We studied the diffusion of Zn in dense SnO2 ceramics by using secondary ion mass spectrometry (SIMS). Dense SnO2 ceramics with additives of 6 mol.% MgO and 0.2 mol.% Sb2O5 were synthesized, and Zn was implanted in the SnO2 ceramics by ion implantation technique. The implanted samples were annealed at 850-1200℃, and the concentration profiles of Zn were evaluated by SIMS. The temperature dependence of Zn diffusion at 850-950℃ could be expressed as DZn[cm2/s] = 3.3 × 106 exp(−463.5[kJ/mol]/RT). These results in relation to the fabrication process of SnO2 with added ZnO was then discussed.

1. Introduction

Tin oxide (SnO2), which is an n-type semiconductor with a wide band gap (Eg = 3.6 eV), has been extensively studied for use in solar cells and gas sensors as an oxidation catalyst.1-3) These applications use thin films and powders of SnO2. On the other, it is difficult to produce dense SnO2 ceramics because SnO2 decomposes and its constituents evaporate during sintering. Park et al.4) synthesized dense SnO2 ceramics without additives at high temperature and high pressure. Jarzabek and Marton5) reviewed the research prior to 1976. Van Daal6) grew polycrystalline SnO2 from vapor. Samson and Fonstad7) found that doubly ionized oxygen vacancies in SnO2 predominate as a function of oxygen partial pressure and temperature. Their results imply that oxygen vacancies are introduced into SnO2 grains through a decomposition reaction when the ceramics are sintered above 1200℃. Quadir and Readey8) found that sintering SnO2 in H2 gas improved its compactness and reduced its apparent density. Thus, decomposition and evaporation must be suppressed at high temperatures in order to produce dense SnO2 ceramics.

Another route to synthesizing dense SnO2 ceramics is to use additives. Useful additives for SnO2 are MnO2,9) CoO,10) CuO,11) MgO,12) ZnO,13-18) Nb2O5,19) Sb2O5,20) In2O3,21) and Bi2O3.22) Our interest is to keep the transparency of SnO2, and hence, we used Sb oxide, Mg oxide, and Zn oxide as additives. Antimony (Sb)-doped SnO2 is a transparent conductor that is used in solar cells and heat-reflective coatings.23) Previous studies have indicated that the minimum amounts of additives in SnO2 are 6 mol.% of MgO and 0.25 mol.% of ZnO. ZnO is a useful additive for synthesizing dense SnO2 ceramics. The densification model of SnO2 ceramics with ZnO includes oxygen vacancies formed by decomposition of SnO2 at high temperature.15-17) Although transmission electron microscopy (TEM) equipped with energy-dispersive spectroscopy (EDS) revealed a secondary phase in dense SnO2 ceramics with over 1 mol.% of ZnO, Zn was not detected in the grains.12) X-ray diffraction (XRD) analysis revealed that precipitation occurred when 5% ZnO was added to the SnO2. Identification of the secondary phase in ZnO-SnO2 system for example, as Zn2SnO4 or ZnSnO3, remains a problem.24,25) The effect of Zn during SnO2 sintering is unclear. Here, knowledge of the solubility limit and cation diffusion is important for understanding the properties affected by the ZnO additive.

In this study, we report on the diffusion and evaporation of Zn in dense SnO2 ceramics. Dense SnO2 ceramics were synthesized by using MgO and Sb2O5 additives. The Zn source was produced by means of ion implantation. The concentration profile and distribution of Zn in the dense SnO2 ceramics were evaluated by secondary ion mass spectrometry (SIMS). We investigated the effect of Zn on SnO2 during sintering at high temperature.

2. Experimental methods

Polycrystalline samples were prepared by conventional sintering. Dense SnO2 ceramics were synthesized in order to study the diffusion and evaporation of Zn. Reagent-grade powders of SnO2, MgO and Sb2O5 (High-Purity Chemicals Ltd.) were used. Dense SnO2 ceramics were prepared with MgO (6 mol.%) and Sb2O5 (0.2 mol.%) additives, because Pereira and Gouvea26) reported that MgO was an effective additive for making dense SnO2 ceramics. Sb2O5 powder was added to the SnO2 as a donor. The powders were mixed by ball milling (YTZ-3) in ethanol for 20 h. After drying, the powders were pressed into disks (diameter: 10 mm; thickness: 3 mm). The pressed disks were sintered at 1480℃ for 2 h in air. After the sintering, the sample surface was polished and composed of SnO2 grains about 10μm in diameter. The mirror-finished surface was used to evaluate the lateral distribution of Mg and Sb. Direct ion images of (MgO)+, and (SbO)+ in SnO2 ceramics were measured using a secondary ion mass spectrometer (SIMS) (Cameca IMS-1270) equipped with a high-efficiency stacked CMOS active pixel sensor for charged particles.27) Figure 1 shows the distribution of...
Mg and Sb in the ceramics, as obtained by SIMS. These images show that Mg and Sb were segregated at the grain boundary and were not in any of the SnO₂ grains.

