Characterization of oxygen defect and zinc segregation in the dense tin dioxide ceramics added with zinc oxide

Isao SAKAGUCHI,[†] Naoya SAKAMOTO,^{*} Minako HASHIGUCHI,^{**,‡}

Hisayoshi YURIMOTO,^{**} Shunichi HISHITA and Naoki OHASHI

National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^{*}Isotope Imaging Laboratory, Creative Research Institution, Hokkaido University, Sapporo 001-0021, Japan

^{**}Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan

We investigated the effect of zinc oxide addition for the defects in the dense SnO₂ ceramics. Cathode and photoluminescence properties revealed the luminescence originated to oxygen vacancies in SnO₂ grains and the presence of non-radiative defect at the grain boundaries. The oxygen diffusion profile showed that the oxygen diffusion was controlled by the limited process at the surface and uniform concentration of ¹⁸O at the grain boundaries inner side of sample. This sample exhibited a low Zn concentration in grains and a high Zn concentration at grain boundaries. We conclude that segregation of Zn at grain boundaries prevents SnO₂ from decomposing at high temperatures, enabling dense SnO₂ ceramics to be obtained.

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1. Introduction

Tin oxide (SnO₂) is an n-type semiconductor with a wide band gap ($E_g = 3.6$ eV). It has been extensively studied for use in solar cells and gas sensors and as an oxidation catalyst.¹⁻³⁾ While SnO₂ in gas sensors in the form of thin films and porous nanosized SnO₂ were extensively studied and proposed the conduction mechanism,³⁾ dense SnO₂ ceramics have been little investigated because they are difficult to fabricate. The lack of bulk SnO₂ forms such as dense ceramics and single crystals has hindered research on the physicochemical properties of SnO₂. It is generally difficult to produce dense SnO₂ ceramics without employing additives because SnO₂ decomposes and its constituents evaporate during sintering.

Jarzebski and Marton⁴⁾ reviewed research prior to 1976 on preparing SnO₂ and its defect chemistry. Van Daal⁵⁾ grew polycrystalline SnO₂ by vapor transport and realized a bulk density of 95%. Samson and Fonstad⁶⁾ found that doubly ionized oxygen vacancies predominate in SnO₂ for partial oxygen pressures between 10⁻² and 1 atmosphere and in the temperature range 700–1330°C. Their findings strongly imply that when SnO₂ ceramics are sintered above 1200°C, oxygen vacancies are introduced into SnO₂ grains by the decomposition reaction. Quadir and Readey⁷⁾ found that sintering SnO₂ in an H₂ atmosphere improved its compactness and reduced its apparent density. Moreover, SnO₂ decomposed and condensed at temperatures above 1200°C. It is thus critical to suppress decomposition and evaporation at high temperatures to produce dense SnO₂ ceramics. Park et al.⁸⁾ synthesized dense SnO₂ ceramics without additives at a high temperature and a high pressure. Another way to synthesize dense SnO₂ ceramics is to use additives. Useful additives for SnO₂

are MnO₂,⁹⁾ CoO,^{9),10)} CuO,¹¹⁾ ZnO,¹²⁻¹⁷⁾ Nb₂O₅,¹⁸⁾ Sb₂O₃,¹⁹⁾ In₂O₃,²⁰⁾ and Bi₂O₃.²¹⁾ These additives have larger ionic sizes and different charge states from Sn in the host material. Additives that improve sintering of other oxides have a low solubility limit and tend to segregate to grain boundaries.²²⁾ The formation of a secondary phase in ceramics reduces the additive concentration in host grains.

Of the additives that have been used to fabricate dense SnO₂ ceramics, ZnO is an important semiconductor due to its potential application in transparent devices and gas sensors made from SnO₂. Matthews and Kohnke¹²⁾ found that ZnO addition produced dense SnO₂ ceramics. A densification model for SnO₂ ceramics with ZnO addition has been discussed in terms of oxygen vacancy formation.^{14),16)} Perazolli et al.¹⁴⁾ proposed that enhanced oxygen diffusivity is the key cause for densification of SnO₂ ceramics on ZnO addition. Foschini et al.¹⁶⁾ suggested that ZnSnO₃ precipitates at grain boundaries in samples with ZnO contents over 1 mol.% and acts as a barrier that prevents grain boundary motion and inhibits densification. Using transmission electron microscopy/energy-dispersive spectroscopy, they found a secondary phase at triple junctions, but did not observe Zn segregation at grain boundaries. In the system of ZnO–SnO₂, Zn₂SnO₄ and ZnSnO₃ are possible precipitate phases.^{23),24)} Palmer and Poepelmeier²⁵⁾ studied the phase relation of the Ga₂O₃–SnO₂–ZnO system. They reported that the solubility limit of Zn in SnO₂ was less than 0.7%. Zn is incorporated in SnO₂ grains only at relatively low concentrations when SnO₂ is sintered at a high temperature of 1400°C, ZnO has a high vapor pressure.

