

Cerium-doped indium oxide transparent conducting films prepared by dip coating process

K. Shimizu, S. Seki, M. Ogawa and Y. Sawada*

Department of Applied Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics,
1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan

*: corresponding author, e-mail, sawada@chem.t-kougei.ac.jp

Fabrication of cerium-doped indium oxide transparent conducting films was attempted onto silica glass substrates by dip coating process using ethanol solution of indium chloride and cerium chloride. The dip coating and the heating at $\sim 400^{\circ}\text{C}$ on a hotplate for 3 min in air were repeated 30 times to fabricate approximately 200 nm-thick oxide films with 0.7 to 7.8 at.%Ce as indicated by $[\text{Ce}/(\text{In}+\text{Ce})]$. The films were annealed at 600°C in a $\text{N}_2\text{-}0.1\%\text{H}_2$ atmosphere. All films showed the X-ray diffraction peaks of In_2O_3 . The minimum resistivity ($1.1 \times 10^{-3} \text{ ohm}\cdot\text{cm}$) and the maximum carrier concentration ($1.6 \times 10^{20} \text{ cm}^{-3}$) of the annealed films were obtained at approximately 3 at.%Ce. The carrier mobility increased with increasing cerium concentration; the maximum carrier mobility ($35 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) in the present work was obtained at 7.8 at.%Ce. The visible transmittance was approximately 55% in the average.

Keywords: Indium oxide, Cerium-doping, Resistivity, Carrier concentration, Mobility

1. INTRODUCTION

Indium-tin-oxide (tin-doped In_2O_3) is an excellent material for transparent conducting films. Tetravalent ions other than tin were attempted since the early stage in the history of the transparent conducting films. Groth [1] reported the spray deposited films doped with tin, titanium and antimon. Frank et al. [2] reported the spray deposited film doped with tin, titanium and zirconium. In the above cases, tin seemed to be the best dopant for improving the conductivity. Therefore, other tetravalent ions were investigated insufficiently. A comparative study of tetravalent ions may bring us the key for the question why tin is the best. The answer was not proposed in the literature. A novel dopant compatible with tin may be found if optimizing the process parameters. Above in mind, cerium-doping was attempted by a dip coating process as a part of a systematic investigation although the carrier concentration did not increase remarkably in the present work.

2. EXPERIMENTAL

2.1 Coating solutions

Indium (III) chloride, $\text{InCl}_3\cdot 2.7\text{H}_2\text{O}$ (purity 99.99%, Kojundo Chemical Laboratories Co., Ltd.) and, cerium (III) chloride, $\text{CeCl}_3\cdot n\text{H}_2\text{O}$ (purity 99.9%, Kojundo Chemical Laboratories Co., Ltd.) were used as received. The chlorides were dissolved in ethanol (purity 99.5%, Wako Pure Chemical Industries, Co. Ltd.). The total metal ions in the solution was 0.1 mol/l. The $\text{Ce}/(\text{In}+\text{Ce})$ molar ratios were 1, 3, 5, 7 and 10 at.%. The solution was stirred at room temperature for 24 hours.

2.2 Film fabrication

Silica glass substrates ($40 \times 25 \times 1 \text{ mm}^3$) were ultrasonically cleaned in water with detergent (Semicoclean 56, Furuuchi Chemical Co., Ltd.) for 10 min, rinsed with water and boiled in acetone (purity 99.0%, Wako Pure Chemical Industries, Ltd.) for 10 min. The glass substrate was dipped into the coating solution for 1 min and pulled up into the air at a rate of 30 cm/min. The ethanol solution of indium chloride

repelled the glass substrate remarkably as reported in our previous paper [3]. The addition of cerium chloride improved the contact between the solution and the substrate. Therefore, an extremely low concentration of cerium (1 at.%) was attempted in the present study instead of the undoped one (cerium-free In_2O_3). Since both surfaces of the substrate were simultaneously coated with the solutions, one of the surfaces was wiped with ethanol. The specimens were placed on a laboratory hot plate (Corning PC-400) preheated at approximately 380°C for 3 min. The dipping and the heating were repeated 30 times. The specimens were then annealed at 600°C for 1 h at a heating rate of $10^\circ\text{C}/\text{min}$ in a N_2 -0.1% H_2 gas (flow rate, 300 ml/min) in a silica tube (inner diameter, 44 mm) then cooled to 100°C before being removed.

