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# Preparation and electrical properties of ITO thin films by dip-coating process

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Indium tin oxide (ITO) thin films were prepared on quartz glass substrates by a dip-coating process. The starting solution was prepared by mixing indium chloride dissolved in acetylacetone and tin chloride dissolved in ethanol. The ITO thin films containing $0 \sim 20$ mol% $SnO_2$ were successfully prepared by heat-treatment at above 400 °C. Chemical stability of sol were investigated by using a FTIR spectrometer. The electrical resistivity of the thin films decreased with increasing heat-treatment temperature, that is carrier concentration increased, and mobility decreased with increasing $SnO_2$ content. The ITO thin films containing 12 mol% $SnO_2$ showed the minimum resistivity of $\rho = 1.2 \times 10^{-3}$ ($\Omega$ cm). It also showed high carrier concentration of $N = 1.2 \times 10^{20}$($cm^{-3}$) and mobility $\mu_H = 7.0$($cm^2\,V^{-1}\,s^{-1}$).

## 1. Introduction

It is well known that tin oxide ($SnO_2$) or indium tin oxide (ITO) are quite transparent and show low electrical resistivity. These thin films are used as transparent electrodes for many devices, such as electrochromic displays (ECDs), and liquid crystal displays (LCDs). It is very important to coat such films on large and complicated-shaped substrates for conventional devices. The sol–gel process is superior for forming thin films on such substrates to sputtering process [1, 2] or chemical vapour deposition (CVD) [3, 4] methods.

The sol–gel process uniformly mixes a solution of the starting materials, allowing the production of high-purity films, with uniform compositions even for multi-component systems [5]. In general, the sol–gel process uses metal alkoxides as raw materials, but it is very difficult to obtain indium and tin alkoxide. Therefore, we prepared ITO thin films from the sol–gel process using metal salts as raw materials and organic solvents. Metal salts are cheaper than metal alkoxides, and these are very easy to handle. Several organic solvents can form stabilized metal ions in solution [6]. We investigated the stability of the starting solution and the electrical properties of the thin films with different concentrations of Sn. In addition, we examined the crystallographic structure dependence of the resistivity of these films.

## 2. Experimental procedure

### 2.1. Preparation and analysis of starting solution

Anhydrous indium trichloride ($InCl_3$) was dissolved in acetylacetone and the solution was refluxed at 60 °C. Anhydrous tin(IV) chloride ($SnCl_4$) was dissolved in ethanol and this solution was mixed with the refluxed solution. IR spectra of an indium-acetylacetone solution were measured in the range of 400 to 2000 $cm^{-1}$ at room temperature by using a Shimadzu FTIR-4200. Differential thermal analysis and thermogravimetric analysis were performed on a Rigaku MJ800KT2 system at a heating rate of 3 °C $min^{-1}$.

### 2.2. Preparation and electrical properties of ITO thin film

Fig. 1 shows the preparation procedure for a thin film of the $(100 - x)In_2O_3 \cdot xSnO_2$ system. Substrates were dipped in the starting solution and withdrawn at a rate of 0.2 cm $s^{-1}$. The coated substrates were heated at a given temperature in air or oxygen atmosphere to form the thin films.

Crystalline phases of these films were identified by using an X-ray diffractometer (Rigaku Model CN4148) with a thin film attachment and a carbon monochromator. Thickness of these films were measured by using a high precision thin film height difference meter (Kosaka Model ET-10S).

Electrical resistivities of these films were measured by using the four terminal method (substrate-shape 15 × 10 mm, electrode interval is 1 mm, electrode length is 10 mm). Hall coefficients of the films were measured (Toyo thecnica Resist 8200) following the Van Der Paw method.

Transmittance of those films were measured by a UV-spectrophotometer (Shimadzu UV-3000).

