Indium-tin oxide thin films prepared by chemical vapor deposition

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Transparent conductive indium-tin oxide thin films were prepared by an atmospheric-pressure chemical vapor deposition method. The source materials were indium acetylacetonate and tin (II) acetylacetonate which are nontoxic and easy to handle. The polycrystalline films were obtained at a reaction temperature in the range of 350–500 °C. For the 215-nm-thick film deposited at 450 °C, the resistivity was 1.8×10^{-4} Ω cm, and the transmittance was more than 90% in the wave number range of above 400 nm. The atomic ratio Sn/In of the film was 0.031. The effects of tin doping on the structure and characteristics of the film were discussed on the basis of the carrier concentration and mobility which were measured by using the Hall effect.

I. INTRODUCTION

Indium oxide (In_2O_3) thin films have a wide range of applications, e.g., transparent electrodes of liquid crystal and other displays, with developing preparation methods of thin films of high quality. In particular, In_2O_3 films doped with tin [In_2O_3:Sn (ITO)] are widely used as transparent conductive films.

High-quality In_2O_3:Sn film has been prepared by various physical vapor deposition methods such as vacuum evaporation, rf sputtering, dc sputtering, and rf ion plating. However, reports on the use of the chemical vapor deposition (CVD) method[1–6] are few in spite of the fact that the CVD method does not require a high vacuum and accordingly has the advantage of relative ease for large-scale application, granting the possibility of coating complicated shapes. For the preparation of In_2O_3, indium acetylacetonate is known to be a volatile material. Korzo and Chernyaev[2] used indium acetylacetonate as a source material of photochemical vapor deposition of In_2O_3. Ryabova *et al.*[3] deposited films of atomic ratio Sn/In = 0.08 by using a mixture of indium and tin acetylacetonates as the reactant. The In_2O_3:Sn films of low resistivity ($1.6–1.8 \times 10^{-4}$ Ω cm) were obtained by annealing the deposited films in a vacuum of about 10^{-4} Torr at 400 °C for 30–45 min.

In this paper, a CVD method is proposed to prepare In_2O_3:Sn films from indium acetylacetonate and tin (II) acetylacetonate. This method can make films of low resistivity and high transparency without annealing the deposited film.

II. EXPERIMENT

Indium acetylacetonate [$In(C_5H_7O_2)_3$, Nihon Kagaku Sangyo Co., Ltd.] and tin (II) acetylacetonate [$Sn(C_5H_7O_2)_2$, Matsumoto Chemical Industry Co., Ltd.] of reagent grade were used as the source materials. Figure 1 shows a schematic representation of the experimental setup. Indium acetylacetonate was placed in a container maintained at 180 °C. Tin (II) acetylacetonate was placed in a container maintained at 80 °C. The generated gas was entrained by N_2 carrier gas and injected into the container of indium acetylacetonate; where indium acetylacetonate and tin (II) acetylacetonate were mixed with O_2 gas which was injected independently to the container. The flow rate of O_2 gas was 200 cm^3/min. The flow rate of N_2 carrier gas for tin (II) acetylacetonate was changed, while the total flow rate of the N_2 carrier gas was kept constant, i.e., 550 cm^3/min, by changing the flow rate of the N_2 carrier gas which is injected into the container of indium acetylacetonate.

A 76×26 mm borosilicate glass plate and quartz glass plate were used as the substrate. The substrate was placed in the reactor heated by an external electric furnace. The reaction temperature ranged from 350 to 500 °C.

The composition of the film was measured by x-ray photoelectron spectroscopy. The crystallinity of the film was analyzed by the x-ray diffraction method with Cu $K\alpha$ radiation. The electric resistivity of the film was measured by the van der Pauw method. The carrier concentration and mobility were measured by using the Hall effect. The optical transmittance of the film was obtained by means of a multipurpose recording spectrophotometer. A blank glass substrate was inserted into the reference beam path of the spectrophotometer.

