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Tin oxide thin films deposited by spray CVD using ethanol solution of tin (II) chloride

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Indium-tin-oxide (tin-doped In_2O_3) thin films are widely used for flat panel displays and solar cells etc. The authors reported elsewhere low resistivity ITO films deposited by spray chemical vapor deposition using ethanol solution of indium chloride and tin (II) chloride. Indium is a rear element whose price is increasing as the results of mass production of flat panel displays. Recently the powders of indium oxide including ITO damage the human lungs. As an approach to fabricate environmentally-benign alternative transparent conducting materials, undoped tin oxide (SnO_2) was deposited by the same process using ethanol solution of tin (II) chloride although the resistivity is much higher since doping with antimony or fluorine was avoided. The lowest resistivity of the as-deposited films was 6.2×10^{-3} ohm cm for the 138 nm-thick film deposited at 255°C. The resistivity increased at the higher temperature. Excellent step coverage was observed when deposited on silicon substrates with stripes (depth, 1 micron).

Key words: tin oxide, spray CVD, transparent conducting films, step coverage

1. INTRODUCTION

Transparent conducting films (TCFs) are indispensable for all solar cells and all flat panel displays such as liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs). Windows coated with TCDs absorb near infrared radiation from the Sun in summer and reflect far infrared emission from the interior in winter so that the energy for cooling and the heating can be reduced. The heat shielding is improved when a space between a pair of glasses were evacuated. Transparent heater for defogging and/or deicing is also possible. The TCF-coated glass can be applied to the bugler alarm [1-8].

Tin-doped indium oxide (In_2O_3) is called ITO (Indium-Tin-Oxide) and a typical TCF material with low resistivity. However, indium is a rare and expensive element whose price is increasing as the markets of flat panel displays are expanding. Furthermore, ITO has been found to be poisonous recently [9]; the powders of indium oxide including ITO damage the human lungs. The present authors reported chemical spray CVD (chemical vapor deposition) of low-resistivity ITO films using a simple and inexpensive hardware [10, 11]. In the present work spray CVD was attempted to fabricate the alternative TCF, i.e. tin oxide (SnO_2) films. Antimony or fluorine-doped tin oxide films were often reported [12-19] although antimony and fluorine is hazardous. The present work is focused to environmentally-benign undoped tin oxide film. The resistivity of the present TCF is higher than ITO so that applications to touch panels, transparent heaters and antistatic coating will be expected. The deposition on to low temperature (approximately 250°C) silicon substrate and on to less flat Si substrate is also reported.

2. EXPERIMENTAL

The fabrication and evaluation of the films was basically identical with our previous paper of depositing ITO films [10, 11] except for the spray solution. Tin (II) dichloride ($SnCl_2.2.01H_2O$, KOJUNDO CHEMICAL LABORATORY CO., LTD.) were dissolved into ethanol (0.1 mol/l) and stirred for more than 12 hours. The content of water in the chloride was determined by thermogravimetry. The solution was manually sprayed with a commercially available atomizer for perfumes etc. onto a silicon substrate (RARE METALLIC CO., LTD., $25 \times 25 \times 0.7$ mm^3) heated on the hotplate with the interval of 5 seconds. The distance from the spray nozzle to the substrate is approximately 15 cm. The Si wafers with grooves were also used as the substrate as reported elsewhere [20]. Film thickness was determined by the X-ray fluorescence analysis (EDX, fundamental parameter method). Crystalline state was evaluated by X-ray diffraction analysis using Cu Kα radiation (40 kV, 300 mA). The resistivity was measured by four-point-probe method. The carrier concentration and mobility was measured by van der Pauw method. The fractured surface of the film deposited on the Si substrate was observed by field-emission scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 *Formation of SnO_2 films*

The X-ray diffraction spectra for the films deposited at various substrate temperatures are indicated in Figure 1. The spectrum of SnO_2 powders is indicated for reference in this figure. The diffraction peaks of SnO_2 were observed for the films deposited at 255 and 305°C. The (200) and (101) peaks were stronger and weaker, respectively, than those of powder specimens. The weak peak at 24° was unidentified. At the lowest substrate temperature (205°C) no clear diffraction peak was observed although very weak halos at 27 and 34° may correspond to (110) and (101) peak, respectively.