2.3 Film characterization

All the oxide films were examined by energy dispersive X-ray fluorescence analysis (Model JSX-3200, JEOL, Ltd.) with Rh radiation (30 kV) to determine the film thickness and the film composition. The crystalline state of the oxide film was evaluated by X-ray diffraction analysis (Model RINT-2500V, Rigaku Co., Ltd.) with a high-power X-ray source (Cu radiation, 40 kV, 300 mA) with a graphite monochromator at a scan speed of $2.0^\circ/\text{min}$. The optical transmission of the film was measured at wavelengths between 250 and 2500 nm using a UV-Vis.-IR spectrometer (Model Ubest V-570DS, JASCO Co., Ltd.). The resistivities of the films were measured by the four-point-probe method (probe distance, 0.6 mm; probe diameter, 0.5 mm; probe current, 1 mA) with a digital multimeter (Model 34401A, Hewlett Packard Co., Ltd.). The carrier concentrations and mobilities were measured by the van der Pauw method (magnetic field, 3.0×10^3 G; DC probe current, 1 mA) with a Hall coefficient analyzer (Model MI-675, Sanwa Radio Measurement Works Co., Ltd.).

3. RESULTS AND DISCUSSION

The film composition [$\text{Ce}/(\text{In}+\text{Ce})$, at.%] was equal to the solution composition. The film thickness was approximately independent of the film composition. The average film thickness was 200 nm in the present study.

The X-ray diffraction spectra of the oxide films after the annealing are shown in Fig. 1. All peaks were assigned to In_2O_3 [4] in case when the films were prepared using the solutions with the various compositions. The peak intensities (peak areas) decreased with increasing tin concentration. The (222) diffraction peak was the strongest; the intensity ratios were approximately identical with those for the powder specimen. The only exception was the film with 0.8 at.%Ce; the (400) diffraction peak was as strong as the (222) peak.

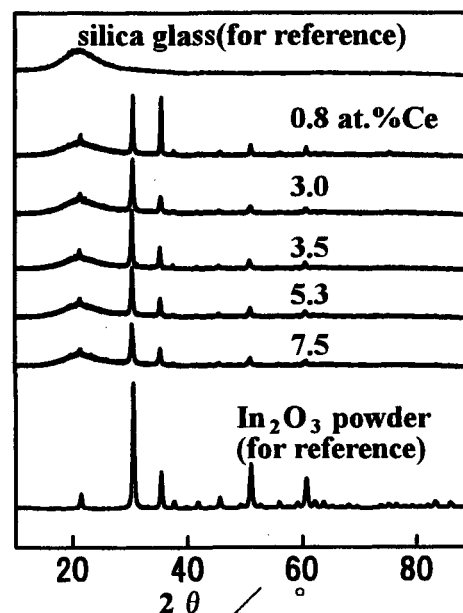


Fig. 1 X-ray diffraction spectra of the oxide films. The films were annealed at 600°C in N_2 -0.1% H_2 .

The dependence of the resistivity on the film composition is shown in Fig. 2. In case of the as-deposited films, the resistivities were relatively high and increased with increasing the concentration of the cerium; the minimum resistivity for the as-deposited

films was 2.9×10^{-2} ohm·cm at 0.7 at.%Ce (thickness, 224 nm). Annealing in N_2 -0.1%H₂ lowered the resistivity to approximately 1 to 2×10^{-3} ohm·cm. The resistivities were rather independent of the cerium concentration although the films with the lowest cerium concentration (0.6 at.%) showed exceptionally high values (2.2×10^{-3} ohm·cm). The minimum resistivity (1.2×10^{-3} ohm·cm) after annealing was obtained at 3.0 at.%Ce (thickness, 200 nm) in the present study. This value is much higher than the reported minimum (3.2×10^{-4} ohm·cm) for the dip-coated films by Takahashi et al. [5].

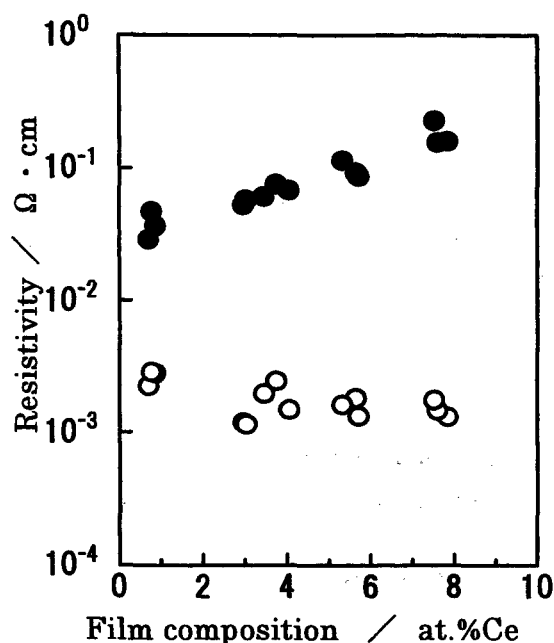


Fig. 2 Dependence of the resistivity on the film composition. ● and ○; as-deposited at 380°C in air and annealed at 600°C in N_2 -0.1%H₂, respectively.