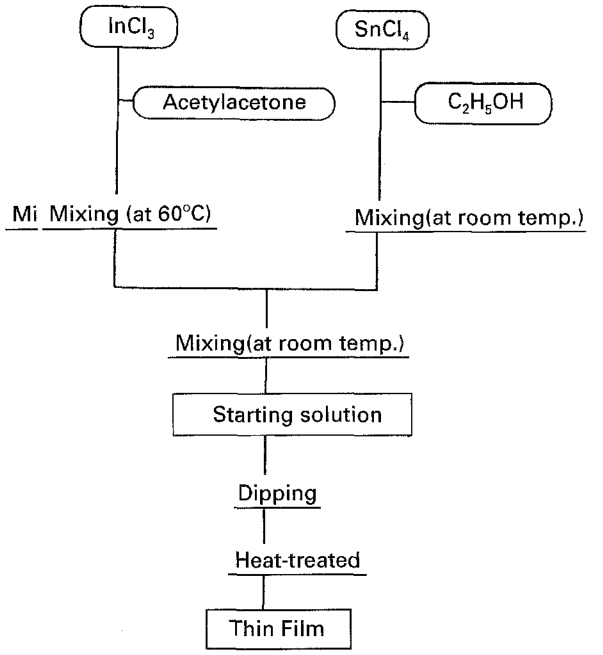

*Figure 1* Preparation procedure of ITO thin film.

## 3. Results and discussion

### 3.1. Stabilization of the starting solution

When anhydrous indium chloride was dissolved in acetylacetone, the colour of the solution was light yellow. The colour of the solution changed to dark reddish-brown after it was refluxed at 60 °C.

IR spectra of acetylacetone (a), a mixture of acetylacetone and isopropanol (b), and indium chloride dissolved in the mixture of acetylacetone and isopropanol (c), are shown in Fig. 2. Generally 70% of acetylacetone is enol and the remainder is keto. The position of C=O stretching peak in keto is very close to that of enol. In solutions (a) and (b), the C=O stretching vibrations appeared at 1640 $cm^{-1}$. In solution (c), they are widely separated and appeared at 1600 and 1630 $cm^{-1}$.

Indium ions form chelate with acetylacetone [7], and stabilize with chelate formation in the solution. This chelate solution is expected to play a similar role to the alkoxide, since the metal ions are surrounded by oxygen.

Fig. 3 shows differential thermal analysis and thermogravimetric analysis (DTA–TGA) curves. The DTA–TGA curves for anhydrous indium chloride dissolved in $H_2O$ (a) and mixture of acetylacetone, HCl and isopropanol (b) are very similar. These curves show endothermic peaks with weight loss between room temperature and 130 °C. The DTA–TGA curve for anhydrous indium chloride dissolved in acetyl acetone and isopropanol and refluxed at 60 °C (c) is very different from the other curves and shows several endothermic or exothermic peaks with weight loss. These DTA–TGA and i.r. spectra suggest that indium chloride and acetylacetone form some compound.

Fig. 4 shows schemes of indium–acetylacetone chelate. This reaction is shown in Equation 1.

$$In^{3+} + CH_3COCH_2COCH_3 \rightarrow [In(CH_3COCHCOCH_3)]^{2+} + H^+ \qquad (1)$$

