Effects of Annealing Temperature on the Characteristics of Nanocrystalline Tin Dioxide Thin Films

Imad H. Kadhim and H. Abu Hassan

Universiti Sains Malaysia, School of Physics, Nano-Optoelectronics Research and Technology Laboratory, 11800, Penang, Malaysia.

Ministry of Education, Iraq-Baghdad

INTRODUCTION

Metal oxide semiconductors extensively studied in recent years because of their properties and applications. For example, tin dioxide is a n-type semiconductor with a large band gap of 3.6 eV at 300 K (Li, H., et al., 2010; Sun, S.H., et al., 2003, Briand, D., et al., 1998), which have different advantages such as a low cost, mechanical and chemical stabilities. SnO2 used in different applications, especially for detection of inflammable gases and for toxic gases (Zhang, Z., et al., 2012). SnO2 thin films could be prepared by various methods, including sol-gel (Jeng, J.S., 2012; Liu, J., et al., 2010), solvothermal (Kang, S.Z., et al., 2007), thermal evaporation (Katti, V.R., et al., 2003), laser ablation (Sasaki, T., et al., 2004), chemical vapor deposition(Liu, Y., et al., 2005), RF magnetron sputtering (Gubbins, M.A., et al., 2002), and spray pyrolysis (Chacko, S., et al., 2006). The sol–gel method has been chosen to prepare SnO2 thin films because it has a lot of preferences compared to others used. It could be done at low reaction temperatures, easy processes, and is not expensive (Liu, J., et al., 2010). The nanoparticles and nano-sized elements can improve the material properties, such as better electrical conductivity, band gap, magnetic properties, and strength because of the very high surface-to-volume ratio (Mahdi, M.A., et al., 2012; Nagrajan, R., et al., 2008). In recent years, several studies have attempted to discover a good candidate for the fabrication of thin films benefits into different application such as gas sensors (Wang, Y., et al., 2006; Ansari, Z.A., et al., 2002). Both the crystallinity and crystal size generally increase as aging heat time increases (Shahini, S., et al., 2011). Temperature plays a decisive role in controlling particle sizes (Adnan, R., et al., 2010). According to (Li, Y., et al., 2012), as-deposited SnO2 film was initially amorphous, thereafter began to crystallize gradually with increased annealing temperature and began at 400 °C for 30 min. The electrical resistance of SnO2 thin films decreased with increasing the thickness of films (Sakai, G., et al., 2001). A blue shift of A1g phonon mode peak was observed in SnO2 thin films with increased grain size (Li, Y., et al.,2012; Shek, C. H., et al., 1999). The main goal of the study is to fabricate a high-quality, crack-free and no agglomerations appear for nanocrystalline SnO2 thin films at low temperature using a low cost method. Also it was found the best conditions to
enhance nanocrystalline SnO$_2$ thin films which were prepared via sol-gel spin coating method.

1. Methodology:

Si substrates have been cleaned using the Radio Corporation of America (RCA) method. Nanocrystalline SnO$_2$ thin films prepared by the sol-gel spin coating method according to the previous studies (Jeng, J. S., 2012; Liu, J., et al., 2010). The sol solution prepared by dissolving 0.1 M tin chloride dehydrate (SnCl$_2$·2H$_2$O) into 70 mL of pure ethanol (C$_2$H$_5$OH). Eliminate cracks by adding glycerin (C$_3$H$_8$O$_3$) to a volume ratio of (1:12) (Gong, S., et al., 2009), and put in a closed flask. The mixture in the covered flask was stirred using a magnetic stirrer for 3 h and kept at 70°C for 8 h. The aging heats for 8 h applied to enhance the solubility of tin chloride dehydrate in pure ethanol, which is to reduce defects and to produce a sol-gel solution with high viscosity. The sol solution was completed for the remainder of the 24-hour at room temperature. Thereafter, the sol solution was spin-coated on p-type Si (100) substrates at a rotation speed of 900 rpm for the first 6 s and then 3000 rpm for the succeeding 30 s to ensure that the film layers were uniformly distributed. The as-deposited thin films were then oven-dried at 100°C for 10 to 12 min. Both spin-coating and drying were repeated ten times for all thin films. Thereafter the obtained thin films are annealed at 400, 500, and 600°C in air for 2 h. In current study, the crystal structure of the production samples have been characterized by X-ray diffraction (XRD) PANalytical X’pert Pro MRD equipped with a Cu Kα radiation of (λ = 0.154060 nm). The morphologies were characterized by a FESEM (model Leo-Supra 50VP, Carl Zeiss, Germany). Raman backscattering measurements were performed at room temperature using Jobin Yvon HR800UV.

