Characterization of Spray Deposited ZnMn$_2$O$_4$ Nanostructured Thin Films

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ABSTRACT

In this study, the undoped MnO$_2$ was deposited using spray pyrolysis technique. The manganese (II) acetate tetra hydrate was taken as 0.1M. The film was then annealed at 450°C for 5 h to obtain crystalline peak. The XRD result for the undoped MnO$_2$ film shows (110) plane peak with maximum intensity. Optical property shows an increase in transmittance for annealed film and band gap was found to be 2.4 eV. The Electrical property indicates the semiconducting nature of the film. The ZnMn$_2$O$_4$ film was obtained from aqueous solution manganese (II) acetate tetra hydrate and Zinc acetate dihydrate salt of 0.01:0.01 molar concentration. After annealing the film at 450°C for 5 h, the crystalline peak was observed. The XRD results of ZnMn$_2$O$_4$ film shows crystalline peaks of (211) and (111) plane. The optical properties shows an increase in transmittance than MnO$_2$ film. The structural, electrical and morphology properties of the film as a function of annealing temperature were analysed and reported.

Key words: MnO$_2$ thin films, ZnMn$_2$O$_4$ thin film, spray pyrolysis

INTRODUCTION

Manganese dioxide is a low band gap, high optical constant semiconductor that exhibits ferroelectric properties (Bhide et al., 1959; Koops, 1951). Manganese dioxide (MnO$_2$) is a widely used material featuring low-cost, high energy density, environmental pollution free and nature abundance (Komaba et al., 2008; Ma et al., 2008). The principal use of MnO$_2$ is in dry-cell, alkaline and zinc-carbon batteries. ZnO is a wide-bandgap semiconductor and has several favorable properties, including good transparency, high electron mobility, wide bandgap and strong room-temperature luminescence. Most of the research focuses on the optical properties of ZnO due to its excellent ultraviolet, blue and green light emission (Zu et al., 1997; Huang et al., 2001; Jin et al., 2003; Inoue et al., 2006). ZnO is a kind of nontoxic material with good biodegradability and biocompatibility (Zhou et al., 2006). ZnO is a promising semiconductor for optical devices due to its nonlinear optical property and excitonic emission at room temperature (Sakohara et al., 1992; Kind et al., 2002; Look, 2001). The ZnMn$_2$O$_4$ is a promising functional material and has become the focus of various researches owing to its potential applications. The ZnMn$_2$O$_4$ could be used for the negative temperature coefficient thermistors on account of their unique electrical properties.
Ferraris et al. (2002) suggested that ZnMn2O4 was an efficient catalyst for the reduction of NO to N2 and, in all cases, its best selectivity to N2 and CO2 was at almost the maximum conversion temperature (Fierro et al., 2005; Ferraris et al., 2002). ZnMn2O4 has obvious advantages because of its much lower toxicity, cost, and operating voltage (average discharge and charge voltages of 0.5 V and 1.2 V, respectively) compared with the Co or Fe oxides (Yang et al., 2008).

There are various techniques are used to deposit the MnO2 and ZnMn2O4 thin films. They are reactive deposition (Rizzi et al., 2000), sol-gel (Long et al., 2001; Minami et al., 2000), plasma assisted molecular beam epitaxy (Guo et al., 2001), r.f. sputtering (Fau et al., 1994), thermal decomposition (Farid Ul Islam et al., 2005), spray pyrolysis (Farid ul Islam et al., 2007), solid-state reaction (Li et al., 1999; Hao et al., 2011), co-precipitation method (Zhai et al., 2011) and hydrothermal method (Duan et al., 2010; Cheng et al., 2014). Among the various methods are used to deposit the thin films, in this work spray pyrolysis was used. Spray pyrolysis having many advantages comparing to other deposition techniques. Some of their advantages are; they can cover large area during deposition, low cost and the surface volume ratio can be controlled here. In this work, the undoped MnO2 and ZnMn2O4 thin films were deposited on glass substrates and their structural, optical and electrical properties are studied and the results are discussed.

