Preparation and Characterization of Jet Nebulizer Sprayed MnO$_2$ Thin Films

M. Balaji $^{a,*}$, M. Ramamurthy $^b$, M. Raja $^c$, M. Thirumoorthy $^a$

$^a$Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam – 638401, Tamil Nadu, India
$^b$Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore - 641020, Tamil Nadu, India.
$^c$Department of Physics, RVS College of Engineering and Technology, Coimbatore - 641402, Tamil Nadu, India.

*Corresponding Author

balayours555@gmail.com

(M. Balaji)

Tel.: +91 9003555938

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ABSTRACT: We report that the jet nebulizer spray (JNS) coating is a promising route to acquire Manganese dioxide (MnO$_2$) thin films for different substrate temperatures, mole concentrations and volume of solution. The structural, optical, dc electrical conductivity properties of prepared MnO$_2$ thin films were measured by various techniques. In thickness measurement, the minimum thickness values were obtained for the substrate temperature of 500°C, mole concentration of 0.1 M and volume of solution 5 ml. From the X-ray diffraction (XRD) analysis, the films were polycrystalline with a tetragonal structure of MnO$_2$. The scanning electron microscope (SEM) images displayed the dissimilarities of the sub-micromized flower-like structure. The elements of Mn and O presence and functional group analysis were confirmed by the energy dispersive X-ray spectroscopy (EDX) analysis and Fourier-transform infrared spectroscopy (FTIR). From the ultraviolet-visible (UV-vis) analysis and current-voltage (I-V) characterization, 6% Ru doped MoO$_3$ film exhibited maximum transmittance in the visible region and maximum conductivity for the substrate temperature of 500°C, mole concentration of 0.1 M and volume of solution 5 ml.

Keywords: MnO$_2$ thin films, JNS pyrolysis, Optimization, Substrate temperature

1 Introduction

Manganese dioxide (MnO$_2$) is a transition metal oxide. It has many opto-electronic applications. It is black in color and is used as electrode materials [1, 2], rechargeable batteries, catalysts, sensors [3], electrochemical capacitors [4, 5], magneto electronic devices [6]. The MnO$_2$ was used as a substrate in the synthesis of magnetic oxide perovskite compounds, which have a variety of electrical and magnetic properties like metal-insulator transistors and a colossal magneto resistance [7–9]. MnO$_2$ of different structures are deposited using several techniques such as sol-gel [6], MOCVD [10], thermal evaporation in vacuum [11], spray pyrolysis. Manganese oxide of different structure (MnO, Mn$_2$O$_3$, MnO$_2$ and Mn$_3$O$_4$) is usually prepared by varying calculations condition of starting chemical precursor bulk or film. They can also be prepared each other by varying the temperature and atmosphere (vacuum or air, oxygen, hydrogen etc.,) of the calcinations. Electrochemical capacitor, also known as supercapacitor, is a promising energy storage device for meeting the high-power electric market [12,13]. Several metal oxides and hydroxides for example, those of Ni, Co, V, and Mn, have been studied extensively for high power redox supercapacitor applications [14–15]. Among the metal oxides, manganese dioxide (MnO$_2$) is one of the promising materials due to its availability, cost-effectiveness and non-toxicity.

In the present work, the process of jet nebulizer spray (JNS) pyrolysis technique is optimized to prepare MnO$_2$ films with good adherence, uniformity and stability. The structure, composition and optoelectronic properties
of the MnO$_2$ thin films depend on the heat treatment temperature. A detailed study has been carried out to prepare MnO$_2$ thin films by the JNS spray technique and their properties are presented.

2. Experimental

2.1 Synthesis of material

The solution was prepared with 0.1 M of manganese chloride in 100 ml of triple distilled water. For increasing the solubility of the solute few drops of concentrated hydrochloric acid was added to the solution. The mixed solutions were stirred well and heated for three hours at 60°C. This solution was sprayed onto glass substrates heated at temperatures 300, 350, 400, 450 and 500°C in air. So that, pinhole free and uniform MnO$_2$ films of thickness about 246 – 295 nm were obtained.

3. Results and Discussion

3.1 Variation of film thickness with temperature, concentration and volume of solution

The variation in thickness about 246 – 295 nm of the JNS coated MnO$_2$ films with the different temperature 300, 350, 400, 450 and 500°C are shown in Fig 1 (a). The variation was found to be linear up to 450°C and no appreciable change in film thickness was observed. Beyond 450°C, the thickness variation is saturated. Hence, in the present study 450°C was fixed for all other studies. The variation in thickness 206 – 266 of the JNS coated MnO$_2$ films with the concentration of solution 0.05, 0.10, 0.15 and 0.20 M is shown in Fig 1 (b). The variation was found to be linear up to 0.10 M and no appreciable change in film thickness was observed when heated at a temperature of 450°C. Beyond 0.10 M, the thickness is increased. Hence, in the present study 0.10 M concentration was fixed for all other studies. The variation in thickness 223 – 298 nm of the JNS coated MnO$_2$ films with volume of solution 1, 3, 5 and 7 ml is shown in Fig 1 (c). The thickness was found that for 5 ml is minimum. Hence, in the present study 5 ml volume of solution was fixed for all other studies [16].

