JOURNAL OF MATERIALS SCIENCE 25 (1990) 1403–1406

# The effect of gas atmospheres on resistivity of indium tin oxide films at high temperature

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The effects of heat treatment in $O_2$, $O_2$ and $N_2$, and Ar gases on the high temperature (500° C) electrical resistivity of indium tin oxide (ITO) film 52 nm thick prepared by chemical spray pyrolysis method were studied. The partial oxygen pressure effect on the resistivity was found to be $P_{O_2}^{1/5}$ to $P_{O_2}^{1/3.5}$. The resistivity changes for cyclic exchange of $O_2$ by Ar gas at 500° C. These lead to the conclusion that chemisorption of oxygen atoms in the film surface is dominant for this thin film, for thicker films such as 640 nm oxygen diffusion is found to occur. The Langmuir model of the monolayer isothermal adsorption of oxygen atoms in the surface is applicable to the rapid change of resistivity.

## 1. Introduction

Numerous studies of ITO (indium tin oxide) films, n-type semiconductors, have been performed because of the usefulness of the optically transparent and electrically conducting properties of this oxide in electronic and opto-electronic devices. In these studies, it is reported that the resistivity of the ITO films were highly affected by post-heat treatment in various atmospheres. Annealing in air [1–4] or in oxygen [5] caused increases in the resistivity of ITO films while in nitrogen [6, 7] or in argon [6] or in vacuum [1, 3–5, 8] it decreased.

Two models have been proposed to explain these phenomena. According to the oxygen diffusion model, oxygen atoms diffuse into oxygen vacancies in the film when it is heating in $O_2$ gas which results in a decrease in electron carrier concentration [7, 9, 10].

On the other hand in the oxygen adsorption model, oxygen atoms adsorbed onto the film surface influences highly the conductance [11, 12]: free carriers close to the film surface are trapped by absorbed oxygen atoms. This produces an electron deficient layer with a high potential barrier for transition in to the conduction band, thus the space charged layer produced by the oxygen adsorption extends the electron deficient layer. This causes effectively a decrease in the number of carrier electrons.

The present study aims at clarifying the mechanism of the conductivity changes of the ITO films in different gas atmospheres at high temperatures since, irrespective of the above two theories, the conductivity changes in thin or thick ITO film in various atmospheric gases have not been studied in detail.

## 2. Experimental details

### 2.1. Film preparation and measurements

ITO films were prepared from indium and tin chlorides by the chemical spray method [13]. For spraying, a methanol solution of chlorides $InCl_3 \cdot 4H_2O$ and $SnCl_4 \cdot xH_2O$ ($x = 3 \sim 5$) containing $0.1\,g\,cm^{-3}$, respectively. We used polished pyrex glass for substrate. Figure 1 shows a schematic diagram of the experimental apparatus. The cleaned substrate was heated in an electric furnace to 600° C. After the heated substrate was drawn vertically to a preset position, the solution was immediately sprayed normally to the substrate in air using a spray gun (Iwata Air Compressor Mfg. Co., Ltd, type W-71) with $N_2$ carrier gas. The flowrate of the carrier gas and spray solution volume were $10\,l\,min^{-1}$ and $3\,cm^3$ respectively, the spray time was about 3 sec. As 52 nm thick ITO films were obtained in the above spraying conditions, these films were used throughout the experiments.

The electrical resistance of the ITO films was measured by the four probe technique at various temperatures in the heat treatment furnace in Fig. 2. The film thickness measurements were made by use of surface profile-meter Talystep (Rank-Taylor-Hobson) or Surfcorder (Kosaka Lab.).

### 2.2. Heat treatment of deposited films

Figure 2 shows schematically the apparatus for heat treatment of the ITO films. The specimen was heated in a pyrex tube set in the electric furnace 3a (in Fig. 2). Atmospheric gases after dehydration were flowed into this furnace with a constant flowrate of $1.0\,l\,min^{-1}$. This gas then flowed through the furnace 3b for measuring oxygen partial pressure kept at 500° C and

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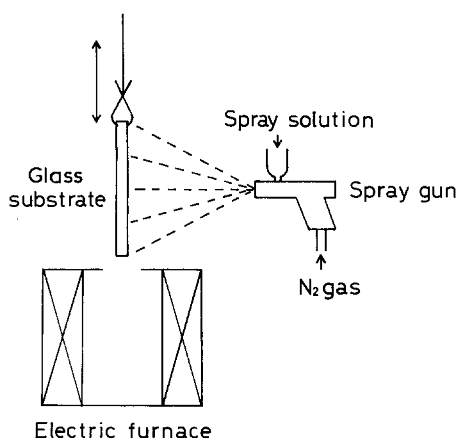


*Figure 1* Schematic diagram of the experimental apparatus.

flowed out. We used an oxygen sensor made of stabilized zirconia, where the reference gas was air.

