Effect of Different Oxidation Temperature on Nano and Micro TCO’s Film

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ABSTRACT

In the present work, electrical structural and surface morphology of tin oxide thin films prepared using simple conventional method known as (CTO) was carried out. The obtained result insures the formation of Nano crystalline SnO$_2$ films as a tetragonal structure. The atomic force microscope results show that film roughness depended on oxidation temperature. Minimum electrical resistivity found to be about (5.35 x 10$^{-5}$ $\Omega$.cm) at (300°C) oxidation temperature.

Keywords: Tin Oxide; Electrical Properties and Measurements, Structural Properties.

INTRODUCTION

SnO$_2$ thin films are an n-type semiconductor material. Because of its good adsorptive properties and chemical stability, it can be deposited on glass, ceramics, oxides, and substrate materials of other types. It has a high melting point and good transmission, and it does not easily react with oxygen and water vapor in the air [1].

SnO$_2$ thin films are used for film resistors, electric conversion films, heat reflective mirror, semiconductor-insulator-semiconductor (SIS) heterojunction structure and surface protection layer of glass. At present, its most common application is as anode material of solar cells [2]. Transparent conducting oxide (TCO) films are widely used in a variety of
optoelectronic devices such as solar cells, displays and electro chromic devices. In recent years; there has been growing interest in the application of TCO films as electrodes in solar cell devices [3]. Among the TCO films, the most appropriate material for the application seems to be tin oxide films, which are chemically inert, mechanically hard and heat-resistant. In addition, they exhibit low electrical resistivity and high optical transmittance. Either doped or non-doped tin oxide thin films can be fabricated by a number of techniques: chemical vapor deposition [4], sputtering [5], spray pyrolysis [6], and physical vapor deposition (PVD) [7]. Transparent Conducting Oxides (TCO) film is a material that is highly transparent in the range of visible light, and at the same time, electrically conductive [8]. Each deposition technique with its associated parameters yields films of different properties.

Depending on the deposition technique, the substrate can have a significant influence on the properties of the films. Glass substrates are most commonly used [9].

The aim of this research was to establish a relationship between the oxidation temperature and the film properties. The properties of the films were characterized by X-ray diffraction analysis (XRD), atomic force microscopy (AFM), and two conductivity method experiment.

EXPERIMENTAL DETAILS

Test glass slides, each of 2×2 cm² area, were used as substrates. They were cleaned by alcohol with ultrasonic waves produced by Alkattl, in order to remove the impurities and residuals from their surfaces.

A thermal evaporation system type (Edwards) was used to evaporate high purity (99.9 %) Tin on glass slides substrate at room temperature under low pressure (~ 10⁻⁶ torr), the source material (element Sn) was evaporated from a tungsten boat and the substrate was placed at a distance of 20 cm from the source.

Thin film thickness (t) is measured by using laser interferometer and applying the following equation [10], as shown in Figure (1).

\[ t = \frac{\Delta x \cdot \lambda}{x \cdot 2} \]  

Where x is the fringes spacing, \( \Delta x \) is the displacement between two fringes and \( \lambda \) is the wavelength of the used laser light (632.8nm).

Figure (1) shows the set-up of thin film thickness technique.
The evaporated films at room temperatures were oxidized using classical oxidation method by using a tube furnace operated at different temperatures (150, 200, 250 and 300°C).

A hot plate was used, and k-type thermocouple was used to monitor samples temperature.

The particle size distributions and surface morphology of SnO$_2$ nanostructure film prepared under various conditions were analyzed by atomic force microscope (AFM) (from a very high-resolution type of scanning probe microscopy AA3000).

X-ray diffraction measurement has been done and compared with the International centre for Diffraction Data (ICDD) cards, using Philips PW1050 X-ray diffractometer of $\lambda=1.5406$ Å from Cu-K$_\alpha$.

The electrical conductivity of the films was determined by two-point probe method at the temperature range 318-368 K.

The activation energy ($E_a$) which can be calculated using the equation:

$$\sigma_{dc} = \sigma_o \exp \left( \frac{-E_a}{kT} \right)$$

Where $\sigma_o$ is the high temperature limit of conductivity, $E_a$ is the activation energy and $kT$ is associated with temperature variation in the measurement where $k$ is Boltzmann constant and $T$ is absolute temperature [11].

**RESULTS AND DISCUSSION**

**Electrical properties**

The logarithmic conductivity as a function of temperature for SnO$_2$ oxide samples prepared at the optimum condition and fixed film thickness are given in Figure (2). It is clear that the values of conductivity increases with temperature, such as the general characteristics of the semiconductor with increasing temperature lead to an increase in the number of electron–holes pairs resulting in increased conductivity. The linear proportionality in the curve is related to the increase in the number of ionized carriers from the valance band to the conduction band as the substrate is heated.

