Annealing Effect of Magnesium Tin Oxide Thin Films Prepared by Nebulizer Spray Pyrolysis Technique for DSSC applications

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Abstract. In the present work, Magnesium Tin Oxide (MTO), transparent conducting oxide thin films (TCO) are prepared by Nebulizer Spray Pyrolysis Technique and the properties are compared with the available ITO substrate. Magnesium acetate (MA), Tin (II) chloride (TC) are taken in three different ratios (0.1:0.1M, 0.1:0.2M, 0.1:0.3M) and the thin films are prepared onto the glass substrate at 400°C. The prepared films were annealed at 400°C for three hours. The structural analysis show the presence of Magnesium Tin Oxide with maximum intensity showing the crystallinity of the prepare samples. Also, the peak corresponds to magnesium oxide and Tin oxides were also observed with less intensity. The crystallite size was found to be around 5 nm and the thickness of the film is found to be 0.23, 0.27 and 0.32 μm for the films prepared at MA: TC in the ratio of 0.1:0.1M, 0.1:0.2M and 0.1:0.3M. The sign of bulk carrier concentration shows that the coated film is having n-type conductivity and the resistivity value is very low in the range of 7 x10⁻³Ω cm which is very close to the resistivity value of ITO (8 x10⁻⁴Ω cm). The Percentage of Transmittance is between 75 to 85% in the visible region and the band gap value is 3.8 eV. From the results, it is concluded that MTO is a Best alternative for ITO and can be used in Dye-Sensitized Solar Cell (DSSC).

1. Introduction
The direct conversion of solar energy into electrical energy by photovoltaic solar cells has been studied for over 30 years [1, 2]. However we are still far from making these sources cost-effective and our aim is substantially reducing the cost of PV systems. The basic requirement for the thin film solar cell are i) Small thickness for high absorption ii) Small diffusion length and high recombination velocity iii) Material economy iv) Very low weight per unit power, v) Various simple and sophisticated deposition techniques. Among various thin film solar cells, DSSC, a third generation solar cells, plays an important role because of its simple fabrication method, environment friendly and low cost. It consists of TiO₂ material coated onto the transparent conducting substrate, acts as the photoanode and pt/c coated onto the conducting substrate, and acts as the photo cathode. An ideal transparent conducting oxide (TCO) should possess high optical transparency and electrical

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conductivity along with good chemical and thermal stabilities when it is subjected to high temperature processes. As Magnesium Tin Oxide MgSnO₃ material has high transparency in the visible and near infrared region of the spectrum and has significant electrical conductivity [1], it is used as substrate for the solar cell applications. Starting from 1990s, multi-cation of TCOs began to be develop [5, 6] and reported. The alkali earth stannates have recently been studied as potential electronic ceramics in thermally stable capacitors which has low permittivity and small loss tangent. Magnesium stannates has found to be a good candidate for a wide range of applications at high temperature and high frequencies. The recent and most useful application of magnesium tin stannate is solar energy conversion, in which they serve as transparent protective coatings as well as terminals to make connectors. The behaviour of magnesium metastannate MgSnO₃ and magnesium orthostannate Mg₂SnO₄ is totally different from the corresponding Ca, Sr and Ba counterparts. MgSnO₃ is unstable and disproportionate to Mg₂SnO₄ and tin oxide at high temperature [4]. Also, relatively limited amount of research is available on the sintering behaviour of Mg-Sn-O system [5]. In the present work is finding alternative TCO substrate for ITO and FTO due to its high cost and scarcity. The film is prepared by the simplest and cost effective nebulizer spray pyrolysis technique. The major interest in spray pyrolysis is due to its low cost, and is widely used in the deposition of a transparent layer on glass [6], SnO₂ layer for gas sensor applications [7], YSZ layer for solar cell applications [8], anodes for lithium-ion batteries [9], and optoelectronic devices [10].

