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Physical and Quasi-chemical Study of Point Defects in Aluminium or Niobium-doped Polycrystalline Tin Dioxide

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Abstract

The influence of aluminium or niobium doping on the thermoluminescence (TL) of polycrystalline tetravalent tin dioxide is studied. The non-stoichiometry of SnO_{2-x} *is characterised by the presence of oxygen vacancies. These vacancies, once or twice ionised behave as donor centres. Introduction of trivalent or pentavalent impurities in the matrix constitute an efficient way to control the native defects of* SnO_2*. Thus, tin oxide samples are doped with aluminium(III) or niobium(V) by impregnation technique. Hydroxyl groups OH are also supposed to play an important role in the TL of the oxide The deconvolution of* SnO_2 *TL curve is carried out in order to identify the trap parameters of the defects Besides, a quasi-chemical model is developed. This theoretical approach allows to foresee the behaviour of points defects versus dopant species concentration. Correlations with experience lead to the identification of these point defects. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Tin dioxide is the most commonly used material in industrial and domestic gas detection (CO, NO_x, CH_4). At a given temperature, its electrical conductivity depends on the gas amount to detect in the atmosphere of measurement.[1] The high reactivity of tin oxide is related to its non-stoichiometry. This last is responsible for the presence of oxygen vacancies, predominant native point defects in tin oxide. But the material not only reacts with the gas to detect, but also with the whole environmental gaseous phase. This may affect the stability of the SnO_2 electrical response with time. Thus, a best knowledge of the defect chemistry in SnO_2 is necessary. A possible method of control of defects is to compensate their electrical charge by introduction of a suitable impurity. A cation with valence different from that of tin(IV) is required. The doping elements used are aluminium(III) and niobium(V). Their ionic radii and electronegativities are 50 pm, 1·5 for Al and 70 pm and 1·7 for Nb respectively. These are near from those of tin(IV) (71 pm and 1·96). Thus, Al or Nb elements are supposed to be substituted to Sn, in the lattice. Aluminium valence (III) confers to it an acceptor-type character. At the opposite, niobium is donor-like element in SnO_2.

Furthermore, the thermoluminescence technique brings quantitative evolution of the point defects acting as trap centres, and gives valuable informations for their identification. Considering that the oxygen vacancies contribute to the electrical conductivity mechanisms, TL technique turns out to be appropriate to characterise these defects. The aim of this work is to study the influence of doping on tin dioxide thermoluminescence in order to characterise its point defects.

2 Experimental Procedure

Commercial tin dioxide (ACRÕS) powders are annealed in air at 1175 K for 2 h. The specific area is about 5 m^2/g. Doping is achieved by impregnation of the commercial powder by a solution of organic salt containing the impurity cation (aluminium nitrate or niobium ethoxide). Then samples are baked at 285 K and annealed at 1175 K.

Thermoluminescence is carried out after 3 min 365 nm excitation at liquid nitrogen temperature. The samples are linearly heated ($0{\cdot}5\,K\,s^{-1}$) in a

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secondary vacuum chamber up to 300 K. TL signal is detected by a photo-multiplier (PHILIPS XP 2018 B) owning S13 response (250–600 nm range) and plotted versus temperature.

3 Results

TL glow curve of nominally undoped tin dioxide is given in Fig. 1. It exhibits 3 peaks located at about 110 K (I), 140 K (II) and 190 K (III). Their relative intensifies vary according to the experimental conditions. We assume that these peaks should be linked to oxygen vacancies and hydroxyl groups.

3.1 Aluminium doping

TL measurements of aluminium doped SnO_2 samples are carried out for concentrations c of Al ions up to 10 000 ppm. The general trend is a whole increase of the glow curve with c, followed by a decrease for larger values of c. The peak intensifies are enhanced for an increase in c: they vary like $c^{0.61}$ (up to 2000 ppm), $c^{0.48}$ (up to 3500 ppm) and $c^{0.55}$ (up to 1000 ppm) for peaks I, II and III respectively (Fig. 2).

3.2 Niobium doping

TL curves are recorded for tin dioxide samples doped from 20 to 200 ppm niobium ions. The variation of the TL peak intensities versus niobium concentration c is plotted on Fig. 3. The peak intensities decrease when niobium is added to SnO_2; quickly below 20 ppm and faster over. The variation laws are $c^{-0.66}$, $c^{-0.76}$ and $c^{-1.02}$ for peaks I, II and III respectively within the whole concentration range.