3.2 Structural properties of MnO$_2$ thin films

3.2.1. XRD results of MnO$_2$ film deposited with different volume of spray

With the deposition temperature fixed at 450°C, the volume of manganese dioxide precursor solution was changed as 1, 3, 5 and 7 ml. XRD spectra were recorded.

![Figure 1](attachment:image.png)
Fig 2 shows these XRD spectra, where broad peaks are observed at minimum volume. Peaks at (200), (301), (400) and (310) correspond to the formation of tetragonal structure. The well defined peaks are observed with the 5 ml solution points to the optimum solution volume. Above this, the intensity of the peaks becomes less.

**Figure 2** XRD pattern of MnO₂ films prepared at different volume of solution a) 1ml b) 3ml c) 5ml and d) 7ml.

### 3.2.2. XRD results of MnO₂ film deposited with different concentration

With the deposition temperature and volume fixed at 450°C and 5ml, the manganese dioxide concentration was changed as 0.05, 0.10, 0.15 and 0.20 M. XRD spectra were recorded.

**Figure 3** XRD pattern of MnO₂ films prepared at different concentration a) 0.05 M b) 0.10 M c) 0.15 M d) 0.20 M.

Fig 3 shows these XRD spectra, where broad peaks are observed at larger concentration. Peaks at (301), (311) and (321) correspond to the formation of tetragonal (β-MnO₂) structure. The well defined peaks are observed with the 0.10 M concentration points to the optimum concentration. Above this, the peaks become very broad revealing reduced crystallinity.

### 3.2.3. Structural properties of MnO₂ films with temperature

Study of varying the temperature of deposition is the main step, which will increase the crystallinity, stoichiometry and other structural related defects of oxide films. Fig 4 shows the XRD of MnO₂ films deposited at different substrate temperatures of 300, 350, 400, 450 and 500°C in air atmosphere. At a lower temperature of 350°C, the peaks corresponding to MnO₂ phase started appearing. From the figure, it is observed that the films are polycrystalline with preferred orientation along (301). Other XRD peaks pertain to (200), (211), (212) and (310) directions are also present. All the diffraction peaks seen in the Fig. 4 confirm the tetragonal structure [17] of the JNS spray coated MnO₂ films. Temperature increases the intensity of the preferred orientation of (301) indicating an increased crystallinity with temperature. The intensity of the (200), (211), (212) and (310) peaks also increase with temperature. However no other phases usually found at elevated temperatures, have been observed in the present JNS coated MnO₂ films prepared by spraying in the temperature range 300 - 500°C.
Figure 4 XRD pattern of MnO$_2$ films prepared at different substrate temperatures a) 300°C b) 350°C c) 400°C d) 450°C e) 500°C. It is an interesting result that the developed XRD peaks are found in the films heated even at a relatively low temperature of 350°C in the present study.

Table 1 shows the micro structural properties of MnO$_2$ films deposited at different substrate temperatures. The hkl and d values for the MnO$_2$ films deposited at different temperatures are agreeing well with the values found in JCPDS card. The calculated value of lattice parameter, a = 8.9634 Å and 9.809 Å [17, 18].

The crystallite size (D) was calculated from the full width at half maximum (FWHM) $\beta$ of the prominent XRD peaks using the Scherrer-Bragg relation.

The variation of micro structural parameters like grain size, dislocation density, micro strain and number of crystallites with deposition temperature is shown in Table 1. It shows that the grain size reaches a maximum at 450°C and then decreases as shown in Table 1. The crystallite size varies in the range 49.16 nm to 137.68 nm as the temperature of MnO$_2$ film deposition increases from 350 to 500°C. Dislocation density and micro strain are found decreasing up to 450°C and then increase as and FWHM is found increasing up to 450°C and then deceases (Table 1).

