Zn and Sb interaction and oxygen defect chemistry in dense SnO2 ceramics co-doped with ZnO and Sb2O5

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1. Introduction

Tin oxide (SnO2) is an n-type semiconductor with a wide band gap (Eg = 3.6 eV). In its thin-film and powder forms, SnO2 has been widely used in solar cells, gas sensors, and as an oxidation catalyst. However, SnO2 ceramics with good sinterability have not been extensively investigated because they are difficult to fabricate. The lack of bulk SnO2 forms such as dense ceramics has hindered research on the physicochemical properties of SnO2. It is generally difficult to produce dense SnO2 ceramics without using additives because SnO2 decomposes and its constituents evaporate during the high temperature (>1200°C) sintering process. In order to fabricate dense SnO2 ceramics, several additives, such as MgO, MnO2, Fe2O3, CoO, and ZnO, have been utilized as sintering aids. ZnO and MgO have been found to be particularly effective for densification of transparent SnO2 ceramics. From a technological viewpoint, ZnO is a suitable additive because the fabrication of dense SnO2 is possible by the addition of just a small amount (0.25 mol%) of ZnO.

From the viewpoint of electroceramics, Sb oxides have been added to SnO2 ceramics to improve their electrical properties. It is expected that Sb in the SnO2 lattice acts as a donor. Saadeddin et al. confirmed by means of X-ray photo-emission spectroscopy (XPS) that Sb mainly substitutes at the Sn sites in Sb-doped SnO2 ceramics.

A previous study revealed that co-doping of Zn and Sb into SnO2 increases the solubility of Sb, although the dense SnO2 ceramics only Sb oxide added were not fabricated due to the severe evaporation of Sb oxide. They suggested that the increase in Sb solubility into SnO2 is resulted from charge compensation without oxygen vacancy formation. However several problems due to the additives still remain for SnO2 ceramics. The first problem is that the interaction reaction of Zn, Sb, and Sn ions and oxygen vacancies in SnO2 grains are unclear. Zn and Sb incorporated into a Sn site in SnO2 can act as a double-charged acceptor and a singly charged donor, respectively. More generally, the incorporation reactions of an acceptor (M) and donor (N) in SnO2 can be written as

\[ M^+ + e \rightarrow M \quad \text{(1)} \]

Equation (1) shows the increase in oxygen vacancy concentration by the double acceptor.

\[ N^+ + V^0_0 \rightarrow 2N^0_0 + 5O^0 + 2e^- \quad \text{(2)} \]

Equation (2) indicates that the donor incorporation needs oxygen vacancy in the SnO2 lattice.

Equations (1) and (2) indicate that the incorporation reaction of the acceptor and donor in SnO2 is connected to the oxygen vacancy. From the charge compensation, improvement of electrical property is not expected because complex (M – 2N)^+ defects would remains in the lattice. However, the electrical properties are influenced by the microstructure of the materials. Therefore, further investigation of the behavior of a donor and acceptor in SnO2 is required.

The second problem with SnO2 ceramics with co-additives is the segregation and secondary phase formation related to the additives in SnO2. Zn segregation has been observed at the grain boundaries in SnO2 ceramics doped with ZnO. A secondary phase with Zn and Sb was also reported in Zn, Sb co-doped SnO2 ceramics. The behavior of doped elements in SnO2 is the key for improving the sinterability of the elements and electrical properties of SnO2 ceramics. It is thus necessary to investigate the distribution and concentration of Zn and Sb in the SnO2 grains.

Equations (1) and (2) indicate that the oxygen vacancy is an important defect for the incorporation reaction of Zn and Sb into the SnO2 lattice. Therefore, we also need to understand the behavior of the oxygen vacancies in the SnO2 ceramics. For
studying defects chemistry based on the quantitative analysis of cation and oxygen diffusion in solids, secondary ion mass spectrometry (SIMS) has been used. In this work, we investigated the distribution and concentration of Zn and Sb in dense SnO2 ceramics using SIMS observations performed at a lateral resolution of 100 nm. Additionally, oxygen diffusion measurements were carried out to determine the bulk diffusion coefficient. The interaction of Zn and Sb, and the oxygen defect chemistry in the dense SnO2 ceramics are discussed below based on the results of the observations and measurements.