III. RESULTS AND DISCUSSION

Prior to the experiment of depositing In_2O_3:Sn films, experiments on the preparation of the In_2O_3 film were conducted without introducing tin (II) acetylacetonate into the reaction system. The transparent conductive In_2O_3 film was obtained from indium 2-ethylhexanoate and oxygen at the deposition temperature ranged from 350 to 500 °C. If O_2 gas was not supplied, transparent insulating films were obtained. These reaction schemes are different from those observed in the preparation of In_2O_3 film from indium carbonate.[5–7] The thermal decomposition of indium car-

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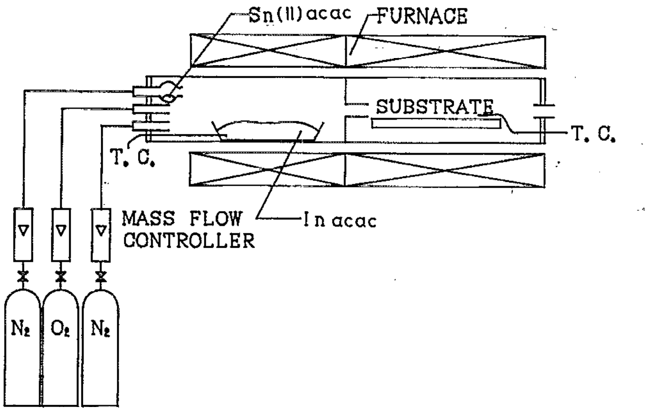

FIG. 1. Schematic diagram of experimental equipment.

bonate yields transparent conductive In_2O_3 film with no need of supplying an oxygen.

By introducing tin (II) acetylacetonate into the carrier gas, In_2O_3 films were doped with tin; that is, In_2O_3:Sn films were obtained. Figures 2(a) and 2(b) show typical examples of the x-ray diffraction patterns of the films on a borosilicate glass. Both of the In_2O_3 and In_2O_3:Sn films show the (222) plane texturing. This preferred orientation is different from that observed in the authors previous studies[5–7] on dopings for In_2O_3 film. The In_2O_3 films prepared from indium acetate and indium 2-thylhexanoate show a nonoriented polycrystalline nature, while a trace quantity of tin or fluorine doping promotes (400) plane texturing.

Figures 3(a) and 3(b) show the electric resistivities, carrier concentrations and Hall mobilities for both In_2O_3 and In_2O_3:Sn (Sn/In = 0.01) films as a function of the reaction temperature. The In_2O_3 film shows the maximum value of the carrier concentration at the reaction temperature of 450 °C, while the Hall mobility is nearly independent of the reaction temperature. As a result, the In_2O_3 film gives the minimum value of resistivity at 400–450 °C. About the In_2O_3:Sn film, the atomic ratio Sn/In = 0.01 is equivalent to the Sn contents 3.4×10^{20} cm^{-3}, which is reflected by the carrier concentration of In_2O_3:Sn film at above 400 °C. At the same time, however, the doping decreases the Hall mobility at reaction temperature lower than 400 °C. The Hall mobility is not affected by the doping at above 450 °C. As a result, the doping effectively decreases the resistivity at above 450 °C. The minimum value of the resistivity is obtained at 450 °C. The following data are based on the films prepared at the reaction temperature 450 °C.

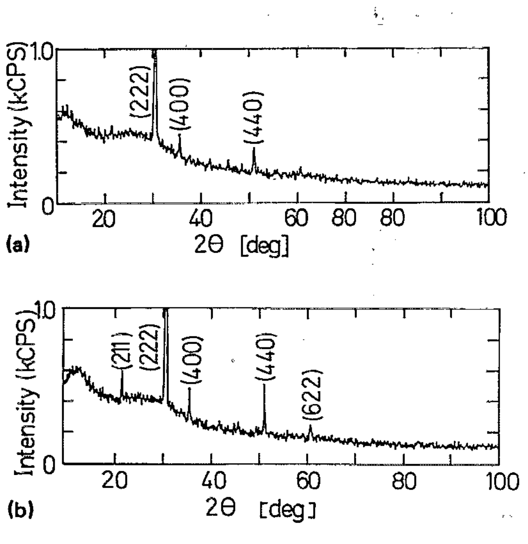

FIG. 2. X-ray diffraction patterns of the (a) 255-nm-thick In_2O_3 film and (b) 156-nm-thick In_2O_3:Sn film on borosilicate glass.