4 Modelling

In order to identify the defects, we use two kinds of modelling. The first consists in a quantitative approach of the problem via TL curve deconvolution, whereas the second constitutes an approach based on the quasi-chemical equilibria involving point defects.

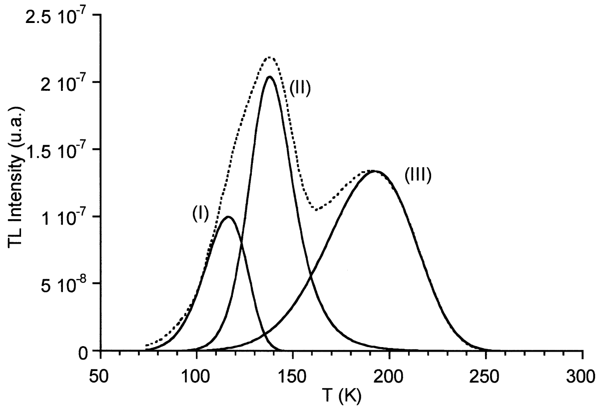

Fig. 1. Numerical deconvolution of undoped SnO_2 TL curve.

4.1 TL glow curve deconvolution

The experimental undoped SnO_2 TL curve is fitted to a numerically generated curve (based on Chen generalised equation[2]). By this way, we are able to extract the trapping parameters of the defects involved in thermoluminescence, especially the trap activation energy (Fig. 1). This method is very useful in the case of the SnO_2 complex glow curve because most method apply only with isolated peaks. By this way, the activation energy of the point defects is estimated to 0·10, 0·19 and 0·12 eV for peaks I, II and III, respectively. The value for the peak III is abnormally weak (0·12 eV) in comparison with that of the peak II. These can be compared to $\Delta H_1 = 0.03$ eV and $\Delta H_2 = 0{\cdot}15$ eV, enthalpies of ionisation of V_o° and $V_o^{\circ\circ}$ respectively.[3] The numerical energy values obtained by our model are not in disagreement with the enthalpy values of the literature. The interpretation concerning the peak III is more complex. Besides, the initial rise method is also a valuable experimental way to get trapping parameters of points defects.[4] Its application to tin dioxide samples gives activation

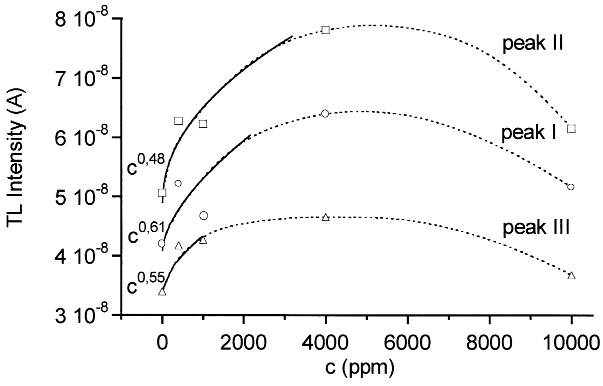

Fig. 2. Intensity variations of TL peaks I, II and III versus aluminium concentration c.

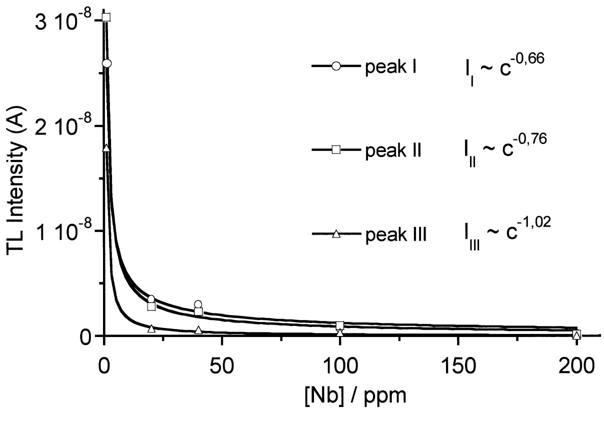

Fig. 3. Intensity variations of TL peaks I, II and III versus niobium concentration c.

energy values (0·1 eV for peak I, and 0·2 to 0·3 eV for peaks II and III) in the same energy range than those obtained by deconvolution method but now they increase with the temperature of the peak.

Since ionisation energy of $V_o^{\circ\circ}$ is greater than that of V_o°, the peak relative to simply ionised vacancies is expected to appear before peak relative to doubly ionised ones.

