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New model for the In_2O_3–SnO_2 system

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The In_2O_3–SnO_2 (ITO) solid solution system was formulated and a model for the ITO material derived. The model starts from the formation of a solid solution – giving rise to a doping effect up to the solid solubility of tin in the In_2O_3 lattice, together with the formation of a new associated vacancy $(V_{In}V_O)^x$. The mechanism is discussed by which the $(V_{In}V_O)^x$ dissociates, reducing the number of free carriers through trapping, which in turn affects the electrical characteristics.

1. Introduction

The indium oxide–stannic oxide (ITO) system has been widely prepared by various techniques and in different forms, up to the solid solubility limit of SnO_2 in In_2O_3 [1–5]. In this doping range, the material in thin film form is of great interest. It has high electrical conductivity, optical transparency (in the visible solar spectrum) and high reflectivity in the infrared region. This satisfies the requirements of many applications such as solar cells [6, 7], microelectronics [8], electrochromic displays [9], heat mirrors [10], and gas sensors [11].

Both In_2O_3 [12] and SnO_2 [13] are *n*-type materials as a result of oxygen vacancies in the undoped state. To analyse the In_2O_3–SnO_2 (ITO) system, a review of the activity of one oxide doping the other oxide will be given.

Extensive X-ray analysis done by Frank *et al.* [16] shows that ITO material retains the cubic In_2O_3 structure up to the solid solubility limit of SnO_2 in In_2O_3, the SnO_2 phase not appearing until a doping level of 6 ± 2 at % Sn. This means that each tin atom substitutes for an indium atom. Mössbauer spectroscopy [17] has shown that in high-quality ITO material the tin is tetravalent, each In^{3+} being replaced by a Sn^{4+}. This process donates a free electron, for conductivity. This is in addition to the contribution by the oxygen vacancies, which is limited by their chemical stability [18]. Beyond the solubility limit, and up to 50 at % Sn, Köstlin *et al.* [19] proposed a model in which a solid solution of $(SnO_2)_2$ in In_2O_3 may take place. Above 60 at % Sn, a distinct SnO_2 phase may be observed beside the In_2O_3 structure [19].

The solubility limit of In_2O_3 in SnO_2 is less than 1 at % In [16, 20], in which the In^{3+} replaces the Sn^{4+} [21]. This decreases the conductivity, because if exactly two In^{3+} ions are present for each missing O^{2-} ion, the defects become locked in the SnO_2 lattice, which decreases the number of free carriers and thus increases the resistivity [20, 22].

2. Discussion

2.1. Qualitative analysis

A model is proposed to characterize fully the ITO material, outlined in Fig. 1a–d. Accordingly, let δ_{Sn} be the solubility of tin in the In_2O_3 lattice, and δ_{In} be the solubility of indium in the SnO_2 lattice. The general behaviour in the indium oxide–stannic oxide system [4, 16, 17, 19, 23, 24] can be summarized as follows.

Let x be the number of moles of SnO_2 used to form a solid solution with $(1 - x)$ moles In_2O_3. Then, up to the solid solubility limit of tin in In_2O_3 we have

$$\delta_{Sn} = x \tag{1}$$

(see Fig. 1a). Beyond the solid solubility limit, on increasing the SnO_2 content, the solubility of tin is nearly constant (δ_{Snm}) until $x = \delta_m$ (where δ_m is the maximum value of x for the ITO material to retain the In_2O_3 structure). For concentrations of SnO_2 greater than δ_m, the solubility starts to decrease and the SnO_2 lattice is built up.

It has been reported [16] that for values of $x > 0.95$ the solubility of In_2O_3 in the SnO_2 lattice starts to increase (Fig. 1b). For values of $x > 0.98$ (within the solid solubility limits of indium in the SnO_2 lattice) this becomes a linear dependence and can be expressed as

$$\delta_{In} = (1 - x) \tag{2}$$

2.2. Mathematical analysis

The above qualitative analysis can be mathematically formulated as follows.