Oxygen vacancy in SnO₂ has been investigated by optical methods such as photoluminescence (PL) and cathodoluminescence (CL) measurements. Such measurements revealed that oxygen vacancies in SnO₂ generate deep level luminescence of the peak at 1.94 eV (wavelength: 640 nm).^{26),27)} Another method to evaluate the oxygen vacancy, self-diffusion experiments provided further direct evidence of oxygen vacancies in SnO₂. For example, oxygen isotope diffusion can be used to directly

[†] Corresponding author: I. Sakaguchi; E-mail: SAKAGUCHI.Isao@nims.go.jp

[‡] Present address: National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

determine the relation between oxygen vacancies and dopants in oxide semiconductors.²⁸⁾ Oxygen diffusion in SnO₂ has been used to investigate the kinetics processes of sensors.²⁹⁾

The present study focuses on dense SnO₂ ceramics produced by ZnO addition because the ZnO–SnO₂ system is expected to give transparent ceramics. CL and PL measurements were used to detect oxygen vacancies in ZnO doped SnO₂ ceramics. Oxygen tracer diffusion and zinc distribution in ZnO doped SnO₂ ceramics were investigated by ion beam techniques such as secondary ion mass spectrometry (SIMS) to find ways to improve the sinterability of SnO₂ ceramics. Direct measurements of oxygen diffusion using ¹⁸O tracers are suitable for investigating the chemistry of oxygen defects in SnO₂. Finally, we propose a model for the formation of dense SnO₂ ceramics by ZnO addition.

2. Experimental methods

Dense SnO₂ ceramics were prepared by conventional sintering technique. The reagent-grade powders of SnO₂ and ZnO (High-Purity Chemicals Ltd.) were used as the starting materials. From previous studies, X-ray powder diffraction analyses indicated that ZnO–SnO₂ secondary phases were not present in SnO₂ ceramics with a ZnO concentration of below about 5 mol.%.^{14)–16)} Since these results indicate that it is possible to fabricate dense SnO₂ that does not contain secondary phases. Consequently, we selected ZnO concentration of 0.25 mol.% in the present study, from the preliminary experiments to fabricate the dense SnO₂ ceramics added with ZnO. 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). These disks were sintered at 1440°C for 2 h in air. The sintered disks were polished and finished with several grades of diamond pastes. After the sample surfaces had been mirror finished, they were washed with ethanol. The samples were annealed at 1000°C for 30 min in air, to remove the polishing damages. The ZnO doped SnO₂ ceramics (Zn–SnO₂) with the relative density of 91% were used as the substrate.

Zn–SnO₂ ceramics were characterized by photoluminescence, PL, (Accent Technology Co. Ltd., RPM-2000; $\lambda = 266$ nm). The following measurements were performed. Their microstructures were evaluated by scanning electron microscopy (SEM; JEOL, JSM-7000F) equipped with a cathode luminescence, CL, detector (Gatan, Mini CL). SEM and CL images were obtained by using a focused electron beam (acceleration voltage: 15 kV).

Zn–SnO₂ ceramics were used to evaluate diffusion of ¹⁸O₂ gas (95% purity). The sample was loaded into an exchange system to achieve ¹⁸O diffusion. This was then annealed at 1000°C for 3 h. The oxygen tracer diffusion profiles and Zn distribution in SnO₂ ceramics were measured by SIMS (Cameca, IMS-6f and IMS-1270 at Hokkaido university). In the measurement of oxygen tracer concentration profiles, the ¹⁶O and ¹⁸O intensities were measured as a function of time. After analysis, the SIMS crater depth was measured using a laser scanning microscope (Keyence, VK-9710; wavelength: 408 nm). The obtained depth profiles were converted to ¹⁸O concentration profiles using the following equation: $C_{(x,t)}[^{18}\text{O}] = I[^{18}\text{O}] / [I[^{16}\text{O}] + I[^{18}\text{O}]]$, where $C[^{18}\text{O}]$ and $I[^{18}\text{O}]$ are the ¹⁸O concentration and the ¹⁸O intensity. Moreover, direct ion images of ¹⁶O[–], ¹⁸O[–], (ZnO)[–], and (SnO)[–] in SnO₂ ceramics were obtained using IMS-1270 equipped with a high-efficiency stacked CMOS active pixel sensor for charged particles.³⁰⁾ This instrument can directly measure ion images with high signal-to-noise ratios in the high-resolution mode of a mass spectrometer because the lateral resolution of ion images is independent of the primary ion beam size. The signal ratio of ZnO

and SnO negative ions was converted into the ZnO concentration using the inner standard produced by Zn ion implantation.