2. Experimental procedure

Zn and Sb co-doped SnO2 polycrystalline samples were prepared by conventional sintering. Reagent-grade powders of SnO2 (99.9% purity), ZnO (99.999% purity), and Sb2O5 (99.999% purity) (High-Purity Chemicals, Ltd.) were used as starting materials. We prepared three SnO2 samples with different ZnO and Sb2O5 concentrations: sample A (ZnO 0.6 mol %, Sb2O5 0.2 mol %), sample B (ZnO 0.6 mol %, Sb2O5 2.0 mol %), and sample C (ZnO 6.0 mol %, Sb2O5 2.0 mol %), as listed in Table 1. The powders were mixed by ball milling (YTZ-3) in ethanol for 20 h, dried, and then pressed into disks of 10 mm diameter and 3 mm thickness. The pressed disks were then sintered at 1440°C for 2 h in air. After sintering, the sample surfaces were polished and finished with diamond paste to obtain mirror surfaces. All samples were then annealed at 1000°C for 0.5 h in air using an electric furnace, to remove polishing damage from the surfaces. The resulting samples were dense ceramics with theoretical densities >95%.

The Zn and Sb concentrations in the SnO2 grains for all samples were then measured by SIMS (Cameca IMS-4f and Cameca NanoSIMS 50) using Zn- or Sb-implanted SnO2 ceramics as the standard. The lateral distributions of Zn, Sb, and Sn in the dense SnO2 ceramics were observed using high-resolution scanning ion images of (ZnO)−, (SbO)2−, and (SnO)2− obtained by SIMS (Cameca NanoSIMS 50).

Oxygen diffusion experiments using 18O as a tracer were then performed on all three samples. These samples were annealed in 18O2 gas at 1000°C for 7 h to obtain their diffusion coefficient. Details of the experimental set-up for the oxygen diffusion measurements are described elsewhere. Before the oxygen diffusion experiments, we checked for evaporation of SnO2. No evidence of SnO2 powder evaporation was observed during annealing for the experimental settings used in this work.

After the oxygen diffusion experiment, 16O and 18O isotopic analysis of the samples was carried out using SIMS (Cameca IMS-4f) to reveal their oxygen self-diffusion characteristics. The secondary ion intensities of 16O and 18O were measured as a function of time. SIMS crater depth was also measured using a surface profiler (Dektak 150). The depth profiles were converted to 18O concentration profiles by the following equation:

\[ C(x,t) = \text{erfc} \left( \frac{x}{2 \sqrt{D_b} t} \right) \]

where \( C(x,t) \) is the surface 18O concentration, \( C_0 \) is the background 18O concentration, \( x \) is the penetration depth, \( t \) is the diffusion treatment time, and \( \text{erfc} = 1 - \text{erf} \) (where \( \text{erf} \) is the Gaussian error function). This equation is a solution for the diffusion equation obtained by assuming that the 18O concentration is constant at the sample surface and that diffusion occurs in a semi-infinite medium.

3. Results

3.1 Elemental distribution and concentration of Zn and Sb

Figures 1–3 show high-resolution ion images obtained from samples A, B, and C, respectively. As can be seen in Fig. 1, shows the highest intensity in the current analysis, and the 18O− image is helpful to observe the surface morphology. The 18O− images clearly indicate that all samples are dense ceramics.

In sample A, the (SbO)2− image shows a uniform distribution of Sb in SnO2 grains (Fig. 1). In contrast, Zn segregation at all grain boundaries was observed in the (ZnO)2− image (Fig. 1). Some particles (<5 μm) with a high intensity of (ZnO)2−, which are precipitates related to ZnO−SnO2−, were found at the grain triple junctions and at grain boundaries.

In sample B, both Zn and Sb were distributed in the SnO2 grains (Fig. 2). The SnO2 grains were identified by the distribution of these ions. The intensities of Zn and Sb near the grain boundaries were smaller than those of the SnO2 grains (Fig. 2). No secondary phase or Zn segregation was observed in this sample.

