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IDENTIFICATION OF POINT DEFECTS IN TIN DIOXIDE : EXPERIMENTAL AND THEORETICAL APPROACH

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Abstract

Thermoluminescence (TL) glow curves of polycrystalline tin dioxide samples exhibit three main peaks below room temperature. Their relative intensities depend on experimental conditions. Especially, they are modified by aluminium doping or by wet air exposition. It is well known that the presence of TL peaks is associated to point defects. In SnO₂, we suggest that ionised oxygen vacancies and hydroxyl groups are responsible for thermoluminescence. This assumption is discussed. In order to explain the behaviour of these defects, two kinds of modelling are proposed.

Introduction

Tin dioxide gas sensors are based on a variation of the electrical conductivity at a given temperature. This variation depends on the gas amount to detect in the atmosphere of measurement. Though, lack of selectivity and temporal drift still affect electrical properties of these detecting devices, which can be interpreted in term of the oxide ageing. Thus, a best knowledge and the control of the parameters governing these properties are important. Commercial samples are characterised from morphological, microstructural and electronic point of view.

X-ray diffraction shows that tin dioxide has really the rutile-like structure. A systematic thermal treatment of the sample powder is carried out at temperature of 1173 K in air during 2 hours. This allows to obtain convenient grain size, specific area, and temperature of conductivity measurement. Some characteristic parameters obtained by specific techniques (laser granulometry, BET isotherm) are given in table 1.

SnO ₂	Granulometry (µm)	S _{BET} (m ² .g ⁻¹)	Pore diameter (nm)
as received	0.5	7.6	10
annealed	0.7	6.3	8

Table 1 : Characteristic morphologic parameters of tin dioxide before and after annealing in air for 2 hours at 1173 K.

The gap of SnO₂ measured in diffuse-reflection spectrometry is about 3.5 eV. Some discrete energy levels exist in the forbidden band, which are associated with point defects of SnO₂ lattice. The oxygen deficiency tin dioxide (SnO_{2-x}) presents a n-type electrical conduction.

The intrinsic predominant defects are therefore oxygen vacancies. These can be neutral (V_O), once (V_O°) or twice ionised ($V_O^{\circ\circ}$) vacancies. A preliminary work on tin dioxide thin films [1] pointed out a possible relation between its curve of thermoluminescence (TL) and the presence of these defects. It was suggested that V_O° , $V_O^{\circ\circ}$ and OH_O° are responsible for the presence of TL peaks I, II and III respectively (fig.1). Considering that the oxygen vacancies contribute to the electrical conductivity mechanisms, TL technique turns out to be appropriate to characterise these defects.

Besides, TL method allows to get quantitative evolution of the species mentioned above and gives valuable informations for their identification. On the other hand, introduction of chemical impurities is a convenient way to control the oxygen vacancy content in oxygen dominated compounds. In example, the substitution of Sn(IV) by a trivalent element results in an enhancement of oxygen vacancies concentration. The aim of this study is to characterise the effect of doping precisely by Al element. The role of wet air exposition will also be investigated.

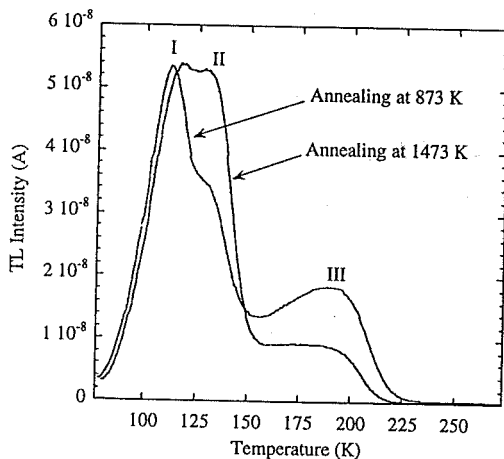


Figure 1 : Typical TL glow curve of tin dioxide (after [1]).

