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

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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.

Key-words : Oxygen vacancy, Segregation, SnO₂, Secondary ion mass spectrometry

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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,⁴ 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 without constituents evaporate during sintering.

Jarzebski and Marton⁵ reviewed research prior to 1976 on preparing SnO₂ and its defect chemistry. Van Daal⁶ grew polycrystalline SnO₂ by vapor transport and realized a bulk density of 95%. Samson and Fonstad⁷ 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 Readey⁸ 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.⁹ synthesized dense SnO₂ ceramics without additives at high temperature and high pressure. Another way to synthesize dense SnO₂ ceramics is to use additives. Useful additives for SnO₂ are MnO₂,¹⁰ CoO,¹⁰ CuO,¹¹ ZnO,¹²–¹⁷ Nb₂O₅,¹⁸ Sb₂O₃,¹⁹ In₂O₃²⁰ 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, Zn₃SnO₄ and ZnSnO₃ are possible precipitate phases.²² Palmer and Poppelmeier²³ 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...
determine the relation between oxygen vacancies and dopants in oxide semiconductors.\textsuperscript{26,27} Oxygen diffusion in SnO\textsubscript{2} has been used to investigate the kinetics processes of sensors.\textsuperscript{28}

The present study focuses on dense SnO\textsubscript{2} ceramics produced by ZnO addition because the ZnO–SnO\textsubscript{2} system is expected to give transparent ceramics. CL and PL measurements were used to detect oxygen vacancies in ZnO doped SnO\textsubscript{2} ceramics. Oxygen tracer diffusion and zinc distribution in ZnO doped SnO\textsubscript{2} ceramics were investigated by ion beam techniques such as secondary ion mass spectrometry (SIMS) to find ways to improve the sinterability of SnO\textsubscript{2} ceramics. Direct measurements of oxygen diffusion using \textsuperscript{18}O tracers are suitable for investigating the chemistry of oxygen defects in SnO\textsubscript{2}. Finally, we propose a model for the formation of dense SnO\textsubscript{2} ceramics by ZnO addition.

2. Experimental methods

Dense SnO\textsubscript{2} ceramics were prepared by conventional sintering technique. The reagent-grade powders of SnO\textsubscript{2} and ZnO (High-Purity Chemicals Ltd.) were used as the starting materials. From previous studies, X-ray powder diffraction analyses indicated that ZnO–SnO\textsubscript{2} secondary phases were not present in SnO\textsubscript{2} ceramics with a ZnO concentration of below about 5 mol.\%\textsuperscript{14-16} Since these results indicate that it is possible to fabricate dense SnO\textsubscript{2} 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 SnO\textsubscript{2} 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 SnO\textsubscript{2} ceramics (Zn–SnO\textsubscript{2}) with the relative density of 91% were used as the substrate.

Zn–SnO\textsubscript{2} 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–SnO\textsubscript{2} ceramics were used to evaluate diffusion of \textsuperscript{18}O\textsubscript{2} gas (95\% purity). The sample was loaded into an exchange system to achieve \textsuperscript{18}O diffusion. This was then annealed at 1000°C for 3 h. The oxygen tracer diffusion profiles and Zn distribution in SnO\textsubscript{2} ceramics were measured by SIMS (Cameca, IMS-6f and IMS-1270 at Hokkaido university). In the measurement of oxygen tracer concentration profiles, the \textsuperscript{18}O and \textsuperscript{16}O 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 \textsuperscript{18}O concentration profiles using the following equation: 
\[
C_{C} = \frac{I_{[18O]}}{I_{[18O]} + I_{[16O]}},
\]
where \(I_{[18O]}\) and \(I_{[16O]}\) are the \textsuperscript{18}O and \textsuperscript{16}O intensities. Moreover, direct ion images of \textsuperscript{18}O\textsuperscript{+}, \textsuperscript{16}O\textsuperscript{+}, (ZnO)\textsuperscript{+}, and (SnO\textsubscript{2})\textsuperscript{+} in SnO\textsubscript{2} ceramics were obtained using IMS-1270 equipped with a high-efficiency stacked CMOS active pixel sensor for charged particles.\textsuperscript{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 SIMS image in Fig. 1(a) reveals that the sample is dense and contains grains with the diameter of about 2–10 \(\mu\)m. 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 SnO\textsubscript{2} 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, \(V_{O}^{\bullet}\), in SnO\textsubscript{2}.\textsuperscript{27} From Fig. 1(b), the SnO\textsubscript{2} grains contain oxygen vacancy as the radiative defect. On the other, it seems that oxygen vacancy as the non-radiative defect present near the grain boundaries.

Figure 3 shows oxygen diffusion profile obtained for Zn–SnO\textsubscript{2} annealed at 1000°C for 3 h. It has an \textsuperscript{18}O surface concentration of 0.09, which is considerably smaller than that for \textsuperscript{18}O\textsubscript{2} 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 \(2 \times 10^{-10} \mathrm{cm}^{2} / \mathrm{s}\).\textsuperscript{31} A high-resolution image of \textsuperscript{18}O was obtained in the tail region, and result shows the inset of Fig. 3. The grain boundaries exhibited a constant intensity of \textsuperscript{18}O. 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 SnO\textsubscript{2} ceramics. Figure 4(a) shows a concentration
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 \(3 \times 10^{18}\) and \(1.4 \times 10^{18}\)/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 Readey\(^7\) 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

\[
\text{SnO}_2 \rightarrow \text{Sn}_\infty^0 + O_\infty^0 + V_{\text{Sn}}^{-0} + 2e^- + 1/2\text{O}_2(g). \quad (1)
\]

SnO\(_2\) behaves n-type conduction, if parts of Vo state as the charged vacancy. Another possible equation to form the defects in SnO\(_2\) lattice is considered as the partial decomposition of SnO\(_2\).

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.\(^{13}\) and Foschini et al.\(^{16}\) gave the following equation for incorporation:

\[
\text{ZnO} \rightarrow \text{Zn}_\infty^0 + V_{\text{O}}^{-0} + O_\infty^0. \quad (3)
\]

The Zn concentration of \(3 \times 10^{18}\)/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 atmosphere\(^{12}\) 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 \(^{18}\text{O}\) 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 \((\text{Zn}_\infty^0 - V_{\text{O}}^{-0})\) from the charge neutrality. However, the feature of oxygen grain-boundary diffusion, which is the uniform intensity of \(^{18}\text{O}\) in Fig. 3, is not explained by first model. Second model is the formation of secondary phase at the

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**Fig. 3.** \(^{18}\text{O}\) diffusion profile obtained for Zn-SnO\(_2\). The inset shows an \(^{18}\text{O}\) 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.
grain boundaries during the sintering. Previous studies reported the secondary phase of Zn$_2$SnO$_4$ 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.\textsuperscript{33} proposed that sintering to produce Zn$_2$SnO$_4$ 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$_2$SnO$_4$ ceramics. A similar phenomenon between sintering and the additive was found for transparent alumina (Al$_2$O$_3$) ceramics fabricated by MgO addition.\textsuperscript{34} In this case, Mg segregation at 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 $^{16}$O indicates that the diffusion is controlled by the surface reaction. Additionally, the uniform intensity of $^{16}$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.