MATERIALS AND METHODS

The materials used for the deposition of undoped MnO2 and ZnMn2O4 thin films are Zinc acetate dihydrate (C6H5O2Zn.2H2O) in reagent grade (RA) and Manganese (II) acetate tetra hydrate (CH3COO)2Mn.4H2O) in analytical reagent grade. The chemicals were purchased from Sigma Aldrich and Merck and the purity form of Manganese (II) acetate tetra hydrate is >99.5% and for Zinc acetate dihydrate, it is 99.9%.

The undoped MnO2 thin film samples were deposited by spray pyrolysis technique. The spray solution was prepared from 0.1 M of Manganese (II) acetate tetra hydrate and dissolved in 50 mL of de-ionized water. The thin films were deposited on glass substrate (Labtech Medico (P) Ltd). The distance between the spray gun and substrate was kept at 50 cm. The nozzle angle was kept at 45°. The substrate temperature was maintained at 250°C. The solution was sprayed at the glass substrates. The prepared thin films were annealed at 420°C for 5 h.

The ZnMn2O4 thin films were prepared from the precursor solution containing Zinc acetate dehydrate and Manganese (II) acetate tetra hydrate with 0.01M. The films were deposited on glass substrate (Labtech Medico (P) Ltd). The deposition parameters for undoped MnO2 and ZnMn2O4 thin films were given in Table 1. The substrate temperature was maintained at 220°C. The deposited thin films were annealed at 400°C for 5 h to attain the crystalline nature.

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Undoped MnO2</th>
<th>ZnMn2O4</th>
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</thead>
<tbody>
<tr>
<td>Precursor salt</td>
<td>Manganese (II) acetate tetra hydrate</td>
<td>Manganese (II) acetate tetra hydrate and Zinc acetate dehydrate</td>
</tr>
<tr>
<td>Molarity of precursor salt</td>
<td>0.1M</td>
<td>0.01M</td>
</tr>
<tr>
<td>Volume of the solution</td>
<td>50 mL</td>
<td>50 mL</td>
</tr>
<tr>
<td>Nozzle angle</td>
<td>45°</td>
<td>45°</td>
</tr>
<tr>
<td>Distance between gun and the substrate</td>
<td>50 cm</td>
<td>50 cm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>250°C</td>
<td>220°C</td>
</tr>
<tr>
<td>Spray time between each cycle</td>
<td>15 sec</td>
<td>15 sec</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Compressed air</td>
<td>Compressed air</td>
</tr>
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thin films were allowed to cool on room temperature and then they are used for various studies. During the spray process, compressed air was used as a carrier gas for both films.

The structural properties were characterized by X-ray diffraction (XRD) (D8, Focus Bruker). The optical properties were studied by using UV-Visible-Perkin Elmer make-Model-Lambada 35 (Range 190-1000 nm) spectrophotometer. The surface morphology of the undoped MnO$_2$ and ZnMn$_2$O$_4$ films were studied using Atomic Force Microscopy (AFM, Park System, XE170, Germany). The variation in resistance along with the temperature for the undoped MnO$_2$ thin films was studied using four probe methods. The photoluminescence properties for the deposited undoped MnO$_2$ and ZnMn$_2$O$_4$ thin films were studied using photoluminescence spectroscopy.

RESULTS AND DISCUSSION

X-ray diffractometer: The XRD pattern of the undoped MnO$_2$ and ZnMn$_2$O$_4$ thin films are shown in Fig. 1. From the diffracted XRD peaks the observed for both the films are found to be

![XRD pattern for undoped MnO$_2$ film and XRD pattern for ZnMn$_2$O$_4$ film](image)

Fig. 1(a-b): (a) XRD pattern for undoped MnO$_2$ film and (b) XRD pattern for ZnMn$_2$O$_4$ film

polycrystalline in nature. The phase identification is done by measure d-spacing of obtained diffraction pattern is matched with the standard JCPDS card numbers 24-0735 and 24-1133 for undoped MnO$_2$ and ZnMn$_2$O$_4$ films, respectively. The peaks observed for MnO$_2$ thin film are identified and assigned to the planes (110), (101) and (111) respectively. Similarly, the observed peaks for the ZnMn$_2$O$_4$ are identified and assigned to (211) and (111) planes. There is no characteristics peak for other elements are observed, which is confirmed by the previous research work done by Xiao et al. (2009).

