed to the fact that the mobility change of the charge carriers through the thin films is regular one.

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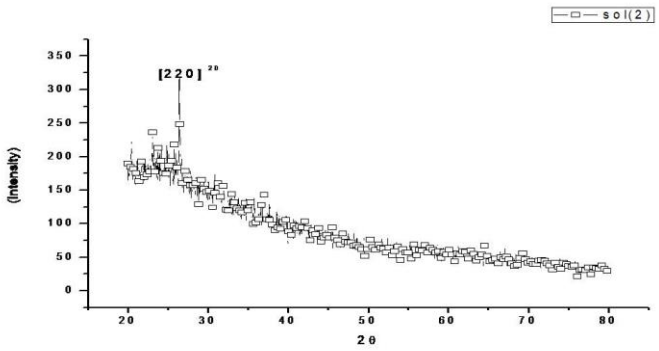
### 3.1 Structural properties

To determine structural properties, XRD studies were carried out. From the XRD, the diffracting planes, lattice parameters and crystalline behaviour of the thin films were determined. The diffractometer was Pan analytical make. From the XRD graph, it was determined that the films is amorphous in nature with sole peak obtained at an angle of $26^0$ corresponding to the diffracting plane [220].

The lattice parameters of 'a = 9.61 Å' and 'c= 6.45Å' indicate that the films have tetragonal structure.




4. **Conclusions:** From the absorbance spectra, it has been concluded that the absorbance is high and transmittance is low. This is due to the greater thickness of the films which is in micrometer range. The thin films have wide energy band gap, which agrees with the energy band gap values reported in the literature. These films can be used as electrodes for batteries and pigment in paints. Also the films deposited have amorphous structure.

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