Crystal Orientation and Electrical Properties of Tin Oxide Transparent Conducting Films Deposited on Rutile Surface

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Abstract. Thin films of tin oxide (SnO₂) without doping are attractive transparent conducting film since environmentally unfavorable elements of antimony or fluorine are eliminated. Tin oxide films without doping were fabricated very cheaply on (001) and (100) planes of single crystal of rutile (TiO₂) by spray chemical vapor deposition (mist CVD). The film deposited on rutile (001) surface was poorly epitaxial (double domain) but with higher mobility (24 cm² V⁻¹ s⁻¹) and lower resistivity (1.6×10⁻³ Ω cm) than that deposited on glass substrate (16 cm² V⁻¹ s⁻¹ and 2.4×10⁻³ Ω cm) for reference. Deposition on rutile (100) surface resulted in better epitaxial growth (single domain). The mobility (39 cm² V⁻¹ s⁻¹) and the carrier electron density (2.7×10²⁰ cm⁻³) were much higher. The resistivity (6.2×10⁻⁴ Ω cm) was compatible with those doped with antimony or fluorine and will be the lowest among tin oxide films without doping.

1. Introduction

Transparent conducting films are necessary for solar cells, displays, touch panels etc. A typical TCF material at present is tin-doped indium oxide (indium-tin-oxide, ITO) is often fabricated by physical vapor deposition such as magnetron sputtering. The authors reported elsewhere [1, 2] very cheap ITO films fabricated by original spray chemical vapor deposition (mist CVD). The lowest resistivity (7.5×10⁻⁵ Ω cm) when deposited on a glass substrate and annealed in reducing atmosphere agreed with the value reported by Ohata et al. [3] who deposited on an yttrium-stabilized zirconia single crystal substrate by expensive pulsed laser deposition.

Indium is a rare element and fine powders of indium oxide damage human lungs. Aluminum or gallium-doped zinc oxide (AZO or GZO) has been developed as an alternative material. Low resistivity in the order of 10⁻⁴ Ω cm has been possible by physical vapor deposition such as magnetron sputtering or ion plating while deposition of AZO or GZO films has been impossible or very difficult by chemical process including our spray CVD.

Another alternative material, tin oxide (SnO₂), needs doping of antimony or fluorine which are environmentally unfavorable. The authors reported elsewhere [4] tin oxide film without doping on glass substrate by spray CVD. The resistivity (6.2×10⁻³ Ω cm) as-deposited at 255°C unfortunately did not seem sufficiently low; the mobility, 21 cm² V⁻¹ s⁻¹ and carrier electron density, 4.3×10¹⁹ cm⁻³.

Exceptionally low resistivity (7.5×10⁻⁵ Ω cm) was reported by Banerjee and Das [5] for undoped tin oxide film deposited on glass by electron beam evaporation and annealing in air; mobility, 29 cm² V⁻¹ s⁻¹ and carrier electron density, 2×10²⁰ cm⁻³.

Crystal structure of SnO₂ (cassiterite) is rutile type, tetragonal system. Tin oxide films without doping were deposited in the present research on single crystal of rutile (TiO₂) substrates to improve...
crystallinity and mobility of the carrier electron to lower the resistivity. Post-deposition annealing in reducing atmosphere was also executed to increase the carrier electron density.

Undoped tin oxide films on rutile substrate were deposited by magnetron sputtering [6], metal-organic CVD (MOCVD) [7], atomic layer deposition (ALD) [8] and CVD [9]. However, none of them reported the resistivity. Undoped tin oxide films were deposited on sapphire substrate by pulsed-laser deposition (PLD) [10], CVD [11, 12] and molecular beam epitaxy (MBE) [13]. These achieved high mobility but failed to achieve sufficient carrier electron density and resulted in high resistivity. Exceptionally low mobility tin oxide film was deposited on sapphire by PLD [14]. These reported values were scattering. The electrical properties seem to highly depend on the deposition process.

2. Experimental

Mirror-polished rutile (single crystal of TiO$_2$) substrates (10 mm×10 mm×0.5 mm) with (001) and (100) surfaces were supplied from Crystal Base Co. and used without thermal treatment prior to the film deposition. Non-alkali glass substrates (Corning EAGLE XG, 10 mm×10 mm×0.7 mm) were used for reference. These substrates were ultrasonically cleaned in Semicoclean 56 (Furuuchi Chemical Co.), rinsed with pure water and boiled in acetone. Tin chloride, SnCl$_4$·5H$_2$O, (Kanto Chemical) was dissolved in industrial alcohol (Imazu Chemical; ethanol 88.40%, isopropanol 10.49%, methyl ethyl ketone 1.11%) to prepare spray solution. Concentration of tin chloride was 0.1 M. A rutile substrate and a glass substrate were heated simultaneously at 400°C on a hotplate (Corning PC-400D). The surface temperatures of the substrates were measured by contact-type resistance thermometer (RKC Instrument, DP-300). The solution was sprayed manually 300 times at the interval of 5 s using an atomizer (SHO-BI, PV14033-00). Distance between the nozzle and the substrates was 15 cm. The films were annealed in the electric furnace at 600°C for 1 h in reducing atmosphere of N$_2$-0.1%H$_2$ (flow rate, 300 mL/min) to lower the resistivity. The film thickness was determined by X-ray fluorescence analysis (energy-dispersive type, JEOL JSX-3200) using fundamental parameter method assuming the film density as 6.45 g cm$^{-3}$. The film thicknesses were, 180, 145 and 123 nm, respectively, for on glass, (001) and (100) rutile surface. The thickness depended on the substrate. The crystal state of the films was evaluated with MiniFlex300 (θ-2θ mode), Rigaku and SmartLab3kW (in-plane and out-of-plane mode etc.), Rigaku.

