

# Carrier compensation and activation energy studies in pyrolytic $\text{In}_2\text{O}_3$ thin film

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The thermal activation energies of polycrystalline thin films of  $\text{In}_2\text{O}_3$  on a glass substrate have been studied by a post deposition heat treatment in the temperature range 30 to 240°C in air. The temperature dependence behaviour of the film and the various activation energies obtained have been explained by taking the existing grain boundary trapping models and other semiconductor models into account. It has been concluded however that at temperatures above 190°C a dissociative chemisorption process may become active in the film and partially compensate the carriers generated for electrical conduction.

## 1. Introduction

Doped and undoped polycrystalline thin films of  $\text{In}_2\text{O}_3$  are interesting for their transparent conducting properties [1]. Sn-doped  $\text{In}_2\text{O}_3$  films are known for their applications in various energy efficient devices, particularly in heterojunction solar cells where they are used as optically conductive windows and as spectrally selective coating materials [2].

There are several methods by which these films are prepared on glass substrates. The well known chemical spray technique or pyrosol process [3, 4] is one of the simplest and least expensive non-vacuum methods. It is known that polycrystalline oxide films deposited in normal open-air atmospheres are very sensitive to post-deposition heat treatments, particularly when the films are deposited by pyrosol process. This may be due to several reasons, of which the process of oxygen diffusion either into or out of the film is the most significant. To make proper use of these oxide films in electronic devices, therefore, their temperature dependent behaviour should be known in detail, because the temperature stability and reproducibility of the film properties are very important for the device fabrication and operation.

In the present paper we report some studies on undoped and Sn-doped  $\text{In}_2\text{O}_3$  films when they are heat treated after deposition. All the samples are prepared by a modified spray technique using a low cost apparatus designed in our laboratory [4]. These films were highly transparent and electrically conductive and they may be used as transparent electrodes in solar cells.

## 2. Experimental procedure

A solution of  $\text{InCl}_3$  in equal volumes of  $\text{H}_2\text{O}$  and  $\sim 0.4\text{ M C}_2\text{H}_5\text{OH}$  was taken as the working solution for preparing undoped  $\text{In}_2\text{O}_3$  film. For the Sn-doped films  $\text{SnCl}_4$  was added to the working solution at different mole percentages of  $\text{InCl}_3$  to obtain films of different conductivity and carrier concentration. Spraying was performed at an average rate of 0.8 ml

$\text{min}^{-1}$  by a pneumatic spray gun using compressed air as the carrier gas. A constant substrate temperature of 400°C was maintained during the film deposition period. The details of the deposition process may be found in our previous paper [4]. All the experimental samples were prepared on glass substrate supplied by Corning Glass Works (USA). After the deposition of films the substrate and films were cooled down to room temperature at an average rate of  $100^\circ\text{C min}^{-1}$  and were kept in desiccators. Post-deposition heat treatment of the samples was performed in normal atmosphere. While performing heat treatment the heating temperature was raised at an average rate of  $10^\circ\text{C min}^{-1}$  up to a maximum temperature of 250°C. The samples were kept at this temperature for an hour and then they were brought back to room temperature through a cooling cycle. A flat nichrome wire strip heater covered with mica sheet was used to heat the samples. The Hall coefficient and conductivity of the samples were simultaneously measured during the heat treatment by using van der Pauw's method. Digital multimeters (Hewlett-Packard, Model 3465A, USA) were used for electrical measurement. Film thicknesses were determined by interferometric methods.

## 3. Results and discussion

Several samples of  $\text{In}_2\text{O}_3$  and  $\text{In}_2\text{O}_3:\text{Sn}$  thin film were tested in these experiments, and it was observed that the nature of variations of the various electrical parameters due to heat treatment were very similar. We therefore feel it wise to report here the result for only four samples; two of them are undoped and the other two are Sn-doped.