2. Experimental

2.1. Preparation of MTO Thin Films

Magnesium acetate tetra hydrate, [(CH₂COO)₂ Mg₄H₂O] Tin (II) chloride dehydrate SnCl₂.2H₂O and 2-propanol) CH₃CHOCHO₃ with purity (GC) ≥ 99.0 were used for the preparation of precursor solution. Chromic acid H₂CrO₄, Acetone and distilled water were used for cleaning the substrate. Glassware’s used for film coating are blue star glass slides of 1mm thickness and beakers. The solution was prepared in a glass beaker by dissolving the known quantities of magnesium acetate tetrahydrate and tin (II) chloride dehydrate in 50ml 2-propanol. The solution was continuously stirred for about 30 min. MgSnO₃ thin film was deposited onto the amorphous glass substrate by spraying an aqueous solution containing the concentration of MA: TC as 0.1:0.1 M, 0.1:0.2M, and 0.1:0.3M using nebulizer spray pyrolysis technique. The well cleaned glass substrate of dimension 75mm x 25mm x 1mm was kept on the preheated hot plate. The substrate temperature was maintained at 400°C. The
compressed air was used to carry the oxygen gas maintained at 2 Kg/cm² corresponding to average pressure solution rate of 50 ml per 30 minutes. The distance between nozzle and substrate was kept at 5 cm. The sample was kept on the substrate until it reached the room temperature after the deposition was over. The deposited samples are annealed at 400°C for 2 hours.

2.2. Characterisation

The various properties of prepared MgSnO₃ thin films were analyzed by different characterization techniques. The structural analysis is carried out by using X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuKα radiation of wavelength 1.541 Å. Bandgap values and the transmission range is evaluated from UV-Studies. Resistivity, mobility and the carrier concentration values are measured by Hall Effect Studies. The thickness of the prepared film is also calculated which is coated at three different ratios and it is tabulated.

3. Results and Discussion

3.1. Thickness Measurement

Microbalance gravimetric technique is one of the simplest techniques for thickness measurement, which was employed in this study for thickness measurement of the MgSnO₃ thin film deposited by nebulized spray pyrolysis method. The films of different thickness were deposited on 1 mm glass substrate at different molar ratios at 400°C. The thickness was carried out for several samples, but the best fit sample parameters shown in table 1. The weight of the deposited film was calculated from the measurement of substrate weight before and after deposition. For all the deposition film, thickness falls in μm range. We observe that the value of the thickness of the samples agrees well for same concentration. Thickness increases as concentration increases, which indicate the validity of the deposition technique adopted for the film [11].

Table 1. The thickness of the MgSnO₃ thin films (Annealed at 400°C)

| MA: TC (M) | Temperature (°C) | Thickness (μm) |
|------------|------------------|----------------|
| 0.1:0.1    | 400              | 0.23           |
| 0.1:0.2    | 400              | 0.27           |
| 0.1:0.3    | 400              | 0.32           |

From the above table 1 concluded that when molarity ratio of the film is increased then the thickness of the film is also increased.

3.2. Structural Analysis

XRD spectrum reveals the structural details and the crystalline nature of the thin film. The Figure 3.2.1 shows the XRD spectrum of a MgSnO₃ thin film prepared by nebulizer spray pyrolysis on a glass substrate at 400°C with the molar ratio (0.1:0.1M). The first and fourth peak corresponding to 2θ=26.6°, 51.9° is assigned for SnO₂ and due to its reactive nature, it crystallizes in tetragonal phase and preferentially oriented in the (110), (222) plane. The second peak corresponding to 2θ=34.09° shows the formation of Mg₂SnO₄ phase. The third and fifth peak corresponding to 2θ=38.2°, 62.1° corresponds to the rhombohedral structure of magnesium metal stannate phase. The relative intensity of the (303) plane is less for the fifth peak and broader which shows that nanosized crystallites.
Table 2. Interplanar spacing and (hkl) plane of MA:TC with 0.1:0.1 M ratio

| 2theta (deg.) | d (Å)  | (hkl)      | JCPDS Card No. |
|---------------|--------|------------|----------------|
| 26.96         | 3.341  | (110)      | (21-1250) SnO₂  |
| 33.83         | 2.352  | (015)      | (30-0798) MgSnO₃ |
| 38.74         | 1.752  | (222)      | (77-2296) SnO₂  |
| 52.26         | 1.666  | (303)      | (30-0798) MgSnO₃ |
| 62.56         | 1.497  | (310)      | (21-1250) SnO₂  |

Table 3. Interplanar spacing and (hkl) plane of MA:TC with 0.1:0.2 M ratio

| 2theta (deg.) | d (Å)  | (hkl)      | JCPDS Card No. |
|---------------|--------|------------|----------------|
| 26.96         | 3.341  | (110)      | (21-1250) SnO₂  |
| 33.83         | 2.628  | (311)      | (74-2152) Mg₂SnO₄ |
| 38.74         | 2.352  | (015)      | (30-0798) MgSnO₃ |
| 52.26         | 1.666  | (222)      | (77-2296) SnO₂  |
| 62.56         | 1.497  | (310)      | (30-0798) MgSnO₃ |