3.3. SEM studies of MnO$_2$ films

The surface morphology of MnO2 films deposited at 350, 400, 450 and 500°C are shown in Fig 5 (a), (b), (c) and (d) respectively. Non-uniform surface feature is observed for the MnO$_2$ film deposited at 350°C. The grain growth and flower shape nanowires of the surface improved at the temperature 450°C [19]. Nanowires are

<table>
<thead>
<tr>
<th>Substrate temperature °C</th>
<th>(301) Inter planar distance Å</th>
<th>Unit cell side (a) Å</th>
<th>FWHM (degree)</th>
<th>Grain size (D) nm</th>
<th>Micro strain ($\varepsilon$) x $10^{-3}$</th>
<th>Dislocation density x$10^{14}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
<td>2.83449</td>
<td>8.956044</td>
<td>0.110</td>
<td>49.162933</td>
<td>0.193288</td>
<td>0.000414</td>
</tr>
<tr>
<td>400</td>
<td>2.83204</td>
<td>8.955697</td>
<td>0.140</td>
<td>58.996254</td>
<td>0.191430</td>
<td>0.000287</td>
</tr>
<tr>
<td>450</td>
<td>2.83215</td>
<td>8.963445</td>
<td>0.168</td>
<td>137.68306</td>
<td>0.189723</td>
<td>0.000053</td>
</tr>
<tr>
<td>500</td>
<td>2.82521</td>
<td>8.934099</td>
<td>0.060</td>
<td>75.080589</td>
<td>0.196405</td>
<td>0.000177</td>
</tr>
</tbody>
</table>

It is an interesting result that the developed XRD peaks are found in the films heated even at a relatively low temperature of 350°C in the present study.

3.4. EDX analysis

The stoichiometry analysis of the elements present in the MnO$_2$ thin film was carried out by EDX results. Fig 6 shows the EDX pattern of the MnO$_2$ film deposited under the optimized conditions deposited at different temperatures of 350°C, 400°C, 450°C and 500°C. From the EDX spectrum it is observed that the prepared MnO$_2$ has nearly the stoichiometric ratio of Mn and O but with oxygen deficiency. The ratio of Mn:O is found to be 46.94 : 31.16. This is clear evidence that this oxygen deficiency gives lower resistivity to MnO$_2$ films heated at 450°C.
450°C in the present study. EDX spectrum and atomic composition of the nano and micro structured MnO₂ on the glass substrates are shown in Fig 6. The atomic and mass percent values of the elements in the MnO₂ structures on the glass substrates are presented in table 2. The concentrations of these elements are indicated by the peaks, which clearly show that the elements corresponding to the peaks comprise the MnO₂ on the glass substrate [20].

**Figure 5** SEM pictures of the MnO₂ films deposited at different substrate temperatures a) 350°C b) 400°C c) 450°C d) 500°C.

**Figure 6** EDX spectra of MnO₂ films with different substrate temperatures a) 350°C b) 400°C c) 450°C d) 500°C.
Table 2 Atomic and mass percentage of the MnO2 films prepared at different substrate temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Mn Atomic %</th>
<th>O Atomic %</th>
<th>Mn Mass %</th>
<th>O Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>36.47</td>
<td>46.24</td>
<td>45.79</td>
<td>33.07</td>
</tr>
<tr>
<td>400</td>
<td>37.16</td>
<td>44.42</td>
<td>46.31</td>
<td>31.54</td>
</tr>
<tr>
<td>450</td>
<td>37.65</td>
<td>44.86</td>
<td>46.94</td>
<td>31.16</td>
</tr>
<tr>
<td>500</td>
<td>31.16</td>
<td>44.10</td>
<td>37.22</td>
<td>31.85</td>
</tr>
</tbody>
</table>

3.5. Optical properties of MnO2 thin films

3.5.1. UV-vis results of MnO2 film deposited with different volume of spray

Fig. 7 shows the transmission spectra in the wavelength region of 320 – 900 nm for the MnO2 films deposited at different volume 1, 3, 5 and 7 ml. The transmittance maximum is around 85% at 650 nm. However, the transmission value decreases steeply in the UV region i.e. less than 400 nm [16].

![Figure 7 Optical transmission spectra of MnO2 films with different volume](image1)

The average percentage transmission for all the MnO2 films is in the recorded wavelength region of 320-900 nm. It is observed that as the volume increases, the percentage of transmission increases. Maximum percentage transmission is recorded for the MnO2 film deposited at a volume of 5 ml, which is optimized for all studies.

3.5.2. UV-Vis results of MnO2 film deposited with different concentration of spray

Fig 8 shows the transmission spectra in the wavelength region of 350 – 900 nm for the MnO2 films deposited at different concentration 0.05, 0.10, 0.15 and 0.20 M. The transmittance maximum is around 85% at 650 nm. However, the transmission value decreases steeply in the UV region i.e. less than 400 nm.

![Figure 8 Optical transmission spectra of MnO2 films with different concentration](image2)

The average percentage transmission for all the MnO2 films is in the recorded wavelength region of 350-900 nm. It is observed that as the concentration increases, the percentage of transmission decreases. Maximum percentage transmission is recorded for the MnO2 film deposited at a concentration of 0.10 M, which is optimized by high transmission.