4.2 Quasi-chemical model of SnO$_2$ point defects

In this approach, we carry out a numerical resolution of the equations describing the quasi-chemical equilibria involving point defects. The principle of this method is described elsewhere.[5] The defects taken into account for the calculation are the following: free electrons (e') and holes (h°), neutral (V_o), simply ionised (V_o°), doubly ionised ($V_o^{\circ\circ}$) oxygen vacancies for native defects. Then substitutional ($\mathrm{Al}'_{\mathrm{Sn}}$), interstitial ($\mathrm{Al}_i^{\circ\circ\circ}$) aluminium ions or substitutional ($\mathrm{Nb}_{\mathrm{Sn}}^{\circ}$), interstitial ($\mathrm{Nb}_i^{5^{\circ}}$) niobium ions and hydroxyl groups (OH_o°) for extrinsic defects. These are bound together by the equations of electrical neutrality, ionisation and interaction with the gaseous phase.

Ionisation equilibria of oxygen vacancies in non-stoichiometric SnO$_2$ can be written as:

$$V_o = V_o^{\circ} + e' \quad (\Delta H_1 = 0.03\ \mathrm{eV})^3 \tag{1}$$

and

$$V_o^{\circ} = V_o^{\circ\circ} + e' \quad (\Delta H_2 = 0.15\ \mathrm{eV})^3 \tag{2}$$

where ΔH_1 and ΔH_2 correspond to enthalpies of extraction of an electron from oxygen vacancies once and twice ionised respectively.

Oxygen is incorporated into the bulk according to eqn (3):

$$\frac{1}{2}\mathrm{O}_2 + V_o^{\circ\circ} + 2e' = \mathrm{O}_o^x \quad (\Delta H_3 = 1.1\ \mathrm{eV})^3 \tag{3}$$

Exposition to oxygen gas tends to fill the V_o species, but weakly affect the hydroxyl groups OH_o°.

The action of water vapour on point defects can be written as:

$$\mathrm{H_2O} + V_o^{\circ\circ} + \mathrm{O}_o^x = 2\mathrm{OH}_o^{\circ} \quad (\Delta H_4) \tag{4}$$

Exposition to wet air also consumes oxygen vacancies, but generates hydroxyl groups. During the introduction of samples in the TL vacuum chamber, the equilibrium state between $V_o^{\circ\circ}$ and OH_o° may be displaced in order to favour the formation of vacancies. Therefore, we think that one of the peaks of the SnO$_2$ glow curve could be due to the OH_o° groups.

On the other hand, in the case of aluminium or niobium ions doping, an equilibrium state between substitutional and interstitial dopant species involving tin vacancies is supposed to take place during introduction in the SnO$_2$ lattice. This can be written, in the case of aluminium by:

$$\mathrm{Al}_i^{\circ\circ\circ} = \mathrm{Al}'_{\mathrm{Sn}} + V_i^x + 2V_o^{\circ\circ} \tag{5}$$

eqns (5) and (7) result from equilibria described in the Appendix.

Assuming that substitutional position is favoured, the equation of electrical neutrality [eqn (6)] shows that aluminium doping is able to control the ionised oxygen vacancies and hydroxyl groups content in the oxide:

$$\begin{aligned}[e'] + \left[\mathrm{Al}'_{\mathrm{Sn}}\right] = \left[V_o^{\circ}\right] + 2\left[V_o^{\circ\circ}\right] + \left[\mathrm{OH}_o^{\circ}\right] \\ + 3\left[\mathrm{Al}_i^{\circ\circ\circ}\right] + [h^{\circ}]\end{aligned} \tag{6}$$

An increase of aluminium concentration c makes $\left[V_o^{\circ}\right]$, $\left[V_o^{\circ\circ}\right]$ or $\left[\mathrm{OH}_o^{\circ}\right]$ rise because $\mathrm{Al}'_{\mathrm{Sn}}$ is in the opposite side of eqn (6) from V_o°, $V_o^{\circ\circ}$ and OH_o°.