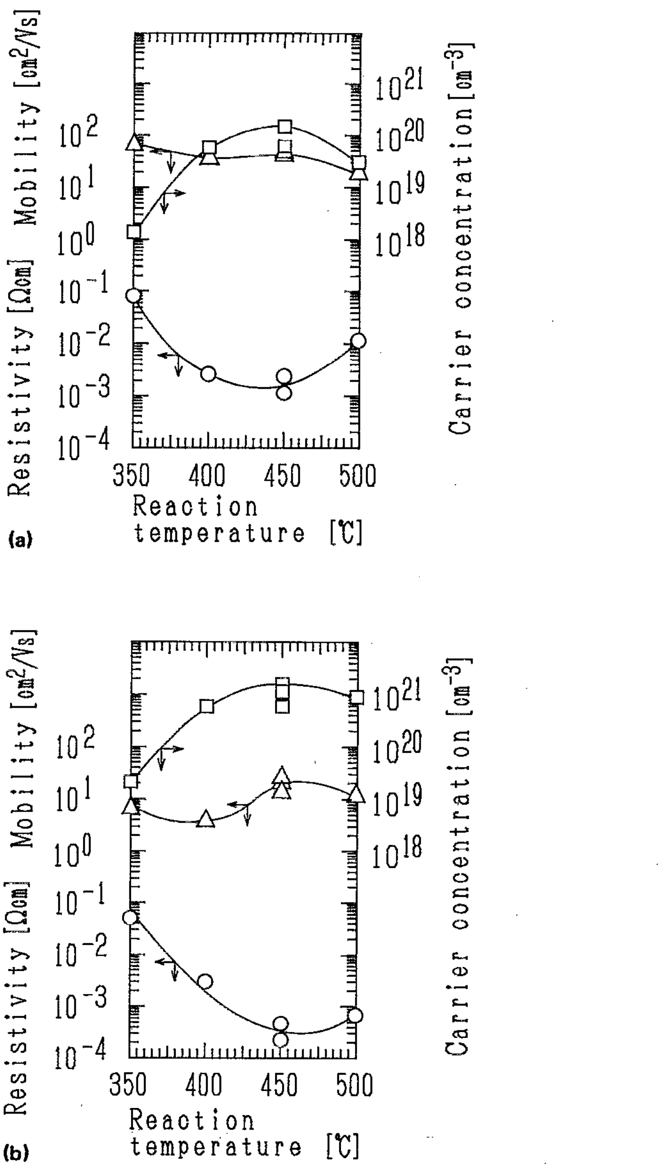

FIG. 3. Electric resistivities, carrier concentrations, and Hall mobilities for (a) In_2O_3 and (b) In_2O_3:Sn (Sn/In = 0.01) films as a function of reaction temperature.

Figures 4(a) and 4(b) show the electric resistivity of the In_2O_3:Sn film as a function of the atomic ratio Sn/In of

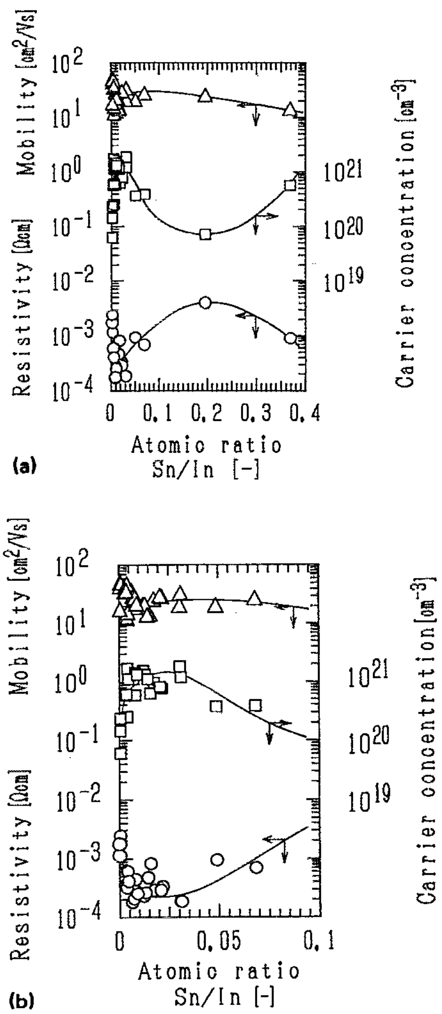

FIG. 4. Electric resistivity, carrier concentration, and Hall mobility for In_2O_3:Sn film as a function of atomic ratio Sn/In: (a) 0<Sn/In<0.4 and (b) 0<Sn/In<0.1.

the film. The resistivity shows the minimum value at the atomic ratio Sn/In of 0.01–0.035. With increasing atomic ratio Sn/In from 0.05, the carrier concentration decreases, while the Hall mobility keeps a constant value. These facts suggest that in this reaction the extra Sn atoms over Sn/In = 0.035 are not effectively incorporated into the lattice structure of In_2O_3. The lowest resistivity was obtained at Sn/In = 0.031, where the resistivity of the 215-nm-thick film was 1.8×10^{-4} Ω cm, and the sheet resistance was 23 Ω/□.