### 3.1. Temperature dependence of resistivity

The variation of resistivity with temperature  $T$  of the samples are shown by two sets of curves in Figs 1a and 1b. It can be seen that up to  $\sim 70^\circ\text{C}$  initially the resistivity increases slightly (region I), then it gradually decreases with the rise of temperature up to

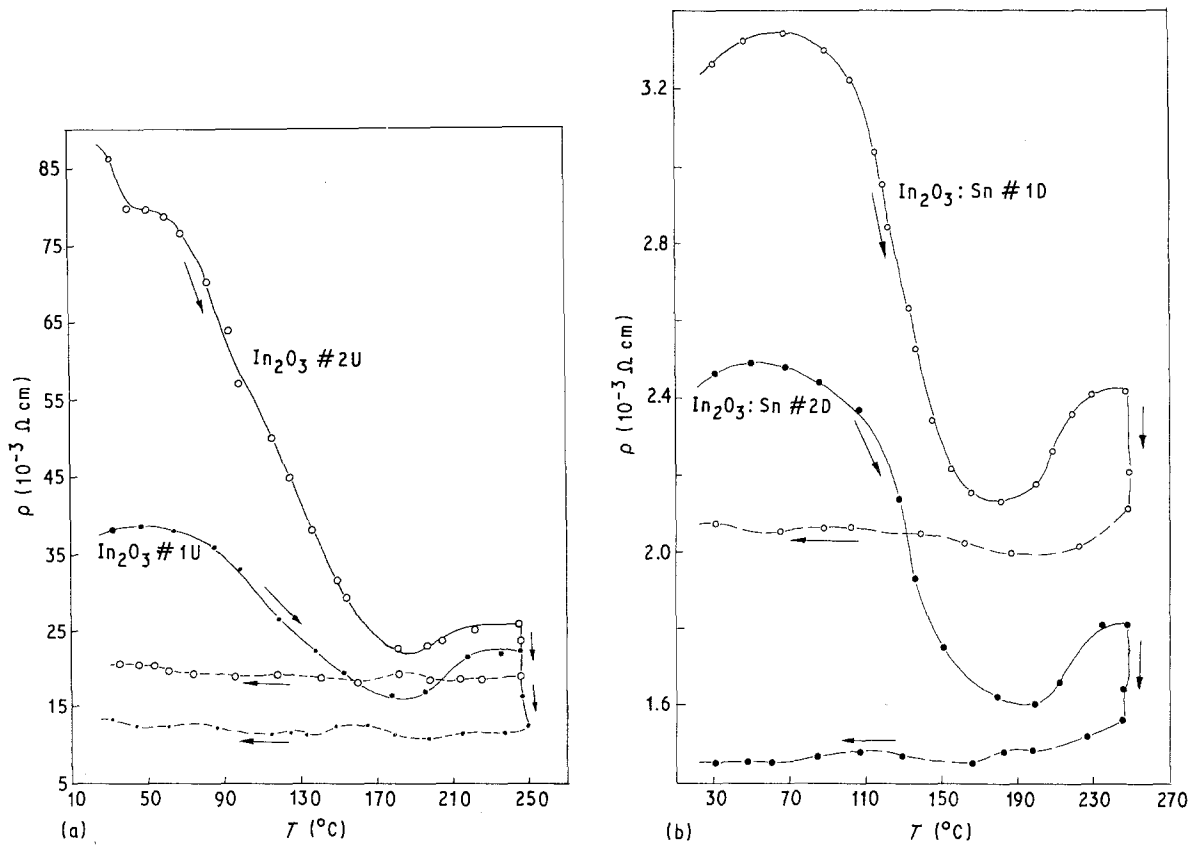


Figure 1 The variation of resistivity  $\rho$  with temperature  $T$  of (a) undoped  $\text{In}_2\text{O}_3$  film, and (b) Sn-doped  $\text{In}_2\text{O}_3$  film. The solid line indicates the heating cycle and the broken line indicate the cooling cycle.

