Large-Area Deposition of Tin Oxide Film by Photochemical Vapour Deposition

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The tin oxide (SnO2) films are thermally and chemically stable, and have been applied to various fields. The SnO2 (non-doped) films were prepared by a photochemical vapour deposition (photo-CVD) process. TMT (Sn(CH3)4) and O2 (containing 4 mol.% O3) were used as the source materials, and a low-pressure mercury lamp was used as the light source. By the combination of a linearly focused low-pressure mercury lamp through a semi-cylindrical suprasil window and a reciprocation of the substrate, a good uniformity along the 8 cm × 10 cm area was realised at a substrate temperature of 200 and 250°C. The SnO2 films prepared at lower temperature had better uniformity. The minimum resistivity of 6.8 × 10⁻³ Ω·cm was obtained at a substrate temperature of 250°C.

1. Introduction

The tin oxide (SnO2) films are thermally and chemically stable, and have been applied to various fields such as liquid crystal displays, transparent electrical heaters, solar cells, etc. Many fabrication processes for the SnO2 films have been proposed such as spray pyrolysis⁶, sol-gel technique⁶, RF sputtering⁷, atmospheric pressure chemical vapour deposition⁵, and photochemical vapour deposition (photo-CVD)⁵,⁶. The photo-CVD is expected to be a low-temperature processing⁵,⁶. We have prepared the SnO2 films by the photo-CVD: the minimum resistivity of a non-doped SnO2 film has been 3 × 10⁻³ Ω·cm at a substrate temperature of 300°C⁷, and that of F-doped SnO2 film has been 4.5 × 10⁻⁴ Ω·cm at 350°C⁸. We have also shown that the photo-CVD could realise higher growth rate compared with the thermal-CVD⁷,⁸. For the practical use of the photo-CVD, a large-area deposition technique is indispensable as well as the low-temperature fabrication process.

In the following, our experimental results on the large-area photo-CVD of the non-doped SnO2 films at a low substrate temperature are shown.

2. Experiment

A schematic diagram of the photo-CVD system (UVD-200TS: SAMCO Inc.) is shown in Fig. 1. A low-pressure mercury lamp (200 W) irradiates a substrate through a semi-cylindrical suprasil window. On the inner surface of the suprasil window, a polymer film was put in order to prevent the window being contaminated. Two local exhausters were also set under the suprasil window in order to prevent the window being contaminated. The estimated gas flow in the chamber is shown in Fig. 1. The pressure in the lamp house was kept at 7.5 × 10⁴ Pa. This photo-CVD system can realise the large-area deposition by the combination of a linearly focused light and a reciprocation (12 sec/cycle) of the substrate (Fig. 2–(a)). The light intensity distribution (254 nm) on the substrate along the direction of the reciprocation of the substrate is shown in Fig. 2–(b). The light intensity along the central axis of the lamp was uniform. The distance between the window and the substrate is 90 mm.

TMT (Sn(CH3)4) and O2 (containing 4 mol.% O3) were used as the source materials. In our previous results, it is proved that O3 contributes to
higher growth rate\(^7,8\). The doping material was not used in this experiment. The deposition parameters are shown in Table 1. The SnO\(_2\) films were deposited on the slide glass substrates (11 cm × 11 cm).

The electrical resistivity of the film was measured by the van der Pauw method. The optical transmittance was measured by a Shimadzu spectrophotometer UV-1600PC. The XRD pattern was measured by a Rigaku X-ray diffractomator RV-200. A total of 36 points were sampled for the measurement of the thickness and the resistivity, and a total of 5 points for the measurement of the transmittance.