## 3. Results and discussion

### 3.1. Effect of oxygen partial pressure

The resistivity of the ITO films lowered with increase in tin doping [2, 7–9, 14–16], and a minimum resistivity of $1.23 \times 10^{-3}$ Ωcm was obtained for Sn/In = 5 at %. We used these films for samples. The resistivity of the ITO film was determined in mixed gases of oxygen and nitrogen atmospheres with various $O_2$ partial pressures at various temperatures. During the measurements, total gas flowrate was fixed to $1.0\,l\,min^{-1}$.

Figure 3 shows the resistivity at a baking temperature (270° C) of the ITO film as a function of baking time at various partial oxygen pressures ($P_{O_2}$). In this experiment, we heated the specimen rapidly in flowing $O_2 + N_2$ gas, and after the temperature of specimen had reached to 270° C the resistance measurement was started. As Fig. 3 shows, the film resistivity which was initially $2 \times 10^{-3}$ Ωcm lowered in 2 ~ 3 min after the beginning of baking then gradually increased to saturated values [4, 9, 15, 17], for more than 1 h, while for $P_{O_2} = 0$ ($N_2$ = 100%) the resistivity remained a low value [6] of $1.04 \times 10^{-3}$ Ωcm. At 90 min baking, the resistivities were higher as $P_{O_2}$ was higher.

The saturated resistivities against oxygen partial pressure for different baking temperatures are shown in Fig. 4. The saturated resistivity values were taken from the same kinds of experiments as those shown in Fig. 3. From Fig. 4, it was found that the resistivity of the film was proportional to $P_{O_2}^{1/5}$ for baking temperatures from 300 to 500° C. Providing that the resistivity change of the $In_2O_3$ films by heat treatment in oxygen is governed by diffusion of oxygen into the films, the resistivity should be proportional to $P_{O_2}^{1/6}$ by applying Baumbach–Wagner theory on ZnO [18] to nonstoichiometric decomposition equation of undoped $In_2O_3$. However, our results showed a higher dependence than $P_{O_2}^{1/6}$ [19]. This can not be explained only by oxygen diffusion into the film [7, 9, 10], rather the oxygen chemisorption effect occurs considerably for such a thin ITO film of 52 nm in thickness.

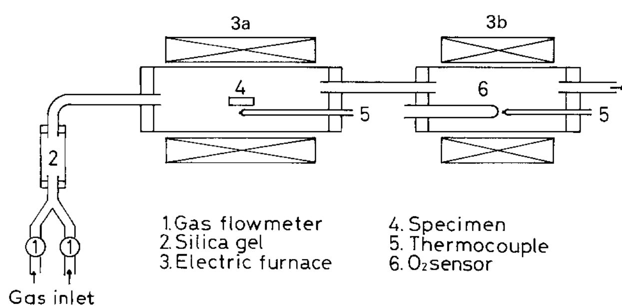


*Figure 2* Schematic diagram of apparatus for heat treatment.

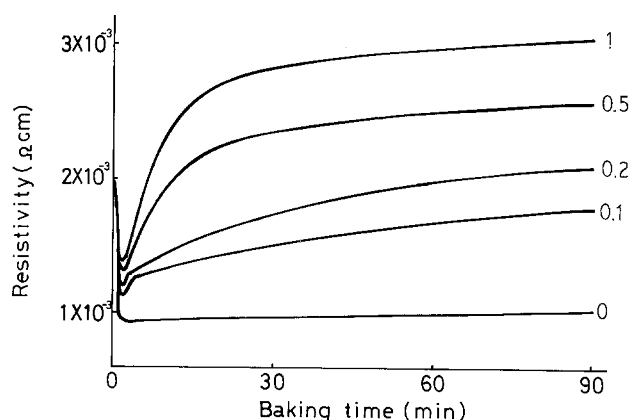


*Figure 3* Resistivity changes of ITO films against baking time for different $P_{O_2}$. Baking temperature: 270° C. Film thickness: 52 nm, Sn/In ratio : 5 at %.

Effect of tin doping on resistivity of ITO films in different partial oxygen pressures is shown in Fig. 5. In the case of the ITO film doped with a low tin content, Sn/In = 1 at %, the resistivity was found to be proportional to $P_{O_2}^{1/3.5}$, giving a higher dependence than $P_{O_2}^{1/5}$ for the film doped with a tin content of Sn/In = 5 at %. The contribution of donner carrier electrons from oxygen vacancies is much higher for the film of Sn/In = 1 at % than that for Sn/In = 5 at %. For such a film with Sn/In = 1 at % including higher oxygen vacancy concentration, diffusion of oxygen at high temperature is expected to affect the resistivity of the film, which results in a proportionality of the resistivity to oxygen partial pressure, approaching the theoretical one, $P_{O_2}^{1/6}$. However a much higher proportional relationship $P_{O_2}^{1/3.5}$ was obtained. From this, we considered that the oxygen chemisorption effect on