In sample C, some precipitates (<5 μm) with high intensity of 18O−, (ZnO)2−, and (SbO)2− and low intensity of (SnO)2− were observed in SnO2 grains (Fig. 3). Zn and Sb were found to be homogeneously distributed in the SnO2 grains. No segregation or 18O concentration and 18O intensity, respectively.

To evaluate the diffusion coefficient (Db), the observed profile was fitted using the following equation:

\[ \frac{C(x,t) - C_0}{C_0 - C_s} = \text{erf} \left( \frac{x}{2 \sqrt{D_b} t} \right) \]

where \( C_s \) is the surface 18O concentration, \( C_0 \) is the background 18O concentration, \( x \) is the penetration depth, \( t \) is the diffusion treatment time, and \( \text{erf} = 1 - \text{erf} \) (where \( \text{erf} \) is the Gaussian error function). This equation is a solution for the diffusion equation obtained by assuming that the 18O concentration is constant at the sample surface and that diffusion occurs in a semi-infinite medium.

In principle, the application of Eq. (3) is limited when the surface concentration is maintained constant value during annealing.

Table 1. Concentration of Zn and Sb doped in dense SnO2 ceramics and concentration in SnO2 grains as measured by SIMS

| Sample | Zn (mol%) | Sb (mol%) | Concentration in SnO2 grains (atoms/cm²) |
|--------|-----------|-----------|----------------------------------------|
| A      | 0.6       | 0.2       | 3.2 × 10¹⁸ (1.1)                         |
| B      | 0.6       | 2.0       | 6.4 × 10¹⁸ (1.8)                         |
| C      | 6.0       | 2.0       | 8.0 × 10¹⁸ (1.3)                         |

Fig. 1. High-resolution ion images of 16O−, (ZnO)2−, (SnO)2−, and (SbO)2− obtained from sample A.
The concentration of Zn and Sb in the SnO$_2$ grains of samples A–C were determined and are listed in Table 1. The measured concentrations of Zn in samples A, B, and C were 3.2 $\times$ 10$^{20}$, 2.8 $\times$ 10$^{20}$, and 1.9 $\times$ 10$^{20}$ atoms/cm$^3$, respectively. The measured concentrations of Sb in samples A, B, and C were 1.3 $\times$ 10$^{20}$, 2.8 $\times$ 10$^{20}$, and 4.0 $\times$ 10$^{20}$ atoms/cm$^3$, respectively. The doped concentration of Zn in sample A and B is the same, however, the measured concentration in sample A is about a half of that for sample B. The Zn concentration in sample B and C is approximately comparable to its doped concentration. In the case of Sb, measured Sb concentration in sample B and C is only slightly larger than that in sample A, even though a one order of magnitude larger amount of Sb was doped in samples B and C than in sample A.

### 3.2 Oxygen diffusion

The $^{18}$O depth profiles in samples A–C showed that almost all surface oxygen was exchanged to $^{18}$O [see Fig. 4(a)]. The profiles indicate two contributions: one is well fitted by Eq. (3), showing bulk diffusion, while the other has a long tailing. The bulk diffusion coefficients ($D_b$) of oxygen in samples A, B, and C were obtained by fitting Eq. (3), to be 4.5 $\times$ 10$^{-19}$, 1.2 $\times$ 10$^{-18}$, and 3.8 $\times$ 10$^{-18}$ cm$^2$/s, respectively (Table 2).

To identify the mechanisms that contribute to the long tailing, high-resolution ion images of the $^{18}$O in the samples were obtained from the tail region. In all samples, the $^{18}$O was found to be concentrated at the grain boundaries [Fig. 4(b)], thus suggesting that the long tailing could be attributed to grain boundary diffusion. This grain boundary diffusion was observed in all samples. Here, the distribution of Zn and Sb at the grain boundaries in the samples was found to be different depending on their concentration. More specifically, Zn segregation was observed at grain boundaries in sample A (Fig. 1), Zn and Sb were lost around the grain boundaries in sample B (Fig. 2), and the interface of the SnO$_2$–precipitates seemed to be at the grain boundaries in sample C (Fig. 3). Since the distributions of Zn and Sb make it difficult to compare and discuss grain boundary diffusion among samples A–C, grain boundary diffusion in the profile was not analyzed in this study.

