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Electrical conductivity of polycrystalline tin dioxide and its solid solution with ZnO

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Electrical conductivity (σ) of "pure" and ZnO doped SnO_2 has been measured at different temperatures and oxygen partial pressures (p_{O_2}). From the variation of electrical conductivity of these materials three partial pressure ranges have been identified. In the high partial pressure range σ increases with decreasing p_{O_2} followed by a p_{O_2} independent region at lower p_{O_2}'s and finally increases once again with a further decrease of p_{O_2}. These variations have been explained on the basis of an anti-Frenkel type defect structure and an interstitial solid solution of ZnO in SnO_2. The activation energy for the conduction process has been estimated and the values are found to differ in two different temperature ranges. In the low temperature range the conductivity is attributed mainly to the chemisorption of oxygen on the surface of the specimen.

1. Introduction

Tin dioxide is generally considered as a broad band n-type semiconductor. Some of its important applications include resistors [1], transparent heating elements [2], transistors [3, 4] and anti-static coatings [5]. In recent years tin dioxide has also been used as electrodes in glass melting furnaces [6]. There have been numerous investigations on electrical properties of this oxide mainly in the form of thin film and single crystal [7–11]. However, only limited attempts have been made to investigate the defect structure and electrical behaviour of the polycrystalline bulk material. Samson and Fonstad [12] and Mar [13] have concluded from the electrical measurement data that the oxygen vacancy is the predominant defect in this oxide. Addition of several oxides to tin dioxide is known to increase the electrical conductivity either by increasing the defect concentration or by the formation of additional energy states within the band gap. In the present investigation the variation of electrical conductivity has been measured at different temperatures over a wide range of oxygen partial pressures and an attempt has been made to establish the defect structure of polycrystalline tin dioxide and its solid solution with ZnO.

2. Experimental details

The tin dioxide used in this study was 99.9% pure (obtained from Keeling and Walker Ltd., England). The ZnO (AR grade), varying in amount from 0.5 wt% to 20 wt%, was mixed with SnO_2 in an 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 removed by a sharp blade to avoid contamination from the die wall. The pellets containing ZnO were sintered in an electrically heated furnace at 1250° C for 4 h. For "pure" SnO_2 pellets, sintering was carried out at 1450° C for 3 h. The bulk densities of the sintered pellets were found to be 85 to 95% of theoretical density. For the measurement of electrical conductivity the flat surfaces of the specimen were ground and an unfluxed platinum paste (Engelhard 6082) was used as the electrodes. The specimen was then placed in the specimen holder (Fig. 1) kept in a tubular furnace, the temperature of which was controlled within ± 1° C. The a.c. conductivity was measured by an universal bridge (Wayne Kerr B224) at an internal frequency of 1592 Hz. The desired oxygen partial pressure was obtained by controlling the oxygen content in a stream of inert

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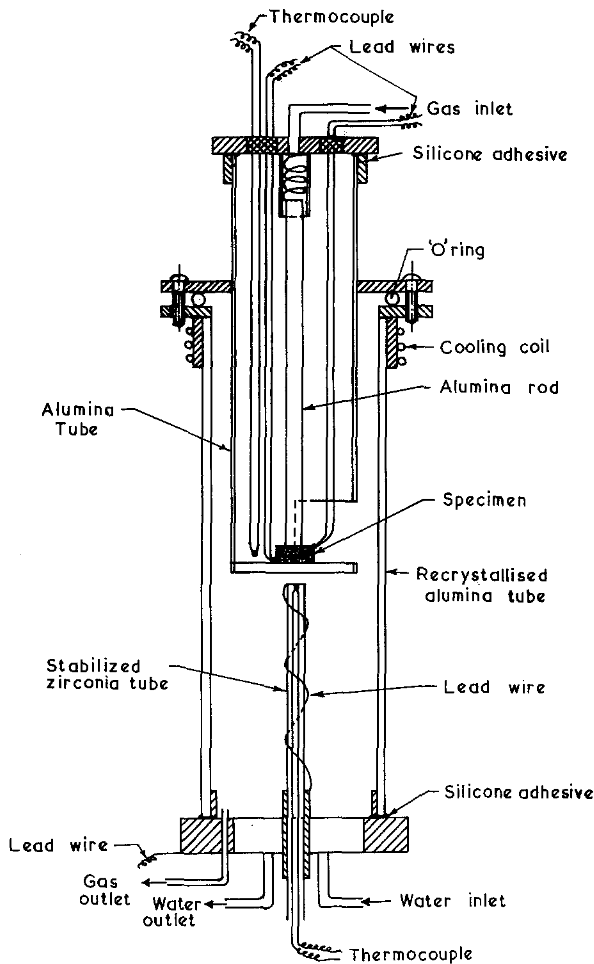


