

Colors and resistivities of sintered bodies of indium oxide doped with various tetravalent ions

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Thin films of indium oxide (In_2O_3) doped with tin (indium-tin-oxide; ITO) are widely used as transparent conducting films for flat panel displays and solar cells etc. Only a few papers reported the sintered bodies and doping with other tetravalent ions. The relation between the colors and the resistivities were not examined systematically although the engineers have understood that dark blue sputtering targets were empirically preferable to light green ones. A color meter was used in the present study to examine quantitatively the correlation with the resistivity of the In_2O_3 sintering bodies doped with Ti^{4+} , Sn^{4+} , Hf^{4+} and Zr^{4+} whose resistivities (2.9×10^{-4} , 8.5×10^{-4} , 5.7×10^{-3} , 4.3×10^{-3} and 3.0×10^{-2} ohm cm, respectively) were lower than that of pure indium oxide (4.8×10^{-2} ohm cm). The resistivities were approximately correlated with the color of the sintered bodies expressed by the coordinates in the chromaticity diagram.

Key words: indium oxide, color, doping, resistivity, transparent conducting film

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1. INTRODUCTION

Tin-doped indium oxide, In_2O_3 , is called ITO (indium-tin-oxide) and widely used as a typical transparent conducting film for all flat panel displays, solar cells, touch panels, infrared-shielding windows, transparent heaters, etc. Doping of tetravalent ion such as tin (Sn^{4+}) is thought to substitute trivalent indium ion (In^{3+}) to form a carrier electron and reduce the resistivity. Reviewing briefly the history of doping elements to indium oxide transparent conducting films, Groth¹⁾ (spray CVD) and Vossen²⁾ (sputtering deposition) reported, respectively, that titanium and tin doping, and tin doping were effective.

Solov'eva and Shvangiradze³⁾ reported that doping of

various tetravalent ions (Ti^{4+} , Sn^{4+} , Hf^{4+} and Ce^{4+}) to bulk indium oxide at 1450-1600°C caused a systematic change in the lattice constant suggesting the formation of solid solution. The present paper traced their results except for cerium doping at the heating temperature of 1450°C and measured the color and the resistivity which have not been reported. The present study focused to low doping concentration at which the formation of the solid solution was expected to occur. The relation between the colors and the resistivities were not reported in the literature although the engineers of ITO sputtering targets understood empirically that the dark blue sputtering targets were preferable to light green ones. A color meter was used

in the present study to examine quantitatively the correlation between the color and the resistivity of the sintered bodies.

2. EXPERIMENTAL

The powder mixtures (30 g) of indium oxide (In_2O_3) and the predetermined amount of titanium oxide (TiO_2), tin oxide (SnO_2), zirconium oxide (ZrO_2) or hafnium oxide (HfO_2) was prepared by wet-milling with ethanol and alumina balls (177 g) in a plastic container rotated at 125 rpm for 24 hours before evaporating the ethanol. The following powders were used; indium oxide (Kojundo Chemical Laboratory Co., Ltd; purity 99.99%; particle size, 4 micron), titanium oxide (Kojundo Chemical Laboratory Co., Ltd; purity 99.9%; particle size, 1 micron), tin oxide (Kojundo Chemical Laboratory Co., Ltd; purity 99.9%), zirconium oxide (Wako Pure Chemical Industries, Ltd.; purity 99.9%) and hafnium oxide (Rare Metallic Co., Ltd.; purity 99.95%).

The mixed powders were pressed at a pressure 200 kgf/cm^2 to form pellets (mass, 3 g; diameter, 16 mm). The pellets were placed in an alumina boat and heated in air at the heating rate of $5^\circ\text{C}/\text{min}$ to hold at 1450°C for 2 hours before the electric supply of the furnace was shut down.

The central portion of the sintered pellets were pulverized into powders and evaluated by X-ray fluorescence analysis (model JSX-3200, JEOL; energy dispersive type, fundamental parameter method) and X-ray diffraction analysis (model RINT 2500, Rigaku; copper target, 30 kV, 300 mA; graphite monochromator). The composition of the sintered specimen agreed approximately with the expected composition. The average of the deviations were 0.40, -0.62, 0.17 and 0.46 at.%, respectively, for titanium, tin, zirconium and hafnium addition. The positive deviations were interpreted as the sublimation of In_2O . The exceptionally negative deviation of tin was

attributed to more volatile nature of SnO . The lattice constant of indium oxide was calculated from the diffraction peaks which did not duplicate with the corresponding doping compounds.