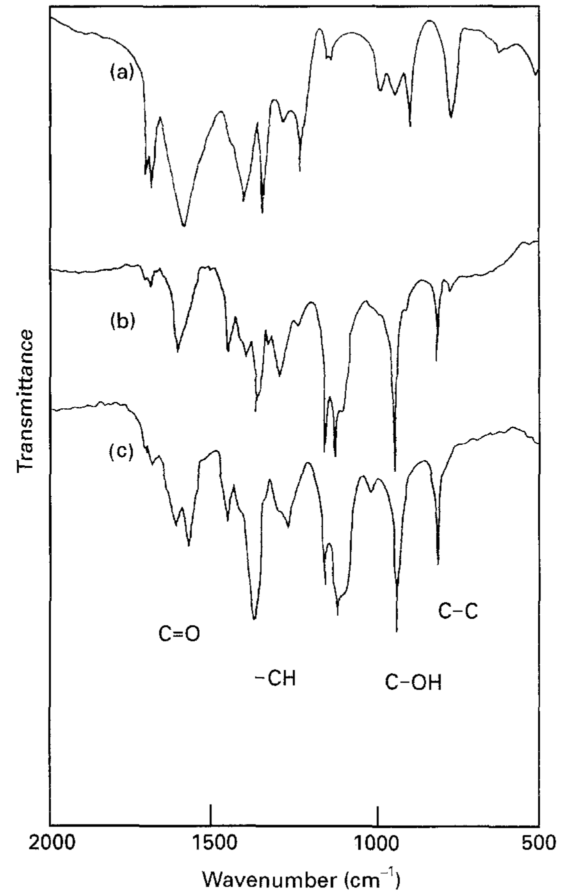

*Figure 2* IR spectra of following solution: (a) acetylacetone (AcAc); (b) AcAc, isopropanol; (c) AcAc, isopropanol and $InCl_3$.

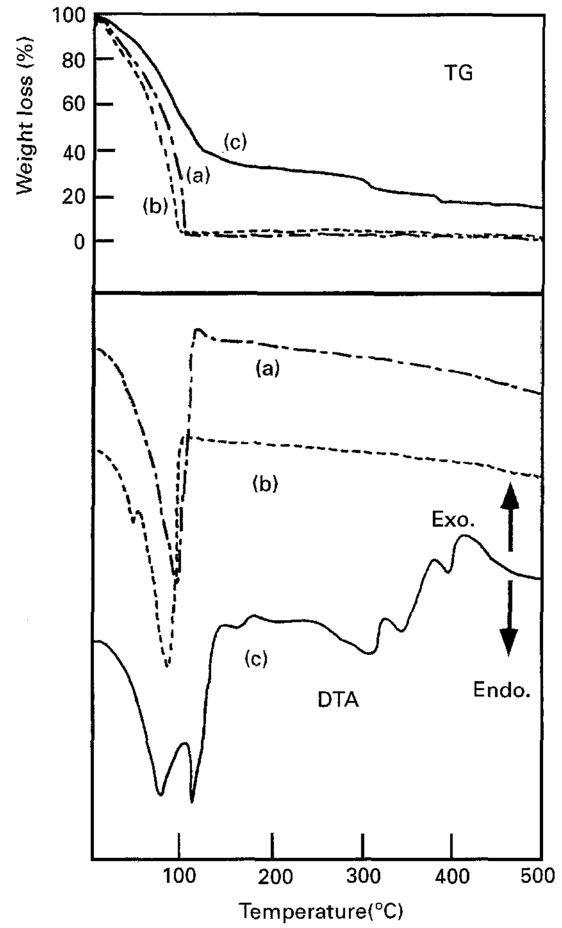

*Figure 3* DTA–TGA curve: (a) acetylacetone (AcAc); (b) AcAc, isopropanol; (c) AcAc, isopropanol and $InCl_3$.

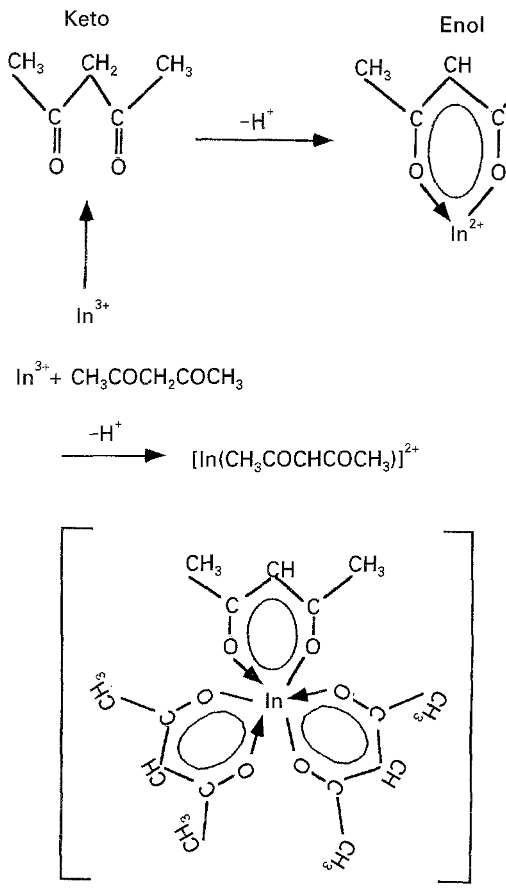

*Figure 4* Schemes of indium–acetylacetone chelate.