The value of the activation energy has been estimated using equation (2). Table (1) shows the activation energy with film oxidation temperature. It has been found that the minimum value of activation energy at 200 °C.

The variation of conductivity as a function of temperature and oxidation temperature were given in Figure (2).

**Table (1) SnO$_2$ activation energy of variation oxidation temperature.**

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>$E_d$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.351817</td>
</tr>
<tr>
<td>200</td>
<td>0.128673</td>
</tr>
<tr>
<td>250</td>
<td>0.420643</td>
</tr>
<tr>
<td>300</td>
<td>0.135218</td>
</tr>
</tbody>
</table>
Surface morphology

The crystalinity of the produced material characterized using x-ray diffraction (XRD). This technique was also employed by other group which gives an indication about the grain size and formation material type of the prepared thin film. The following figures show the XRD patterns for samples grown at different oxidation temperature. For Sn films depositing on quartz substrate. One peak could be recognized in Figure (3), the film is single crystalline with a tetragonal structure according to the ASTM standards where (200) Sn, with lattice constant of (5.8285) respectively could be recognized. This is related to the formation of tin thin film and such result indicates that no formation of the oxide film occurs on quartz substrate.
Figure (4) XRD pattern of SnO\textsubscript{2} thin film at oxidation temperature (200°C).

Figure (5) XRD pattern of SnO\textsubscript{2} thin film at oxidation temperature (300°C).
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Table (2) Data extracted from the XRD analysis as a function of substrate temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Angle θ (deg)</th>
<th>hkl</th>
<th>Lattice constant (Å)</th>
<th>FWHM (deg)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>13.995</td>
<td>101</td>
<td>3.1881</td>
<td>0.1200</td>
<td>68.25</td>
</tr>
<tr>
<td>200</td>
<td>15.12</td>
<td>111</td>
<td>2.9554</td>
<td>0.2000</td>
<td>41.16</td>
</tr>
<tr>
<td></td>
<td>31.695</td>
<td>132</td>
<td>1.4674</td>
<td>0.2000</td>
<td>46.70</td>
</tr>
<tr>
<td></td>
<td>11.795</td>
<td>110</td>
<td>3.7684</td>
<td>0.86</td>
<td>9.44</td>
</tr>
<tr>
<td></td>
<td>5.67</td>
<td>020</td>
<td>2.85195</td>
<td>0.44</td>
<td>18.76</td>
</tr>
<tr>
<td></td>
<td>10.25</td>
<td></td>
<td>4.3289</td>
<td>0.28</td>
<td>28.84</td>
</tr>
<tr>
<td>300</td>
<td>15.14575</td>
<td></td>
<td>2.94823</td>
<td>0.1282</td>
<td>64.21</td>
</tr>
<tr>
<td></td>
<td>16.28175</td>
<td></td>
<td>2.74753</td>
<td>0.1671</td>
<td>49.54</td>
</tr>
<tr>
<td></td>
<td>15.8402</td>
<td></td>
<td>2.82207</td>
<td>0.1358</td>
<td>60.82</td>
</tr>
</tbody>
</table>

The AFM images of SnO₂ thin films as shown in Figure (6) revealed the distribution of particles become more consistent and the size is larger especially at (200°C). During the oxidation process, the atoms of the film get enough energy, so that position of the atoms changes and recrystallization occurs.

We have studied the surface morphology of the produced TCO films by atomic force microscope. We recognize that surface roughness of prepared film depended on oxidation temperature, the film roughness decrease from (11 nm) to about (6.53 nm) at (200°C) and increase to bout (29.1 nm) at higher temperature as given in Table (2).
Figure (6) AFM image of SnO₂ thin film at oxidation temperature (150°, 200° and 300° C)

Table (3).

<table>
<thead>
<tr>
<th>Oxidation Temp. (°C)</th>
<th>Roughness (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>200</td>
<td>6.53</td>
<td>8.85</td>
</tr>
<tr>
<td>300</td>
<td>29.1</td>
<td>39.7</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The SnO\textsubscript{2} TCO’s thin films prepared by classical thermal oxidation method on biological glass substrates result in a good orientation of preferred growth. The film structure becomes more symmetrical and compact, the degree of crystallization tends to be perfect, and moreover the minimum grain size is about 9.44 nm at 200°C oxidation temp. the lowest resistivity (about 5.35 x 10^-5 Ω cm) was obtained for the certain thin film at specific temperature of oxidation.

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