Difference of the responses between SnO₂ and ZnO to reducing gases at 300°C and below via optical and electrical approaches

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The responses of SnO₂ and ZnO were investigated to several atmospheres via optical and electric approaches. Optical absorption spectroscopy was adopted to detect the formation of the defect levels in the energy-band-gaps by the reducing treatments, while the changes in the electric properties of the materials were evaluated by Hall effect measurements. The electric measurements revealed that the response of the SnO₂ films to 0.5% H₂/N₂ consisted of two components. One was steep rise of the electric conductance as the films were exposed to the gas, and the second was gradual increase after the conductance jump, which lasted for several hours until reaching a plateau. The SnO₂ films after reaching the plateau exhibited the enhancement of optical absorption between 340 and 800 nm and it was attributed to the formation of oxygen vacancies by the reducing treatment. The Hall effect measurements revealed that the increase of the electric conductivity of the SnO₂ films was a consequence of increase of both the carrier concentration and the mobility. On the other hand, a change of the optical absorption was not observed for ZnO and Al-doped ZnO films against 0.5% H₂/N₂ up to the treatment temperature of 400°C. The Al–ZnO films showed the carrier concentration dependence in the responses. When Al was doped in ZnO to enhance the carrier concentration at a relatively low level (≈10¹⁹ cm⁻³), the change of the electric conductivity according to the atmosphere did follow the change of the mobility. As the carrier concentration increased to ≈10²¹ cm⁻³ with higher Al doping, the response became dominantly influenced by the change of the carrier-concentration according to the atmosphere. Even though SnO₂ and ZnO are both typical semiconductive oxides, the interaction with the atmospheres is different from each other.

Key-words : Oxygen vacancy, SnO₂, ZnO, Optical absorption, Gas sensor, Semiconductive oxide, Defect

1. Introduction

Semiconductive oxides have been widely used in various applications such as transparent electrodes, gas sensors and thermisors. SnO₂, ZnO and In₂O₃ are typical n-type semiconductive oxides which have attracted a great interest for many years. Each oxide would be an insulator with a certain width of band-gap energy if it has the ideal, stoichiometric composition. However, the real materials often show electric conductivity because of the inevitably included defects. The oxygen vacancies in oxide materials have been considered to be an origin of the electric conductivity and they work as electron donors according to the conventional Kröger-Vink notation [Eq. (1)].

\[ \text{O}_2^\text{–} \rightarrow \text{V}_\text{O}^{2\text{–}} + 2e^- + 1/2 \text{O}_2 \uparrow \quad (1) \]

On the other hand, it is still controversial whether or not oxygen vacancies themselves solely act as donors. For example, S. Samson et al. evaluated the energy depth of the oxygen vacancies in SnO₂ by measuring the electric conductivity under different oxygen partial pressures. According to them, the defect levels of the oxygen vacancies in SnO₂ were 30 and 150 meV deep for the first (V₀⁰) and second (V₀¹) ionized levels from the bottom of the conduction band. Theoretical approaches suggested that the donor levels of the oxygen vacancies were not shallow as electron donors at room temperature (RT). Other defect types such as a defect pair of an interstitial tin atom and an oxygen vacancy, and hydrogen solved in the lattice are proposed for the shallow donors for SnO₂ and ZnO, respectively.

The electric conductivity of the semiconductive materials varies according to the atmosphere at the moderately heated conditions between about 200 and 500°C. Such a nature has been used in the gas sensor application. The conductivity of the n-type oxides is enhanced when they are exposed to the reducing, flammable gases. The mechanism has been explained with the attachment and detachment of the chemisorbed oxygen atoms on the material surfaces. According to the model, the chemisorbed oxygen atoms capture the carrier electrons near the surfaces. The electrons are released when the chemisorbed oxygen atoms are removed by the gas molecules from the surfaces. It results in the increasing number of the carrier electrons and, hence, enhances the electric conductivity of the materials. The change of the potential-barrier-height at the grain boundaries in different atmospheres also affects the electric conductivity, and these models successfully explain the so-called ‘grain size effect’ of the semiconductor-type gas sensors.