For niobium doping, an equilibrium takes place between niobium and the oxygen vacancies:

$$\mathrm{Nb}_i^{5o} = \mathrm{Nb}_{\mathrm{Sn}}^{\circ} + V_i^x + 2V_o^{\circ\circ} \tag{7}$$

In this case, the introduction of niobium makes $\left[V_o^{\circ}\right]$, $\left[V_o^{\circ\circ}\right]$ and $\left[\mathrm{OH}_o^{\circ}\right]$ decrease, all the defects lying in the same side of the electrical neutrality equation:

$$\begin{aligned}[e'] = \left[V_o^{\circ}\right] + 2\left[V_o^{\circ\circ}\right] + \left[\mathrm{OH}_o^{\circ}\right] + \left[\mathrm{Nb}_{\mathrm{Sn}}^{\circ}\right] \\ + 5\left[\mathrm{Nb}_i^{\circ\circ\circ\circ\circ}\right] + [h^{\circ}]\end{aligned} \tag{8}$$

The influence of doping on the point defect concentration is then given by solving the precedent set of equations. The knowledge of the equilibrium constants of the reactions makes possible the plotting of the concentration evolution versus the concentration c of doping element. This allows to study the behaviour of the oxygen vacancy and the hydroxyl group concentrations in function of the aluminium (Fig. 4) or niobium amount (Fig. 5). Three domains of concentration reported as 1, 2 and 3 are considered in each graph.

For aluminium, the general trend is the control of intrinsic defects by substitutional aluminium in the zone 2 of the graphic. $V_o^{\circ\circ}$, V_o°, and OH_o° concentrations follow c, $c^{1/2}$ and $c^{1/2}$ laws respectively. The most affected species are the doubly ionised oxygen vacancies. The simply ionised oxygen vacancies and the hydroxyl groups are less sensitive to the aluminium concentration. In the zone 1, e' and $V_o^{\circ\circ}$ prevail. The amount of aluminium is not

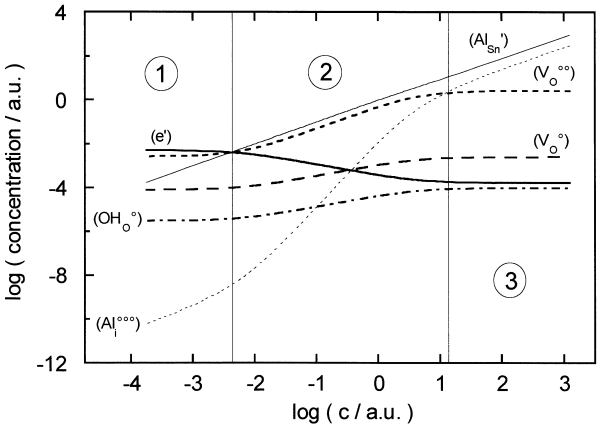

Fig. 4. Point defect concentrations versus aluminium concentration in tin dioxide given by the quasi-chemical model.

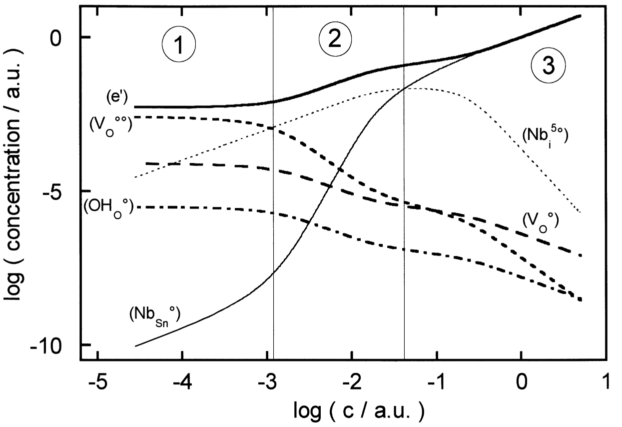

Fig. 5. Point defect concentrations versus niobium concentration in tin dioxide given by the quasi-chemical model.

sufficient to have an effect on defects ; the regime is intrinsic-like. In the zone 3, the limit of aluminium solubility in SnO_2 is exceeded. Interstitial and substitutional aluminium ions are both the majority species; the control of defects is not efficient anymore.

For niobium, the control of native defects is efficient by interstitial niobium in the zone 2 and by substitutional niobium in the zone 3 of the graphic.

The zone 1 is intrinsic-like; e' and $V_o^{\circ\circ}$ are predominant. Then niobium becomes sufficient enough to control the defects: by $\left(Nb_i^{5o}\right)$ in the zone 2 and by $\left(Nb_{Sn}^{\circ}\right)$ in the zone 3. Both imply the same, variations for native defects. Thus $V_o^{\circ\circ}$, V_o°, and OH_o° vary like c^{-2}, c^{-1} and c^{-1} respectively. There is no saturation zone like in the case of aluminium.

To resume, by compensation phenomena, aluminium favours the creation of oxygen vacancies and hydroxyl groups in the tin dioxide lattice whereas that is the opposite for niobium.