At the final state, the indium–acetylacetone compound changes to $In(CH_3COCHCOCH_3)_3$. Several new peaks associated with the reaction were observed in the DTA–TGA curve for (c). Weight loss of solution (c) finished at 400 °C, and the DTA curve does not change above 450 °C. IR spectra show there is no carbon following treatment at 450 °C. Indium oxide was obtained from indium–acetylacetone chelate by heat treatment at above 450 °C.

## 3.2. Heat-treatment

Fig. 5 shows the relationship between film thickness of the heat-treated film and the number of dippings. Film thickness increased linearly with the number of dippings. Film thickness increased by approximately 40 nm with each dipping.

Fig. 6 shows X-ray diffraction patterns of the indium tin oxide films containing 10 mol % $SnO_2$ and heat treated at different temperatures ranging from 400 to 800 °C. Peaks of indium oxide already appeared at 400 °C, and the intensity of these peaks increased with increasing temperature up to 600 °C. These results suggest that these films begin to crystallize at above 400 °C and are fully crystallized at 600 °C.

Fig. 7 shows SEM of thin films obtained by heat treatment at 500 °C and 700 °C for 1 h.

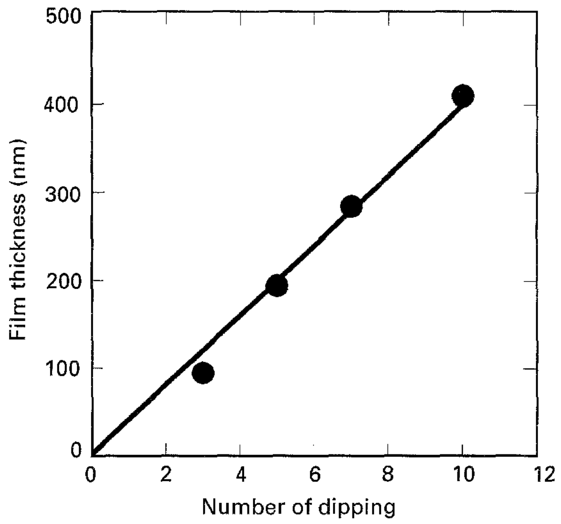

*Figure 5* Film thickness versus number of dipping on ITO films.

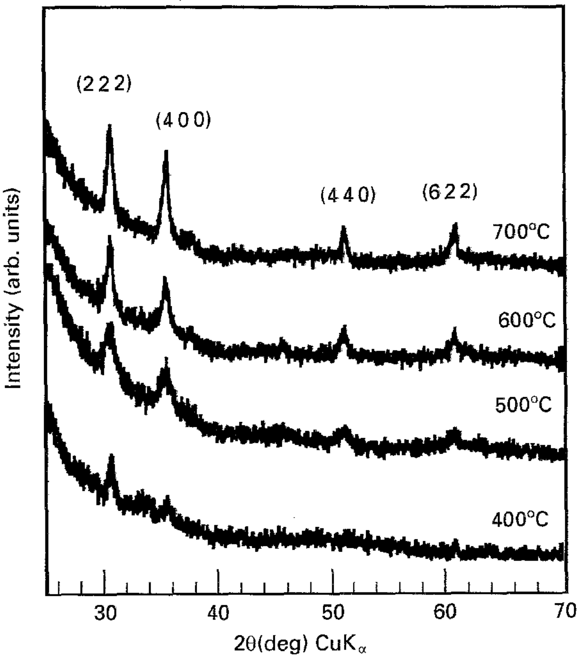

*Figure 6* X-ray diffraction patterns of ITO film prepared by various heat treatments.