3. Results and discussion

Figure 1 shows the results of microstructure by SEM and optical properties by CL measurements. The SEM image in Fig. 1(a) reveals that the sample is dense and contains grains with diameters in the range 2–10 μm . The CL image in Fig. 1(b) indicates the distribution of radiative and non-radiative defects in the sample. Figures 1(a) and 1(b) reveal that CL signal is emitted from grains, but not near grain boundaries. These are evident of the different state around the defect.

Figure 2 shows PL spectrum of the SnO₂ sample. Sample contains a simple peak at a wavelength of 640 nm. Orange luminescence at a wavelength of 640 nm was observed in a previous study and it was assigned to oxygen vacancies, $V_{\text{O}}^{\bullet\bullet}$, in SnO₂.²⁷⁾ From Fig. 1(b), the SnO₂ grains contain oxygen vacancy as the radiative defect. On the other, it seems that oxygen vacancy as the non-radiative defect presents near the grain boundaries.

Figure 3 shows oxygen diffusion profile obtained for Zn–SnO₂ annealed at 1000°C for 3 h. It has an ¹⁸O surface concentration of 0.09, which is considerably smaller than that for ¹⁸O₂ gas, indicating that the surface reaction became a limited process in the experiment and O isotopic exchange is dominant at grain boundaries. The oxygen bulk diffusion coefficient was estimated roughly to be $2 \times 10^{-16} \text{ cm}^2/\text{s}$.³¹⁾ A high-resolution image of ¹⁸O was obtained in the tail region, and result shows the inset of Fig. 3. The grain boundaries exhibited a constant intensity of ¹⁸O. The grain boundary diffusion coefficient could not be determined because selective sputtering during SIMS measurements.

Figure 4 shows a high-resolution concentration map and line analysis of the SnO₂ ceramics. Figure 4(a) shows a concentration

Fig. 1. Microstructure and optical property of Zn–SnO₂. (a) SEM image and (b) CL image.

Fig. 2. Photoluminescence spectrum obtained in Zn–SnO₂ sample.

image of $(\text{ZnO})^-$ in which Zn segregates at all grain boundaries. The Zn concentration in this image varies at grain boundaries. The Zn concentration in SnO_2 grain is enough small rather than that of grain boundary segregation. Some particles with high Zn concentration were found at the triple junctions and grain boundaries. These were secondary phase related with Zn– SnO_2 . Figure 4(b) shows the results of line analysis between the line I–II in Fig. 4(a). The grain boundaries of SnO_2 grains have Zn concentrations of about 3×10^{18} and $1.4 \times 10^{19}/\text{cm}^3$ in this figure. The above results indicate a considerably low Zn concentration in SnO_2 grains and grain boundary segregation of Zn. These findings suggest that Zn segregation at the grain boundaries is a critical phenomenon for densification of SnO_2 ceramics.

Our results in Figs. 1(b) and 2 indicate that the defect, oxygen vacancy, is different state in the grains and the grain boundaries. So, we discuss by separating the oxygen defect in grain and at the grain boundaries. On the oxygen defect in the grains, the oxygen defect such as vacancy acts as the radiative defect [Figs. 1(b) and 2]. The oxygen defect formation relates with the sintering process. Quadir and Readey⁷⁾ studied sintering of SnO_2 in a hydrogen atmosphere. They found that SnO_2 disks expanded due to agglomerate growth of grains due to evaporation and condensation above 1200°C . The process can be expressed by

Fig. 3. ^{18}O diffusion profile obtained for Zn– SnO_2 . The inset shows an ^{18}O ion image at the depth of 400 nm.

Fig. 4. High-resolution ion image (a) and line analysis (b) of Zn for Zn– SnO_2 . (a) high-resolution Zn image and (b) line analysis along I–II in Fig. 4(a). GB in Fig. 4(b) shows the grain boundary.

SnO_2 behaves n-type conduction, if parts of V_{O} state as the charged vacancy. Another possible equation to form the defects in SnO_2 lattice is considered as the partial decomposition of SnO_2 . For example, the reaction is written as

As described in the above, two possible equations are considered to decompose SnO_2 . In order to improve the sinterability, several sintering aids have been used to produce dense SnO_2 ceramics. The sinterability of SnO_2 can be improved by using these aids based on the supposed enhancement in the oxygen diffusivity. Perazolli et al.¹⁴⁾ and Foschini et al.¹⁶⁾ gave the following equation for incorporation:

The Zn concentration of $3 \times 10^{18}/\text{cm}^3$ in SnO_2 grain in Fig. 4 is enough small rather than the added concentration. If above reaction is a dominant reaction, it is expected that its effect is found in the oxygen diffusion feature. Diffusion profile in Fig. 3 shows that oxygen diffusion is limited by the exchange reaction between $^{18}\text{O}_2$ and O at the surface. This reflects the lack of charge in sample and the exchange reaction depended on the atmosphere³²⁾ and temperature. Result in Fig. 3 was obtained from the diffusion experiment at 1000°C , because SnO_2 causes the decomposition and evaporation at high temperature. At this time, it is difficult to understand that diffusion phenomenon reflects the Zn incorporation in SnO_2 . So, we conclude that the origin of oxygen vacancy in SnO_2 grain is mainly described by Eqs. (1, 2).