Figure 1 Specimen holder with stabilized zirconia oxygen probe.

gas (argon) by an electrochemical "oxygen pump" [14] using a stabilized zirconia solid electrolyte tube (obtained from Corning Glass Works, USA). The inert gas, with a controlled oxygen content, was transferred to the specimen holder through a copper tube. The exact oxygen partial pressure prevailing inside the specimen holder was also measured by an electrochemical oxygen sensor made of a stabilized zirconia tube which was kept very close to the specimen.

3. Results and discussion

Electrical conductivity of "pure" tin dioxide specimen is measured as a function of oxygen partial pressure in the temperature range 500 to 700° C and the results are plotted in Fig. 2. The complete range of oxygen partial pressure used in the present investigation may be divided into three distinct ranges. In the highest partial pressure range the conductivity at each temperature increases with a decrease of p_{O_2} indicating an n-type semiconductivity in the specimen. The slope of the plot is found to vary between $-1/3.7$ and $-1/4.5$. In the intermediate p_{O_2} range the conductivity becomes independent of p_{O_2}. This is quite apparent specially at lower temperatures of measurement (500 and 550° C) where the p_{O_2} independent region extends down to the lowest partial pressure (10^{-16} atm) used in this investigation. The extent of the flat region, however, decreases as the temperature is increased and it is almost non-existent at the highest temperature of measurement (700° C). At lower oxygen partial pressures beyond the flat region the conductivity once again increases with a decrease in p_{O_2}. This is apparent especially at high temperatures. In this case however, the slope is much lower ($-1/13.5$ to $-1/15$) than that observed in the higher partial pressure range.

Similar measurements of electrical conductivities at different oxygen partial pressures and temperatures have been made for SnO_2–ZnO solid solutions

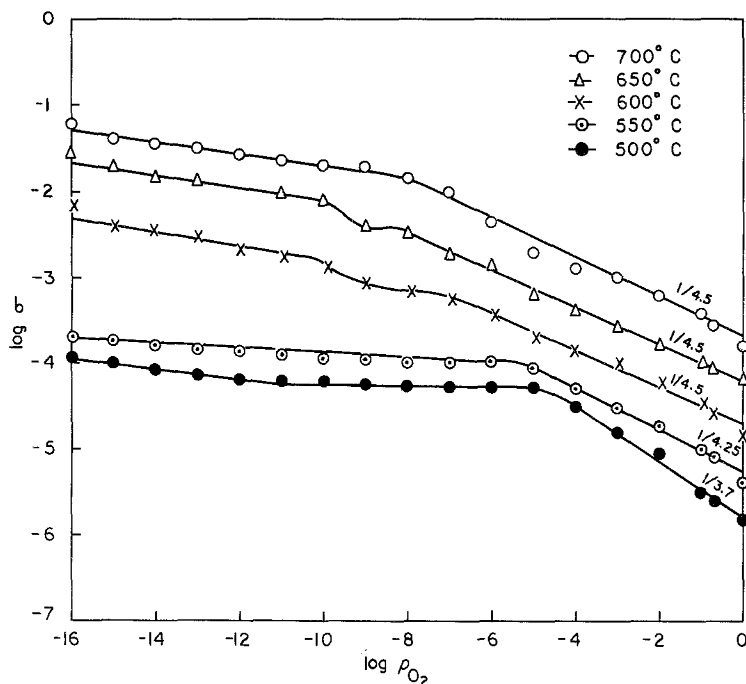


Figure 2 Electrical conductivity of "pure" SnO_2 as a function, of oxygen partial pressure at different temperatures.

containing 1 and 5 wt% ZnO and the results are shown in Figs. 3 and 4, respectively. The results are very similar to that observed in "pure" SnO_2 except that (a) the p_{O_2} independent conductivity region extends down to much lower partial pressures at each temperature as the ZnO content is increased, (b) the p_{O_2} dependent conductivity in the lower partial pressure range is observable at comparatively higher temperatures and (c) the slope of the plots in the highest p_{O_2} range is lower compared to that observed in "pure" SnO_2.