3. Results and Discussion

3.1 Crystal Orientation

Figure 1 shows X-ray diffraction spectra for SnO$_2$ films after post-deposition annealing in reducing atmosphere.

The spectrum of the film deposited on a glass is amplified by 10 times since the peak intensity was weaker. Ten SnO$_2$ peaks were detected. The crystal orientation was approximately random. The average crystallite size determined from the peaks were approximately 41 nm. Unidentified weak peaks were detected at 63.92 and 77.14°.

The XRD spectrum for SnO$_2$ film deposited on rutile (001) surface showed weak and wider (002) and (301) peaks of SnO$_2$. The crystallite sizes were, respectively, 16 and 14 nm which were much smaller than that deposited on glass substrate. Results of in-plane and out-of-plane measurement are omitted. Epitaxial growth (double-domain) as TiO$_2$ 001 // SnO$_2$ 001 // SnO$_2$ 301/031 (out-of-plane direction) and TiO$_2$ 010 // SnO$_2$ 010 // SnO$_2$ 101/011 (in-plane direction). It should be kept in mind that the film was low crystallinity with small crystallite size although epitaxial. Unidentified weak peaks were detected at 31.52 and 56.14°.

The X-ray diffraction spectrum for SnO$_2$ film deposited on rutile (100) surface showed very sharp and strong (200) and (400) peaks of TiO$_2$ substrate and (200) and (400) peaks of SnO$_2$ film. The crystallite size (63 nm) was larger than those deposited on glass substrate (41 nm). Successful epitaxial growth (single-domain) of SnO$_2$ film was confirmed as TiO$_2$ 100 // SnO$_2$ 100 (out-of-plane direction) and TiO$_2$ 010 // SnO$_2$ 010 (in-plane direction). Very weak (101) and (212) peaks of SnO$_2$ were detected. Unidentified weak peaks at 35.24 and 72.18° were detected.
3.2 Electrical Properties

Figure 2 shows dependence of mobility on the carrier electron density. The dotted lines show the resistivity $1 \times 10^{-3}$ and $1 \times 10^{-2} \ \Omega \ \text{cm}$.

In case of SnO$_2$ film deposited on glass for reference, the mobility $(16 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1})$ was approximately same with our previous film [4]. Post-deposition annealing in reducing atmosphere increased remarkably (4 times) the carrier electron density $(1.7 \times 10^{20} \ \text{cm}^{-3})$ than the previous as-deposited film. The resistivity $(2.4 \times 10^{-3} \ \text{cm}^{-3})$ was much lower than the previous film although much higher than that that deposited by Banerjee and Das [5] by physical process.

Deposition on single crystal substrates increased the mobility and lowered the resistivity remarkably. Deposition on rutile (001) surface increased the mobility to $24 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$, which is 1.5 times of that deposited on glass. Thus poorly-epitaxial growth (double domain) lowered the resistivity to $1.6 \times 10^{-3} \ \Omega \ \text{cm}$ although the carrier electron density $(1.7 \times 10^{20} \ \text{cm}^{-3})$ unchanged from that deposited on glass.

Deposition on rutile (100) surface increased the mobility drastically to $39 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$, which is 2.4 times of that deposited on glass. This should be attributed to the successful epitaxial growth (single domain) of the SnO$_2$ film. The carrier electron concentration also increased to $2.7 \times 10^{20} \ \text{cm}^{-3}$, which is 1.6 times of that deposited on glass. The reason of increasing carrier electron concentration is not clear but tentatively attributed to the crystal growth dependent on the substrate surface. Thus, the resistivity...
was lowered to $6.2 \times 10^{-4} \, \Omega \, \text{cm}$. This value seems the lowest among the SnO$_2$ films without doping and compatible with antimony or fluorine-doped tin oxide (ATO or FTO) films.

![Graph of Dependence of Mobility on Carrier Electron Density for SnO$_2$ Films after Post-deposition Annealing](image)

**Figure 2.** Dependence of mobility on carrier electron density for SnO$_2$ films after post-deposition annealing.

### 3.3 Optical Properties

Average transmittance in visible range was approximately 80% when deposited on a glass substrate. Reflection from the rutile substrate is high (approx. 35%) because of high refractive index of rutile (approximately 2.7). Transmittance improved slightly by depositing SnO$_2$ film. This should be attributed to lower refractive index of SnO$_2$ film. Low visible transmittance will be no problem in many cases since deposition of antireflective coating with much lower reflective index on SnO$_2$ film will increase the transmittance if necessary.

### 4. Conclusions

Thin films of tin oxide (SnO$_2$) without doping were fabricated on single crystal substrate of rutile (TiO$_2$) by spray CVD.

The film deposited on rutile (001) surface was poorly epitaxial (double domain). The mobility (24 cm$^2$ V$^{-1}$ s$^{-1}$) was higher than that (16 cm$^2$ V$^{-1}$ s$^{-1}$) deposited on glass. The carrier electron density (1.7×10$^{20}$ cm$^{-3}$) was same as on glass. The resistivity (1.6×10$^{-3}$ Ω cm) was lower than that deposited on glass substrate (2.4×10$^{-3}$ Ω cm).

The film deposited on rutile (100) surface was epitaxial (single domain) with much higher mobility (39 cm$^2$ V$^{-1}$ s$^{-1}$) and higher carrier electron density (2.7×10$^{20}$ cm$^{-3}$). The resistivity (6.2×10$^{-4}$ Ω cm) was compatible with those of tin oxide films doped with antimony or fluorine which are environmentally unfavorable elements.

### 5. References

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