The dependence of the carrier concentration on the film composition is shown in Fig. 3. The carrier concentration increased with cerium concentration until 3 at.%. The maximum carrier concentration in the present study was 1.6×10^{20} cm⁻³ at 3.0 at.%Ce. The values are much lower than those of the ITO films.

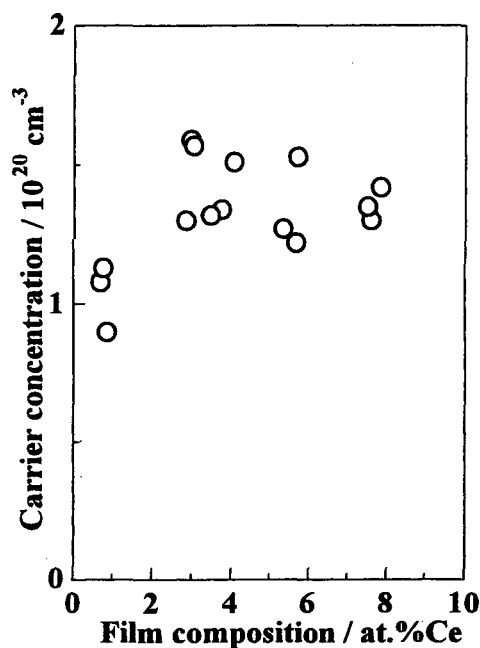


Fig. 3 Dependence of the carrier concentration on the film composition. Films were annealed at 600°C in N_2 -0.1%H₂.

The dependence of the carrier mobility on the film composition is shown in Fig. 4. Although scattered, the mobility was relatively high as dip-coated films. The maximum mobility in the present case ($35 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) was much higher than the reported values of dip-coated ITO films, for example, $21 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ reported by Takahashi et al. [5].

A typical example of the optical transmittance is shown in Fig. 5. The transmittance (average 55 %) in the visible range (wavelength 380-780 nm) was lower than those of the ordinary ITO films. In this figure, the spectrum of the uncoated silica glass substrate is indicated for reference.

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The authors mourn over the sudden death of a co-worker Prof. M. Ogawa.

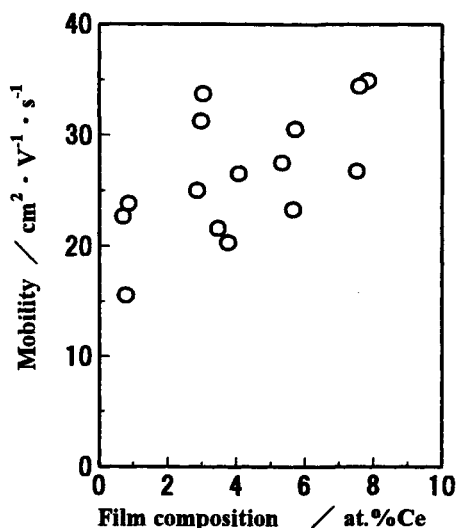


Fig. 4 Dependence of the carrier mobility on the film composition. Films were annealed at 600 °C in N_2 -0.1% H_2 .

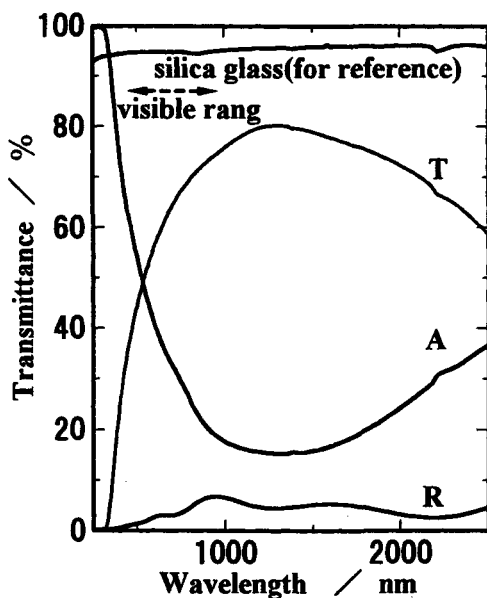


Fig. 5 A typical example of the optical transmittance for the annealed film. 3.4 at.%Ce; thickness, 232 nm.

4. CONCLUSION

Cerium-doped indium oxide thin films (thickness, approximately 200 nm) were fabricated by dip coating process. The films were annealed at 600°C in a N_2 -0.1% H_2 atmosphere. The minimum resistivity (1.2×10^{-3} ohm·cm) was obtained at approximately 3 at.%Ce where the carrier concentration (1.6×10^{20} cm $^{-3}$) was maximum. The maximum carrier mobility (35 cm 2 ·V $^{-1}$ ·s $^{-1}$) was obtained at 10 at.%Ce. The visible transmittance (55% in the average) was relatively low.

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