### 3. Results and Discussion

The average resistivity, the thickness, the distribution of the thickness and the average transmittance at 550 nm (including the substrate) of the non-doped SnO\(_2\) films are shown in Table 2. The XRD measurements were made at CuK\(\alpha\) in the \(\theta-2\theta\) geometry. The SnO\(_2\) films prepared at 200°C and

**Table 1** Deposition parameter of SnO\(_2\) films

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Light intensity (center)</td>
<td>8 mW/cm(^2) (254 nm)</td>
</tr>
<tr>
<td>TMT flow rate</td>
<td>3 sccm</td>
</tr>
<tr>
<td>(\text{O}_2) (4 mol.%O(_3)) flow rate</td>
<td>300 sccm</td>
</tr>
<tr>
<td>Total Pressure</td>
<td>1.33 × 10(^3) Pa</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>200, 250, 300°C</td>
</tr>
<tr>
<td>Deposition time</td>
<td>60 min</td>
</tr>
</tbody>
</table>

**Table 2** Average resistivity, thickness, distribution of thickness, average transmittance (including the substrate) at 550 nm of non-doped SnO\(_2\) films prepared by photo-CVD

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Average resistivity (Ω·cm)</th>
<th>Thickness (µm)</th>
<th>Distribution of thickness (%)(^a)</th>
<th>Distribution of thickness (%)(^b)</th>
<th>Average transmittance at 550 nm(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>(9.2 \times 10^{-3})</td>
<td>0.13 – 0.16</td>
<td>±10</td>
<td>±7</td>
<td>88</td>
</tr>
<tr>
<td>250</td>
<td>(6.8 \times 10^{-3})</td>
<td>0.20 – 0.26</td>
<td>±13</td>
<td>±6</td>
<td>79</td>
</tr>
<tr>
<td>300</td>
<td>(3.6 \times 10^{-2})</td>
<td>0.22 – 0.42</td>
<td>±31</td>
<td>±13</td>
<td>87</td>
</tr>
</tbody>
</table>

\(^a\) 11 cm × 11 cm area (indicated by the symbol □ and ■ in Fig. 3)

\(^b\) 8 cm × 10 cm area (indicated by the symbol □ in Fig. 3)
250°C were amorphous. The SnO$_2$ film prepared at 300°C was polycrystalline: the SnO$_2$ (110) peak and the SnO$_2$ (211) peak were observed.

The minimum resistivity of $6.8 \times 10^{-3}$ Ω·cm was obtained at a substrates temperature of 250°C. The existence of the minimum peak of the resistivity is quite similar to our previous result obtained by our another experimental apparatus. The resistivity of the SnO$_2$ film at 300°C is higher than that at 250°C, which could be due to the reduction of carrier concentration at the crystalline film. The resistivity of the SnO$_2$ film at 200°C is also higher than that at 250°C, which could be due to the reduction of mobility at the amorphous film. In our preliminary experiment, the resistivity of the film increased abruptly below the substrate temperature of 200°C.

The measured points (36 points) of the film thickness are shown in Fig. 3. As shown in Table 2, the SnO$_2$ films prepared at lower temperature had better uniformity to the whole area (11 cm × 11 cm: indicated by both symbol □ and ■ in Fig. 3). To a limited area (8 cm × 10 cm: indicated by the symbol □ in Fig. 3), the uniformity was improved for all samples (Table 2). It may be said that the distribution of the thickness is affected by the spatial distribution of the CVD-source materials and the distribution of the substrate temperature. It may also be said that the effect of these factors becomes remarkable at higher substrate temperature. The distribution of thickness of the SnO$_2$ film (prepared at 250°C) for each row of 6 points is shown in Fig. 4. The rows are labeled as (a)−(f) from the top as shown in Fig. 3. In Fig. 4, the dot-dash lines show the average thickness and the broken lines show the deviation level of 5%. In order to realise a good uniformity to the whole area (11 cm × 11 cm), the improvement of the nozzle arrangement is required.

4. Conclusions

The tin oxide (SnO$_2$: non-doped) films were prepared by a photo-CVD process. The minimum resistivity of $6.8 \times 10^{-3}$ Ω·cm was obtained at a substrate temperature of 250°C. By the combination of a linearly focused low-pressure mercury lamp and a reciprocation of the substrate, a good uniformity along the 8 cm × 10 cm area was realised. The SnO$_2$ films prepared at lower temperature had better uniformity.

References