3. Results:

Fig. 1 shows XRD patterns for as-deposited and annealed SnO$_2$ thin films prepared by sol-gel spin coating method on Si substrates. Fig. 1(a) indicates that as-deposited thin films emerged as amorphous and does not appear any X-ray diffraction peaks related to SnO$_2$ (Jeng, J. S., 2012; Li, Y., et al., 2012; Ke, C., et al., 2011). All annealed thin films show different reflection peaks which have been matched to a standard bulk SnO$_2$ and showed as tetragonal rutile structure (JCPDS card No. 041-1455). Table 1 emerged the comparison of the 2-values found from the measurement XRD patterns for the thin films annealed at different annealing temperatures. Fig. 1(b) shows diffraction peaks for the thin films annealed at 400°C which correspond to (110), (101), (200), (211) and (220) planes. It was found that with increasing annealing temperature leads to increase the intensities of diffraction peaks which became stronger and sharper (Jeng, J. S., 2012; Li, Y., et al., 2012). Fig. 1(d) shows the diffraction peaks that compatible with (110), (101), (200), (211), (220), (002), (310) and (112) planes for thin films annealed at 600°C.

Fig. 1: XRD patterns for SnO$_2$ thin films prepared from sol solution at 70°C for 8h aging heat time: (a) as-deposited and annealed for 2 h in air at (b) 400°C, (c) 500°C and (d) 600°C.
The average of crystallite size (D) of nanocrystalline SnO$_2$ thin films was calculated for the annealed thin films from the main and the first diffraction peak (110) using Debye-Sherrer formula, (Chandramouleeswaran, S., et al., 2007):

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$

where $\beta$ is the full width at half-maximum of the major peak, $\lambda$ is the X-ray wavelength of the radiation, and $\theta$ is the diffraction angle.

It was found a significant increase in the crystallite size of thin films prepared from 400 to 500°C. No significant change in the crystallite size of thin films prepared from 500 to 600°C. Where nanoparticles still have the same crystallite size and clumped together until formed agglomerations. This result is consistent with surface morphology measurements as shown in Fig. 2(d). These findings indicate the heat of annealing that enhance the crystallization in thin films, increased crystallite size, and reduced defect (Li, Y., et al., 2012; Ke, C., et al., 2011) as shown in Table 2.

**Table 1**: The comparison of the 2- values found from the measurement XRD patterns for the thin films annealed at different annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Plane (110)</th>
<th>Plane (101)</th>
<th>Plane (211)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.59°</td>
<td>31.88°</td>
<td>51.78°</td>
</tr>
<tr>
<td>400</td>
<td>26.591</td>
<td>31.888</td>
<td>51.787</td>
</tr>
<tr>
<td>500</td>
<td>26.562</td>
<td>31.876</td>
<td>51.635</td>
</tr>
<tr>
<td>600</td>
<td>26.531</td>
<td>31.812</td>
<td>51.668</td>
</tr>
</tbody>
</table>

**Table 2**: The crystallite size of SnO$_2$ thin films prepared from sol solution at 70°C for 8h aging heat time at different annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>8.30</td>
</tr>
<tr>
<td>500</td>
<td>33.19</td>
</tr>
<tr>
<td>600</td>
<td>53.20</td>
</tr>
</tbody>
</table>

