Effect of substrate temperature on the structural properties of SnO\textsubscript{2} thin films

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Abstract - SnO\textsubscript{2} thin films were coated on a glass substrate by the simple homemade spray pyrolysis (SP) technique at substrate temperature in the range 250-320°C using stannous chloride dehydrate (SnCl\textsubscript{2}.2H\textsubscript{2}O) as precursors, and mixture of water and methanol as solvent. The prepared samples were characterized by X-ray diffraction (XRD) and optical spectroscopy. The X-ray diffraction studies confirmed the prepared films were tetragonal structure with polycrystalline nature. Both crystallinity and the grain size were found to increase with increasing substrate temperature. The film thickness and the crystallite size vary from 380 to 312 nm, from 20.03 to 32.97 nm, respectively. The films exhibited maximum transmittance (62% - 89%) in infra-red (IR) region. The average visible transmittance (800 nm) of the deposited films is 70.64 %. In the visible region of the spectrum, the transmission is very high. For films prepared at 350°C, relatively higher transmittance of about 78.9% at 800 nm has been observed. The obtained results revealed that the structures and properties of the films were greatly affected by substrate temperature.

Key Words: Spray pyrolysis, SnO\textsubscript{2} thin films, substrate temperature, XRD.

1. INTRODUCTION

Currently, the development goes hand in hand with the explosion of scientific and technological breakthrough in micro electronics, optoelectronics and nanotechnology. Tin dioxide is a n-type wide-band gap semiconductor (E\textsubscript{g} = 3.6 eV) [1]. The SnO\textsubscript{2} films have several potential applications such as in solar cells, light emitting diodes [2], anti reflective coatings [3], transparent electrodes in electroluminescent lamps and displays [4], transistors [5], photovoltaic cell [6], gas sensors [7]. Protective and wear resistant coating on glass containers [8], Infrared reflectors for glass windows [9]. The SnO\textsubscript{2} thin films are synthesized by a variety of methods such as RF magnetron sputtering, metal organic chemical vapor deposition[10], vacuum evaporation, pulsed laser deposition, electron beam deposition, spray pyrolysis [11], sol-gel[12], chemical vapor deposition, and successive ionic layer adsorption and reaction, CBD [13]. Among various techniques homemade perfume spray pyrolysis is a simplified spray pyrolysis technique. This is cost effective, low volume of spray solution and time saving technique by which tiny droplets of particles can be deposited [14].

In the present investigation, nanocrystalline SnO\textsubscript{2} thin films were prepared by using a simple homemade spray pyrolysis method. The prepared films were characterized for their structural and optical properties using XRD and UV-visible spectroscopy measurement.

2. EXPERIMENTAL DETAILS

SnO\textsubscript{2} thin films were prepared on commercial microscopic glass slide by using the homemade spray pyrolysis technique. The substrates were washed using soap solution and subsequently kept in hot chromic acid and then ultrasonically cleaned with deionized water for 10 min and wiped with acetone and stored in a hot oven. As a precursor for tin used stannous chloride dehydrate (SnCl\textsubscript{2}.2H\textsubscript{2}O). 10g of SnCl\textsubscript{2}.2H\textsubscript{2}O dissolved in 5 ml of concentrated hydrochloric acid (HCl) was heated at 90°C for 10 min. The addition of HCl was required in order to break down the polymer molecules that were formed when diluting with methanol. This mixture was diluted by adding 20 ml of diluted methanol and 25 ml of doubly distilled water served as starting solution. In each case, the amount of spray solutions prepared was 50 ml. All the spray solutions were magnetically stirred for 1h and finally these solutions were filtered by syringe filter with 0.2 μm pore size before spraying on substrate. The substrates were preheated to the required temperature like 250°C, 300°C and 350°C. After deposition, all the films were allowed to cool down naturally to room temperature. The flow rate (2 ml/min.), total spraying quantities (50 ml) were all kept fixed. The total deposition time was maintained at 30 minutes for each film, including waiting times. To avoid excess cooling of the substrates 10 minutes waiting time was allowed between spraying applications. The substrate temperature (working temperature) was varied from 250°C to 350°C.
3. RESULTS AND DISCUSSION

3.1. Thickness Measurement

Thickness is the most important film parameter, which controls the film properties. Hence, precise knowledge of the film thickness is necessary for the intensive study of the properties of thin films. Thickness of the prepared film was estimated using weight method. The well-cleaned glass plate is weighted in a high precision microbalance. After the deposition the coated glass plate is weighted. The difference in weight gives the mass of the deposited film "m". The area over which the film deposited is measured as "A". The standard value of density "ρ" has been taken and the thickness is calculated using the expression.

\[ t = \frac{m}{(Aρ)} \] (microns) \hspace{1cm} (1)

Where,
- \( t \) – is the thickness of the film.
- \( m \) – is the weight difference (Mass of the film)
- \( A \) – is the area of the sample.
- \( ρ \) – is the density of the film.