2.2.1. Definitions

The active metal oxide lattice point is a cation lattice point which is surrounded by its own metal oxide atoms.

δ is a measure of the portion of indium or tin which is not present in the form of its own metal oxide and

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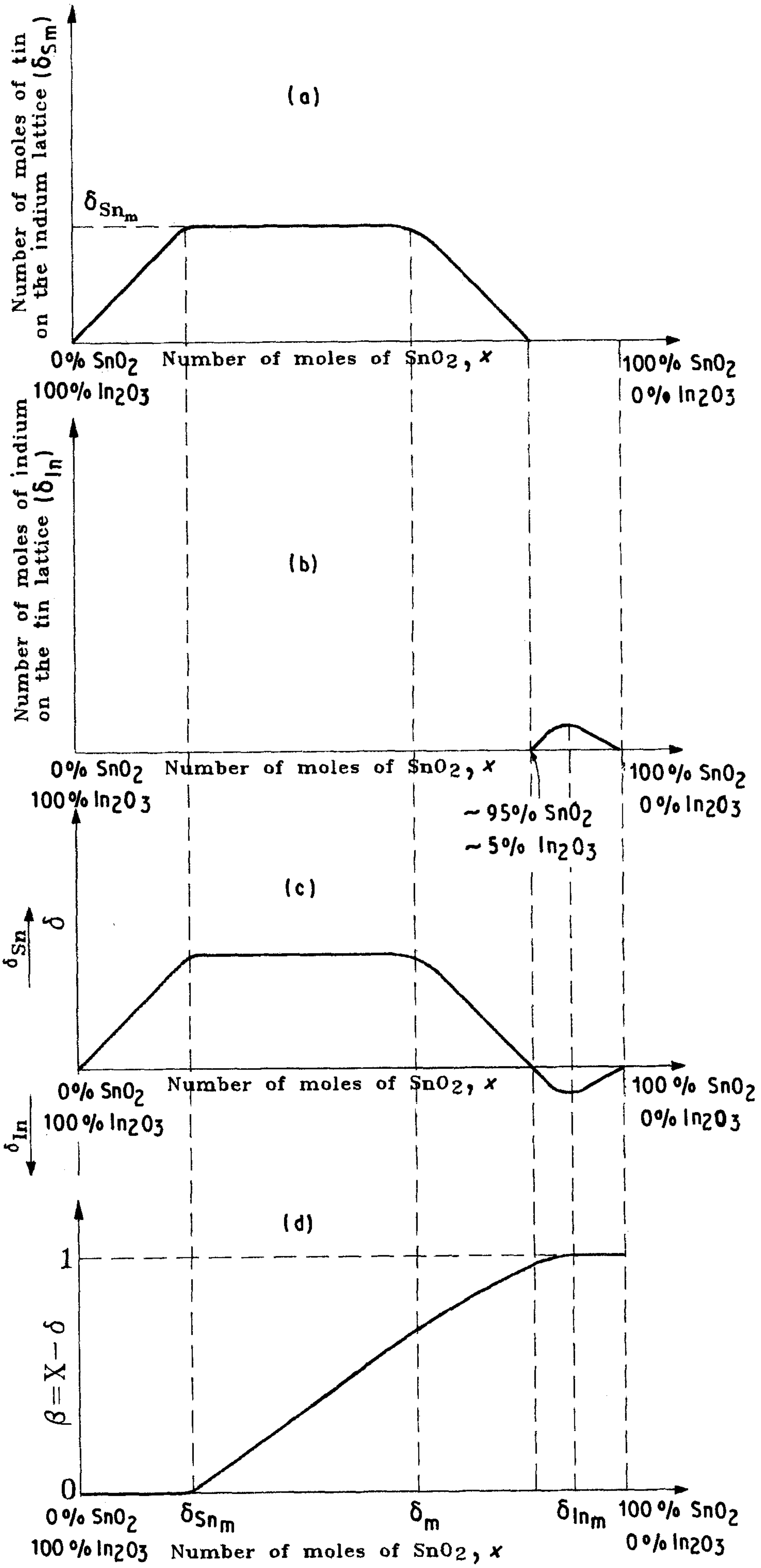

