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Electrical conductivity and defect structure of polycrystalline tin dioxide doped with antimony oxide

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Electrical conductivity (σ) of tin dioxide doped with antimony has been measured as functions of temperature and oxygen partial pressure (p_{O_2}). Variation of electrical conductivity is explained by assuming that the antimony oxide forms a substitutional solid solution and doubly ionized oxygen vacancies are predominant defects. Above $\sim 10^{-5}$ atm oxygen partial pressure antimony ions are present predominantly in the pentavalent state in tin dioxide lattice. However, it is converted to the trivalent state below this oxygen partial pressure accompanied by a sudden rise in conductivity.

1. Introduction

Tin dioxide is a n-type semiconductor having doubly ionized oxygen vacancies as predominant defects. There have been a large number of investigations [1–5] on its electrical properties mainly in the form of thin films or single crystals. Defect structure and electrical properties of polycrystalline tin dioxide has recently been studied by the present authors [6]. One of the important applications of the polycrystalline tin dioxide is as electrodes in some glass melting furnaces. It has been known that addition of antimony oxide significantly increases the electrical conductivity of SnO_2 [7–9]. However, the effect of oxygen partial pressure on the electrical conductivity has not been studied extensively. Confusion also exists regarding the exact state of the antimony ion in the SnO_2 lattice. In the present investigation the electrical conductivity of tin dioxide doped with antimony has been measured over a wide range of oxygen partial pressure and temperature. An attempt has been made to investigate its defect structure and the relative stabilities of trivalent and pentavalent antimony ions as functions of oxygen partial pressure and temperature.

2. Experimental details

Tin dioxide used in this study was 99.9% pure (obtained from Keeling and Walker Ltd, England). Sb_2O_3 (Analar grade) varying in amount from 0.05 to 0.4 wt % was mixed with SnO_2 in acetone slurry and dried in an air oven at 110° C. The samples were pressed into cylindrical pellets of 1.28 cm diameter and 0.5 to 0.6 cm height at a pressure of 240 MPa. The surface of the green pellets was scraped to avoid contamination from the die wall. The pellets were sintered in an electrically heated furnace at 1450° C in air for 3 h on a platinum plate. In order to avoid the loss of Sb_2O_3 due to volatilization, the pellets were enclosed in powder of the same composition during sintering.

For the measurement of electrical conductivity the flat surfaces on the specimen were polished and electroded with unfluxed platinum paste (Engelhard 6082). The specimen was then placed inside a spring-loaded specimen holder kept inside a tubular furnace. The oxygen partial pressure inside the specimen holder was varied by controling the oxygen content of the flowing inert gas (argon) by an electrochemical "oxygen pump". The a.c. conductivity was measured by an universal bridge (Wayne Kerr B224) at an internal frequency of 1592 Hz.

3. Results and discussion

Electrical conductivity of "pure" and Sb_2O_3-doped SnO_2 has been measured in air over the temperature range 150 to 700° C. The results

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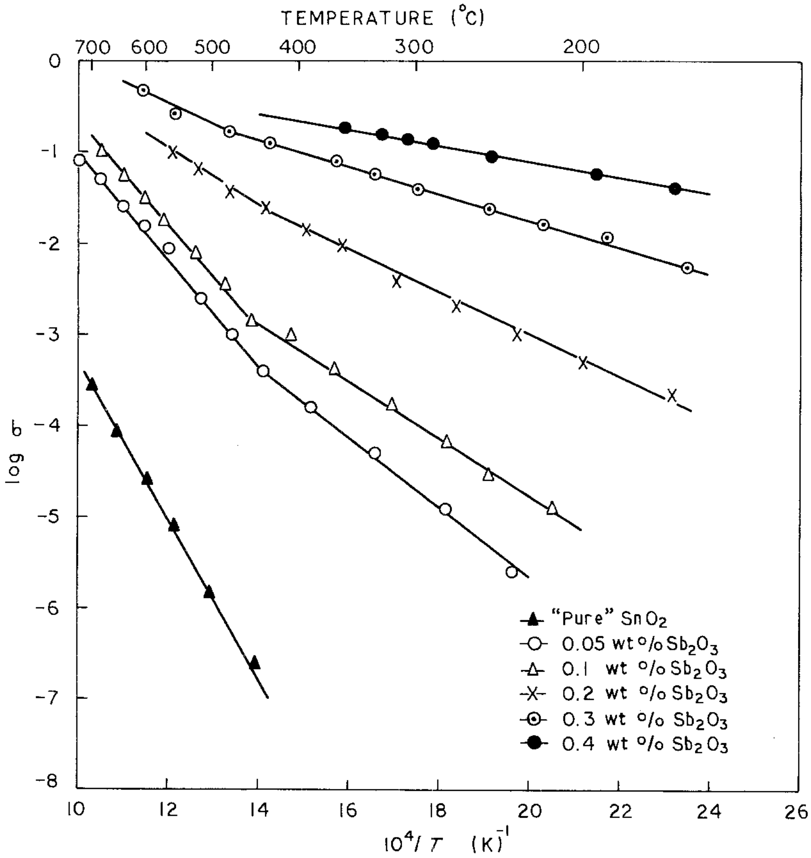