## 4. Electrical properties

### 4.1. Resistivity and heat-treatment temperature

Fig. 8 shows the effect of heat-treatment temperature on resistivity of $90In_2O_3{\cdot}10SnO_2$ films heat treated in air. Samples were heat treated for 1 h at each temperature. The resistivity decreased significantly with heat-treatment temperature up to 600 °C, and then remained at an almost constant value up to 800 °C. This result was in good agreement with the peak intensity of the X-ray diffraction, and indicated that the decrease in resistivity was due to an improved crystallinity of the thin films.

### 4.2. Resistivity and composition

It is known that electrical conduction of ITO is caused by electrons from doped Sn and oxygen-deficient defects. For Figs 9 and 10, the thin films were heat treated in air or an oxygen atmosphere at 700 °C for 1 h.

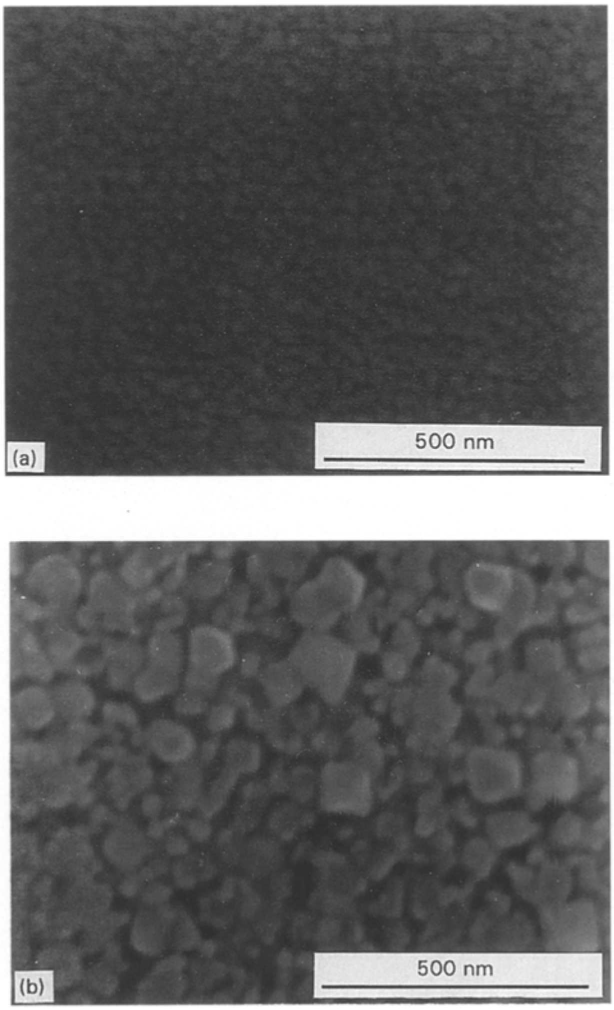

*Figure 7* SEM micrograph of ITO thin films surface (heated for 1 h). (a) Heat treated at 500 °C and (b) heat treated at 700 °C.

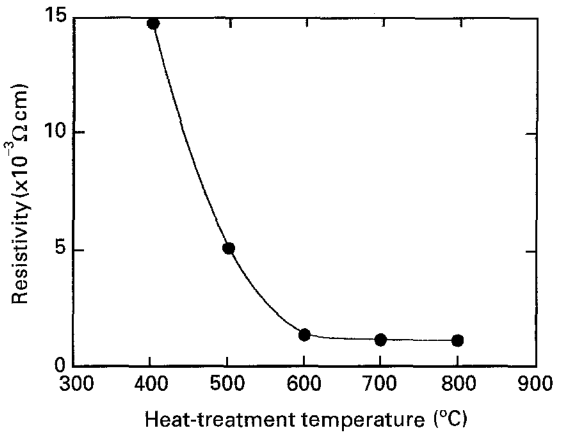

*Figure 8* Heat-treatment temperature dependence on thin film resistivity.

