

Greener Spray CVD Process with Water Solution to Fabricate Transparent IR-Shielding Films on Glass Windows

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Indium-tin-oxide (tin-doped In_2O_3) thin films are indispensable for flat panel displays and solar cells. The ITO coated glass windows absorb near-infrared radiation from the Sun in summer and reflect far-infrared radiation from the interior in winter to reduce the energy consumption for cooling and heating, respectively. The ITO films are usually deposited by sputtering process which requires expensive vacuum system and ceramic targets whose sintering needs heating at high temperature. The authors reported elsewhere the inexpensive spray CVD (chemical vapor deposition) using ethanol solution of indium chloride and tin chloride. The solvent is replaced in the present study by water as a more environmentally-benign one for easier recycling of uncoated raw materials and the by-product of hydrogen chloride. The lowest resistivity was 9.7×10^{-5} ohm cm after the post-deposition annealing at 600°C in N_2 -0.1% H_2 flow. This value was compatible with our previous report using ethanol solvent and the one deposited by sputtering process. An ITO film deposited with a less green solvent, 2-propanol at approximately is briefly demonstrated.

Key words: ITO, transparent conducting films, indium-tin-oxide, water, indium chloride

1. INTRODUCTION

Indium-tin-oxide (tin-doped indium oxide, In_2O_3) is a typical transparent conducting material and its thin films are widely used as transparent electrodes for all flat panel displays including liquid crystal displays (LCDs), plasma display panels (PDPs), organic light-emitting diodes (OLEDs) and various kinds of solar cells. The ITO-coated glass windows, so-called low-E windows, absorb near-infrared radiation from the Sun beam in summer and reflect far-infrared radiation from the interior in winter so that the energy consumption for cooling and heating, respectively, is expected. Transparent infrared-shielding windows can be applied to oven front windows, housings for incandescent lamps, cover glasses for flat plate solar collectors and coatings for low emissivity as reported since the early stage of the research history [1-8]. The ITO films are deposited mainly by magnetron sputtering process using an expensive vacuum system. Deposition of low-resistivity films requires dense ceramic targets whose sintering must be executed at high temperature ($>1400^\circ\text{C}$) in oxygen atmosphere in a special furnace. Therefore, large-area deposition is difficult and costly high. The target must be replaced after only a limited portion was engraved during the sputtering process. A

lot of sputtered materials are deposited onto the inner wall of the deposition chamber. The above in mind, the present paper describes an inexpensive chemical processes, spray CVD (chemical vapor deposition) which is sometimes called as spray pyrolysis or mist CVD. The authors reported elsewhere the process using stable and cheap raw materials (indium chloride and tin chloride) and a stable and environmentally-benign solvent (ethanol) [9-10]. In the present study, the solvent was replaced by water which is greener i.e. more environmentally benign and much cheaper than ethanol. The spray CVD process accompanies a lot of unused raw materials stuck on the cold wall of the deposition chamber. The unused raw materials is can be washed by water relatively easily for the reuse. Water is safer against the fire accident compared with ethanol which ignites at approximately 500 - 550°C according to our experience. The resistivities of the present ITO films were compatible with the ones in our previous report and those deposited by sputtering process. The results using a less greener solvent, 2-propanol, was demonstrated briefly for comparison.

2. EXPERIMENTAL

Indium (III) chloride and tin (II) chloride were

dissolved in water instead of ethanol. Concentration of the total metal ions was 0.1 mol/l. The spray CVD process was executed by spraying (100 times) the solution using an atomizer on to a glass substrate (Corning 7059) heated on a laboratory hotplate at 300-350°C as described elsewhere [9, 10]; the distance between the atomizer and the substrate was 25 cm. The as-deposited films were thermally reduced at 600°C in order to lower the resistivity in $N_2-0.2\%H_2$ flow for 2 hours, respectively. A less environmentally-benign solvent, 2-propanol, was also attempted for comparison; 0.1 mol/l solution of 3 at.% Sn was sprayed 200 times onto Corning 1737 glass substrate.

The film thickness and composition (Sn/(In+Sn) atomic ratios) were determined by X-ray fluorescent analysis (Energy dispersive type, fundamental parameter method; model JSX-3200, JEOL). The crystalline states of the films were examined by an X-ray diffraction analysis using a $CuK\alpha$ radiation (acceleration voltage, 40 kV; target current, 300 mA; model RINT 2500T, RIGAKU).