Figure 1 Electrical conductivity ($\Omega^{-1}\,cm^{-1}$) of the SnO_2–Sb_2O_3 system as a function of temperature, in air.

are presented in Fig. 1, in which log conductivity has been plotted against reciprocal of temperature. The conductivity of tin dioxide is increased significantly by small additions of Sb_2O_3. For each composition the plots show two straight lines of slightly different slopes. In the low-temperature region (below 450° C) the slopes are lower than those in the high-temperature range. It may also be noted that the slopes in both the regions decrease with increasing amount of Sb_2O_3. The activation energies for conduction calculated from these slopes are given in Table I.

TABLE I Activation energy for conduction obtained in "pure" and Sb_2O_3-doped SnO_2

Sb_2O_3 (wt %)	Activation energy (eV)	
	High temperature	Low temperature
"pure" SnO_2	1.73	–
0.05	1.14	0.76
0.1	1.09	0.62
0.2	0.59	0.46
0.3	0.44	0.29
0.4	–	0.16

The lowering of activation energy in the low-temperature range is possibly due to chemisorption of oxygen on the surface of the specimen. The effect of oxygen chemisorption on electrical properties of SnO_2 doped with ZnO was earlier discussed by Matthews and Kohnke [10] and has also been observed by the present investigators [6]. In this region it is most likely that the bulk of the material is not in equilibrium with the surrounding atmosphere. However, the surface of the specimen attains equilibrium rapidly. So the observed variation in conductivity is mainly due to the change of defect concentration on the surface of the specimen.

For two of these SnO_2 specimens, doped with 0.1 and 0.3 wt % Sb_2O_3, the conductivity has been measured as a function of oxygen partial pressure at different temperatures. The variation of conductivity with oxygen partial pressure for these specimens are plotted in Figs. 2 and 3. It may be observed that the complete p_{O_2} range of measurement can be divided into two regions. In the high p_{O_2} range ($> 10^{-5}$ atm) the conductivity increases