Fig. 9 shows the compositional dependence of the resistivity of the thin films. The resistivity of each film decreased with increasing $SnO_2$ content up to 12 mol %. The resistivity of 12 mol % $SnO_2$ content thin films exhibited the minimum value. The resistivity of thin films heat treated in air was lower than that of the films heat treated in an oxygen atmosphere.

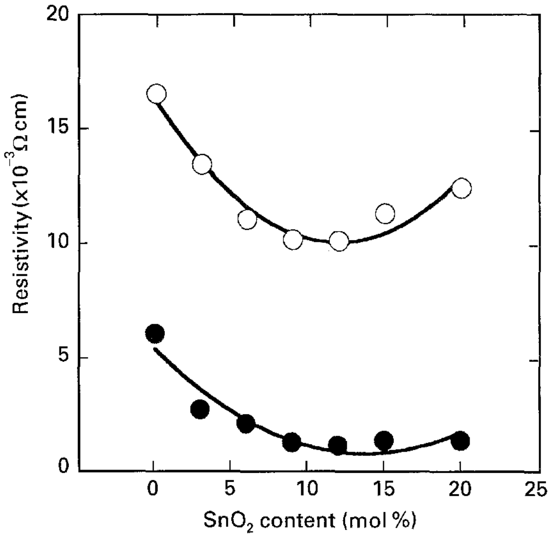

*Figure 9* Compositional dependence of resistivity in the (100 − *x*)-$In_2O_3$·$xSnO_2$ system. Key: —○— $O_2$ atmosphere; —●— air atmosphere.

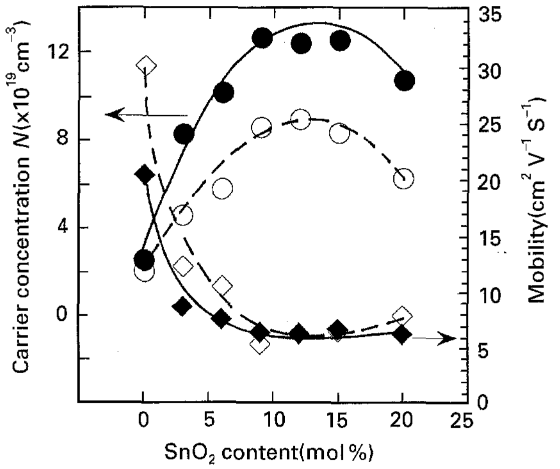

*Figure 10* Compositional dependence of mobility and carrier concentration in the (100 − *x*)$In_2O_3$·$xSnO_2$ system. Key: —●— —◆— in air; —○— —◇—in $O_2$.

Fig. 10 shows the compositional dependence of the mobility and carrier concentration in the (100 − $x$)-$In_2O_3 \cdot xSnO_2$ system. The carrier concentration of both films increased with increasing $SnO_2$ content up to 12 mol %. The 12 mol % $SnO_2$ thin films showed the minimum value. Carrier concentration of the films prepared in air and in oxygen atmospheres showed almost the same value at 0 mol % $SnO_2$ content. The difference between these increased with increasing $SnO_2$ content. Mobility of films prepared in oxygen was higher than that of films prepared in air at 0 mol % $SnO_2$ content. But these values approached each other with increasing $SnO_2$ content.

Thus difference in resistivity between the two atmospheres was caused by the difference in carrier concentration.

Mobility of $In_2O_3$ single crystal is 160 cm$^2$ V$^{-1}$ s$^{-1}$ [8]. However, mobility of the prepared ITO thin film was about 7 cm$^2$ V$^{-1}$ s$^{-1}$.