4. Defect structure

Tin oxide is known to be an oxygen deficient n-type semiconductor as also observed in the present investigation. Variation of electrical conductivity throughout the oxygen partial pressure range observed in this investigation may be explained

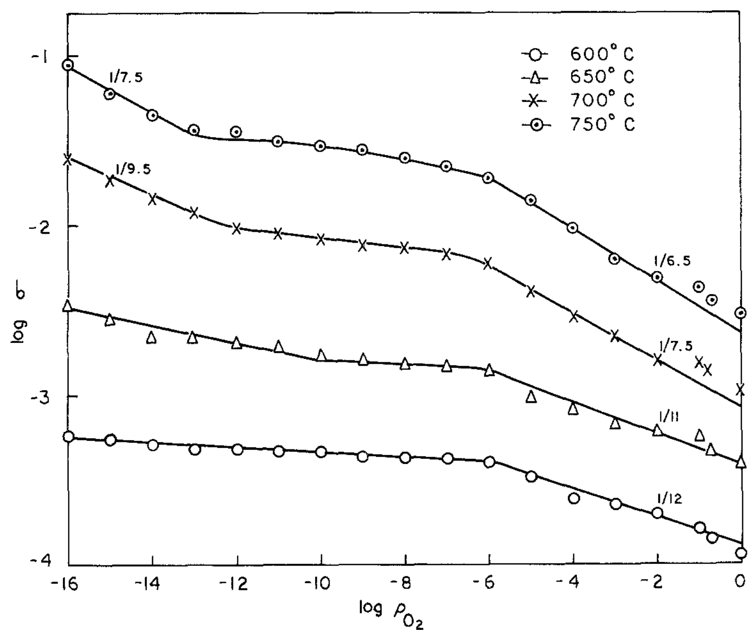


Figure 3 Electrical conductivity of SnO_2 + 1 wt% ZnO as a function of oxygen partial pressure at different temperatures.

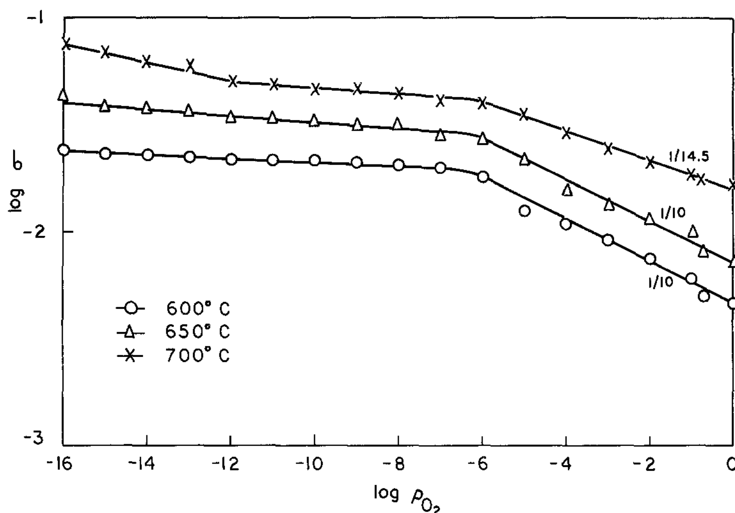
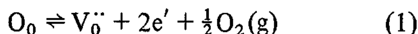


Figure 4 Electrical conductivity of SnO_2 + 5 wt% ZnO as a function of oxygen partial pressure at different temperatures.

satisfactorily assuming an anti-Frenkel type defect structure in this material. In the range of oxygen partial pressures studied, the predominant ionic defect may be considered as doubly ionized oxygen vacancies as also suggested by some of the earlier workers [12, 13]. Accordingly, using conventional defect notations the defect reaction may be written as



$$O_0 \rightleftharpoons V_0^{\cdot\cdot} + 2e' + \tfrac{1}{2}O_2(g) \qquad (1)$$

Even though this defect reaction is valid over the whole range of p_{O_2} used in this investigation, the variation of electrical conductivity depends on the particular neutrality condition existing at different ranges.