Figure 1 The proposed model to characterize fully the ITO material.

which occupies active cation positions on the metal oxide lattice of the other. If tin substitutes for indium, then δ is positive. Conversely, if indium substitutes for tin, then δ is negative. According to this definition of δ we have

$$\delta = x \qquad \text{for } x = (0, \delta_{\mathrm{Snm}}) \tag{3}$$

$$\delta = \delta_{\mathrm{Snm}} \qquad \text{for } x = (\delta_{\mathrm{Snm}}, \delta_{\mathrm{m}}) \tag{4}$$

$$\delta = ax + c \qquad \text{for } x = (\delta_{\mathrm{m}}, \delta_{\mathrm{Inm}}) \tag{5}$$

$$\delta = (x - 1) \qquad \text{for } x = (\delta_{\mathrm{Inm}}, 1) \tag{6}$$

where

$$a = \frac{\delta_{\mathrm{Inm}} - \delta_{\mathrm{Snm}} - 1}{\delta_{\mathrm{Inm}} - \delta_{\mathrm{m}}} \tag{7}$$

$$c = \frac{\delta_{\mathrm{Snm}}\delta_{\mathrm{Inm}} - \delta_{\mathrm{Inm}}\delta_{\mathrm{m}} + \delta_{\mathrm{m}}}{\delta_{\mathrm{Inm}} - \delta_{\mathrm{m}}} \tag{8}$$

The general behaviour of δ is illustrated in Fig. 1c.

β is a function which describes the concentration of tin (or indium) which occupies any position except for those substituting for indium (or tin) on the active metal lattice points. Thus

$$\beta = x - \delta \tag{9}$$

According to this definition of β we have

$$\beta = 0 \qquad \text{for } x = (0, \delta_{\mathrm{Snm}}) \tag{10}$$

$$\beta = \mathrm{x} - \delta_{\mathrm{Snm}} \qquad \text{for } x = (\delta_{\mathrm{Snm}}, \delta_{\mathrm{m}}) \tag{11}$$

$$\beta = (1 - a)x - c \qquad \text{for } x = (\delta_{\mathrm{m}}, \delta_{\mathrm{Inm}}) \tag{12}$$

$$\beta = 1 \qquad \text{for } x = (\delta_{\mathrm{Inm}}, 1) \tag{13}$$

The general behaviour of β is illustrated in Fig. 1d.

2.3. The ITO model

Consider the interaction between x mol SnO_2 and $(1 - x)$ mol In_2O_3 to give 1 mol solid solution

$$x\mathrm{SnO_2} + (1 - x)\mathrm{In_2O_3} \rightleftharpoons \mathrm{In}_{2-2x}\mathrm{Sn}_x\mathrm{O}_{3-x} \tag{14}$$

Because δ represents the value of tin which substitutes for indium in the In_2O_3 lattice, then

$$\begin{aligned} x\mathrm{SnO_2} &+ (1 - x)\mathrm{In_2O_3} \\ &\rightleftharpoons \mathrm{In}_{2-2x+\delta-\delta}\mathrm{Sn}_x\mathrm{O}_{3-x+3/2\delta-3/2\delta} \\ &\rightleftharpoons \mathrm{In}_{2-x-\beta}\mathrm{Sn}_x\mathrm{O}_{3-\beta}(\mathrm{V_{In}V_O})^{x}_{\delta\mathrm{Sn}} \end{aligned} \tag{15}$$

where $(V_{In}V_O)^x$ is an associated In–O vacancy.