The resistivity was measured by four-point-probe method (the probe distance, 0.65 mm; the probe current, 1 mA) with a digital multi-meter (model 34401, Hewlett Packerd). The Hall coefficient was measured by van der Pauw method (probe current, 1 mA; model MI675, Sanwa Radio Measurement Corp. Inc.). The optical transmittance and reflectance was measured with a conventional spectrometer (model Ubest V-570DS, JASCO); an aluminum plate was used as the reference for 100% reflectance.

3. RESULTS AND DISCUSSION

3.1 Crystalline state, composition and thickness of the films

The X-ray diffraction spectra for all deposited films agreed with that for the cubic indium oxide, In_2O_3 . No extra phase was detected. Indium oxide and tin-doped indium oxide were successfully deposited using water solution as well as ethanol solution. Strong 400 diffraction peaks indicated preferred orientation of the crystallites.

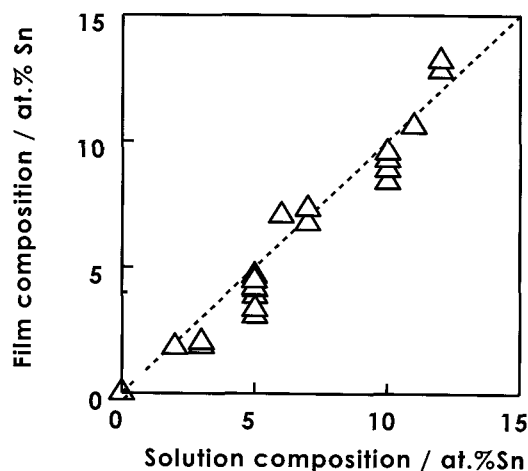


Fig. 1 Film composition determined by X-ray fluorescence analysis.

Film compositions (Sn/(In+Sn) ratios in at.%) are indicated in Fig. 1 as a function of the solution concentration. The both compositions agreed approximately although the values are scattered.

Film thicknesses (mass thickness) are indicated in Fig. 2 as a function of the film composition. The values scatter between 220 and 300 nm. A slightly thicker film fabricated using 3 at.% Sn and 2-propanol solution is due to extra times of spraying (200 times).

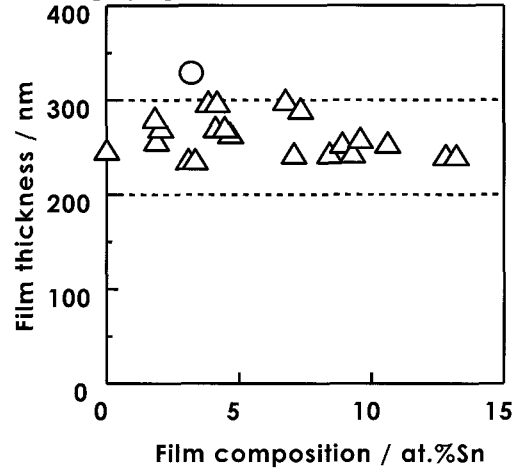


Fig. 2 Film thicknesses (mass thickness) determined by the X-ray fluorescent analysis.

Δ and \circ : fabricated using water and 2-propanol solvent, respectively.

3.2 Electrical properties

Resistivity of the films fabricated with water solutions are indicated in Fig. 3. The resistivity was lowered by tin doping. Annealing in reduced atmosphere (thermal reduction) lowered the resistivity.

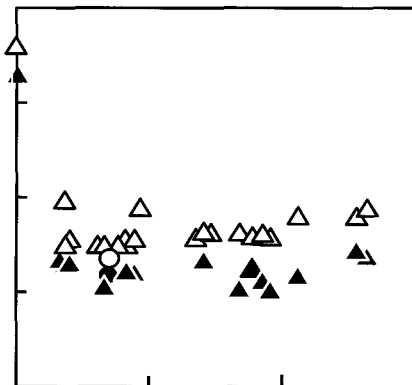


Fig. 3 Resistivity for the ITO films fabricated with water solution as a function of the film composition.

Δ and \blacktriangle , as-deposited and after annealed, respectively;

○, as-deposited fabricated using 2-propanol solutions for comparison.