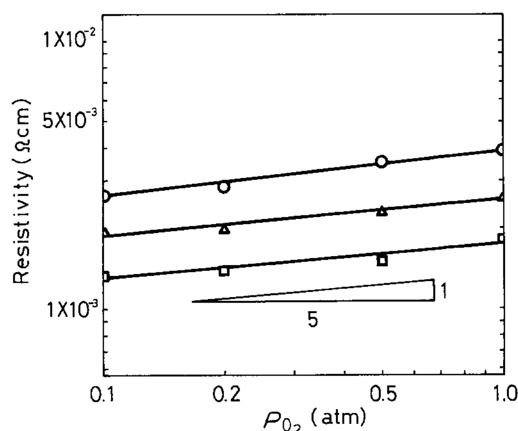


*Figure 4* Resistivity of ITO film against $O_2$ partial pressure at different baking temperatures: (□) 300° C; (△) 400° C; (○) 500° C. Film thickness: 52 nm, Sn/In ratio : 5 at %.

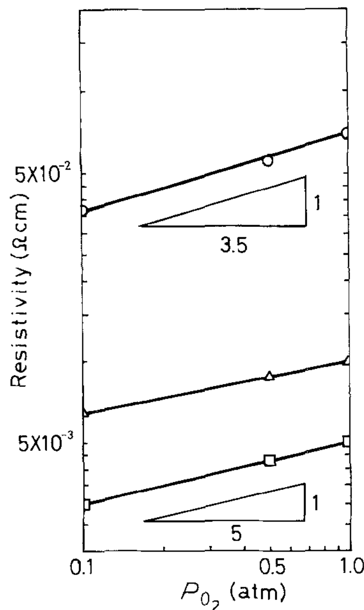

*Figure 5* Resistivity of ITO films with various Sn/In ratios against $O_2$ partial pressure. (○) 1 at %; (△) 10 at %; (□) 5 at %. Baking temperature: 500° C.

a film of such a thin thickness as 50 nm was higher than the oxygen diffusion effect.

## 3.2. Changes of resistivity in alternate atmospheres of oxygen and argon

Figure 6 shows variations of resistivity for ITO films at 500° C when atmospheric gases of $O_2$ and Ar alternately switched every hour. In this experiment, after the resistivity of the specimen had been saturated by a sufficient heat treatment in Ar, we started the resistance measurements. As shown in Fig. 6, the resistivity of the ITO film in 52 nm thickness reversibly changed and was rapidly sensed by the exchange of atmospheric gases. The variations of the resistivity for ITO films 52 nm thick was much larger than that in the 640 nm thick film, this means that the effects of oxygen chemisorption [11, 12] in an oxygen atmosphere and oxygen desorption in an argon atmosphere on and from the film surface were more dominant in thinner films than in thicker films. For instance, the effect of oxygen chemisorption has been studied previously on ZnO [11, 20]. On the other hand, it was observed that the resistivity of a 640 nm thick film gradually increased as heat treatment time passed on which undulating changes of the resistivity by exchanges of Ar with $O_2$ gas were superposed. This gradual increase may be caused by oxygen diffusion because the rate of the diffusion is lower than that of chemisorption and desorption. In Fig. 6 is drawn a dotted curve showing a measure of the resistivity increase due to oxygen diffusion into the film for the duration of 5 h baking time. It is expected from this curve that the resistivity change is almost determined by oxygen diffusion for the films of several micrometres in thickness.

Next we discuss in detail the effect of surface oxygen chemisorption shown in Fig. 6. Oxygen chemisorption on the surface of the ITO causes the trapping of an electron at the surface. Since the electron affinity of oxygen molecule is larger than work function of ITO, the trapping of an electron from the bulk of the ITO will result in a decrease in the surface conductivity as a strong depletion layer is formed. The depth $d$ of the depletion layer is given by as follows [21],

$$d = \left(\frac{2\varepsilon\varepsilon_0\,\phi}{eNd}\right)^{1/2} \qquad (1)$$

where $N_d$ is donner density, $\varepsilon$ and $\varepsilon_0$ are dielectric constant for the film and vacuum respectively, e is electron charge and $\phi$ is surface potential. And $Nd = fN_s$, where $N_s$ is density of surface chemisorped oxygen and $f$ is a constant. The chemisorped oxygen results in change in the space charge density $\Delta N$ per unit surface area in the space charge region, so $N_s = \Delta N$. Thus $\Delta N$ results in the change $(\Delta N)$ in total carrier density $n$, i.e., $n' = n - \Delta N$, and $\Delta n \equiv n' - n = -\Delta N$. Assuming that the electron mobility of the film does not change throughout the oxygen chemisorption, the change in conductivity of the film $\Delta\sigma$ can be described as, $\Delta\sigma = \Delta n \cdot e\,\mu$ as stated in previous study [11].