$\sim 190^\circ\text{C}$  (region II), then it again increases very slightly with the rise of temperature up to about  $240^\circ\text{C}$  (region III). Finally  $\rho$  drops down at a constant temperature of  $250^\circ\text{C}$  during a period of one hour and attains a steady state value. The return operation of cooling does not appreciably alter the value of  $\rho$  that is attained at the maximum temperature. During the variation of  $\rho$ , the carrier concentration  $n$  and the Hall mobility  $\mu$  of the samples were also found to vary with the temperature. All the samples show  $n$ -type conductivity in this temperature range.

### 3.2. The activation energy

It is known that the thermal activation energy for electronic conduction in semiconductors and in dielec-

trics is traditionally interpreted in three possible ways.

- (a) It is half the bandgap when the material is intrinsic;
- (b) some trap depth when the material is extrinsic or
- (c) half the trap depth when the material is extrinsic but highly doped.

For doped polycrystalline semiconductor, grain boundary trapping models have been proved adequate for interpreting the various activation energies [5-7]. According to this model, when carrier concentration of a sample becomes quite high compared to its available trap density, a depletion region exists adjacent to the grain boundary, the carrier distribution is

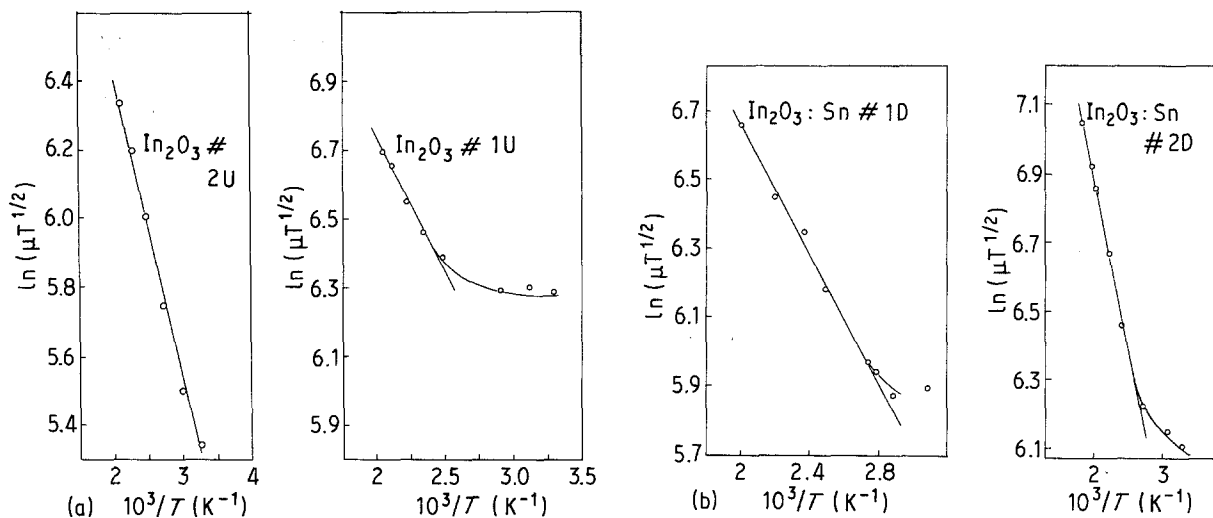


Figure 2  $\ln(\mu T^{1/2})$  against  $10^3/T$  curve plotted for (a) 2U and 1U undoped  $\text{In}_2\text{O}_3$  film, and (b) 1D and 2D Sn-doped  $\text{In}_2\text{O}_3$  film.