The lowest one in the present study for the annealed film was 9.7×10^{-5} ohm cm (9.5 at.% Sn; thickness, 256 nm). This value was compatible with our previous work using ethanol solvent (9.5×10^{-5} ohm cm, 4.4 at.% Sn; thickness, 190 nm [9]) and compatible with those deposited by the sputtering process. Thus deposition using a greener water solvent was successfully achieved.

A similar resistivity (1.6×10^{-4} ohm cm) was obtained when deposited using a less greener solvent, 2-propanol solvent (3 at.% Sn; thickness, 340 nm). These similar results should be attributed basically to the similar boiling temperature of the solvents; 78.3, 100 and 97.2°C, for ethanol, water and 2-propanol, respectively.

The carrier concentration is indicated in Fig. 4 as a function of the film composition. The carrier concentration was increased by tin doping and annealing (thermal reduction). The carrier mobilities were scattered so that interpretation was abandoned in the present study.

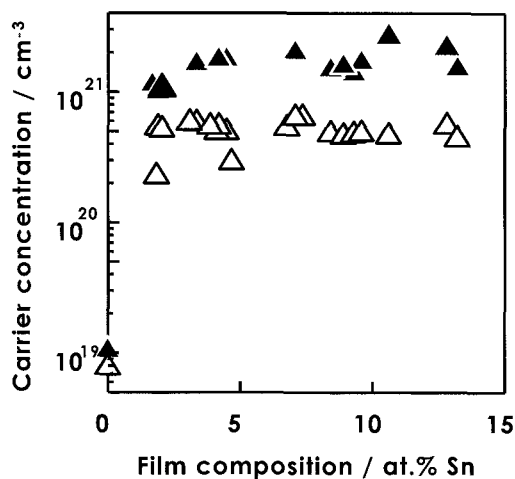


Fig. 4 Carrier concentration for the films fabricated using ethanol solution as a function of the composition.

▲ and △; as-deposited and after annealed, respectively.

3.3 Optical spectra

Optical spectrum for the films after the annealing are indicated in Fig. 5. The average visible transmittance was 77%. This value is slightly lower than that deposited using ethanol solvent (81%) but will be sufficient for most application. The infrared reflectance initiated at 1030 nm which is approximately similar to that deposited using ethanol solvent.

4. CONCLUSIONS

The ITO transparent conducting films were fabricated successfully with water solution of indium chloride and tin chloride as a greener spray CVD process. The film properties after the post-deposition annealing in reducing atmosphere were summarized in Table I. The resistivities were compatible with our previous results

and those deposited by sputtering process.

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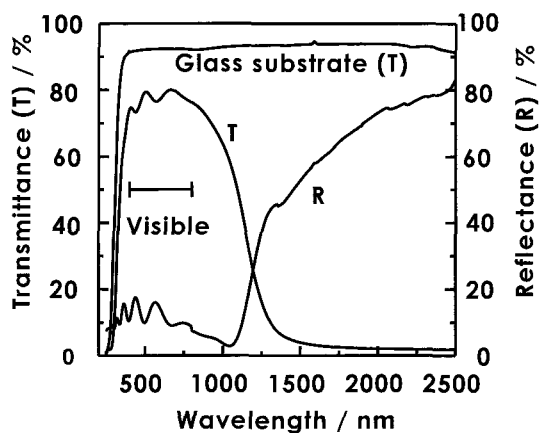


Fig. 5 Optical spectrum for a typical annealed ITO film fabricated with water solvent.

Table I Summary of the ITO films fabricated by spray CVD process after the post-deposition annealing in reducing atmosphere.

| | Present work | Previous work [9] |
|-----------------------|--|--|
| Solvent | Water | Ethanol |
| Thickness | 256 nm | 190 nm |
| Resistivity | 9.7×10^{-5} ohm cm | 9.5×10^{-5} ohm cm |
| Carrier concentration | 1.7×10^{21} cm ⁻³ | 1.8×10^{21} cm ⁻³ |
| Carrier mobility | 38 cm ² V ⁻¹ s ⁻¹ | 40 cm ² V ⁻¹ s ⁻¹ |
| Transmittance | 77% | 81% |
| IR reflection | @>1030 nm | @>1000 nm |

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