The initial stage of the oxygen chemisorption may be interpreted by the Langmuir monolayer adsorption because of the reversible character of the resistivity change in Fig. 6. So we tried to apply the Langmuir isothermal adsorption theory to our data of the resistivities of each film for baking time from 2 to 3 h in Fig. 6. The isothermal adsorption equation is given by,

$$dv/dt = (k_1 + k_2)(v_c - v) \qquad (2)$$

or by integration

$$v = v_c[1 - \exp^{-\psi t}] \qquad (3)$$

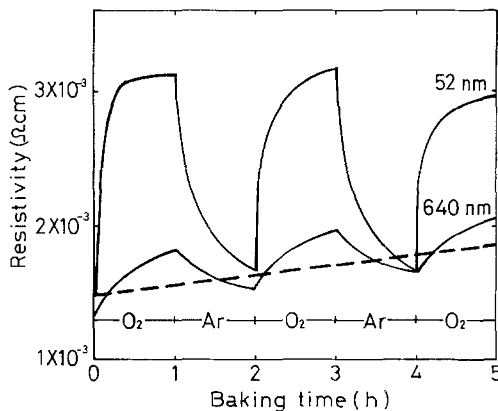

*Figure 6* Changes in resistivity of thin and thick ITO films against baking time. Baking temperature: 500° C.

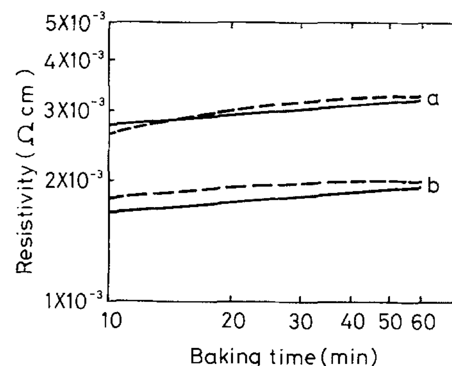

*Figure 7* Resistivity of ITO films against baking time. Baking temperature: 500° C, film thickness: (a) 52 nm, (b) 640 nm. (– – – –) theoretical curve; (———) experimental curve.

where $V$ is adsorption volume at time $t$, $v_e$ is equilibrium adsorption volume, $k_1$ is rate constant for adsorption, $k_2$ is rate constant for desorption, and $\psi = k_1 + k_2$, respectively. In Fig. 7, we plotted theoretical curves due to adsorption by choosing optimized parameters of $v_e$ and $\psi$ from experimental curve shown in Fig. 6. It is seen that experimental curve and calculated curve agree relatively well. From this, it may be concluded that the rapid change of resistivity for ITO films on exposing at oxygen or argon gases at a high temperature of 500° C is caused by adsorption of these gases on the film surface. This may also possibly explain the result that resistivity of the ITO films was proportional from 1/5 to 1/3.5 power of partial oxygen pressure larger than 1/6 power, theoretical value [18] for oxygen diffusion, (see Figs 4 and 5). Our treatments of the phenomenon may be useful for designing gas sensors using semiconducting ceramics. For rapid sensing and high sensitivity, larger $k_1$ and $k_2$ and larger $v_e$ are necessary respectively, depending on kinds of gases and substrate materials.

## 4. Conclusion

We prepared ITO films having resistivity of $1.23 \times 10^{-3}\,\Omega$cm for tin doping of 5 at % by chemical spray technique, and the effects of heat treatments in various atmospheres on the resistivity of the films 52 nm thick were investigated at a high temperature of 500° C.

1. The dependences of partial oxygen pressure ($P_{O_2}$) on the resistivity were proportional from $P_{O_2}^{1/5}$ to $P_{O_2}^{1/3.5}$ which were higher than $P_{O_2}^{1/6}$, theoretical relationship from the non-stoichiometric decomposition equation of $In_2O_3$. Accordingly, in addition to oxygen diffusion into the film, oxygen chemisorption occurred considerably in thin ITO films.

2. The cyclic exchange of $O_2$ by Ar gas at 500° C caused rapid changes in the resistivity for the film of 52 nm in thickness because of the dominant chemisorption and desorption effects of oxygen on the film surface. For a film of 640 nm in thickness a gradual increase in the resistivity due to oxygen diffusion into the film occurred, on which the rapid change of the resistivity due to the chemisorption and desorption was superposed.

3. The rapid changes of the resistivity could be explained by the Langmuir model of monolayer isothermal adsorption of $O_2$ gas on the surface of the ITO films 52 nm thick.

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*Received 20 December 1988*
*and accepted 14 April 1989*