MgSnO₃ films prepared with a molar ratio (0.1:0.2M) at substrate temperature 400° C on the glass substrate are shown in Figure 3.2.2. The observed peak and value is compared with JCPDS card no.
In this molar concentration ratio, XRD reveals that the peak corresponding to magnesium ortho stannate at $2\theta = 34.25^\circ$ The third and fourth peak corresponding to $2\theta = 52.15^\circ$, $61.9^\circ$ is SnO$_2$ tetragonal structure. Although the concentration of the stannic chloride is low, due to its highly reactive, it crystallizes in tetragonal phase and preferentially oriented in the (310) plane.

| $2\theta$ (deg.) | d (Å) | (hkl)   | Phase      | JCPDS Card No. |
|------------------|-------|---------|------------|----------------|
| 26.96            | 3.430 | (113)   | MgO        | (27-0759)      |
| 33.83            | 2.624 | (311)   | Mg$_2$SnO$_4$ | (74-2152)     |
| 38.74            | 2.349 | (015)   | MgSnO$_3$  | (30-0798)      |
| 52.26            | 1.755 | (222)   | SnO$_2$    | (77-2296)      |
| 62.56            | 1.673 | (220)   | SnO$_2$    | (77-2296)      |

XRD pattern of MgSnO$_3$ film prepared with molar ratio (0.1:0.3M) at substrate temperature 400$^\circ$C on glass substrate is shown in Figure 4.4. The observed peak and’ value are compared with JCPDS data. The first peak at $2\theta = 27.2^\circ$ small amount of MgO is present in the precursor and it shows hexagonal phase with JCPDS card no. (27-0759), the second peak $2\theta = 34.4^\circ$ corresponding to magnesium ortho stannate with JCPDS card no. (74-2152). The third peak $2\theta = 38.2^\circ$ correspond to magnesium metal stannate with JCPDS card no. (30-0798). The other two peak $2\theta = 52.0^\circ$, $54.8^\circ$ are comparable with SnO$_2$ phase and it is obvious to say that the precursor concentration of stannic chloride is higher than magnesium acetate [12].

The average crystallite size of Annealed MgSnO$_3$ thinfilms are determined using the Scherrer equation

\[
D = \frac{k\lambda}{\beta \cos \theta} \text{ nm}
\]

Where $\lambda$ is CuK$\alpha$ radiation of X-rays with wavelength 1.541 Å, $K$ is shape factor. Microstructural parameters are shown in table 4. It is noted that the average crystallite size improves when the concentration of the tin increases and the increased FWHM shows the improved crystallinity of the doped samples.

### 3.3. Optical Analysis

The optical properties of the films were studied using a UV-Vis spectroscopy. The absorption and transmission measurement was made in the range of 200 nm to800 nm for three different molar ratio. From the figure, we can observe that the annealed MgSnO$_3$ possess higher transmittance in the visible and IR region. Hence it is clear that the films obtained were highly transparent. Because of higher transmittance (above 80%) the indium tin oxide can be replaced by MgSnO$_3$. The value of the energy bandgap is found to increase with increasing annealing time. The direct energy bandgap of the films was calculated using Tauc relation and the values are found to be 3.85 eV, 3.80 eV and 3.91 eV for the annealed films at 360$^\circ$C. The value of the energy bandgap is found to increase for 0.1:0.3M. The absorption spectra of the MgSnO$_3$ films with different molar ratios deposited and annealed at 400 $^\circ$C for 2 h as shown in the figure 4. From the absorbance spectrum of MgSnO$_3$ films, it is observed that MgSnO$_3$ films with molar ratios MA:TC with 0.1:0.1 M, 0.1:0.2 M, 0.1:0.3 M is observed at 0.39, 0.67 and 0.16 which is in the UV range. This is important for an application such as transparent conducting device and solar cell window. The bandgap of the deposited MgSnO$_3$ films is shown in Table 4.8.
Figure 3. % of Transmission of MgSnO$_3$ Thin film at different MA:TC molar ratio and annealed at 400°C for 2 hours

Table 7. Cut off wavelength of the annealed MgSnO$_3$ thin film

| MA:TC (M) | Cut Off Wavelength (nm) | Band Gap (eV) |
|-----------|-------------------------|---------------|
|           | Transmittance (%)       | Absorbance (a.u) |       |
| 0.1:0.1   | 615                     | 336           | 3.85  |
| 0.1:0.2   | 554                     | 360           | 3.80  |
| 0.1:0.3   | 470                     | 371           | 3.91  |
3.4. Hall Effect Studies

The Hall Effect studies were conducted for thin films of different molar ratios (0.1:0.1M, 0.1:0.2M and 0.1:0.3M) at substrate temperature 400 °C and the film is annealed for three hours at the same substrate temperature.