In the region of the solid solubility limit of tin in the In_2O_3 lattice, $\beta = 0$, therefore

$$\begin{aligned} x\mathrm{SnO_2} + (1 - x)\mathrm{In_2O_3} &\rightleftharpoons \mathrm{In}_{2-x}\mathrm{Sn}_x\mathrm{O_3}(\mathrm{V_{In}V_O})^{x}_{x} \\ &\rightleftharpoons \mathrm{In}_{2-x}\mathrm{Sn}^{\cdot}_x\mathrm{O_3}e'_x(\mathrm{V_{In}V_O})^{x}_{x} \end{aligned} \tag{16}$$

As the In_2O_3 structure is evolved (during growth) then the deduced associates $(V_{In}V_O)^x$ are distributed over the matrix, except for those which dissociate during the ITO preparation.

There are two mechanisms by which the associate $(V_{In}V_O)^x$ may dissociate.

1. During the ITO material preparation or during heat treatment [25].

$$2(\mathrm{V_{In}V_O})^x \rightleftharpoons \tfrac{1}{2}\mathrm{O_2(g)} + \text{an Indium oxide vacancy which migrates to the surface} \tag{17}$$

The liberation of oxygen during the thin film deposition process is predicted by Hamberg *et al.* [3]. The oxygen evolved in a high oxygen environmental partial pressure (during preparation) may dissolve again in the ITO lattice, thus occupying interstitial positions and causing some complexes to appear according to [23]

$$\tfrac{1}{2}\mathrm{O}_2^{(g)} + 2e' + 2\mathrm{Sn}^{\cdot} \rightleftharpoons (\mathrm{Sn_2}^{\cdot}\mathrm{O}_i'') \text{ complex} \tag{18}$$

The above dissociation reaction could explain the mechanism by which the thickness of a thin film decreases during heat treatments and/or reduction processes [23].

2. The associate may be ionized [26] to give

$$(\mathrm{V_{In}V_O})^x \rightleftharpoons (\mathrm{V_{In}V_O})' + \mathrm{h}^{\cdot} \tag{19}$$

The ionized associate plays the role of a trapping centre which decreases the number of free carriers.

In reduced (oxygen deficient) ITO material, the following mechanism may take place

$$2(\mathrm{V_{In}V_O})' + (\mathrm{V_O^{\cdot\cdot}}) \rightleftharpoons \text{an Indium oxide vacancy which migrates to the surface} \tag{20}$$

The dependence of the number of free carriers on the oxygen partial pressure as calculated through this model [25] shows that

$$n = kp_{\mathrm{O_2}}^{-1/8} \qquad \text{for } [\mathrm{Sn}^{\cdot}] \geq 2\mathrm{V_O}^{\cdot\cdot} \tag{21}$$

$$n \approx [\mathrm{Sn}^{\cdot}] \qquad \text{for } [\mathrm{Sn}^{\cdot}] \leq 2\mathrm{V_O}^{\cdot\cdot} \tag{22}$$

These predictions are in complete agreement with the experimental data published by Frank *et al.* [23].

The general form of the In_2O_3–SnO_2 system can now be written as

$$x\mathrm{SnO_2} + (1 - x)\mathrm{In_2O_3} \rightleftharpoons \mathrm{In}_{2-x-\beta}\mathrm{Sn}_x\mathrm{O}_{3-\beta}(D)_{x-\beta} \tag{23}$$

where

$$\begin{aligned} (D)_{x-\beta} &= (\mathrm{V_{In}V_O})_{x-\beta} \qquad \text{for positive } \delta \\ &= (\mathrm{InO})_{\beta-x} \qquad \text{for negative } \delta \end{aligned} \tag{24}$$

3. Conclusion

The In_2O_3–SnO_2 system has been modelled on the basis of its defect chemistry. The model predicts a new associate $(V_{In}V_O)^x$. This associate is a result of the incorporation of tin atoms into the active lattice points of the indium oxide. The ionization and dissociation of the associate represent the dominant mechanisms controlling the properties of the ITO material.

This model is capable of being extended to analyse the behaviour of other binary oxide systems.

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