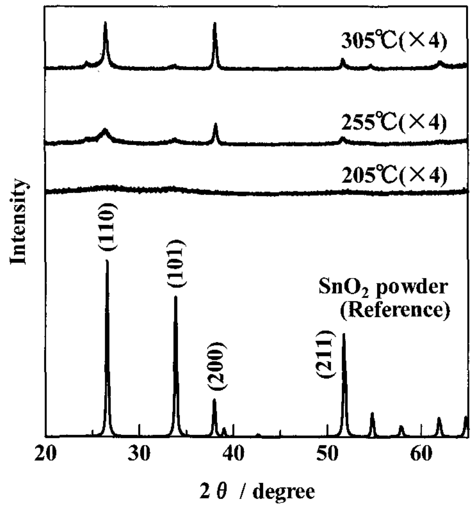

Fig. 1. X-ray diffraction spectra for SnO_2 films deposited at various deposition temperatures.

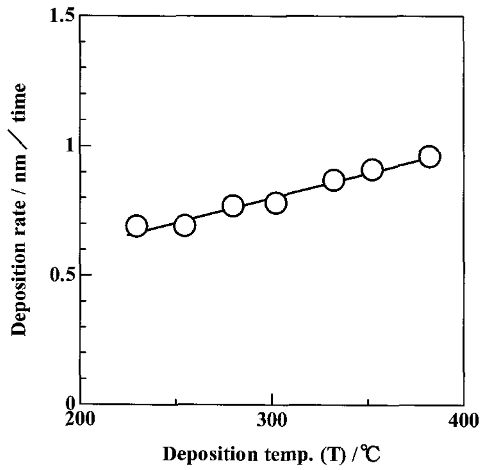

Fig. 2. Dependence of the deposition rate on the deposition temperature for SnO_2 films.

Figure 2 shows the dependence of the deposition rate on the deposition temperature. The deposition rate here is defined as the film thickness formed par a spraying time. The deposition rate increased in proportion to the deposition temperature unlike that of ITO films reported in our previous paper [20]. The higher deposition rate at the higher temperature suggested that the reaction would be the rate-determining factor.

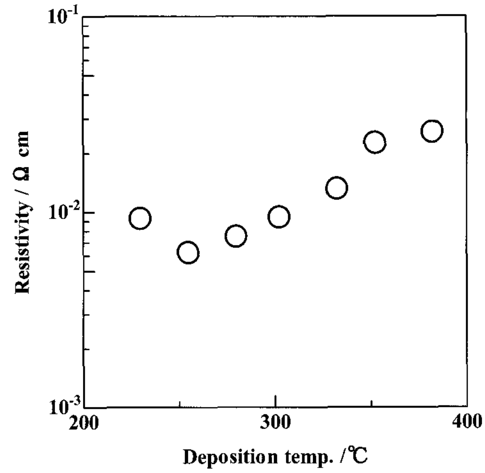

Fig. 3. Dependence of the resistivity on the deposition temperature for SnO_2 films.

3.2 Properties

The dependence of the resistivity on the deposition temperature is shown in Figure 3. The resistivities of the present SnO_2 films were higher by one order or more than those of ITO films [10, 11]. The present films can be used for touch panels, antistatic coating and transparent heater driven by AC power supply etc. The resistivity increased as temperature increased this tendency is opposite to that of ITO films. The lowest and the highest respectively of SnO_2 films was, respectively, 6.2×10^{-3} ohm cm (deposited at 255°C; thickness, 138 nm) and 2.6×10^{-2} ohm cm (deposited at 383°C; thickness, 192 nm). This lowest value was compatible with value for undoped tin oxide film deposited by electron beam plasma deposition at room temperature (6.6×10^{-3} ohm cm, after annealing) [21].

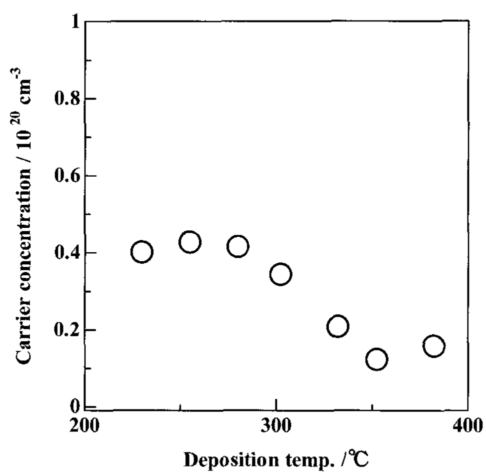

Fig. 4. Dependence of the carrier concentration on the deposition temperature for SnO_2 films.