![Figure 8 Optical transmission spectra of MnO2 films with different concentration](image2)
3.5.3. UV-Vis results of MnO₂ film deposited with different substrate temperature

Fig 9 shows the transmission spectra in the wavelength region of 320 – 900 nm for the MnO₂ films deposited at different heating temperatures 300, 350, 400, 450 and 500°C. The transmittance maximum is around 80% at 650nm. However, the transmission value decreases steeply in the UV region i.e. less than 400 nm [21,22]. The average percentage transmission for all the MnO₂ films is in the recorded wavelength region of 320 – 900 nm. It is observed that as the heating temperature increases, the percentage of transmission increases. Maximum percentage transmission is recorded for the MnO₂ film deposited at a temperature of 450°C.

![Figure 9 Optical transmission spectra of MnO₂ films with different substrate temperatures a) 300°C b) 350°C c) 400°C d) 450°C e) 500°C.](image)

The variation of \((\alpha h \nu)^2\) versus \((h \nu)\) for the MnO₂ films deposited at different temperatures is shown in Fig 10. The straight line portion indicates that the optical transition is direct in nature. The direct gap value has been determined by extrapolating the vertical straight line portion of the plot to the energy axis. The intercept on energy axis gives the values of band gap energy 2.25, 2.08, 2.15, 2.36 and 2.28 eV for the MnO₂ films heated at 300, 350, 400, 450 and 500°C respectively, which is in good agreement with the reported value of 1.4eV and 2.30 eV [16,22]. Here 450°C exhibits higher band gap energy. These results show that MnO₂ film deposited at 450°C with 5 ml sprayed coating has good optical transmission property and higher band gap value.

![Figure 10 Band gap energy of MnO₂ films with different substrate temperatures a) 300°C b) 350°C c) 400°C d) 450°C e) 500°C.](image)

5.6. FTIR results of MnO₂ film deposited with different substrate temperature

FTIR spectra of MnO₂ thin film samples in the range 4000–800 cm⁻¹ are shown in Fig 11. FTIR spectroscopy analysis was also utilized to characterize the obtained samples, with an intention to get more information about the sprayed MnO₂ thin films.

![Figure 11 FTIR Spectra of different substrate temperatures.](image)

Generally, it was accepted that the peak observed at 1003–780 cm⁻¹ indicate Mn-O bond characteristically and the peak at around 2924 and 1589 cm⁻¹ [23,24] stands for the presence of structural and bending vibrations of OH groups in the mineral structure.
of manganese oxide. Thus results indicated that, as MnO₂ film contained hydroxide and Mn–O bonds, which indicates that formation of hydrous MnO₂ that may play important role in capacitive behaviour [25]. Additionally, any other functional groups are not involved. Therefore, the FTIR spectra, further confirm the formation of the product.

5.7. Electrical properties of MnO₂ thin films

The four probe measurement gives all the JNS deposited MnO₂ films resistivity (ρ) and conductivity (σ) of the MnO₂ films measured at room temperature are shown as a function of the deposition temperature in Fig 12.

![Figure 12 (a) Variation of resistivity of MnO₂ films with substrate temperature.](image)

As the temperature is increased, resistivity is found decreasing. This is due to the observed increase in grain size with temperature. The electrical values measured in the present work are showing similar trend with the reported values [26]. Fig. 12 (a) shows the variation of ‘p’ values with deposition temperature. The values are in the range of 1.275 x 10² Ω cm to 3.456 x 10² Ω cm. Minimum value of 1.275 x 10⁻³ Ω cm is observed for the MnO₂ film deposited at 450°C. Fig 12 (b) shows the conductivity variation starting from 3.23 x 10⁻⁵ to 5.84 x 10⁻⁵ S/cm for the film heated at 300°C - 500 °C, reaching a maximum of 5.84 x 10⁻⁵ S/cm for the film deposited at 450°C. Then it shows a slight decreasing trend, showing 4.82 x 10⁻⁵ S/cm for the 500°C film.

6. Conclusions

The JNS pyrolysis coating has been used to prepare highly transparent as well as conducting MnO₂ films. At the optimum deposition temperature of 450°C with 5 ml solution volume, the transmittance is about 80 % with a band gap of 2.08 to 2.36 eV and the resistivity is found to be a minimum of 1.275 x 10² Ω cm. The present study clearly shows that device quality and uniform grained MnO₂ films can be prepared with a resistivity of about 10⁻² Ω cm with nano grains. A high band gap of 2.36 eV can be prepared by the JNS technique by depositing at a temperature of 450°C. The SEM and XRD studies confirm the presence of MnO₂ nano crystallites with tetragonal structure.
References


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**Competing Interests:**

The authors declare that they have no competing interests.

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