The color of the sintered bodies was measured using a commercially available colorimeter, Topcon Spectral Radiometer SR-3. The colorimeter was looking straight down on the samples illuminated by two Xenon lamps set to a 45° angle. Color temperature of the lamp was about 6500K. The spectrum baseline was calibrated using a white standard of barium sulfate.

The dc resistivity was measured by four-point-probe method with silver paste electrodes (distance, approximately 10 mm) formed on the specimens (approximately $5.2 \text{ mm} \times 4.5 \text{ mm} \times 24 \text{ mm}$) sintered by the process similar to the described above; the averages of five measured values were used.

3. RESULTS AND DISCUSSION

3.1. Phases and lattice constant

The X-ray diffraction analysis indicated that the cubic indium oxide (bixbyite structure⁴) was the main phase. No other phase was detected in case of low doping concentration suggesting the formation of solid solution of the tetravalent ions in indium oxide lattice. The highest solubility limits of hafnium (3 at.%) and zirconium (2 at.%) should be interpreted as their ionic radii (71 and 72 pm, respectively⁵) which are close to that (80.0 nm) of indium ion. Solubility limit of tin ions (69.0 pm^5) into indium oxide (2 at.%) were much lower than that of the films prepared by Frank and Köstlin⁶ who reported the lattice constant of ITO films with 0.8-22 at.%Sn. The solubility limit of the smallest doping ion, titanium (ionic radius, 60.5 pm^5), was the lowest (1 at.%) in the present study.

The lattice constants are plotted in Figure 1 as a function of the ionic radius of the tetravalent doping ions in case of 0.5 at.% doping concentration. The lattice constant of undoped indium oxide (1.0118 nm) is

plotted at the ionic radius of In^{3+} (80.0 pm) for reference. This measured values agreed with the reported one⁴⁾ (1.0118 nm). Lattice shrinkage was remarkable when doping smaller ions; 1.0102, 1.0107, 1.0107 and 1.0111 nm, respectively, for the lattice constant of 0.5 at.% doping of Ti^{4+} , Sn^{4+} , Hf^{4+} and Zr^{4+} , respectively. The evaluation of the specimens at the high doping concentration was abandoned in the present study since the peaks for the intermediate compounds such as $\text{In}_2\text{Ti}_2\text{O}_5$ ⁷⁾, $\text{In}_2\text{Sn}_2\text{O}_7$ ⁸⁾, $\text{In}_4\text{Sn}_3\text{O}_{12}$ ⁹⁾, unreacted oxides (TiO_2 , SnO_2 , HfO_2 and ZrO_2) and weak peaks for some unknown compounds were detected.

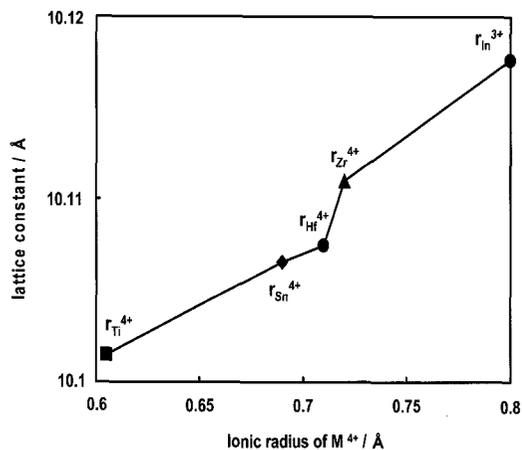


Fig. 1. The lattice constants as a function of the ionic radius of the tetravalent doping ions in case of 0.5 at.% doping concentration.

3.2 Resistivities

The resistivities of the sintered bodies are shown in Figure 2 as a function of the radius of the doping ions for the doping concentration 1 at.%. The resistivities of the all doped specimens were lower than that of the pure indium oxide (4.8×10^{-2} ohm cm) although this value was slightly higher than those of the pure indium oxide thin films (approximately 1×10^{-4} ohm cm)¹⁰⁾. The smaller tetravalent ions are preferable to lower the resistivity. The lowest resistivity (2.9×10^{-4} ohm cm) was achieved by titanium doping. This value is lower than that by tin doping (8.5

$\times 10^{-4}$ ohm cm) in the present study and slightly higher than the reported values for excellent ITO films deposited by sputtering¹¹⁾ (1.3×10^{-4} ohm cm) and spray CVD¹⁰⁾ (1.7×10^{-4} ohm cm). The resistivities in case of hafnium and zirconium doping were higher by one order, 5.7 and 4.3×10^{-3} ohm cm, respectively. The difference in the resistivities should be attributed mainly to difference in the carrier electron concentrations since the carrier mobility doesn't seem to change so much in case of sintered bodies with large crystallites. If the above assumption is correct, titanium and tin ions will be more active to generate the carrier electron compared with hafnium and zirconium ions.