The crystallite size (D) of the samples are calculated using the following equation:

$$D = \frac{K \lambda}{\beta \cos \theta}$$  (1)

where, $\lambda$ is the wavelength, $\beta$ is the Full width at half maximum intensity and $\theta$ is the Bragg angle. The obtained crystallite size for the undoped MnO$_2$ and ZnMn$_2$O$_4$ films are 148 and 69 nm, respectively. This result is satisfy the Scherer's formula, were $\beta$ is inversely proportional to D. The observed D values and FWHM values varies depends due to Zn incorporated with Mn$_2$O$_4$.

To identify the crystalline homogeneity, texture of a particular plane, (referred as the deviation from unity used to know plane of preferred growth) can be calculated by following texture co-efficient (TC) Eq. 2.

$$TC_{(hkl)} = \frac{I_{(hkl)} / I_{0(hkl)}}{N \sum i I_{(hkl)} / I_{0(hkl)}}$$  (2)

where, $I_{(hkl)}$ is measured intensity of a plane (hkl), $I_{0(hkl)}$ is standard intensity of plane (hkl) taken from JCPDS data, N is a reflection number and n is the number of diffraction peaks. TC$_{(hkl)} = 1$, for a sample with random oriented crystal percent's and the larger TCs value is larger abundance of crystallites oriented in (hkl) direction. For the undoped MnO$_2$ film it is identified as (110) plane which confirms the $\beta$-phase of MnO$_2$ (JCPDS card number 24-0735) and is well matched with the earlier reports reported by Zheng et al. (2005) and Chandru et al. (2012).

Optical properties: The optical properties of deposited films were studied from absorbance and transmittance spectra, recorded by UV-Vis spectrophotometer in the wavelength ranges from 200-1200 nm. The optical absorbance spectrum of undoped MnO$_2$ and ZnMn$_2$O$_4$ films are shown in Fig. 2a and b. The optical absorption starts to decrease and this may be due the increased grain size.

Figure 3 shows the comparison of optical transmittance spectrum of MnO$_2$ films and ZnMn$_2$O$_4$ films. For both the film samples, the transmittance is obtained in the range of 200-1200 nm. The optical transmittance of MnO$_2$ samples is found to be upto 40%. This reported value is verified with already existing reports by Farid Ul Islam et al. (2005) and it is found to be very low. The reason for the decreasing the transmittance may be due to the preparative condition. However, the transmittance obtained for ZnMn$_2$O$_4$ thin film is found to be 80%. This may be due to the incorporation of the ZnO component on the MnO$_2$.  

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Electrical studies: The resistivity for the undoped MnO$_2$ was calculated by using the following relation:

$$\rho = \frac{V}{I \times \ln 2}$$

where, V is the voltage across the crystal, I is the current through the crystal, d is the thickness of the crystal and \(\rho\) is the resistivity of the semiconductor. The room temperature electrical studies for the undoped MnO$_2$ were studied by using four probe methods. Figure 4 shows the electrical properties of the undoped MnO$_2$ thin films. The resistivity starts to increase with the increase of temperature. This shows the conducting nature of the material, the improvement in crystallinity and grain size induced higher conductivity in sample. The order of resistivity in this study agrees quite well with that of spray-deposited films. However, the resistivity obtained by this method is
so high as compared to the earlier report (Fau et al., 1994). This is because of the preparative condition of thin film. After the transition temperature, the resistivity of the material starts to decrease when the corresponding temperature is increased. This region shows the presence of negative temperature coefficient behavior of a semiconductor and the prepared MnO$_2$ films are semiconducting in nature.

**Atomic force microscopy:** The morphological study for the undoped MnO$_2$ was studied by using AFM. The AFM study is used to visualize the surface of the deposited films. The AFM image for undoped MnO$_2$, thin film is shown in Fig. 5a. The pure MnO$_2$ morphology indicated a smooth surface with flack like structure covered the entire surface. This may be due to increments of metal nucleation center which resulted to the grain growth towards prose surface from nano flacks structure. From the AFM image, it is evident that the grain size was improved upon annealing treatment. For the deposited MnO$_2$ films, the surface skewness was found to be -0.5. It is nearly equal to zero. The surface kurtosis for the prepared MnO$_2$ films was found to be 3.0. From this, we say that the peaks are sharp here.