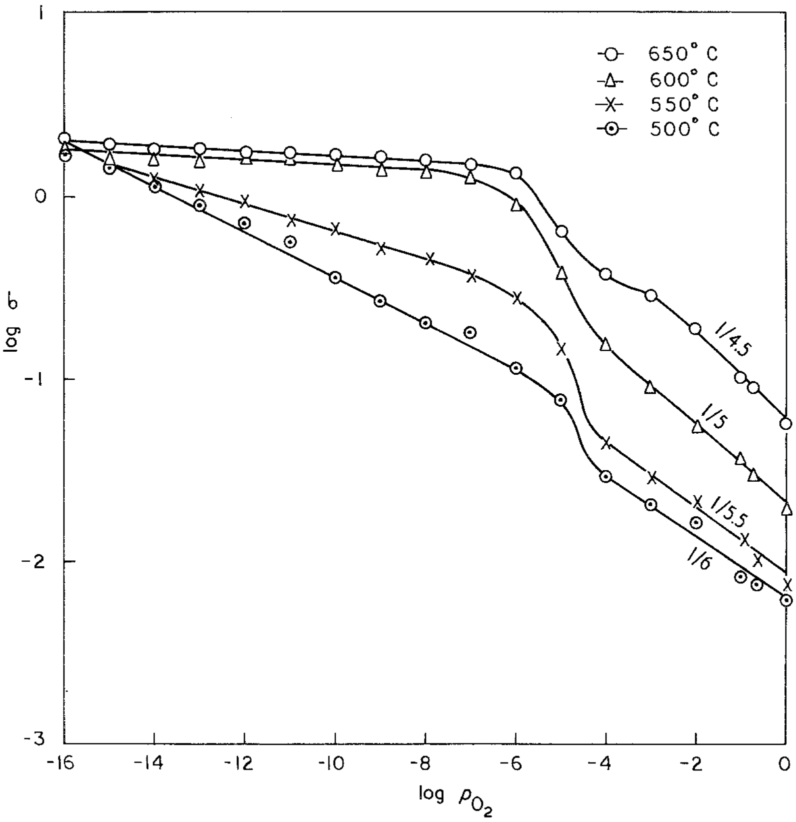

Figure 2 Electrical conductivity ($\Omega^{-1}\,cm^{-1}$) of $SnO_2 + 0.1\,wt\%\ Sb_2O_3$ as a function of oxygen partial pressure at different temperatures.

linearly with decrease in p_{O_2}. For the 0.1 wt% Sb_2O_3-doped specimen the slope of the plot increases from $-1/6$ at 500° C to $-1/4.5$ at 650° C while for the 0.3 wt% Sb_2O_3-doped specimen it varies between $-1/8$ and $-1/10.5$. For both the specimens at each temperature there is a sudden increase of conductivity within a narrow range of oxygen partial pressure at around

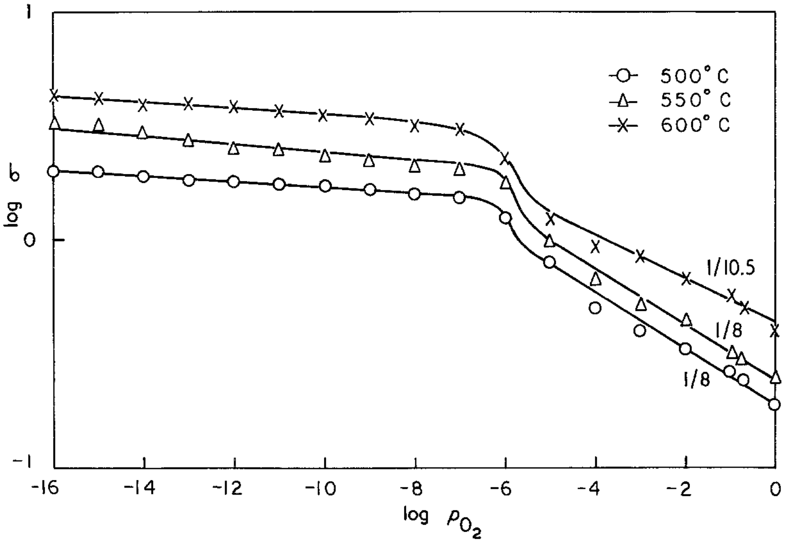

Figure 3 Electrical conductivity ($\Omega^{-1}\,cm^{-1}$) of $SnO_2 + 0.3\,wt\%\ Sb_2O_3$ as a function of oxygen partial pressure at different temperatures.

10^{-5} atm. At partial pressures lower than about 10^{-6} atm the conductivity remains independent of p_{O_2} except for the specimen containing 0.1 wt % Sb_2O_3 measured at 500 and 550° C. In these cases the conductivity continues to increase with decrease in p_{O_2}.

