Nanostructure and properties of solution processed oxide semiconductor films for thin film transistors or transparent conductive electrodes

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1. Introduction

Oxide semiconductor materials possess wide band gap, high visible transmittance, high electron mobility, heat resistance. Due to these properties, they have been used in a wide range of applications in energy devices and electron devices. For example, as transparent conductive films SnO_2 system [1], In_2O_3 system, ZnO system, and composite oxide system are studied. Sn doped In_2O_3 (ITO) films by the sputtering method are well established due to its stability. Moreover, amorphous In-Ga-Zn-O attracts attention as active layer materials for switching or driving thin film transistors of ultra highly resolution liquid crystal display or organic electroluminescence display [2].

Solution processed electronic devices are now attracting research interests because of the benefits of cost-effective mass production. It is important to achieve all components of devices by coating process, such as light emitting device, thin film transistor for switching device, thin film transistor for driving device, interconnection, and transparent conductive electrode. The spray deposition is proven as one of the major techniques to

deposit a wide variety of materials. This technique also offers easy way to dope films by merely adding it to the precursor solution [3].

In this study, we examined the thin film structure and properties which were formed by solution process of the precursor solution of In-Ga-Zn-O and F dope SnO_2 oxide semiconductor. We discuss the relation between process and property considering reaction in the solution, in the gas, and on the substrate.

2. Experimental details

P-type Si (100) substrates or quart substrate were used in this study. They were chemically cleaned by dipping them in a HF solution ($HF:H_2O$ = 1:50). Chloride or acetate salt were used as metal sauces and these precursors were dissolved in H_2O or ethanol. HF was added as sauce of doping F for SnO_2 films. In the “annealing after deposition” process, films were spin coated on the substrate at in the atmosphere. Thermal annealing was performed on these films by a hot plate or tubular furnace. The “heating during deposition” process of oxide film was also studied. The precursor solution was atomized by (1) twin-fluid nozzle or (2) ultrasonic wave (3.6 MHz), and sprayed on the substrate heated between 400 and 530 ^{o}C. The diameter of atomized droplet is one digit smaller by ultrasonic wave than by twin-fluid nozzle. The feature of each process is shown in Table 1.

Table 1. Feature of wet coating processes in this study.

	Mist method (ultrasonic wave)	Spray metod (twin-fluid nozzle)	Spin coating or dipping method
Diameter of atomized droplets	4 μm	40 μm	—
Annealing period	During deposiiton	During deposition	After deposition
Uniformity of films	○	△	×

The crystal phase of the films was determined in the out of-plane direction using ω−2θ X-ray diffraction (XRD) and the crystallite size was determined for the in-plane direction using ϕ−2θχ XRD with Cu Kα radiation operating at 50 kV and 300mA on an X-ray diffractometer. Film composition was determined by Rutherford back-scattering analysis (RBS), X-ray photoelectron spectroscopy(XPS), and energy dispersed X-ray method (EDX). The nanostructure of the films was determined by the scanning electron microscope (SEM), and the transmission electron microscope (TEM).

Transmittance was measured by ultraviolet and a visible light spectrum method (UV-vis). Electrical resistivity was measured by a 4 probe measuring device. Career concentration, and mobility with the Hall effect measuring device was also carried out.

3. Results and Discussions

3-1. Film uniformity

The wettability of the precursor solution on a SiO_2 substrate became higher and the uniformity of the as-deposited film by spin coating was improved when the H_2O/EtOH ratio of precursor solution decreased and solution concentration was small. On the other hand, in ultrasonic atomization, the solution was easy to atomize as the H_2O/EtOH ratio of precursor solution increased and solution concentration was small.

In ultrasonic atomization method, the diameter of atomized droplet was achieved with 4 μm and it was able to form a film uniformly on SiO_2 substrate even with the precursor solution in which a uniform film was not obtained in spin coating process.

3-2. Film composition and structure

Since the residual Cl in F-doped SnO_2 film is impurities, it is considered to reduce electrical properties. The amount of residual Cl decreased when the substrate temperature during the deposition was higher in any process, mist method by ultrasonic wave and spray method by twin-fluid nozzle. However, the amount of residual Cl was lower by the atomization and coating method than by spin coating method, especially the atomization by ultrasonic wave and coating method conducted the lower amount of residual Cl in the film as shown in Fig. 1.

The In-Ga-Zn-O films were amorphous in both atomization process by twin-fluid nozzle and ultrasonic wave. F doped SnO_2 films had the same crystal structure as rutile type SnO_2, and crystallinity of the F doped SnO_2 films improved where the substrate temperature during deposition in both atomization process, twin-fluid nozzle and ultrasonic wave. Crystallinity of the F doped SnO_2 films was better by mist process than by spray process.

3-3. Electrical properties of the films

The carrier density and carrier mobility increased with increasing process temperature causing the electrical resistivity decreasing in F-doped SnO_2 films. The spray deposition was effective to improve the electrical properties.

In In-Ga-Zn-O films, the carrier density and mobility increased with increasing process temperature as well as F-doped SnO_2 films.

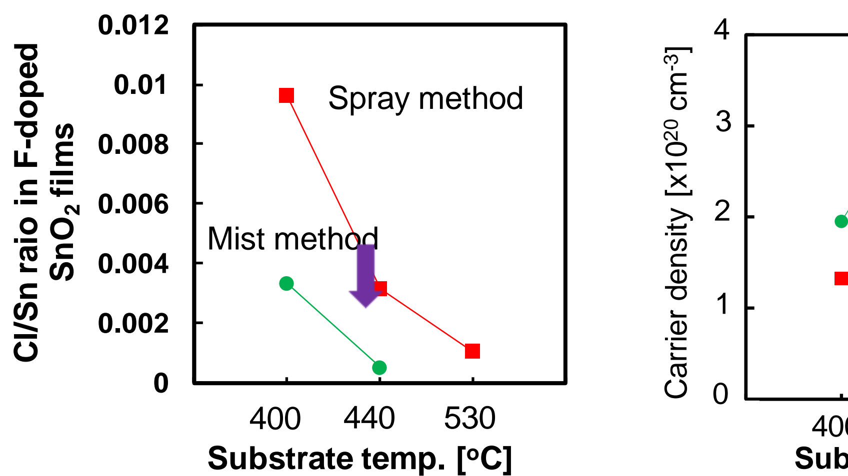

Fig. 1. Residual Cl in F-doped SnO_2 films

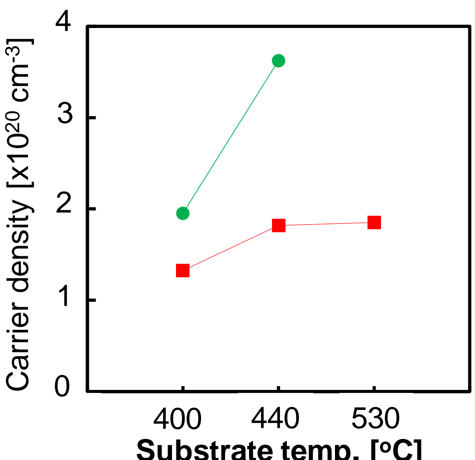

Fig. 2. Electrical properties of F-doped SnO_2 films

4. Conclusions

The composition and the diameter of atomized droplet influence the reaction process, causing the improvement of electrical properties of films in solution process. We will discuss the F state in the F-doped SnO_2 films and composition ratio of In, Ga, Zn in In-Ga-Zn-O films in the presentation.

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