TABLE I Various characteristics of In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>:Sn films. Regions II and III are temperature regions explained in the text

Sample number and type	Resistivity, $\rho$ ( $10^{-3} \Omega \text{ cm}$ )	Hall mobility $\mu$ ( $=\mu_{\text{eff}}$ ) ( $\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ )	Barrier height, $E_{\mu}$ (meV), (for Region II)	$(E_c - E_d)^*$ (meV) (for region II)	$(E_c - E_d)^\dagger$ (meV) (for region III)	$E_a$ (meV) (for region II)	TCR ( $10^{-3} \text{ deg}^{-1}$ ) (for region II)
1U In <sub>2</sub> O <sub>3</sub>	38.0	31.08	69.0	97.0	100	119	-5.45
2U In <sub>2</sub> O <sub>3</sub>	86.0	12.0	76.0	85.0	83	118	-6.35
1D In <sub>2</sub> O <sub>3</sub> :Sn	3.27	21.78	79.0	81.0	83	120	-3.31
2D In <sub>2</sub> O <sub>3</sub> :Sn	2.46	25.87	71.0	69.0	67	104	-3.67

\*Determined by using uncompensated semiconductor model.

†Determined by using partially compensated semiconductor model.

inhomogeneous and the carrier transport occurs by thermionic emission over the grain boundaries. In this situation the free carrier concentration and Hall mobility both are thermally activated [8, 9]. For degenerate semiconductor where this situation exists the effective mobility  $\mu_{\text{eff}}$  is given by

$$\mu_{\text{eff}} = A\mu'_0 T^{-1/2} \exp(-E_{\mu}/k_B T) \quad (1)$$

where  $E_{\mu}$  is the mobility activation energy or the grain boundary barrier height, and  $\mu'_0$  is a function of grain size  $L$  and effective mass  $m_c^*$  given by

$$\mu'_0 = eL/(8\pi m_c^* k_B)^{1/2} \quad (2)$$

$A$  is a parameter which accounts for the various reflection, transmission and scattering coefficients at the grain boundaries and their slow temperature dependence [10]. Thus when mobility is thermally activated then  $E_{\mu}$  is determined from Equation 1 by plotting curves as shown in Figs 2a and 2b.

The temperature dependence of carrier concentration  $n$  for such a material can be expressed as

$$n = n_0 \exp(-E_n/k_B T) \quad (3)$$

where  $E_n = (E_c - E_d)/2$  is the activation energy for the carrier concentration, and  $(E_c - E_d)$  is the position of donor level  $E_d$  with respect to the conduction band edge  $E_c$ .  $E_n$  depends on the relative concentration of carriers in the grains  $n_1$  and those in the barrier regions  $n_2$ . Petritz [11] has given the relation between  $E_{\mu}$ ,  $n_1$  and  $n_2$  as

$$E_{\mu} = k_B T \ln(n_1/n_2). \quad (4)$$

Similarly the thermally activated conductivity can be expressed by

$$\sigma = \sigma_{\infty} \exp(-E_{\sigma}/2k_B T) \quad (5)$$

where  $E_{\sigma} = 2E_a$ , and  $E_a$  is the conductivity activation

energy for uncompensated semiconductor. A simple relation that exists between  $E_n$ ,  $E_{\mu}$  and  $E_a$  is

$$E_n \simeq |E_a - E_{\mu}|. \quad (6)$$

In the light of the above description and using Equations 1-5 the various activation energies and the grain boundary parameters are calculated for our In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>:Sn films and are given in Tables I and II. Here  $n_1$  has been considered to be the carrier concentration corresponding to the measured Hall coefficient and the values of  $n_2$  were determined from Equation 4.

It is observed from Table II that when  $n_1$  of the undoped films increases by about 13% it is accompanied by a ~14% decrease of the  $n_2$  values; whereas for Sn-doped films an ~11% increase of  $n_1$  by the addition of dopant is accompanied by an almost 50% increase of the  $n_2$  values. From such an observation one may tentatively infer that when dopants are added to the film the boundary regions of the grains receive a greater share of the new charge carriers in comparison to that of the grains. On the other hand for undoped films the total number of carriers remains almost constant; a distribution of carriers may only occur between the grain and the boundary regions if the deposition conditions are varied.