The defect structure of "pure" tin oxide and that doped with ZnO has been discussed elsewhere [6] on the basis of an anti-Frenkel type defect model. The variation of electrical conductivity observed in the present investigation can also be explained on the basis of a similar defect model. The situation is, however, complicated due to the presence of antimony oxide having variable valence states, the relative stability of which depends on the oxygen partial pressure and temperature. It is difficult to determine the exact valence state of the Sb-ion in the SnO_2 lattice. However, an indication of the relative stabilities of Sb^{3+} and Sb^{5+} ions may be obtained from the calculation of the standard free energy (ΔG^0_T) for the reaction

$$Sb_2O_3 + O_2 \rightleftharpoons Sb_2O_5 \qquad (1)$$

as functions of temperature and oxygen partial pressure. This has been done by using the following equation

$$\begin{aligned}\Delta G^0_T &= \Delta H^0_T - T\Delta S^0_T \\ &= \Delta H^0_{298} + \int_{298}^{T} \sum c_p \, dT \\ &\quad - T\left[\Delta S^0_{298} + \int_{298}^{T} \sum \frac{c_p \, dT}{T}\right] \qquad (2)\end{aligned}$$

where ΔH^0_T and ΔS^0_T are the standard enthalpy change and entropy change, respectively, at temperature T K for Reaction 1. c_p is the constant pressure specific heat of the individual components and their values are taken from [11]. The variation of ΔG^0_T as a function of temperature is plotted in Fig. 4 which also includes the plots of ΔG^0_T as a function of temperature at constant p_{O_2} calculated on the basis of the equation

$$\Delta G^0_T = RT \ln p_{O_2}. \qquad (3)$$

The equilibrium oxygen partial pressure for the Reaction 1 at different temperatures may be determined from the intersection of these plots. It may be noted from this figure that under atmospheric oxygen pressure trivalent antimony can be present only above 1150 K. Since the temperatures of measurement in the present investigation are between 500 and 650° C, it is most likely that the Sb-ions are present in the SnO_2 lattice in the pentavalent state even though they are added in the form of Sb_2O_3. However, at lower partial pressures it is expected that the pentavalent ion would be converted to the trivalent form even within this temperature range. Fig. 4 indicates that the partial pressure corresponding to the Sb^{3+}–Sb^{5+} equilibrium shifts from 10^{-3} to 10^{-6} atm as the temperature is changed from 635 to 455° C. Such a conversion should not be confused with the reaction

$$2SnO_2 + Sb_2O_3 \rightleftharpoons 2SnO + Sb_2O_5 \qquad (4)$$

which is not feasible in the present system as concluded by Vincent [12] from his thermodynamic calculation.

As suggested by earlier investigators [12, 13] antimony oxide may be assumed to form substitutional solid solution with SnO_2 due to their comparable ionic sizes. Since the specimen behaves as a n-type semiconductor at least in the higher oxygen partial pressure range, doubly ionized oxygen vacancy and compensating electron may be considered as predominant defects. Accordingly, using the conventional defect notations, the defect reaction may be written as

$$O_O \rightleftharpoons V_O^{\cdot\cdot} + 2e' + 1/2\,O_2(g). \qquad (5)$$

In an intrinsic situation the neutrality condition will be

$$[e'] = 2[V_O^{\cdot\cdot}] \qquad (6)$$

and therefore the electron concentration will vary as $-1/6$ power of p_{O_2}. Even though the plot of $\log \sigma$ against $\log p_{O_2}$ (Fig. 2) gives a slope of $-1/6$ at low temperature it is not an indication of intrinsic behaviour of the material. Because in the lower partial pressure range even at higher temperatures the conductivity becomes independent of p_{O_2} representing an extrinsic behaviour. However, in the presence of antimony oxide the neutrality condition in the high oxygen partial pressure range (Figs. 2 and 3), where Sb-ions are considered to be present in the pentavalent state, may be represented as

$$[Sb^{\cdot}_{Sn}] = 2[O_i''] . \qquad (7)$$

This, in addition to the neutrality condition existing for anti-Frenkel defect equilibrium, gives rise to a p_{O_2}-independent concentration of oxygen vacancy. The variation of electron concentration