Figures 5(a) and 5(b) show the optical transmittances for the 255-nm-thick In_2O_3 film and 156-nm-thick In_2O_3:Sn film deposited on the quartz glass substrate at 450 °C. The transmittances are more than 85% for In_2O_3 film and more than 90% for In_2O_3:Sn film in the range above 400 nm. Figures 6(a) and 6(b) show the square absorption coefficients α^2 as a function of photon energy. The extrapolations to the abscissa indicate that the optical energy gap of In_2O_3 for the direct transition is 3.7 eV and that the tin doping brings about 0.2 eV increase in the optical energy gap.

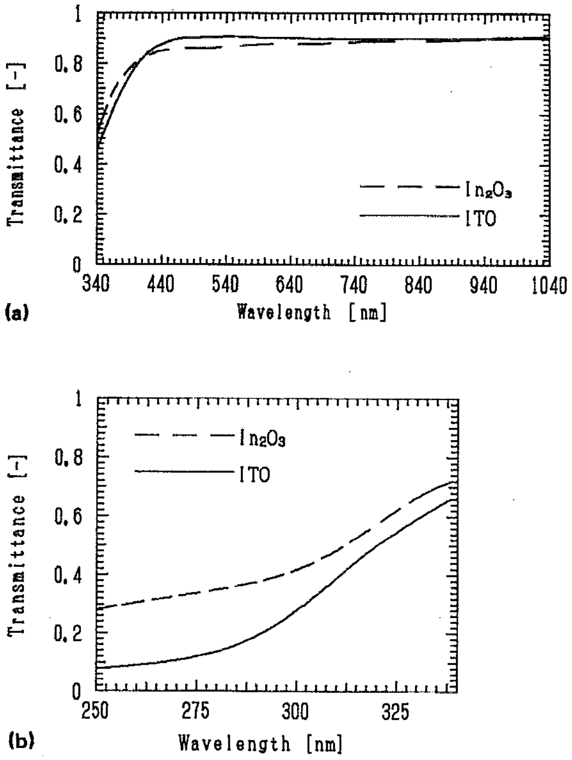

FIG. 5. Optical transmittances for 255-nm-thick In_2O_3 film and 156-nm-thick In_2O_3:Sn film deposited on the quartz glass substrate at 450 °C: (a) wavelength > 340 nm, and (b) wavelength < 340 nm.

IV. CONCLUSIONS

Transparent conductive indium-tin oxide thin films were prepared by an atmospheric-pressure chemical vapor deposition method. The raw materials were indium acetylacetonate and tin (II) acetylacetonate, which are nontoxic and easy to handle. The polycrystalline films were obtained at a reaction temperature in the range of 350–

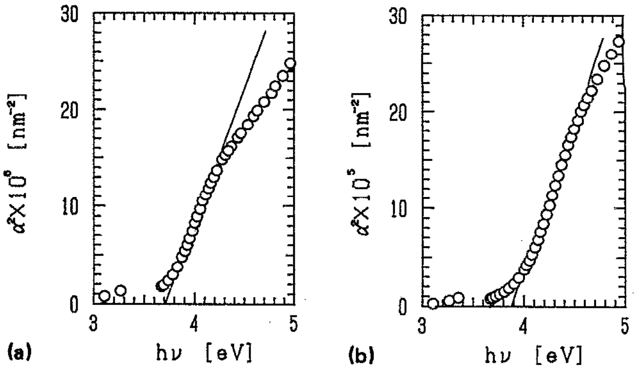

FIG. 6. Square absorption coefficients α^2 for (a) In_2O_3 and (b) In_2O_3:Sn (Sn/In = 0.01) films as a function of photon energy.

500 °C. For the 215-nm-thick film deposited at 450 °C, the resistivity was $1.8 \times 10^{-4}\ \Omega\,\text{cm}$, and the transmittance was more than 90% in the wave number range of above 400 nm. The atomic ratio Sn/In of the film was 0.031.

ACKNOWLEDGMENTS

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[1] J. Kane, H. P. Schweizer, and W. Kern, Thin Solid Films **29**, 155 (1975).
[2] V. F. Korzo and V. N. Chernyaev, Phys. Status Solidi (a) **20**, 695 (1973).
[3] L. A. Ryabova, V. S. Salun, and I. A. Serbinov, Thin Solid Films **92**, 327 (1982).
[4] M. Privman, J. Berger, and D. S. Tannhauser, Thin Solid Films **102**, 117 (1983).
[5] T. Maruyama and K. Tabata, Jpn. J. Appl. Phys. **29**, L355 (1990).
[6] T. Maruyama and K. Fukui, Thin Solid Films (in press).
[7] T. Maruyama and K. Fukui, Jpn. J. Appl. Phys. **29**, L1705 (1990).
[8] T. Maruyama and A. Kojima, Jpn. J. Appl. Phys. **27**, *L*1829 (1988).