The thicknesses of the prepared tin oxide films were tabulated.

3.2. Structural Studies

Fig. 2 shows the XRD pattern of the 0.2 M concentration of SnO\(_2\) thin films deposited using spray pyrolysis method. All the diffraction peaks of XRD pattern could be indexed to tetragonal phase crystal structure of SnO\(_2\), which is in good agreement with the standard data for SnO\(_2\) (JCPDS data file No. 41-1445). The grown SnO\(_2\) films have exhibited strong orientation along (110) plane and also other peaks like (101), (200), (211), (220), (310), (301), (321) and (400) are appears. The intensity of the diffraction peak was also found to decrease with increasing substrate temperature and get sharper with decreasing full width half maximum (FWHM). This can be attributed to the improvement in crystallinity of SnO\(_2\) thin films. No other peaks appear.

The structural parameters of SnO\(_2\) thin films are given in Table 1. The crystallite size is calculated using Debye - Scherrer's formula [15-18]

\[ D = \frac{kλ}{β\cosθ} \] \hspace{1cm} (2)

Where \( k \) is the shaping factor which takes value from 0.89 to 0.94, 'λ' is the wavelength of the Cu-\( k\_α \) line, 'β' is the full width at half maxima (FWHM) in radians and 'θ' is the Bragg's angle. The crystallite size increases with increase of substrate temperature.

Dislocation density (δ) for (110) plane is evaluated using the relation

\[ δ = \frac{1}{D^2} \] \hspace{1cm} (3)

The strain (ε) is calculated from the following relation

\[ ε = \frac{(β \cosθ)}{4} \] \hspace{1cm} (4)

The Number of Crystallites per unit area (N) is calculated from the following relation [19]

\[ N = \frac{t}{D^3} \] \hspace{1cm} (5)

Table 1. Clearly shows that dislocation density (δ), strain (ε) and number of crystallites per unit area (N) are decreases with increases of substrate temperature. It is due to the incorporation of increase of oxygen iron vacancies.
3.3. Optical studies

Fig. 3 shows the variation of transmittance (T) with respect to wavelength of SnO2 thin films deposited at various substrate temperatures. Average visible transmittance (AVT) is calculated as 70.43% in the wavelength 800 nm. The transmission in the visible region has been found to be ranging from 62.3% to 78.9% depending upon the substrate temperature. An increase in transmission is observed with increase in temperature. These values are comparable with the values found in literature [20-23]. At lower temperatures, at 250°C and under, relatively lower transmission is due to the formation of milky films and that is because of incomplete decomposition of the sprayed droplets. In general, in the visible region of the spectrum, the transmission is very high. It is due to the fact that the reflectivity is low and there is no absorption due to transfer of electrons from the valence band to the conduction band owing to optical interference effect, it is possible to maximize the transmission of thin film at particular region of wavelengths. The optical transmission spectrum of the films has been determined on the basis of UV-vis transmission measurements (Fig. 3).

Table 1: Micro structural properties of SnO2 thin films

<table>
<thead>
<tr>
<th>Substrate Temperature</th>
<th>Thickness (t) nm</th>
<th>Crystallite size (D) nm</th>
<th>Dislocation density $\delta \times 10^{14}$ lines/m²</th>
<th>Strain $\varepsilon \times 10^{-3}$</th>
<th>Number of Crystalline per unit Area (N) x10$^{16}$</th>
<th>Transmittance (%) ($\lambda = 900$ nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C</td>
<td>380</td>
<td>20.03</td>
<td>24.91</td>
<td>1.73</td>
<td>4.72</td>
<td>62.3</td>
</tr>
<tr>
<td>300°C</td>
<td>347</td>
<td>22.55</td>
<td>19.65</td>
<td>1.53</td>
<td>3.02</td>
<td>70.1</td>
</tr>
<tr>
<td>350°C</td>
<td>312</td>
<td>32.97</td>
<td>9.19</td>
<td>1.05</td>
<td>0.86</td>
<td>78.9</td>
</tr>
</tbody>
</table>
3. CONCLUSIONS

Tin oxide (SnO$_2$) thin films were prepared on glass substrate by altering substrate temperature from 250°C – 350°C in the steps of 50°C using homemade spray pyrolysis method. The prepared films were characterized. XRD studies revealed that the prepared samples were polycrystalline with tetragonal structure. The thickness and crystallite size of the prepared films increases with increasing substrate temperature and the dislocation density (δ), strain (ε) and number of crystallites per unit area (N) are decreases. From the optical transmittance studies the transmission in the visible region has been found to be ranging from 62.3% to 78.9% depending upon the substrate temperature. An increase in transmission is observed with increase in temperature.

REFERENCES


BIOGRAPHIES

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