Solution molarity effect on electrical properties of SnO\textsubscript{2} thin films

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**ABSTRACT**

Tin oxide thin films of different molarities were successfully deposited by spray pyrolysis technique on preheated glass substrates at a temperature of 500°C. The effect of molarity concentration on film properties was investigated. All deposited films were characterized by various techniques such as X-ray diffraction for structural characterizations, weight difference density method for thickness measurement, the two probe conductivity measurements for electrical characterization. The X-ray diffraction (XRD) patterns showed that the film of 0.1 M tin chloride pentahydrate has amorphous structure. With increasing the molarity concentration of the films to 0.3 M and 0.5 M the patterns showed a polycrystalline structure with preferential orientation along (110) direction. Results showed that the resistivity increases remarkably as the molarity increases. The variation of electrical conductivity as a function of temperature increases with increasing temperature, and tend to decrease with increasing the molarity concentration to 0.5 M. The activation energies increased with increasing the molarity concentration. Hall measurements showed that all films are n-type. The charge carrier concentration, Hall mobility, drift velocity, and mean free path decreases with increasing molarity concentration.

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**KEYWORDS**

SnO\textsubscript{2}; Spray pyrolysis; Electrical properties; Thin films.

**INTRODUCTION**

Transparent conducting oxide (TCO) thin films have attracted considerable attention from scientific and technological point of view due to their unique properties of high electrical conductivity and high optical transmittance\textsuperscript{[1,2]}. They are used for photovoltaic devices, phototransistors, liquid crystal displays, optical heaters, gas sensors, solar cells, transparent electrodes and other optoelectronic devices\textsuperscript{[3-8]}.

Among these TCOs, SnO\textsubscript{2} films are inexpensive, chemically stable in acidic and basic solutions, thermally stable in oxidizing environments at high temperatures and also mechanically strong, which are important attributes for the fabrication and operation of solar cells\textsuperscript{[9,10]}. Their property is resulted from its n-type semiconductor behavior and wide band gap \( E_\text{g} = 3.6-4.0 \) eV\textsuperscript{[11,12]}

Thin films of SnO\textsubscript{2} can be produced by various techniques, such as chemical vapor deposition\textsuperscript{[13,14]}, beam evaporation\textsuperscript{[20]} and spray pyrolysis\textsuperscript{[21,22]}. Among these techniques that used to form SnO\textsubscript{2} films spray pyrolysis technique is the best, it is simple and inexpensive ex-
Experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings\cite{23}. The aim of this work is to investigate the effect of solution molarity effect on electrical properties of SnO$_2$ films produced by spray pyrolysis technique.

**EXPERIMENTAL DETAILS**

![Figure 1: X-ray diffraction pattern of SnO$_2$ films with different molarity](image-url)
Thin films of tin oxide SnO\textsubscript{2} with different molarities have been prepared by spray pyrolysis technique. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500\degree C. The deposition was carried out for different molar concentration of the solution varied from 0.1 M to 0.5 M of tin (IV) Chloride Pentahydrate SnCl\textsubscript{4}.5H\textsubscript{2}O from Fluka Germany, this material was dissolved in deionized water and ethanol, few drops of HCl were added to speed up the dissolving, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 Sec lasted by two minutes to avoid excessive cooling and the spray interval (3 min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm\textsuperscript{-2}, distance between nozzle and the substrate was about 28 cm ± 1 cm, solution flow rate 5 ml/min. The samples were weighted before and after spraying to determine the mass of the films\textsuperscript{[24]}. Knowing the dimensions of the used substrates, the thicknesses can be determined by the following equation\textsuperscript{[25]}:

\[
d = \frac{\Delta m}{\rho_n l L}
\]

(1)

Where \Delta m is the difference between the mass after and before spraying, \rho is the density, l the width and L the length. Thickness of the films was found to be around 300 nm. XRD patterns for SnO\textsubscript{2} thin films were carried out using a Phillips X-ray diffractometer system which records the intensity as a function of Bragg angle. The source of radiation was CuK\textsubscript{\alpha} with wavelength \lambda = 1.5405 Å, the current was 20 mA and the voltage was 30 kV. The scanning angle 2\\theta was varied in the range of (20–60) degree with speed of 2 cm.min\textsuperscript{-1}.