Experimental procedure

Among the various possible dopants, aluminium(III) was first chosen. Its ionic radius (68 pm) and its electronegativity (1.6) are near from those of tin(IV) (83 pm and 1.96). Thus, it is supposed to be substituted to Sn in the lattice, and its valence (III) confers to it an acceptor-type character. Doping is achieved by impregnation of the commercial powder by a solution of aluminium nitrate, and then annealed at 1173 K. A set of samples, doped from 400 to 10000 ppm in molar fraction, was studied in TL, after U.V. excitation (253.7 nm) at liquid nitrogen temperature. As seen before, the glow curve of SnO_2 presents 3 main peaks, whose relative intensities vary according to the experimental conditions. These are located around 113 K (I), 137 K (II) and 192 K (III). In the present case, peak I is the most important (fig.2). The general trend is a whole increase of the glow curve with the concentration [Al] of aluminium. The intensities of the 3 peaks are enhanced for an increase of [Al] up to 2000 ppm and become relatively constant beyond (fig.3). Peaks I and II are subject to the most meaningful variations, whereas peak III seems less affected by the doping.

Another parameter of influence concerns the environmental gaseous phase which acts at different steps of sample preparation and also during the TL measurements. Indeed, mechanisms of desorption of surface species are supposed to disturb the stability of the defects responsible for TL. In particular, hydroxyl groups are suspected of playing a major role in the charge transfers in the oxide, because they share the same adsorption sites that oxygen. This was pointed out in previous work [2,3]. Undoped tin dioxide samples exhibit many thermo-programmed desorption (TPD) peaks located at about 423, 623, 723 K and over 923 K due to hydroxyl groups. Also, it is shown that some of them are still present at the undoped tin oxide surface, even after thermal annealing beyond 1173 K. Additional TPD and conductivity measurements will permit a better knowledge of these phenomena. The evolution of the electronic properties of point defects is probably related to the lack of stability of the gas sensors.

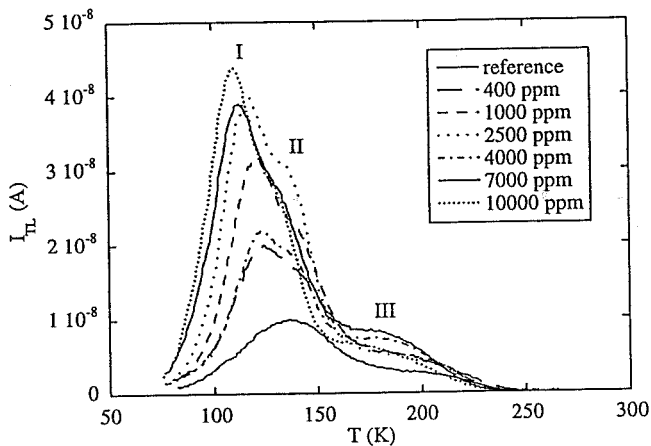


Figure 2 : $\text{SnO}_2:\text{Al}$ glow curves for different aluminium concentrations.

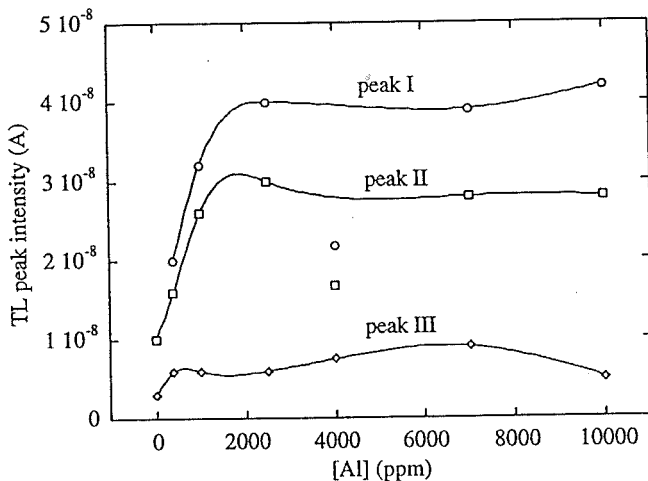


Figure 3 : TL Peak intensities versus aluminium concentration introduced in the lattice.