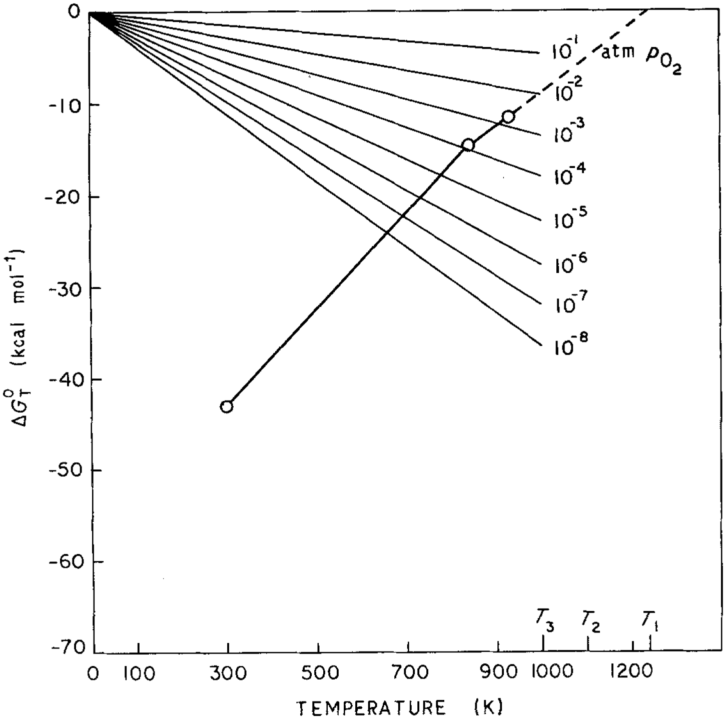

Figure 4 Standard free energy of oxidation of Sb_2O_3 to Sb_2O_5 as a function of temperature.

in this partial pressure range can, therefore, be represented as

$$[e'] = (K/C_v)p_{O_2}^{-1/4} \qquad (8)$$

where C_v is the concentration of oxygen vacancy and K is equilibrium constant for Reaction 5. Equation 8 indicates a slope of $-1/4$ for the plot of $\log \sigma$ against $\log p_{O_2}$. This may be compared with the observed slope of $-1/4.5$ for the specimen containing 0.1 wt% Sb_2O_3 at 650° C (Fig. 2). However, the slope decreases with decrease in temperature. This is due to the small amount of ionic contribution to the conductivity of the doped specimen. The effect is more prominent with increase in dopant concentration as observed in Fig. 3.

It is observed in both Figs. 2 and 3 that there is a steep rise in conductivity within a narrow partial pressure range around 10^{-5} atm. This is an indication of the conversion of Sb^{5+} to Sb^{3+} as predicted from our thermodynamic calculation. The observed p_{O_2} range of conversion, however, does not change significantly with temperature and the values are slightly different than those predicted from standard free energy data. This is expected because of the fact that the calculation has been based on pure antimony oxide while in fact it is present only as a solute in SnO_2.

At oxygen partial pressure below this conversion range the p_{O_2} independent conductivity is fixed by the concentration of impurity ions. In this region the impurities can be regarded to be present predominantly as trivalent antimony ions. The neutrality condition can therefore be written as

$$[\mathrm{Sb}'_{\mathrm{Sn}}] = [\mathrm{h}^{\cdot}], \qquad (9)$$

indicating a p-type conduction in this p_{O_2} range. This has not, however, been confirmed in the present investigation. For the specimen containing 0.1 wt% Sb_2O_3 at lower temperatures (500 and 550° C) the continued increase in conductivity may be explained by assuming that the conversion of pentavalent to trivalent antimony remains incomplete at these low temperatures within the time allowed for equilibrium.

4. Conclusions

(1) Addition of antimony oxide increases the conductivity of tin dioxide quite significantly. Variation of electrical conductivity of SnO_2 doped with antimony with oxygen partial pressure may be explained satisfactorily assuming doubly ionized oxygen vacancies as the predominant defect.

(2) Antimony oxide forms a substitutional solid solution. Above $\sim 10^{-5}$ atm oxygen partial

pressure Sb-ions are present predominantly in the pentavalent state in the temperature range considered. However, it is converted to trivalent state below this partial pressure.

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