The AFM image for ZnMn$_2$O$_4$ thin film is shown in Fig. 5b. From the AFM image, it is evident that the grain size is decreased. The surface skewness for the deposited ZnMn$_2$O$_4$ films was found to be 0.4. The obtained surface skewness was nearer to zero. The surface kurtosis was found to be 2.98. The obtained surface kurtosis value is approximately equal to three. This shows that they have sharp peak.

The line histogram is a bar graph that shows the distribution of heights along a height profile. It can display the entire range of height of the data points in a line. The width of a bar depends on the overall height range of the sample and the number of data points of the line profile.

The histogram graph for MnO$_2$ and ZnMn$_2$O$_4$ thin films was shown in Fig. 6a and b.

**Photoluminescence spectroscopy:** Photoluminescence is the spontaneous emission of light from a material under optical excitation. Photoluminescence studies provide information of different energy states available between valence and conduction bands responsible for radioactive recombination. Figure 7 shows the PL spectra of undoped MnO$_2$ and ZnMn$_2$O$_4$ thin film samples. For both films, a strong and sharp peaks excited at 231 nm was observed. The additional small
Fig. 5(a-b): AFM image for (a) MnO₂ film and (b) ZnMn₂O₄ film

Fig. 6(a-b): Histogram graph for (a) MnO₂ and (b) ZnMn₂O₄ thin films
peaks emitted at 245 nm for both MnO$_2$ and films ZnMn$_2$O$_4$. However, the intensity of the of the undoped MnO$_2$ is high compared to ZnMn$_2$O$_4$ film.

CONCLUSION
From the XRD pattern for the undoped MnO$_2$ thin films, it was clearly shown that the highly oriented peak is (110) plane due to the annealing process. They belongs to polycrystalline in nature. The grain size was calculated using the scherer formula. For the ZnMn$_2$O$_4$ thin films were polycrystalline in nature. The crystallinity of the deposited ZnMn$_2$O$_4$ thin films was improved due to the annealing process. Their grain size was calculated by using the scherer formula and they were found to be decreased. Due to the narrow peak in the undoped MnO$_2$, the grain size was increased here and their absorbance will be decreased. Finally, there was an increase in their transmittance. The transmittance for the undoped MnO$_2$ was obtained in the range of 40%. The band gap for the MnO$_2$ films was found to be 2.4 eV. Due to the broadening of the peaks in the ZnMn$_2$O$_4$ films, their grain size was decreased here, therefore their absorbance was increased and there was an increase in their transmittance. By the addition of ZnO with MnO$_2$, the transmittance of ZnMn$_2$O$_4$ was increased up to 80%. This is due to the addition of ZnO with MnO$_2$ because ZnO is a window material and they increased the transparency. The band gap for ZnMn$_2$O$_4$ films was found to be 2.6 eV. Comparing both the MnO$_2$ and ZnMn$_2$O$_4$ films, the band gap was increased to the ZnMn$_2$O$_4$ films. For the undoped MnO$_2$ thin films, it was clearly observed from the AFM that there is an increase in their grain size. The grain size was increased here and this is due to the annealing effect. In the case of ZnMn$_2$O$_4$ thin films, from the AFM, we can see that the grain size was decreased. Surface kurtosis value for both the films, which is approximately equal to three. This indicates that for both the deposited films have sharp peak. Surface skewness value for both the films was found to be nearly equal to zero. This shows that both the deposited films were found to be symmetry. The electrical studies were studied using four probe method. It shows that there is an increase in the resistivity, when temperature was increased. This shows the conducting state of the material. After the transition temperature, the resistance of the MnO$_2$ film starts to decrease along with the increase of their temperature, this is due to the presence of negative temperature coefficient. This shows that the material is a semiconductor. The FESEM for the ZnMn$_2$O$_4$ thin films, confirms that the decrease in the grain size. It shows that they are well-connected grains.
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