### 4. Discussion

The differences in the distribution and oxygen diffusivity among samples A–C is a result of the interaction between Zn, Sb and oxygen vacancies. For high-temperature sintering of undoped SnO$_2$, oxygen vacancies (V$_{O}$) can be introduced in the SnO$_2$ lattice during the decomposition reaction that can be described as follows:

$$\text{SnO}_2 \rightarrow \text{Sn}^{2+} + O^{2-} + \frac{1}{2} O_2(\uparrow) + 2e^{-}. \quad (4)$$

This reaction has been identified as the major reaction for forming oxygen vacancies in the SnO$_2$ lattice.$^{7,15,16}$

In this study, ZnO and Sb$_2$O$_3$ were used as additives. Previous studies have shown reported that Sb doping in SnO$_2$ enhanced its electrical conductivity, indicating the introduction of free electrons in the SnO$_2$ lattice.$^{15,18}$ Furthermore, those studies proposed that Sb$^{5+}$ is substituted at the Sn$^{4+}$ sites in Sb-doped SnO$_2$ ceramics.$^{14,18}$ Zn doped into SnO$_2$ has been suggested to produce oxygen vacancies. The introduced oxygen vacancies act as a donor in the SnO$_2$ lattice.$^{7}$ The expected incorporation reactions of Sb$_2$O$_3$ and ZnO are expressed as follows:

$$\text{Sb}_2\text{O}_3 + V^*_O \rightarrow 2\text{Sb}^{2+} + 5O^{2-} + 2e^{-}. \quad (5)$$

$$\text{ZnO} \rightarrow \text{Zn}^{2+} + O^{2-} + V^*_O + 2e^{-}. \quad (6)$$

The incorporation reaction of Sb into SnO$_2$ grains needs V$_O$ [Eq. (5)], whereas the incorporation reaction of ZnO produces V$_O$ in the SnO$_2$ lattice [Eq. (6)]. Consequently, the incorporation of ZnO promotes the incorporation of Sb into the SnO$_2$ grains.

In order to discuss the interaction reaction in samples A–C, it is necessary to remove the problems of segregation and secondary phase formation caused by the thermodynamical equilibrium and to determine the concentrations of Zn and Sb incorporated into the SnO$_2$ grains. Quantitative values for the Zn and Sb concentration in SnO$_2$ grains were determined and are listed in Table 1. The Zn concentration in the SnO$_2$ grains of these samples increased with the increase in the Sn concentration. Our results support the above discussion and are consistent with the results of a previous study.$^{10}$

Zn and Sb in SnO$_2$ grains are expected to affect the oxygen diffusivity based on the vacancy mechanism. Figure 5 shows the
Db values of samples A–C as a function of Zn concentration in the SnO$_2$ grains. The Db values in these samples are significantly lower than those for Zn-doped SnO$_2$ ceramics without the Sb doping. The incorporation of Sb into SnO$_2$, Eq. (5) indicates its significant effect to reduce oxygen vacancy concentration during sintering [Eq. (4)] and Zn doping [Eq. (6)]. In samples A–C, the Db values were found to increase slightly with increasing Zn concentration in the SnO$_2$ grains. The increase in the Db value shown as trends (ii) and (iii) in Fig. 5 is due to the increase in the oxygen vacancy concentration due to the Zn incorporation reaction as indicated in Eq. (6).