From consideration of Peason and Bardeen [8], Weiher [9] reported that the donor ionization energy of

$In_2O_3$ is represented by the following formula

$$E_d = E_{d0} - \alpha N_d^{1/3} \qquad (2)$$

where $E_d$ is the donor ionization energy for a given concentration of donors ($N_d$), $E_{d0}$ is the donor ionization energy when the number of donors approaches zero, and $\alpha$ is a constant. For a donor concentration above $1.48 \times 10^{18}$ cm$^{-3}$, the conduction and valence band became degenerate.

The carrier concentrations of prepared films are above $2 \times 10^{19}$ cm$^{-3}$. Therefore the thin films should have degenerate band structures and electrons in these films should show similar behaviour to those in metals. The density of In atoms in crystalline $In_2O_3$ is $3 \times 10^{22}$ cm$^{-3}$. If 10 mol % of indium atoms are substituted by Sn atoms, the carrier concentration should be $3 \times 10^{21}$ cm$^{-3}$. But the carrier concentrations of the substituted thin films were less than $1.25 \times 10^{20}$ cm$^{-3}$. When more than 12 mol % of In were substituted by Sn, the resistivities of films did not decrease with increasing Sn.

Fig. 11 shows compositional dependence of lattice constants in the $(100 - x)In_2O_3 \cdot xSnO_2$ system films ((a) heat treated in air; (b) heat treated in oxygen). The lattice constant of the $In_2O_3$ unit cell is 1.012 nm [10]. The lattice constant of (a) was smaller than (b). In both cases, they were smaller than 1.012 nm. The film heat treated in oxygen is more substituted with Sn atoms than that treated in air. This result is in good agreement with the measured result for the mobility.

It is expected that an interstitial Sn and Sn(II) atoms substituted for In atoms will increase the lattice constant whereas substituted Sn(IV) atoms will decrease it.

With increasing $SnO_2$ content, not all the Sn atoms can be substituted to In atom sites. Sn atoms which cannot substitute to indium sites do not behave as effective donors.

Very little Sn(IV) is changed to Sn(II). They will behave as acceptors.

Köstlin *et al.* [11] reported an optimum value of Sn content for high electrical conductivity. Sn ions are very close to each other when the concentration of Sn ion is very high. When this occurs one of the neighbouring Sn(IV) ion has the tendency to change into Sn(II). Sn(IV) ions are associated with Sn(II) ions by electrostatic force. This association forms a kind of defect complex. The average electrical charge of the complex is + 3. The associated Sn ions that have the average charge + 3 may not contribute to the electrical conduction.

The resistivity results were confirmed as mentioned above by measurement of Hall effect and lattice constant. The carrier concentrations of the thin films prepared in air and in oxygen do not increase much with increasing Sn content. The mobility of these thin films were very low. The reason for the low mobility was considered to be due to the defects in the $In_2O_3$ crystal structure doped with Sn, and the high resistivity, was considered to be due to the very small crystals in the thin film. The mean crystal diameter is about 60 nm obtained from SEM observation. The small crystal grains have many grain boundaries. The grain boundary may disturb the electron moving in the thin film. It was considered that these factors caused high resistivity in these thin films.

## 4.3. Transparency and band gap energy

Fig. 12 shows a transmittance spectrum of $90In_2O_3 \cdot 10SnO_2$ film (having 400 nm thickness) on a $SiO_2$ glass substrate (having 1 mm thickness). The thin film has high transmittance above 80% over the wavelength range 400 to 800 nm. It is high enough for applying as transparent electrodes. The film has an absorption edge at 280 nm. This absorption is caused by electron excitation from a valence band to a conduction band. Relationship between band gap energy ($E_g$) and adsorption coefficient ($\alpha$) follows Equation 3 [12, 13]

$$\alpha \propto (h\nu - E_g)^2 \qquad (3)$$

Band gap energy of the film was estimated to be 3.4 eV. This result almost agreed with the reported values [7, 14].