### 3.3. The donor level

From the temperature dependence of the carrier concentration  $n$ , in region II, the position of the donor level  $(E_c - E_d)$  may be determined by plotting  $\ln(n)$  against  $T^{-1}$  (Fig. 3), considering the samples to be in the uncompensated regime. The obtained values of  $(E_c - E_d)$  with reference to the conduction band edge  $E_c$  are given in Table I. The values are of the order of

TABLE II Estimated grain boundary parameters of In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>:Sn films

Sample number and type	Carrier concentration $n_1$ ( $10^{18} \text{ cm}^{-3}$ )	Carrier concentration $n_2$ ( $10^{18} \text{ cm}^{-3}$ )	Debye screening length $L_D$ ( $\text{\AA}$ )	Estimated grain size $L$ ( $\text{\AA}$ )	Mean free path ( $\text{\AA}$ )
1U In <sub>2</sub> O <sub>3</sub>	5.18	0.357	10.38	273	10
2U In <sub>2</sub> O <sub>3</sub>	5.85	0.307	10.12	332	4
1D In <sub>2</sub> O <sub>3</sub> :Sn	88.0	4.15	2.95	351	19.7
2D In <sub>2</sub> O <sub>3</sub> :Sn	98.1	6.26	2.9	318	27

69–97 meV which is very small, indicating that the possible donor levels are shallow.

Whether this sort of donor level is adequate in these films can be determined by calculating the static dielectric constant  $\epsilon_L$  for the samples. For this purpose a hydrogenic model for the medium could be assumed where the donor ionization energy  $E_d$  is given by [12]

$$E_d = (e^4 m_e^*) / (2\epsilon_L^2 \hbar^2) \quad (\text{in CGS}). \quad (7)$$

The effective mass  $m_e^*$  can be obtained from the thermopower study (see also [13]). For undoped films we obtained the value of  $\epsilon_L$  of 3.9–4, which is in excellent agreement with the value of 4 reported by Kostlin *et al.* [14] and by Clanget [15]. Therefore the obtained donor levels are reasonable and the samples in this region of temperature (region II) could be safely considered as uncompensated.

In undoped films the oxygen vacancies and the interstitial chlorine ions (incorporated in the film from the working solution) may act as the major sources of donors. Interstitial  $\text{In}^{3+}$  ions are also important in this case [16]. For Sn-doped samples  $\text{Sn}^{4+}$  ions may substitute for  $\text{In}^{3+}$  ions in the  $\text{In}_2\text{O}_3$  lattice and can act as additional sources of donors [17]. Apart from these donor levels, there is some excess oxygen occupying the interstitial sites of the host lattice which create acceptor levels [18–22] just above the valence band. With the increase of temperature these acceptor states may be excited and may produce a partial negation of the donor action in the film.

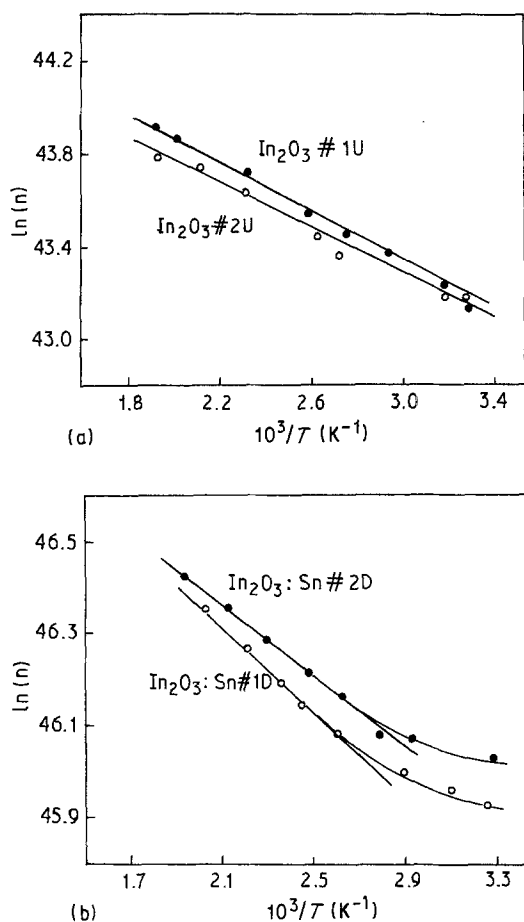


Figure 3 Plots of  $\ln(n)$  against the  $10^3/T$  curve for (a) undoped  $\text{In}_2\text{O}_3$  film, and (b) Sn-doped  $\text{In}_2\text{O}_3$  film.