Fig. 2. shows FESEM images that the levels of evolution for SnO$_2$ morphology were prepared on Si substrates. Fig. 2(a) shows the surface morphologies of as-deposited thin films which have a smooth surface. This morphology is matched with the amorphous nature of SnO$_2$ thin films (Jeng, J. S., 2012; Li, Y., et al., 2012; Ke, C., et al., 2011). After annealing to 400°C, small nanoparticles were observed, and the thin films are polycrystalline with uniform structures as shown in Fig. 2 (b). Particles size increased and became more homogeneous when the annealing temperature was increased to 500°C as shown in Fig. 2 (c). At 600°C annealing temperature, agglomerations of SnO$_2$ particles was observed, as shown in Fig. 2 (d). The increases of agglomerations lead to decrease of gas response (Korotcenkov, G., et al., 2003; Kim, H. R., et al., 2009). These results show that annealing temperature caused to enhance the crystallinity and to reduce defects for thin films (Jeng, J. S., 2012; Li, Y., et al., 2012).

**Fig. 2**: FESEM images for SnO$_2$ thin films prepared from sol solution at 70°C for 8h aging heat time: (a) as-deposited and annealed for 2 h in air at (b) 400°C, (c) 500°C and (d) 600°C.
Fig. 3. shows that the average thickness of as-deposited film was 470 nm. This thickness is related with the high viscosity of the sol solution which produced by the high aging heat time for 8 h. In general, with increasing viscosity produced to increase in the thickness of film at constant spin-coating speeds (Viana, M. M., et al., 2006).

![Cross-section FESEM images for SnO₂ thin films prepared from sol solution at 70°C for 8h aging heat time for as-deposited.](image)

Fig. 3: Cross-section FESEM images for SnO₂ thin films prepared from sol solution at 70°C for 8h aging heat time for as-deposited.

Fig. 4. emerged Raman spectroscopy of nanocrystalline SnO₂ was prepared on Si substrate. Raman spectroscopy measurements were completed. Fig. 4(a) emerged the spectrum of as-deposited SnO₂ thin films, no Raman mode was observed due to of the amorphous nature of the thin film (Ristić, M., et al., 2002). In Figs. 4 (b) to (d), Raman peaks were observed, and their intensities were clearly improved with increasing annealing temperature. Hence, A₁g phonon mode peaks were observed at 614.54, 625.24 and 633.62 cm⁻¹, respectively. These wavenumber values are lower than the bulk SnO₂ value of 638 cm⁻¹. A₁g phonon mode is related to grain size and shifts to a higher wavenumber with increasing in grain size ((Li, Y., et al.,2012; Shek, C.H., et al., 1999; Dieguez, A., et al., 2001).

![Raman spectroscopy for SnO₂ thin films prepared from sol solution at 70°C for 8h aging heat time: (a) as-deposited and annealed for 2 h in air at (b) 400°C, (c) 500°C and (d) 600°C.](image)

Fig. 4: Raman spectroscopy for SnO₂ thin films prepared from sol solution at 70°C for 8h aging heat time: (a) as-deposited and annealed for 2 h in air at (b) 400°C, (c) 500°C and (d) 600°C.
4. Conclusion:
Nanocrystalline SnO$_2$ thin films have been prepared by a simple cost-effective method by adding glycerin via sol-gel spin coating method on p-type (100) Si substrates. The XRD, and FESEM analysis emerged that crystallization of thin films obtained at 400°C, and all annealed thin films for 2h in air are tetragonal rutile structure. With increasing annealing temperature from 400 to 600°C the crystallization of SnO$_2$ thin films enhanced, reduced defects, and increased in crystallite size from 8.30 to 32.20 nm. With increasing annealing temperature, A1g phonon mode of Raman spectroscopy emerged blue shifts due to increase in crystallite size. The findings show that the annealing temperature for thin films at 500°C was selected to fabricate of nanocrystalline SnO$_2$ thin films in order to avoid agglomerations.

REFERENCES