Zn ions (accelerating voltage of 75 keV, dose of $2 \times 10^{15}$ ions/cm²) were implanted at room temperature. The implanted dense SnO₂ (SnO₂:Zn) was annealed at 850–1200°C for 0.5–6 h in air using an electric furnace. A quantitative analysis conducted by means of secondary ion mass spectrometry (SIMS) was carried out to reveal the characteristics of Zn evaporation and diffusion. To evaluate the diffusion coefficient ($D_{0}$), the observed profile was fitted using

$$\frac{C_{i,n} - C_{0}}{C_{i} - C_{0}} = \text{erfc} \left( \frac{x}{2\sqrt{D_{0}t}} \right)$$

where $C_{i}$ is the surface Zn concentration, $C_{0}$ is the background concentration remaining in the implanted region and the other concentration was kept constant during the annealing.

### 3. Results and discussion

Figure 2 shows Zn concentration profiles in SnO₂ ceramics annealed at different temperatures. Profile (i) shows the concentration in the as-implanted standard. Zn has a peak concentration of $6.6 \times 10^{20}$ cm⁻³ at a depth of 0.02 μm. After the annealing, the Zn concentration decreased around the implanted peak and a diffusion profile appeared deeper in the annealed samples. The behavior of Zn in SnO₂ during annealing is described below. Profile (ii) in Fig. 2 indicates the Zn profile of the sample annealed at 900°C for 180 min. The profile indicates that the diffusion starts at a depth of 0.06 μm and a concentration of $7 \times 10^{15}$ cm⁻³. Profile (iii) shows that the implanted Zn evaporated and diffused during annealing at 1000°C for 180 min. The concentration decreased gradually from the surface to 0.8 μm. The discontinuity apparent at a depth of 0.06 μm in concentration profile (ii) has disappeared in this profile. Profile (iv) is that of SnO₂ annealed at 1100°C for 60 min. The Zn concentration decreased sharply at the surface and gradually increased inside the sample. Profile (v) was obtained from a sample annealed at 1200°C for 30 min. The Zn concentration slightly increases deeper inside the sample. Profiles iii, iv, and v show high concentrations of Zn at the surface. This feature has often been observed at the surface of implanted samples.²⁹ In this study, the Zn evaporated from the surface at the annealing temperature and became deposited on the surface during the cooling process because of the high vapor pressure of ZnO.

Two types of Zn profiles were observed. One is of the Zn concentration remaining in the implanted region and the other is for diffusion deeper inside the sample [such as profile (ii)]. In that profile, the Zn concentration at a depth of 0.06 μm was maintained during the annealing, because the concentration at the surface was larger than that at this depth and the maximum concentration in the SnO₂ grains is limited to solubility at that temperature.

Diffusion profile (ii) in Fig. 2(a) is characterized as showing both volume diffusion and grain boundary diffusion away from the surface and into the sample. The volume diffusion curve is well fitted by Eq. (1) [Fig. 3(a)]. The Zn diffusion coefficient at 900°C was calculated to be $7 \times 10^{-15}$ cm²/s. Additionally, a constant concentration of Zn was obtained inside the sample, and it originated from the grain boundary diffusion shown in Fig. 3(b). The tail region of the Zn profiles (iii–v) in Fig. 2 is due to segregation of Zn at the grain boundaries; this indicates that Zn tends to remain at the grain boundaries during high-temperature annealing.

Figure 4 plots the bulk diffusion coefficient of Zn. Because the Zn evaporated at higher temperatures, the temperature dependence of oxygen bulk diffusion was determined for a temperature range of 850–950°C and can be expressed as

$$D_{Zn}(cm²/s) = 3.3 ± 0.395 \times 10^{6} \exp \left( \frac{-463.5 \pm 46.7 [kJ/mol]}{RT} \right),$$

where $D_{Zn}$ represents the bulk diffusion coefficient of zinc, $R$ is the gas constant, and $T$ is the temperature. The plot at 1000°C in Fig. 4 deviates downwards from the value extrapolated from Eq. (2) and it reflects evaporation of Zn.