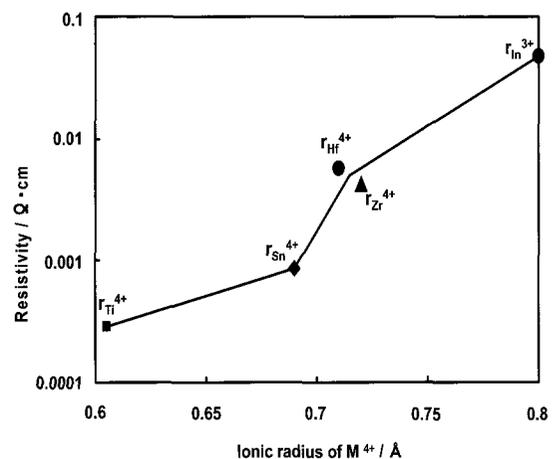


Fig. 2. The resistivities of the sintered bodies as a function of the radius of the doping ions for the doping concentration 1 at.%.

3.3 Colors

The colors of the sintered bodies are indicated in the x-y chromaticity diagram as shown in Figure 3. A straight line correlation was observed. The right end is the yellowish color of pure indium oxide. The left end is blue or dark blue which is well known to the engineers as the color of low-resistivity ITO sputtering target. Between them there exists pale green which is known as a color of low-density ITO sputtering target with slightly high resistivity.

The resistivities of the sintered bodies are indicated

in Figure 4 as a function of the color coordinate x . The color and the resistivity are correlated approximately so that the empirical understanding by the engineers is quantitatively proved. The higher reflectance of blue light (short wavelength visible light) of the low-resistivity sintered bodies should be attributed to the Burstein-Moss shift¹⁵⁻¹⁷⁾ by which the band gap absorption shifts to the shorter wavelength in case of degenerated higher carrier electron concentration.

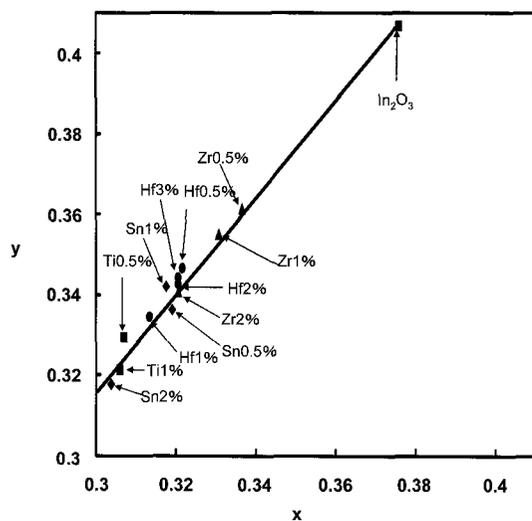


Fig. 3. The colors of the sintered bodies as the x - y coordinate of color matrix (chromaticity diagram).

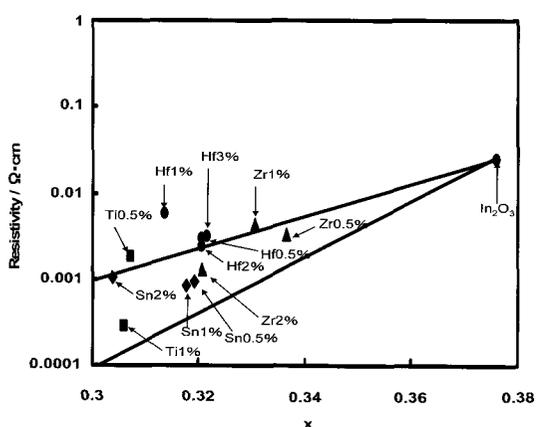


Fig. 4. The resistivities of the sintered bodies as a function of the color coordinate x .

4. CONCLUSION

Sintered bodies of indium oxide doped with various tetravalent ions (Ti^{4+} , Sn^{4+} , Zr^{4+} , and Hf^{4+}) were

prepared at 1450°C in air for 2 hours. The specimen showed narrow solubility limit to indium oxide where the lattice shrinkage were systematically governed by radius of the doping ions. The smaller doping ions were preferable to lower the resistivity. The resistivities were approximately correlated with the color coordinates in the chromaticity diagram.

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