TL measurements are achieved in dynamic vacuum ($\sim 10^{-3}$ Pa), after heating up to 673 K, in the range 77 K to 293 K (with a rate of 0.5 K/s). The chronological evolution of the TL peak intensities of SnO₂:Al doped at 400 ppm is given in figure 4. Exposing the sample to dry air and subsequent heating at 673 K ① or only heating at 673 K ③ reduces the intensity of the peaks I and II of important manner. On the other hand, an exposition to wet air ② regenerates the TL of these 2 peaks, whereas the peak III is less affected.

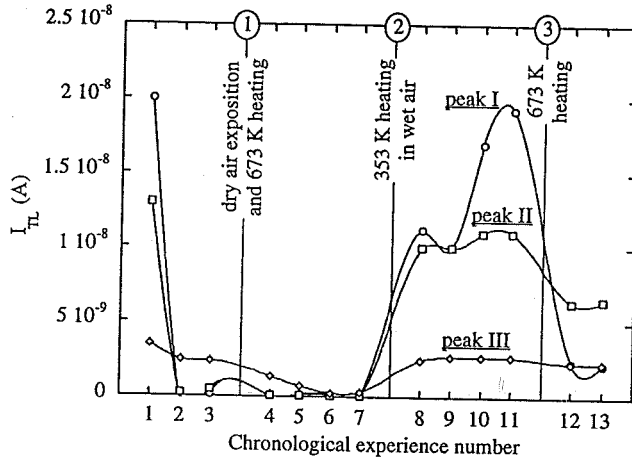
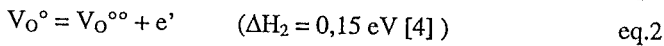
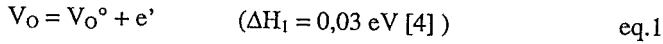


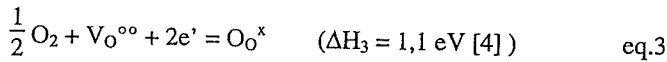
Figure 4 : Chronological evolution of the TL peak intensities of SnO₂:Al (400 ppm Al).

Discussion

Ionisation equilibria of oxygen vacancies in non-stoichiometric SnO₂ can be written as :



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 equation 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 :



Exposition to wet air also consumes oxygen vacancies, but generates hydroxyl groups. During the introduction of samples in the TL vacuum chamber, the equilibrium between $V_O^{\circ\circ}$ and OH_O° may be displaced in order to favour the formation of vacancies. Therefore, we think that one out of the peaks of the SnO₂ glow curve could be due to the OH_O° groups. On the other hand, an equilibrium between substitutional and interstitial aluminium involving tin vacancies is supposed to take place during introduction of aluminium in the SnO₂ lattice :



Combining this reaction with Schottky's one leads to equation 6 :



Thus, aluminium favours the creation of oxygen vacancies in the tin dioxide lattice by compensation phenomenon. Moreover, the increase of the oxygen vacancies content with the aluminium concentration coincides with the global enhancement of the SnO_2 glow curve (see fig.3). Two out of the three TL peaks can thus be linked to these vacancies. This leads to the hypothesis that the origin of the peaks I, II and III would be simply (V_O°), doubly ($\text{V}_O^{\circ\circ}$) ionised vacancies and OH_O° hydroxyl groups. In order to verify this assumption and to identify the defects, we use two kinds of modelling.