The MgO and Sb₂O₅ additives mainly SnO₂ influence the oxygen defect chemistry. MgO can cause oxygen vacancy defects as follows:

$$\text{MgO} \rightarrow \text{Mg}^{2+} + \text{V}_O^{*} + \text{O}_0^{*}$$

### Footnotes

²⁹. This feature has often been observed at the surface of implanted samples.
This equation shows that adding MgO to SnO₂ increases the concentration of oxygen vacancies. Sb₂O₅ could also react with defects of SnO₂ such as oxygen vacancies, as follows: \[ \text{Sb}_2\text{O}_5 + V_{\text{Sn}}^0 \rightarrow 2\text{Sb}^5_\text{Sn} + 5\text{O}_2^+ + 2e^- \] (4)

This equation means that adding Sb₂O₅ reduces the oxygen vacancy concentration. However, the grain boundary segregation of Mg and Sb (see Fig. 1) indicates that the bulk diffusion of Zn is not influenced by the added MgO and Sb₂O₅.

We tried to determine the origin of Zn diffusion in dense SnO₂ ceramics from a previous result on cation diffusion in ZnO, because there have been no studies on diffusion of cations in SnO₂. Watanabe et al. (2012) reported that the activation energy of Zn self-diffusion in ZnO was about 400 kJ/mol. They considered that Zn diffusion was controlled by Zn vacancies. The activation energy obtained in this study (463.5 kJ/mol) is in good agreement with that in ZnO, although the crystal structures of SnO₂ [rutile structure] and ZnO [hexagonal structure] are quite different. Therefore, Zn diffusion in SnO₂ seems to be caused by the vacancy mechanism.

Dense SnO₂ ceramics with added ZnO were fabricated in a conventional sintering process at 1400–1500°C in air. Previous studies indicated that dense SnO₂ ceramics would contain the secondary phases such as Zn₂SnO₄ (spinel) and ZnSnO₃ (perovskite). The secondary phase formed by reacting SnO₂ and ZnO is stable at high temperature. The low solubility limit of the additive in the host materials leads to the secondary phase. The formation of the secondary phase needs a long enough diffusion length through which to supply Zn. From Eq. (2), the Zn diffusion coefficient at 1400–1420°C is calculated to be \(3 \times 10^{-10} \text{ cm}^2/\text{s}\). The diffusion length of Zn is calculated using the expression \(X = 2\sqrt{D_t t}\), where \(X\) is the diffusion length and \(t\) is the annealing time for diffusion. This expression indicates that Zn can diffuse about 25 μm during sintering. This diffusion length is sufficiently long to concentrate Zn at the location of the secondary phase in SnO₂ ceramics. Recently, Sakaguchi et al. (2013) observed Zn segregation at grain boundaries of SnO₂ ceramics and found that it suppresses decomposition of SnO₂. They also found that oxygen diffusivity improves sinterability of SnO₂ ceramics by uniform oxygen transport through the grain boundary in SnO₂ and that oxygen grain-boundary diffusion does not depend on the structure of the grain boundary in SnO₂ ceramics. In this study, Fig. 1 shows Mg and Sb segregation at the grain boundaries in SnO₂. The profiles in Fig. 2 suggest that Zn tends to remain at the grain boundaries at high temperature after the Zn in the SnO₂ grains has completely evaporated. These results indicate that grain boundary segregation of additives is a key to fabricating dense SnO₂ ceramics.

4. Conclusions

We studied Zn diffusion in dense SnO₂ ceramics synthesized with MgO and Sb₂O₅ additives. Mg and Sb in SnO₂ ceramics show grain boundary segregation in the direct ion images of SIMS. The diffusion source of Zn was measured, and bulk diffusion coefficients were obtained by diffusion analysis. The temperature dependence of the diffusion...
was determined in the temperature range of 850–950°C and could be expressed as 
\[ D_{Zn} = 3.3 \times 10^{-6} \exp(-463.5 \text{ [kJ/mol]} / RT) \]. Zn diffusivity is the key to fabricating dense SnO\(_2\) ceramics.