In the highest partial pressure range, p_{O_2} dependence of conductivity in "pure" SnO_2 may be explained assuming that the specimen remains in the stoichiometric condition, in which case the neutrality condition may be expressed as

$$[O_i''] = [V_0^{\cdot\cdot}] \qquad (2)$$

where square brackets represent the concentration of the defects. Since an anti-Frenkel type defect equilibrium also prevails in this partial pressure range, the concentrations of O_i'' and $V_0^{\cdot\cdot}$ are also expressed by

$$[O_i''] \; [V_0^{\cdot\cdot}] = K_A \qquad (3)$$

where K_A is the equilibrium constant for anti-Frenkel defect reaction. Application of the law of mass action in Reaction 1 and the use of Equations 2 and 3 leads to

$$n = K_1 K_A^{-1/2} p_{O_2}^{-1/4} \qquad (4)$$

where n is the electron concentration and K_1 is the equilibrium constant for Reaction 1. Equation 4 predicts $-$ 1/4th dependence of log σ on log p_{O_2} (since $\sigma \propto n$).

A similar p_{O_2} dependence is also obtained if one assumes the presence of a small amount of aliovalent impurities in the "pure" specimen. It has been observed in a number of other oxides that the conductivity behaviour is greatly influenced by an extremely small quantity of impurities, the presence of which is inevitable even in the purest material available. Such impurities may be either higher or lower valent cations compared to the tetravalent tin ion. The presence of such cations will produce compensating ionic defects such as either oxygen vacancy or oxygen interstitial depending on whether the cations are placed in the substitutional or interstitial position. In either case the concentration of defects will be fixed by the amount of impurities present and will be independent of p_{O_2}. Under these circumstances the concentration of the electron will be given by

$$n = (K_1/C_V) p_{O_2}^{-1/4} \qquad (5)$$

where C_V is the concentration of the oxygen vacancy fixed by the presence of an impurity.

It may be noted that the observed p_{O_2} dependence of conductivity closely compares with the predicted value of $-$ 1/4 and, therefore, it may be concluded that the "pure" specimen in this investigation either remains in the stoichiometric condition in the high partial pressure range or its conductivity is mainly controlled by the presence of minor impurities.

The conductivity at an intermediate partial

pressure range signifies a p_{O_2} independent n-type conduction. This is possible only when the conductivity is impurity controlled and electrons are the compensating defects. The neutrality condition in this case can be represented by either of the following two equations:

$$[M_i^{m\cdot}] = m[e'] \qquad \text{where, } m < 4 \tag{6}$$

$$[M_{Sn}^{(m-4)\cdot}] = (m-4)[e'] \qquad m > 4. \tag{7}$$

In these equations M^{m+} denotes an impurity cation. The existence of p_{O_2} independent n-type conduction, therefore, is a clear indication that the "pure" specimen does contain a sufficient amount of impurities which make it behave extrinsically at least at lower temperatures. However, as the temperature increase the intrinsic behaviour predominates with a consequent shortening of the p_{O_2} independent range, which finally vanishes at the highest temperature (700° C).

At higher temperatures and lower partial pressures the conductivity once again increases with a decrease in p_{O_2}. This may be considered as the onset of the intrinsic behaviour of the material for which the neutrality condition is

$$2[V_O^{\cdot\cdot}] = [e'] \tag{8}$$

This leads to $-1/6$th dependence of log σ on log p_{O_2}. The observed slope is, however, much lower than this value. One of the reasons for this discrepancy may be that the mobility of the electron is reduced significantly because of the large concentration of oxygen vacancies present at these low partial pressures.

4.1. Effect of ZnO

As may be observed in Figs. 3 and 4 the behaviour of ZnO doped SnO_2 is very similar to that of "pure" SnO_2. In the intermediate p_{O_2} range the flat region signifies the impurity controlled electron conduction similar to that observed in "pure" SnO_2. Since the zinc has a lower valency than that of the tin ion, Equation 6 applies in this case. This implies that ZnO forms an interstitial solid solution with SnO_2. Such an assumption may not be unrealistic due to the following facts. SnO_2 has a rutile structure in which half of the octahedral and all the tetrahedral sites are vacant. The radius of the Zn^{2+} ion in octahedral coordination is 0.075 nm [15] which compares favourably with 0.069 nm [15] for Sn^{4+}. So it is probable that zinc-ions occupy a part of the vacant octahedral sites.

It may be noted that in the high partial pressure range of Figs. 3 and 4 the observed slopes are lower than the predicted $-1/4$th dependence. In this partial pressure range there is a significant concentration of the ionic defect produced as a result of ionic defect compensation represented by

$$[Zn_i^{\cdot\cdot}] = [O_i''] \tag{9}$$

which will lead to appreciable ionic conductivity. The concentration of the ionic defect in this case is fixed by the amount of ZnO added and is independent of p_{O_2}. Therefore a larger contribution of ionic conduction tends to reduce the slope of the conductivity plot. This is one of the reasons for the observed lower slope. The slope, however, increases with an increase of temperature since at a higher temperature the extent of electronic contribution increases compared to that of the ionic contribution. On the other hand the slope decreases with an increase in the ZnO content because of the larger ionic contribution.