**RESULTS AND DISCUSSION**

**Structure properties**

X-Ray diffraction (XRD) analysis has been performed onto certain the crystal structure and the crystal orientation. The XRD spectra of SnO\textsubscript{2} thin films with various molar concentrations (0.1, 0.3 and 0.5) M recorded in 2\\theta angle in the range of 20–60 are depicted in Figure 1. It can be seen that the film obtained with a concentration of 0.1 M tin chloride pentahydrate has amorphous structure. By increasing the molarities of the films to 0.3 M and 0.5 M one may observe a strong diffraction peak for [110] direction, which is characteristic for the tetragonal structure of the SnO\textsubscript{2} thin films. Also, the [101] direction yields the second most important diffraction peak. This [101] peak is shown in the figures which reveal the polycrystalline structure of these films. Mean crystallite size was calculated for the [110] diffraction peak using Debye–Scherrer formula:

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

(2)

Comparison between observed and standard d-values for 0.1 M and 0.5 M SnO\textsubscript{2} thin films are listed in TABLE 1.

**Electrical properties**

The variation of resistivity of SnO\textsubscript{2} thin films as a

<table>
<thead>
<tr>
<th>Solvent Volume of SnO\textsubscript{2}</th>
<th>(2\theta) (degree)</th>
<th>(d_{exp}) (Å)</th>
<th>((I/I_0)_{exp})</th>
<th>(hkl)</th>
<th>FWHM Degree (SnO\textsubscript{2})</th>
<th>(D \times 10^4) (µm)</th>
<th>(N \times 10^{14}) (m\textsuperscript{-2})</th>
<th>(\delta \times 10^{13}) (Lines/m\textsuperscript{2})</th>
<th>(S \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>26.423</td>
<td>3.370</td>
<td>100</td>
<td>110</td>
<td>2.75</td>
<td>3.617294</td>
<td>10563</td>
<td>7642.4</td>
<td>95.82714</td>
</tr>
<tr>
<td>33.895</td>
<td>2.642</td>
<td>42</td>
<td>101</td>
<td>1.0875</td>
<td>22.4724</td>
<td>440.57</td>
<td>198.01</td>
<td>15.42492</td>
<td></td>
</tr>
<tr>
<td>50.792</td>
<td>1.796</td>
<td>36</td>
<td>211</td>
<td>0.314</td>
<td>26.21634</td>
<td>277.49</td>
<td>145.43</td>
<td>13.22209</td>
<td></td>
</tr>
<tr>
<td>54.897</td>
<td>1.67</td>
<td>8</td>
<td>220</td>
<td>0.1917</td>
<td>61.15883</td>
<td>21.857</td>
<td>26.735</td>
<td>5.667783</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>26.404</td>
<td>3.372</td>
<td>100</td>
<td>110</td>
<td>0.4618</td>
<td>21.38889</td>
<td>510.98</td>
<td>218.58</td>
<td>16.20630</td>
</tr>
<tr>
<td>33.7016</td>
<td>2.657</td>
<td>89</td>
<td>101</td>
<td>0.400</td>
<td>31.42857</td>
<td>161.06</td>
<td>101.23</td>
<td>11.0293</td>
<td></td>
</tr>
<tr>
<td>51.5359</td>
<td>1.7719</td>
<td>65</td>
<td>211</td>
<td>0.374</td>
<td>32.91442</td>
<td>140.22</td>
<td>92.305</td>
<td>10.53140</td>
<td></td>
</tr>
<tr>
<td>54.514</td>
<td>1.6819</td>
<td>12</td>
<td>220</td>
<td>0.275</td>
<td>54.98669</td>
<td>30.074</td>
<td>33.073</td>
<td>6.303981</td>
<td></td>
</tr>
</tbody>
</table>
function of temperature in the range of (303-473) °K at different solution molarity is shown in Figure 2. It’s clear from the figure that the resistivity shows the negative temperature coefficient of resistance for all deposited films. Also, the resistivity increases markedly as the molar concentration of films increases.

