

Nonstoichiometry and Defect Equilibrium in Stannic Oxide

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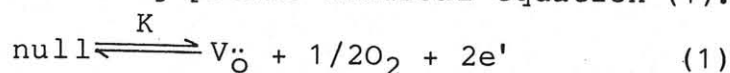
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Stannic oxide has long been noted to show good conductivity and its thin films are widely used for such purposes as transparent electrodes and sensors. Despite the generally accepted notion that the oxygen vacancy is primarily responsible for the carrier formation in stannic oxide, the oxygen deficiency, i.e. the nonstoichiometry of stannic oxide has not been quantitatively analyzed yet. The present paper describes the first success of definite determination of nonstoichiometry and provides an evidence supporting the direct correlation between carrier concentration and defect equilibrium.

The experimental setup for the measurement of nonstoichiometry is schematically represented in Fig.1. The sample was prepared from 5N SnO₂ powder which was pressed into a cylindrical rod and sintered at 1200 °C for three hours. The size and weight of the rod measured in air at room temperature were 10φx15mm and 5.45g, respectively. The weight measurement was carried out by using an electro-microbalance (Shimadzu TG-31H) placed in an atmosphere of circulating argon-oxygen mixed gas in which the oxygen partial pressure was varied in the range between 1.32x10⁻¹ and 1x10⁻⁴ atm. The sensitivity of weight measurement was tuned up to be as high as 2.5μg by controlling the pressure of argon so that the buoyancy effect could be equalized when the oxygen partial pressure was changed. This compensation of buoyancy effect as well as the use of relatively heavy sample made it possible to detect such small weight changes of stannic oxide as shown in Fig.2.

The observed dependences of nonstoichiometry or deviation from the stoichiometric 1:2 ratio in stannic oxide on oxygen partial pressure and on temperature are reversible under the condition of Fig.2, indicating that the defect equilibrium is rapidly reached. At temperatures higher than 1200 °C, the weight change turned out to be irreversible due apparently to the evaporation of stannic oxide. The weight increase observed at temperatures of 950 °C and below and at relatively high oxygen partial pressures should be ascribed to the oxygen adsorption on the sample.

Figure 3 shows the log-log plots of nonstoichiometry vs. oxygen partial pressure P_{O₂}, the slopes of which are approximately -1/6. This result can be interpreted by assuming the following pseudochemical equation (1):



where K is the equilibrium constant represented by eq.(2), [V_O]=δ is the concentration of oxygen vacancy, and [e']=n is carrier concentration.

$$K=[V_{\ddot{O}}]n^2P_{O_2}^{1/2} \quad (2)$$

According to the neutralization, eq.(3) holds,

$$n=2\delta \propto P_{O_2}^{-1/6} \quad (3)$$

Samson and Fonstad measured the conductivity of stannic oxide crystals as a function of $P_{O_2}(1-10^{-2}\text{atm})$ at elevated temperatures and concluded from the observed proportional relationship between the conductivity and $P_{O_2}^{-1/6.5}$ that the conductivity was originated from the native doubly ionizable oxygen vacancy $V_{\ddot{O}}$ in stannic oxide¹⁾.

Thus, the present result strongly supports the direct correlation between the conductivity and defect in stannic oxide.

Reference

- 1) S.Samson and C.G.Fonstad, J.Appl.Phys.,44,4618(1973)

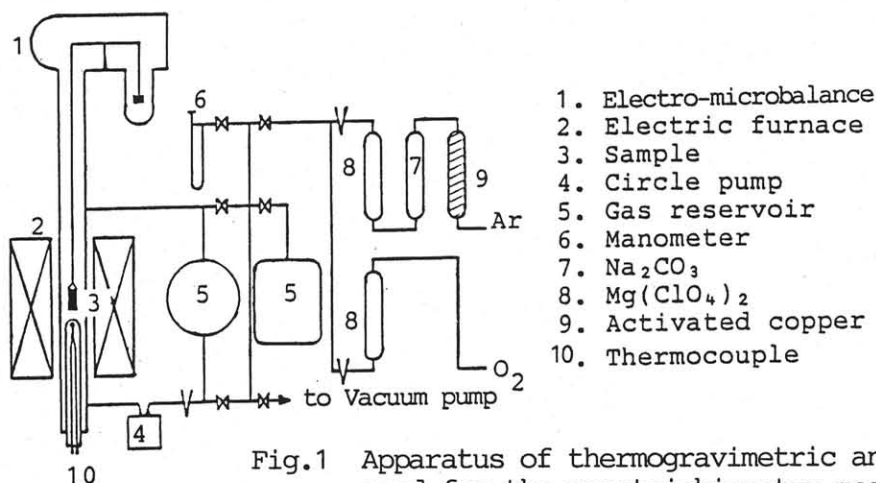


Fig.1 Apparatus of thermogravimetric analysis and gas mixing used for the nonstoichiometry measurement of $SnO_{2-\delta}$

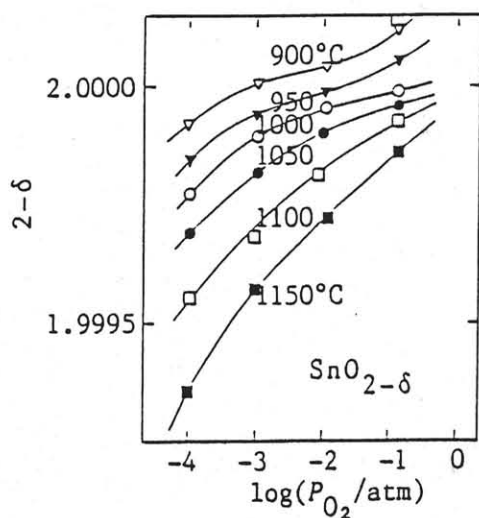


Fig.2 Dependences of nonstoichiometry in stannic oxide on temperature and oxygen partial pressure

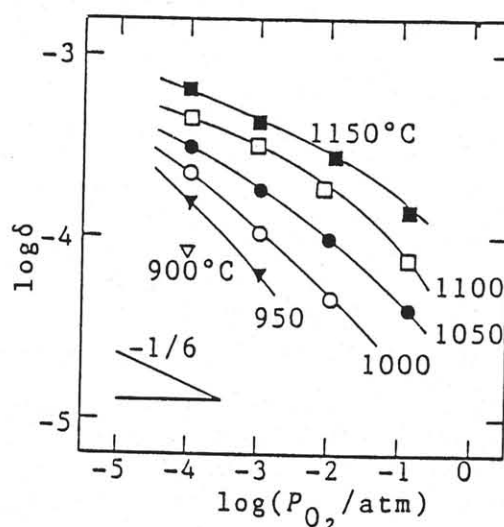


Fig.3 Correlation between $\log \delta$ and $\log P_{O_2}$