Similar to that in "pure" SnO_2 the intrinsic behaviour is observed only at very low oxygen partial pressures and comparatively at higher temperatures (Fig. 3). As expected this range is absent when the ZnO content is increased (Fig. 4).

To determine the activation energy for the conduction process, the conductivity of the specimen was measured over the temperature range 300 to 1100° C at a fixed oxygen partial pressure (air). The results are presented in Fig. 5, in which the logarithm of conductivity has been plotted against the reciprocal temperature. It may be observed that the results cannot be represented by a single straight line for any of the compositions. A break in the plots around 450 to 500° C indicates that the activation energies are different above and below this temperature range. In each region the activation energy has been calculated from the slope of the straight line and is given in Table I. For all the specimens the values of the activation energy in the high temperature region are higher than those at the low temperature range.

The lowering of the activation energy may be attributed to the increasing importance of surface conduction due to the chemisorption of oxygen at the lower temperatures. The effect of oxygen chemisorption on the electrical conductivity in the low temperature range was earlier demonstrated by Matthews and Kohnke [16]. At low temperature, the bulk of the material is not equilibrated

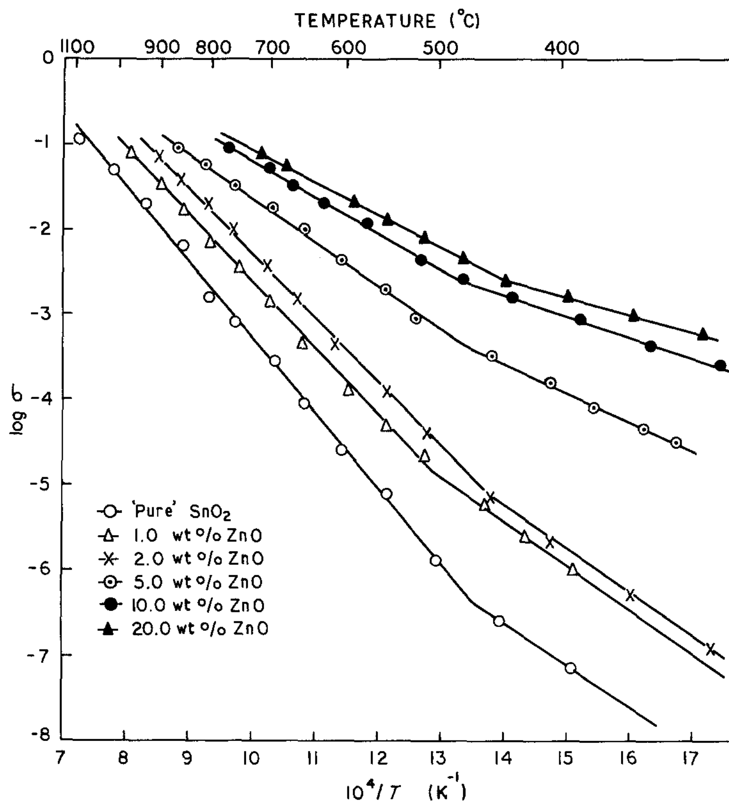


Figure 5 Electrical conductivity of the SnO_2–ZnO system as a function of temperature in air.

with the surrounding atmosphere. However, the suface of the specimen attains equilibrium at a much faster rate. Thus the observed variation in the low temperature range is mainly due to the variation of the surface property.

It may also be noted (Table I) that there is a general trend of decreasing activation energy with an increase in ZnO concentration. This may be attributed to the increasing amount of ionic contribution to the total electrical conductivity, since the addition of ZnO increases the ionic defect concentration in this partial pressure range.

5. Conclusions

1. SnO_2 is an n-type semiconductor and is characterized by an anti-Frenkel type defect structure.

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

ZnO (wt %)	Activation energy (eV)	
	High temperature	Low temperature
"pure" SnO_2	1.73	0.99
1	1.53	0.99
2	1.48	0.99
5	1.04	0.69
10	0.84	0.49
20	0.79	0.39

2. Addition of ZnO significantly increases the electrical conductivity. Variation of conductivity of ZnO doped SnO_2 with the oxygen partial pressure may be explained satisfactorily assuming ZnO forms an interstitial solid solution.

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