Segregation, depletion and precipitation of Zn and/or Sb were observed in samples A–C. The behavior of the elements in Figs. 1–3 reflects the interaction of elements that depends on the concentration of added elements. Previously, Zn in ZnO doped SnO$_2$ ceramics has been reported to act as an incompatible element during the high temperature sintering. Palmer and Poeppelmeier suggested that the solubility limit of Zn in SnO$_2$ was less than 0.7% and only low concentrations of Zn are incorporated in SnO$_2$.[16] Sakaguchi et al. observed the precipitate in SnO$_2$ with 0.25 mol % ZnO added and reported a significantly low concentration of Zn in SnO$_2$. Previously, Zn$_2$SnO$_4$ and ZnSnO$_3$ phases were also observed in SnO$_2$ ceramics added with ZnO over 1 mol % added ZnO by XRD analysis.[12,26] Hashiguchi et al. reported on the behavior of Zn in SnO$_2$ and demonstrated the possibility of explaining the low concentration of Zn in SnO$_2$ grains and the formation of precipitate related to ZnO and SnO$_2$ in SnO$_2$ ceramics. In the present work, the Zn and Sb images of sample A in Fig. 1 showed their different distribution of them, indicating that added ZnO in SnO$_2$ tends to form the secondary phase during the high temperature sintering. In the case of sample C, the secondary phase with high intensity of Zn and Sb was observed in the ion images (Fig. 3). Previously, for SnO$_2$ co-doped with 1 mol % ZnO and Sb$_2$O$_5$, the secondary phases of Zn$_2$SnO$_4$ and Zn$_2$SbO$_4$ were detected.[15] The intensity distributions for Zn, Sb and Sn in sample C (Fig. 3) suggested that Zn$_2$SbO$_4$ is a candidate phase for the secondary phases in this sample. In sample B, the loss of Zn and Sb near grain boundaries was observed (Fig. 2). This is a evidence for the depletion of Zn and Sb along the grain boundaries during the high-temperature sintering. It should be pointed out that there is no evidence a the secondary phases in sample B. This is an important finding for fabricating the SnO$_2$ ceramics. The results indicate that it is possible to suppress the secondary phase formation by the co-doping of acceptor and donor into SnO$_2$.

5. Conclusions

Dense SnO$_2$ ceramics were fabricated with ZnO and Sb$_2$O$_5$ additives. Ion micro-beam analysis using secondary ion mass...
spectrometry (SIMS) was applied to characterize the elemental distribution in the samples. Zn and Sb were observed to be incorporated into SnO$_2$ grains in all samples, and their concentrations increased with increasing concentration of additives. In SnO$_2$ ceramics doped with less than 1 mol $\%$ of ZnO and Sb$_2$O$_5$, Zn segregated at the grain boundaries and precipitated at the triple junctions to form a secondary phase with SnO. In these samples, Sb showed a uniform distribution, indicating that Sb was incorporated into SnO$_2$ grains. Dense SnO$_2$ ceramics doped with more than 1 mol $\%$ of ZnO and Sb$_2$O$_5$ showed secondary phases related to Sn, Zn and Sb. On the other hand, dense SnO$_2$ ceramics doped with 0.6 mol $\%$ ZnO and 2.0 mol $\%$ Sb$_2$O$_5$ showed no precipitate in the sample. Both Zn and Sb were incorporated into SnO$_2$ grains in all samples, and their concentrations increased with increasing concentration of additives. In dense SnO$_2$ ceramics doped with more than 1 mol $\%$ of ZnO and Sb$_2$O$_5$ showed secondary phases related to Sn, Zn and Sb. The present report also indicate that co-doping of Zn as an acceptor and Sb as a donor allows for the fabrication of dense SnO$_2$ ceramics without secondary phases.

Oxygen diffusivity in the dense SnO$_2$ ceramics co-doped with ZnO and Sb$_2$O$_5$ was determined by SIMS. We found that incorporation of Sb significantly decreased the concentration of oxygen vacancies, whereas incorporation of Zn formed oxygen vacancies in the SnO$_2$ grains. The oxygen diffusivity result suggest that incorporation of Zn into SnO$_2$ grains promotes Sb incorporation in dense SnO$_2$ ceramics. This interaction reaction of Zn, Sb, and oxygen vacancies in the SnO$_2$ grains is consistent with the distributions of these in the dense SnO$_2$ ceramics.

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