### 3.4. The experimental curves

In view of the above picture and taking the grain boundary effects into account we may proceed to explain the experimental curves of Figs 1a and 1b. Since the films are all polycrystalline in structure the gross variation of resistivity due to heat treatment would be controlled mainly by the grain boundary effects (by modulating the Hall mobility). It has been observed that in this type of film oxygen chemisorption and desorption may both occur at all temperatures. Which process dominates is determined by their respective rates, which are functions of the ambient temperature and relative concentration of the chemisorption species available in the ambient and in the chemisorption sites [19]. A minor increase of resistivity observed between 30 and 70°C at the beginning of the heating cycle may be due to the predominance of such a chemisorption effect. As the temperature increases further in region II an overwhelming degree of desorption occurs and the resistivity decreases.

During desorption in this region the principal species of the available chemisorbed oxygen, probably  $\text{O}_2^-$ , converts to  $\text{O}_2$  by donating an electron to the indium oxide ( $\text{O}_2^- \rightarrow \text{O}_2 + e$ ) [20]. It is however difficult to explain at present the increase of resistivity in region III when the sample temperature exceeds  $\sim 190^\circ\text{C}$ . Two possible mechanisms may be present here:

- (i) generation of internal stresses in the film [21], and
- (ii) a predominance of partial carrier compensation process via (a) excitation of possible acceptor states [22] or (b) dissociative chemisorption effect [20].

These processes may increase the film resistivity. If at temperatures above  $\sim 190^\circ\text{C}$  the available desorbable oxygen  $\text{O}_2$  of the sample yields  $\text{O}^{1-}$  or  $\text{O}^{2-}$  by accepting electrons from the indium oxide ( $\text{O}_2 + 2e \rightarrow 2\text{O}^{1-}$ , or  $\frac{1}{2}\text{O}_2 + 2e \rightarrow \text{O}^{2-}$ ) then it is the dissociative chemisorption effect which is responsible, otherwise it may be the usual ionization of the acceptor states. The reason for invoking here the process of partial carrier compensation is that the activation energy determined in this region of temperature, region III, using the partially compensated semiconductor model, agrees well with the previously determined donor ionization energy using the uncompensated semiconductor model (Table I). Since a similar type of behaviour was observed for all the doped and undoped films in region III, it is definitely a characteristic of the host lattice  $\text{In}_2\text{O}_3$  rather than of the Sn donors. Therefore it appears that a mechanism like partial carrier compensation may dominate in this region of temperature to increase the resistivity slightly over a general declining background.

Just *et al.* [21] have mentioned that if internal stresses in a film increase due to heat treatment, resistivity increases simultaneously. Since the grain boundary barrier heights are the chief controlling factor of resistivity as mentioned earlier, the cooling cycle does not follow the heating cycle in these as-deposited films.

#### 4. Conclusion

In spray deposited polycrystalline films of  $\text{In}_2\text{O}_3$  various effects at the grain boundary play an important role in controlling the thermal activation energy for the electronic transport phenomena in the temperature range 30 to 250°C. The Hall mobility in these films is thermally activated across a barrier of height about 69 to 79 meV and the possible donor levels are very shallow. At temperatures between 190 and 240°C, irrespective of the concentration of doping in the film, a partial carrier compensation process may set in either via the ionization of available acceptor states or via a dissociative chemisorption process when the films are in the as-deposited condition.

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Received 27 January  
and accepted 17 July 1989