The first consists in a quantitative approach of the problem via TL curve deconvolution. In this way, TL experimental curves of tin dioxide are compared to a numerical model following Rasheedy's method [5]. By curve fitting (fig.5), we are able to extract the trapping parameters of the defects involved in thermoluminescence, especially the activation energy. We give some characteristic data of interest in table 2. This method is available even in the case of complex glow curves like SnO_2 one, which presents no resolved peak. The activation energy of the point defects is estimated to be 0.08 eV for peak I, and 0.17 eV for peak II. The value for the peak III seems abnormally weak ($X \cong 0.12$ eV) ; it is lower than that of the peaks II and II'. We consider that this value is out of scale, and should not be retained. One must remind that the enthalpies (ΔH_1 and ΔH_2) of the ionisation reactions of V_O° and $\text{V}_O^{\circ\circ}$ are equal to 0.03 eV and 0.15 eV respectively [4]. The numerical values obtained by our model are not in disagreement with those of the literature. The interpretation concerning the peak III is more complex, because deconvolution process reveals the existence of two peaks (namely peak II' added to peak III). The reality of the peak II' remains hypothetical. Besides, the initial rise method is also a valuable experimental way to get trapping parameters of points defects in tin dioxide. Its application gives activation energy values (0.1 eV for peak I, and 0.2 to 0.3 eV for peaks II and III) in agreement with those obtained by deconvolution method. These results seem therefore to confirm the assumptions relative to V_O° and $\text{V}_O^{\circ\circ}$. Ionisation energy of $\text{V}_O^{\circ\circ}$ is greater than that of V_O° . So the peak relative to simply ionised vacancies is expected to appear before peak relative doubly ionised ones. The frequency factor of the TL peaks is supposed to not vary during heating.

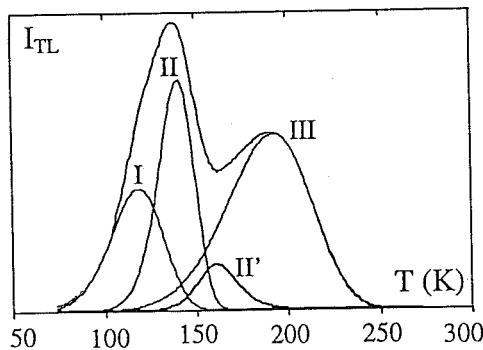


Figure 5 : Numerical deconvolution of undoped SnO_2 TL curve. (Peak temperatures are given in table 2).

	Peak I	Peak II	Peak II'	Peak III
Peak temperature (K) *	113	137	160	192
Kinetic order b *	1.00	1.08	1.80	0.95
Activation energy (eV) *	0.08	0.17	0.27	X
Suggested point defect	V_O°	$V_O^{\circ\circ}$	-	OH_O°
Ionisation reaction enthalpy (eV)	0.03 (ΔH_1)	0.15 (ΔH_2)	-	(ΔH_4)

Table 2 : Trapping parameters of TL peaks in SnO_2 obtained by curve fitting (*), suggested point defects responsible for TL peaks and literature values of ionisation enthalpies of involved defects (after [4]).

The second kind of modelling constitutes a mathematical approach. It is based on a numerical resolution method of the equations describing the quasi-chemical equilibria involving point defects (ionisation, interaction between solid and gaseous phases). The principle of this method is described elsewhere [6]. Point defects in SnO_2 are bound together by the equations of electrical neutrality, ionisation and interaction with the gaseous phase. The influence of one parameter (such as doping, gaseous phase of O_2 or H_2O) on their concentration is then given by solving this set of equations. The first approach concerns the study of the influence of the aluminium amount introduced in the lattice. 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, substitutional (Al_{Sn}), interstitial ($Al_i^{\circ\circ}$) aluminium and hydroxyl groups (OH_O°). Then, equation of electrical neutrality can be written as :

$$(e') + (Al_{Sn}') = (V_O^\circ) + 2(V_O^{\circ\circ}) + (OH_O^\circ) + 3(Al_i^{\circ\circ}) + (h^\circ)$$