Table 7. Hall Parameters of MgSnO₃ Thin film at different MA:TC molar ratio and annealed at 400°C for 2 hours

| MA:TC Molarity ratio(M) | Carrier Concentration Nb x 10¹⁹ (cm²) | Mobility µ(cm²/Vs) | Sheet Concentration Ns x 10¹⁵(cm²) |
|------------------------|----------------------------------------|---------------------|------------------------------------|
| 0.1:0.1                | -3.9450                                | 6.09007             | -2.3670                            |
| 0.1:0.2                | -9.5087                                | 28.85113            | -5.7052                            |
| 0.1:0.3                | -7.0261                                | 12.73647            | -4.2156                            |

From the above table, it is clear that the majority charge carriers are electrons because of the negative values of carrier concentration. For the molarity ratio 0.1:0.2 the mobility is found to be is maximum (28.85113) with less sheet concentration (-5.7052x10¹⁵)

Table 8. Measurement of hall coefficient, conductivity, and resistivity of MgSnO₃ Thin film at different MA:TC molar ratio and annealed at 400°C for 2 hours

| MA:TC Molarity ratio (M) | Hall Coefficient R_H (m²/C) | Conductivity σ (1/Ωcm) | Resistivity P x 10⁻² (Ωcm) |
|--------------------------|-----------------------------|-------------------------|--------------------------|
| 0.1:0.1                  | -0.15823                    | 38.48188                | 2.5986                   |
| 0.1:0.2                  | -6.5647x10⁻²                | 50.69533                | 1.9726                   |
| 0.1:0.3                  | -8.8844x10⁻²                | 143.2584                | 6.9804                   |

From the Table 7, the Hall coefficient of the film is found to be negative which ensures n-type conductivity of the material. Here the conductivity of the solid solution strongly depends on the composition and is increased with increasing the molarity ratio of MgSnO₃ that used for the preparation of thin films [13]. There is a tendency for crystals with small energy gap at direct band edges to have high values of the electron mobility. But here the MgSnO₃ films having the band gap 3.53 eV, so the electron mobility is somewhat decreasing. The hole mobility is smaller than the electron mobility, because of the occurrence of band degeneracy at the valence band edge, at the zone centre, thereby making possible interband scattering processes that reduce the mobility considerably. The carrier concentration will be increased by increasing the temperature. Hence it is clear that the negative hall voltage has been observed for films annealed at 400 °C for 3 hours. The observed negative Hall voltages clearly suggest that the film annealed at 400 °C are of n-type nature with electrons as majority charge carriers [14].
4. Conclusion

For constructing Dye-Sensitized Solar Cells (DSSC) with high efficiency the effective TCO substrate is need to prepare. For achieving this, MgSnO₃ (MTO) substrate is constructed by using nebulized spray pyrolysis technique. Already in industries for DSSC manufacturing, ITO and FTO are being used as TCO substrate. Due to their high cost and lower production rate they need suitable alternative for them. MTO is a promising and better replacement of ITO and FTO substrates due to its lower resistivity value and higher transmission range. For preparing MTO substrate Magnesium acetate, Tin (II) chloride are the starting materials and taken in three different ratios (0.1:0.1M, 0.1:0.2M, 0.1:0.3M) and the thin films are prepared onto the glass substrate at 400°C by nebulized spray pyrolysis technique. The prepared film was annealed at 400°C for three hours. The structural, optical, electrical studies are carried out for the film which is annealed. From the XRD results the structure of the film is analyzed and it is in rhombohedral structure. For the first two ratios i.e, (0.1:0.1M and 0.1:0.2M) most of the peaks corresponds to MgSnO₃ phase and some of the peaks corresponds to SnO₂ phase because SnO₂ is a highly reactive oxide. At the third ratio SnO₂ dominates due to its higher concentration. The crystallite size of the prepared film is observed and it is around 5µm. From the optical studies it is concluded that the percentage of transmission is increased when the molarity ratio is increased and the range is around 80%. The optical band gap values are measured from the Tauc - plot and it is well known that the values are around 3.8eV which is the expected value. From the Hall Effect studies the carrier concentration, mobility and the resistivity values are measured. Due to the negative values of charge carriers the film is having n-type conductivity and the resistivity value is very low in the order of 7 x10⁻³Ω cm which is very closer to the resistivity value of ITO (8 x10⁻⁴Ω cm). The Percentage of Transmittance is between 75 to 85% in the visible region and the band gap value is 3.8 eV. From the results, it is concluded that MTO is a Best alternative for ITO and can be used in Dye-Sensitized Solar Cell (DSSC).

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