5 Discussion

Moreover, the increase or decrease of the oxygen vacancy and OH group content with the dopant species concentration coincides respectively with the global enhancement of the SnO_2:Al glow curve or the drop intensity of the whole SnO_2:Nb TL curve. We can say that the ionised oxygen vacancies and the hydroxyl groups are the point defects responsible for thermoluminescence in tin dioxide. Now let us compare the defect concentration variations with the TL peak intensities.

In the case of aluminium, the variations of $\left(V_o^{\circ}\right)$ and $\left(OH_o^{\circ}\right)$ are similar to those of peak II and III intensities. For niobium doping, the peak III intensity vary like $\left(OH_o^{\circ}\right)$ with c. Thus, we assume that OH_o° are responsible for TL peak III. Comparing the oxygen vacancy concentration with the other TL peak intensity variations with c, it is not obvious to identify V_o° and $V_o^{\circ\circ}$. Regarding now the activation energy values obtained by deconvolution, and assuming that the two low temperature peaks are linked to these vacancies, energetic considerations let us consider that peak I is due to V_o°, and peak II to $V_o^{\circ\circ}$.

6 Conclusion

TL measurements on tin dioxide reveal three main peaks related to point defects. Effect of aluminium or niobium doping are studied. At the same time, thermoluminescence and quasi-chemical modelling are carried out. These approaches are correlated to experimental results. This leads us to propose that once and twice ionised oxygen vacancies V_o°, $V_o^{\circ\circ}$ and hydroxyl groups OH_o° are responsible for TL peaks I (110 K), II (140 K) and III (190 K) respectively. This work is a step of further study which consists in establishing relationships between electrical properties, crystalline microstructure and point defects in tin dioxide.

References

1. Pijolat C., Dutraive M. S. and Lalauze R., Investigation of SnO_2 defect chemistry in relation with the electrical conductivity. In *Ceramics: Charting the Future*, ed. P. Vincenzini, Techna, Faenza, 1995, pp. 2865–2872.
2. Chen, R., Glow curves with general order kinetics. *J. Electrochem. Soc.*, 1969, **116**, 1254.
3. Göpel, W., Schierbaum, K., Wiemhöfer, H. D. and Maier, J., Defect Chemistry of tin (IV)-oxide in bulk and boundary layers. *Solid State Ionics*, 1989, **32/33**, 440–443.
4. Garlick, G. F. J. and Gibson, A. F., The electron trap mechanism of luminescence in sulphide and silicate phosphors. *Proc. Phys. Soc.*, 1948, **60**, 574–590.
5. Spinolo, G. and Anselmi-Tamburini, U., On the calculation of point defect equilibria. *Ber. Bunsenges. Phys. Chem.*, 1995, **99**(1), 87–90.

Appendix

In the course of aluminium doping, Al element is introduced in interstitial position in the lattice and is charge-compensated by tin vacancies [eqn (A1)]. The contribution of the Schottky reaction at high temperature [eqn (A2)] leads to an equilibrium between Al element and the oxygen vacancies [eqn (A3)]. These last species are then able to trap electrons [eqns (1) and (2)].

$$\mathrm{Al}_i^{\circ\circ\circ} + V_{\mathrm{Sn}}^{''''} = \mathrm{Al}_{\mathrm{Sn}}' + V_i^x \qquad \text{(A1)}$$

$$0 = V_{\mathrm{Sn}}^{''''} + 2V_o^{\circ\circ} \qquad \text{(A2)}$$

$$\mathrm{Al}_i^{\circ\circ\circ} = \mathrm{Al}_{\mathrm{Sn}}' + V_i^x + 2V_o^{\circ\circ} \qquad \text{(A3)}$$

Similar thought process can be carried out for niobium. A charge compensation mechanism involving tin vacancies is taken into account [eqn (A4)]. Considering the Schottky disorder once again [eqn (A2)], we can write the reaction between niobium element and oxygen vacancies [eqn (A5)].

$$Nb_i^{\circ\circ\circ\circ\circ} + V_{\mathrm{Sn}}^{''''} = \mathrm{Nb}_{\mathrm{Sn}}^{\circ} + V_i^x \qquad \text{(A4)}$$

$$\mathrm{Nb}_i^{5\circ} = \mathrm{Nb}_{\mathrm{Sn}}^{\circ} + V_i^x + 2V_o^{\circ\circ} \qquad \text{(A5)}$$