Consideration for Oxygen Adsorption Species on SnO₂ Semiconductor Gas Sensors [†]

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1. Introduction

Water vapor is the most important factor to influence on gas sensing properties. We can obtain high gas sensor response in dry atmosphere, but the gas response is decreased gradually by introducing water vapor. Such phenomena are strongly related with oxygen adsorption species on SnO₂ particles. Previously we reported that oxygen adsorption species is O²⁻ and O⁻ in dry and wet atmosphere, respectively [1]. However, the effect of treatment before measurement doesn't have discussed. In this study, we investigated pretreatment of neat SnO₂ and Sb-doped SnO₂ for behavior of oxygen adsorption.

2. Experiments

In this study, we used the following equation for analysis of oxygen adsorption species.

$$\frac{R}{R_0} = \frac{1}{2} \cdot \left(c + \frac{3}{a} \cdot (K_1 P_{O_2})^{\frac{1}{2}} \right) + \left\{ \frac{1}{4} \cdot \left(c + \frac{3}{a} \cdot (K_1 P_{O_2})^{\frac{1}{2}} \right)^2 + \frac{6N_D}{a} \cdot (K_2 P_{O_2})^{\frac{1}{2}} \right\}^{\frac{1}{2}} \quad (1)$$

R is electric resistance (Ω) in measurement condition, R_0 electric resistance (Ω) at flat band, a crystalline size (nm), N_D donor density (nm⁻³), P_{O_2} oxygen partial pressure (atm), K_1 and K_2 adsorption equilibrium constants for O⁻ (nm²/atm) and O²⁻ (nm⁸/atm), respectively, and c constant.

We used SnO₂ and Sb(0.1 mol. %)-SnO₂ particles calcined at 600–700 °C in various atmosphere. After the powders were deposited on alumina substrates with Au electrodes by screen-printing, the elements were calcined at 580 °C in oxygen atmosphere for 3 h. After that, the resulting sensor elements were pretreated at 580 °C for 3 h in N₂, 0.3%O₂, 1%O₂ or 100%O₂. The sensor element was cooled to 350 °C with keeping the atmosphere of the pretreatment, and the oxygen partial pressure dependence of the electrical resistance was measured in dry and wet atmosphere (P_{H_2O} = 0.03 atm).

3. Results and Discussion

At first, neat SnO₂ calcined at 700 °C in O₂ or N₂ atmosphere was investigated after pretreating at 580 °C for 3 h in 0.3%O₂, 1%O₂ or 100%O₂. Figure 1 shows relationship between amount of oxygen adsorption species and oxygen partial pressure in pretreatment. It was revealed that O²⁻ adsorbs with precedence than O⁻. In addition, by reducing oxygen partial pressure at pretreatment, the amount of O²⁻ adsorption decreased and the amount of O⁻ adsorption increased. Figure 2 shows total amounts of [O²⁻] and [O⁻] against oxygen partial pressure in pretreatment. It is found that the total amount of

oxygen adsorption increases by reducing oxygen partial pressure at pretreatment. Furthermore, it is clear that the control of atmosphere at pretreatment gives a big influence on amounts of oxygen adsorption than the control of atmosphere at the powder calcination.

Second, neat SnO_2 and Sb-doped SnO_2 calcined at 600°C in O_2 atmosphere was investigated was investigated in wet atmosphere after pretreating at 580°C for 3 h in N_2 or $100\%\text{O}_2$. Figure 3 shows total amounts of $[\text{O}^{2-}]$ and $[\text{O}^-]$ against oxygen partial pressure in pretreatment (measured in dry and wet atmosphere). The difference in the total amounts of oxygen adsorption species for dry and wet atmosphere was not observed, although Sb- SnO_2 are more on the total amounts of oxygen adsorption than neat SnO_2 . From these results, it is considered that, at the first stage by changing dry to wet atmosphere, the hydroxyl group formation from water vapor may be related with the reduce in electric resistance. However, when the elements are kept for long time in wet atmosphere, the oxygen adsorption species changes O^{2-} to O^- , and the resulting also gives the reduce in electric resistance, as reported previously [1].

Figure 1. Relationship between amount of oxygen adsorption species and oxygen partial pressure in pretreatment (measured in dry atmosphere).

Figure 2. Total amounts of $[\text{O}^{2-}]$ and $[\text{O}^-]$ against oxygen partial pressure in pretreatment (measured in dry atmosphere).

Figure 3. Total amounts of $[\text{O}^{2-}]$ and $[\text{O}^-]$ against oxygen partial pressure in pretreatment (measured in dry and wet atmosphere).

References

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