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References
1) J. F. Wagner, Science, 300, 1245–1246 (2003).
2) D. E. Williams, Sens. Actuators, B, 57, 1–16 (1999).
3) N. Barsan and U. Weimar, J. Electroceram., 7, 143–167 (2001).
4) S. J. Park, K. Hirot and H. Yamamura, Ceram. Int., 10, 115–116 (1984).
5) Z. M. Jarzebski and J. P. Marton, J. Electrochem. Soc., 123, 199C–205C (1976).
6) H. J. van Daal, Solid State Commun., 6, 5–9 (1968).
7) S. Samson and C. G. Fontad, J. Appl. Phys., 44, 4618–4621 (1973).
8) T. Quadir and D. W. Readey, in G. C. Kuczynski, A. E. Miller, G. A. Sargent (Ed.), Microstructure Evolution in SnO\(_2\) and CdO in Reducing Atmosphere in Sintering and Heterogeneous Catalysis, Plenum Publ. Co. (1984) p. 159.
9) J. A. Cerri, E. R. Leite, D. Gouvêa and E. Longo, J. Am. Ceram. Soc., 79, 799–804 (1996).
10) J. A. Varela, J. A. Cerri, E. R. Leite, E. Longo, M. Shamsuzzoha and R. C. Bradt, Ceram. Int., 25, 253–256 (1999).
11) S. A. Pianaro, P. R. Bueno, E. Longo and J. A. Varela, J. Mater. Sci. Lett., 14, 692–694 (1995).
12) G. J. Pereira and D. Gouvea, Ceramica, 49, 116–119 (2003).
13) H. E. Matthews and E. E. Kohnke, J. Phys. Chem. Solids, 29, 653–661 (1968).
14) L. T. Grigoryan, Z. H. Gedakyan and K. A. Kostanyau, Inorg. Mater., 12, 313–314 (1976).
15) L. Perazolli, C. R. Foschini, T. R. Giraldi, R. S. Biscaro, J. A. Varela and E. Longo, Sintering Science Technology, 2, 117–122 (2000).
16) L. Perazolli, A. Z. Simões, U. Coleti, Jr., F. Moura Filho, S. Gutierrez, C. O. P. Satons, J. A. G. Carrió, R. F. C. Marques and J. A. Varela, Mater. Lett., 59, 1859–1865 (2005).
17) C. R. Foschini, L. Perazolli and J. A. Varela, J. Mater. Sci., 39, 5825–5830 (2004).
18) J. Liu and W. Ning, J. Mater. Sci., 44, 2520–2524 (2009).
19) J. Takahashi, I. Yamai and H. Saito, Yogyo Kyokai-shi, 83, 362–366 (1975).
20) Y. H. Hu, H. H. Zhang and H. M. Yang, J. Alloys Compd., 453, 292–297 (2008).
21) G. Z. Zang, J. F. Wang, H. C. Chen, W. B. Su, W. X. Wang, C. M. Wang and P. Qi, J. Non-Cryst. Solids, 351, 941–945 (2005).
22) M. Muraoaka, M. Suzuki, Y. Sawada and J. Matsushita, J. Mater. Sci., 33, 5621–5624 (1998).
23) G. Boschloo and D. Fitzmaurice, J. Phys. Chem. B, 103, 3093–3098 (1999).
24) D. L. Young, D. L. Williamson and T. J. Coutts, J. Appl. Phys., 91, 1464–1471 (2002).
25) I. Stambolova, A. Toneva, V. Blasov, D. Radev, Y. Tsievovna, S. Vassilev and P. Peshev, J. Alloys Compd., 391, L1–L4 (2005).
26) H. Yuirimoto, K. Nagashima and T. Kunihiro, Appl. Surf. Sci., 203/204, 793–797 (2003).
27) J. Crank, The Mathematics of Diffusion. Oxford University Press, London, U.K. (1967).
28) I. Sakaguchi, N. Sakamoto, M. Hashiguchi, H. Yurimoto, S. Hishita and N. Ohashi submitted for J. Am. Ceram. Soc. (2013).
29) I. Sakaguchi, S. Hishita, H. Ryoken, Y. Sato and H. Haneda, Surf. Interface Anal., 37, 332–335 (2005).
30) K. Watanabe, K. Matsumoto, Y. Adachi, T. Ohgaki, T. Nakagawa, N. Ohashi, H. Haneda and I. Sakaguchi, Solid State Commun., 152, 1917–1920 (2012).