On the oxygen defect at the grain boundaries, our results in Fig. 1(b) indicated that the defect presented as the non-radiative defect. The uniform intensity of ^{18}O at the grain boundary was observed in Fig. 3. This is the evidence that the grain boundary diffusion was independent of the grain boundary structure. Moreover, it was found Zn segregation at the grain boundaries in Fig. 4. Here, two possible models were considered the incorporation of Zn near the grain boundary in SnO_2 and the formation of grain boundary phase by Zn segregation. First model is assumed the Zn diffusion into SnO_2 grains. The amount of oxygen vacancy near the grain boundary increases by the Zn incorporation reaction of Eq. (3). From first model, the weak CL intensity near the grain boundaries in Fig. 1(b) seems to be explained such as the increase of oxygen vacancy and/or the formation of complex defect of $(\text{Zn}_{\text{Sn}}^{\prime\prime} - \text{V}_{\text{O}}^{\bullet\bullet})^\times$ from the charge neutrality. However, the feature of oxygen grain-boundary diffusion, which is the uniform intensity of ^{18}O in Fig. 3, is not explained by first model. Second model is the formation of secondary phase at the

grain boundaries during the sintering. Previous studies reported the secondary phase of Zn_2SnO_4 spinel at triple junction in SnO_2 ceramics added with the large amount of ZnO using TEM technique, but not detected Zn segregation and secondary phase at the grain boundaries. Hashemi et al.³³⁾ proposed that sintering to produce Zn_2SnO_4 ceramics could be controlled by the diffusion–evaporation mechanism of ZnO that gave rise to a higher Zn concentration at the walls of inner pores in Zn_2SnO_4 ceramics. A similar phenomenon between sintering and the additive was found for transparent alumina (Al_2O_3) ceramics fabricated by MgO addition.³⁴⁾ In this case, Mg segregation at the grain boundaries suppressed abnormal grain growth. Approach from oxygen diffusion study revealed the uniform oxygen diffusivity at the grain boundaries of alumina by Mg segregation at the grain boundaries.³⁵⁾ Consequently, transparent alumina ceramics results from the good sinterability were produced. In this study, similar results were found such as the oxygen grain-boundary diffusion independent of the grain boundary structure in Fig. 3 and Zn segregation at the grain boundary in Fig. 4. From the analogy, it seems that the secondary phase with ZnO and SnO_2 compositions at the grain boundary is formed during the sintering and SnO_2 grains are covered with the secondary phase. As a result, the Zn segregated grain boundaries suppress the decomposition and evaporation of SnO_2 described by Eqs. (1, 2), and cause the uniform oxygen transport along the grain boundaries. Finally, the dense SnO_2 ceramics are synthesized.

4. Conclusions

We have fabricated the dense SnO_2 ceramics added with ZnO of 0.25 mol.% to study the optical property, oxygen tracer diffusion, and elemental distribution. The following findings were obtained:

- 1) SEM image shows that Zn-SnO_2 ceramics is dense. CL image reveal that radiative and non-radiative oxygen vacancies are concentrated in grains and grain boundaries, respectively. PL measurements gave a simple spectra with a peak centered at a wavelength of about 640 nm, which was assigned to oxygen vacancies.
- 2) Oxygen diffusion using ^{18}O indicates that the diffusion is controlled by the surface reaction. Additionally, the uniform intensity of ^{18}O was observed at the grain boundaries.
- 3) The Zn distribution in dense SnO_2 ceramics was measured by using SIMS loaded with a SCAPS. The Zn concentration in SnO_2 grains is considerably smaller than the added Zn concentration. Zn segregation was observed at grain boundaries.
- 4) The change in the physicochemical properties of SnO_2 induced by Zn segregation at the grain boundaries gave insight into the densification of SnO_2 ceramics. The densification of SnO_2 ceramics by ZnO addition is due to the Zn -rich grain boundaries formed by Zn diffusion and evaporation acting as barriers to suppressing decomposition and condensation of SnO_2 . Consequently, dense SnO_2 ceramics are fabricated.

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