The carrier concentration and the mobility are plotted as a function of the temperature in Figure 4 and 5, respectively. The highest carrier concentration and mobility was 4.3×10^{19} cm^{-3} and 21 cm^2 V^{-1} s^{-1} at 255°C. The lower carrier concentration at the higher temperature was attributed to complete thermal oxidation of the SnO_2 films. The lower carrier concentration at the lowest temperature (230°C) was interpreted as insufficient formation of SnO_2. The lower mobility at the higher temperature was tentatively attributed to grain boundary scattering.

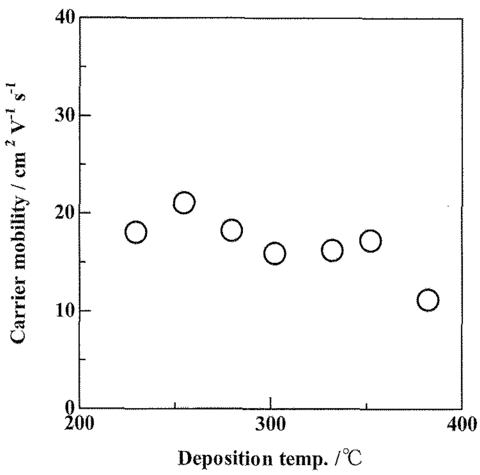

Fig. 5. Dependence of the carrier mobility on the deposition temperature for SnO_2 films.

The averaged transmittance in the visible range was approximately 74% which is lower than those of ITO films [10]. Reflectance in the infrared region (<2400 nm) was not observed; this should be interpreted as low carrier electron concentration.

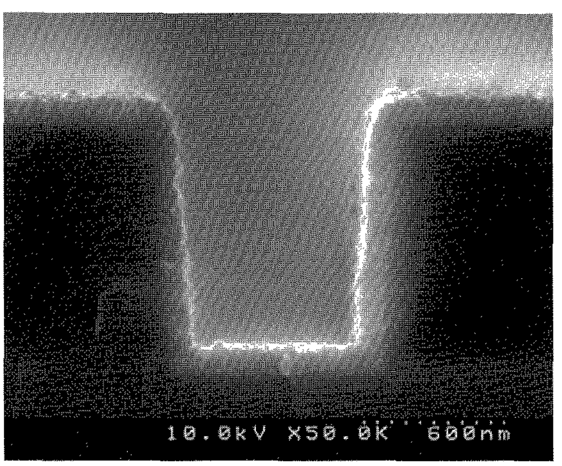

Fig. 6. FE-SEM photo indicating nanostructure of the fractured surface of SnO_2 films deposited at 355°C on a Si wafer with artificially fabricated grooves.

3.3 Nanostructure and step coverage

The authors reported recently [20] that ITO films deposited by spray CVD showed excellent step coverage compared with those deposited by physical vapor deposition (PVD) process such as sputtering deposition. Figure 6 showed a typical example of the fractured surface of the present SnO_2 films on a Si substrate with artificially fabricated grooves. The film consisted of densely packed large crystalline grains. This suggested that relatively high resistivity is not attributed by the grain boundary scattering but the electron scattering in the crystalline grain. Excellent step coverage was achieved even the higher temperature (355°C). Deposition on the concaved surface is expected for fabricating high-density three-dimensional devises.

4. CONCLUSIONS

As an approach to fabricate environmentally-benign transparent conducting films, undoped tin oxide films were successfully deposited by spray CVD process with an inexpensive atomizer at relatively low temperature (255°C). The resistivities of the as-deposited films were higher than that of ITO films in our previous study. The lowest resistivity was 6.2×10^{-3} ohm cm for the 138 nm-thick film deposited at 255°C. The resistivity increased when deposited at the higher temperature. Excellent step coverage was observed deposited at 355°C.

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