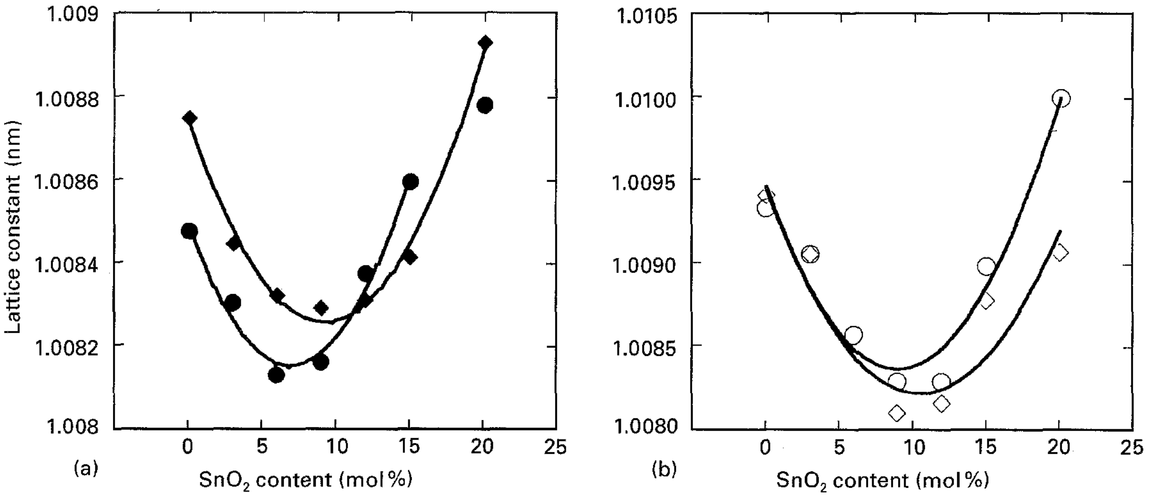

*Figure 11* Compositional dependence of the lattice constant in films of the $(100 - x)In_2O_3 \cdot xSnO_2$ system. ((a) : heat treated in air, (b) heat treated in oxygen atmosphere). Key: —●— (4 0 0); —◆— (2 2 2); —○— (4 0 0); —◇— (2 2 2).

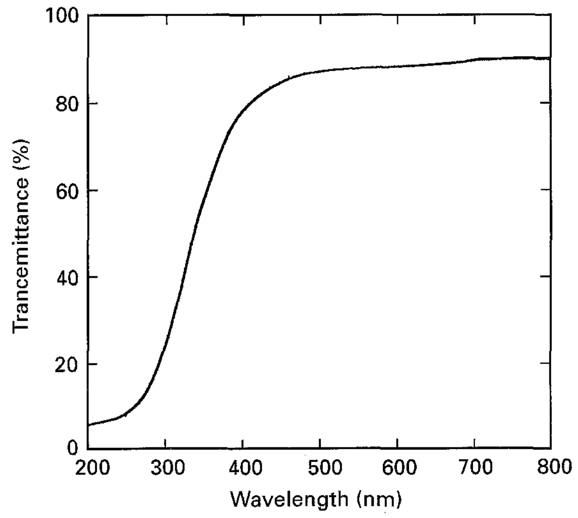

*Figure 12* Visible spectral transmittance of $88In_2O_3{\cdot}12SnO_2$ (film thickness 400 nm).

## 5. Conclusions

ITO transparent conductive thin films of the $(100 - x)$-$In_2O_3{\cdot}xSnO_2$ system were prepared by a dip-coating process. The homogeneous sol for dip-coating was prepared by mixing indium chloride dissolved in acetylacetone and tin chloride dissolved in ethanol. The chelate complexes were formed by the reaction of anhydrous indium chloride and acetylacetone. Films were prepared by heat treating at 700 °C for 1 h. The film substituted with 12 mol % $SnO_2$ showed the minimum resistivity of $\rho = 1.2 \times 10^{-3}\ \Omega$ cm, when the film was heat treated in air. A thin film (88 $In_2O_3{\cdot}12SnO_2$) on a $SiO_2$ glass substrate showed a transmittance of over 90% in the visible wavelength range.

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