The knowledge of equilibrium constants of the reactions makes possible the plotting of the concentration evolution versus the concentration c of doping element (fig.6). This allows to study the behaviour of the oxygen vacancies and the hydroxyl groups in function of the aluminium amount. 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 increase with c , following c , $c^{1/2}$ and $c^{1/2}$ laws respectively. The most affected species are therefore the doubly ionised oxygen vacancies. The simply ionised oxygen vacancies and the hydroxyl groups are less sensitive to the aluminium concentration. This behaviour is similar to the evolution of the TL peak intensity versus aluminium concentration (fig.3). In the zone ①, e' and $V_O^{\circ\circ}$ prevail ; the amount of aluminium is not 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 are both the majority species ; the control of defects is not efficient anymore.

Approaches achieved by the 2 kinds of modelling seem to agree with the assumption that the origin of the TL peaks I, II and III would be the simply (V_O°), the doubly ($V_O^{\circ\circ}$) ionised vacancies and the hydroxyl groups OH_O° respectively.

A band energy scheme is therefore suggested, including the collected data for tin dioxide (fig.7). The nature of the recombination centre is not given in this figure. However, it was suggested [7] that tin vacancies may be responsible for the luminescence in undoped SnO_2 .

We show by spectral analysis that this luminescence is an emission band centred around 1.92 eV, and is identical for all TL peaks. Following our hypothesis, this signifies that a recombination level located 1.92 eV below the conduction band stands. This energy scheme needs to be confirmed. Nevertheless, it constitutes a basis for further studies.

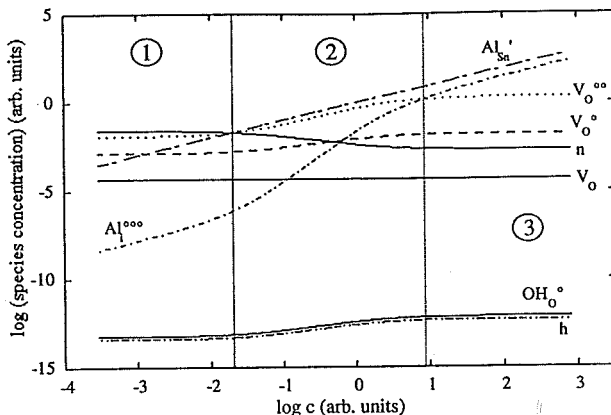


Figure 6 : Effect of aluminium content on point defects concentrations.

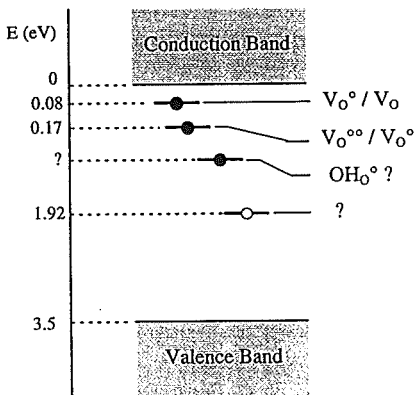


Figure 7 : Possible band energy scheme in SnO_2 .

Conclusion

TL measurements on tin dioxide reveal three main peaks related to point defects. The stability of these peaks depends on experimental conditions. Particularly, hydroxyl groups affect TL in a significant way. Effect of aluminium doping and influence of atmosphere on TL are studied. At the same time, modelling is carried out. These approaches lead us to propose that once and twice ionised oxygen vacancies V_O^\bullet , $V_O^{\bullet\bullet}$ and hydroxyl groups OH_O^\bullet are responsible for TL peaks I (113 K), II (137 K) and III (192 K) respectively.

Some complementary TL measurements on donor-doped tin dioxide samples will complete this work. They should help the interpretation of the evolution of the concentration of point defects in term of charge transfers in the oxide. This work is the first step of a large study which consists in establishing some interrelationships between electrical properties, crystalline micro-structure and point defects in tin dioxide. Besides, one plan to consider the case of other tetravalent oxides such as ZrO_2 , TiO_2 , or CeO_2 . These may probably share similar properties.

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