The variation of electrical conductivity as a function of temperature for SnO$_2$ films at different molarity concentration is shown in Figure 3. It’s clear from this figure that the conductivity for all deposited films increases with increasing of the temperature. Also, it can be seen that the conductivity decreases with the increasing of molarity concentration of the films. This decrease in the conductivity can be understood on the basis of the fact that the conductivity generally decreases when the carrier concentration of the heavily doped semiconductor increases\[^{26}\]. For example, which is attributed to the strong scattering or absorption of photons by the increased number of carrier concentration resulted from the defects created in the lattice\[^{27}\]. In this study, when the solvent volume increases, the spray flux density decreases, which make the growth rate slow and thereby, the carrier concentration increases.

In order to study the conductivity mechanisms, it is convenient to plot logarithm of the conductivity ($\ln \sigma$) as
Figure 4: Ln$\sigma$ versus 1000/T for SnO$_2$ films with different molarity

Table 2: Carries concentration, Hall mobility, $V_d$, $E_{a1}$ and $E_{a2}$ for SnO$_2$ films with different molarity.

<table>
<thead>
<tr>
<th>Solvents volume (ml) SnO$_2$</th>
<th>$\sigma_{e1} \times 10^4$ $(\Omega^{-1} \cdot cm^{-1})$</th>
<th>$R_n \times 10^{-1}$ cm$^2$/C</th>
<th>$\rho \times 10^2$ $(\Omega \cdot cm)$</th>
<th>$\mu_{H} \times 10^2$ (cm$^2$/V.s)</th>
<th>$v_d \times 10^3$ (cm/s)</th>
<th>$N_e \times 10^{18}$ (1/cm$^3$)</th>
<th>Type of con.</th>
<th>$E_{a1}$ (eV)</th>
<th>$E_{a2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.05</td>
<td>57.4</td>
<td>2.466</td>
<td>5.3</td>
<td>5.56</td>
<td>2.36</td>
<td>n-type</td>
<td>0.0043</td>
<td>0.095</td>
</tr>
<tr>
<td>0.3</td>
<td>2.93</td>
<td>8.49</td>
<td>3.4</td>
<td>2.49</td>
<td>2.61</td>
<td>7.35</td>
<td>n-type</td>
<td>0.032</td>
<td>0.103</td>
</tr>
<tr>
<td>0.5</td>
<td>2.02</td>
<td>1.45</td>
<td>4.9</td>
<td>0.59</td>
<td>0.619</td>
<td>42.8</td>
<td>n-type</td>
<td>0.0336</td>
<td>0.121</td>
</tr>
</tbody>
</table>

The obtained results showed that the materials under study are n-type semiconductor possibly due to the donor formation by O$_2$ vacancies. The carrier mobility decreases with increasing of the carrier concentration which is due to increase in the solvent volume. The interpretation of this decrease is attributed to the increase in the localized state near band edge, and also increase in carrier concentration, which leads to decrease in $\mu_{H}$.

CONCLUSIONS

From the obtained results, we can conclude the following. The structural study of the films showed that an amorphous state may exist in the material as in the films with molarity 0.1M. With increasing the molarity to 0.3M and 0.5M a polycrystalline structure with preferred orientation along [110] direction with strong diffraction Peak has been observed. The variation of resistivity of the films with different molarities as a function of temperature showed the negative temperature coefficient of resistance. The resistivity increases remarkably as the molarity increases. The variation of electrical conductivity as a function of temperature increases with increasing temperature, and tend to decrease with the increasing of molarity concentration to 0.5 M. The results indicate that the materials under study are n-type semiconductor possibly due to the donor formation by O$_2$ vacancies. The carrier mobility decreases with increasing of the carrier concentration which is due to...
increase in the molar concentration.

REFERENCES