There are several works investigating the interaction between SnO₂ and the atmospheres on the single crystalline surfaces. K. Shimano et al. investigated the (1 1 0) surface of a SnO₂ single crystal with scanning tunneling microscopy (STM). They found the change of the contrast in the STM images in the different atmospheres and explained it with the adsorption and desorption of O₂⁻ (molecularly adsorption) and O⁻ on the surface. These species have been believed to be adsorbed on the sur-
face and the presence was indicated in electron spin resonance (ESR) in, e.g., a study by S.-C. Chang on the surfaces of SnO$_2$ powder. However, the detection of these species was rather uncommon and some following research failed to detect the signals from paramagnetic O$^-$ and O$_2^-$ on SnO$_2$, although they should exist abundantly on the surfaces. The interpretation of ESR results might have to be carefully done because they are affected by paramagnetic additives or impurities.

D. F. Cox et al. extensively investigated the (1 1 0) surface of SnO$_2$ by ion-scattering spectroscopy (ISS) and ultraviolet photoelectron spectroscopy (UPS). They found that there were two types of oxygen vacancies on the ideal SnO$_2$ (1 1 0) surface, namely ‘bridging’ and ‘in-plane’ oxygen vacancies. According to them, the bridging oxygen vacancies did not affect the surface electric conductivity whereas other types of defects (including in-plane oxygen vacancies) increased the conductivity above 427°C (700 K).

The knowledge from ideal surfaces in ultra-high vacuum or defect chemistry based on the thermodynamically equilibrium conditions above 800°C surely provides an insight of the surface phenomena. On the other hand, the materials in the real situations, such as gas sensors, are usually polycrystalline with a lot of surface defects. They typically work under thermodynamically equilibrium conditions below 500°C, where it is expected that the conditions are quite different from the ideal ones. As seen in the case of semiconductor-type gas-sensors, single crystalline SnO$_2$ did not necessarily exhibit a good performance and, therefore, incompleteness including surface defects and grain boundaries clearly plays important roles in the actual devices. In this work, we focus on the material conditions of polycrystalline SnO$_2$ and ZnO thin-films under air and reducing gases at the moderately heated conditions from 100 to 300°C, which are typical working-temperatures of semiconductor-type gas-sensors. The results may bring a new, useful knowledge to understand the mechanism of gas sensing and also the origin of the semiconductivity. Here, we adopted ultra-violet and visible-light (UV–Vis.) spectroscopy and the Hall effect measurements. Some oxide materials are optically transparent with the sufficiently wide energy-band-gap. The optical absorption edges exist in the UV region near the visible-light region. Suppose that the oxygen vacancies are deep donors as proposed in the literature, the defect levels should arise in the visible-light region near UV and they are readily detected by an optical absorption technique. Besides, the Hall effect measurements would provide an information about the change in the electronic states according to or regardless of the detectable defects in optical absorption. The motivation of this work is providing a new insight about the semiconductive oxides with the combination of the optical and electric techniques. The concept is schematically illustrated in Fig. 1.

2. Experimental

Polycrystalline transparent films were essential for the optical characterization in this work. A liquid phase deposition method and a dip-coating method were used for preparing SnO$_2$ and ZnO, respectively, because these methods offered crack-free, highly-transparent polycrystalline films without any preferred orientation for respective oxides in ordinary laboratory equipment as described in Results and discussion.

In the liquid phase deposition method for SnO$_2$, a commercial reagent of SnF$_2$ (99%, Sigma-Aldrich, USA) was solved in water at 50°C at a concentration of 0.02 mol dm$^{-3}$. A quartz-glass substrate was immersed in the solution for 1 to 48 h, where SnF$_2$ gradually hydrolyzed in the solution and a SnO$_2$ thin-film was spontaneously formed on the substrate surface. After removing the substrate out of the solution, the coated substrate was washed with deionized water and dried at RT. The dried film was heat-treated at 500°C in air for 1 h. The coating procedure was repeated 1 to 4 times to attain an appropriate thickness. The film was finally annealed at 800°C in air for 6 h.

ZnO thin-films were prepared by a dip-coating technique similar to those reported in the literature. Zinc acetate dihydrate Zn(CH$_3$COO)$_2$·2H$_2$O (99.5%, Wako, Japan) was solved in methanol at a concentration of 0.2 mol dm$^{-3}$. 2,2′-iminodiethanol (diethanolamine, DEA) (99%, Kanto, Japan) was added as a sol stabilizer at a ratio of DEA/Zn = 5. Al was added as donors to increase the carrier concentration. Aluminum nitrate enneahydrate Al(NO$_3$)$_3$·9H$_2$O (99%, Kanto, Japan) was solved in methanol. Acetylacetone (acac) (99.5%, Kanto, Japan) was added to the solution as a stabilizer at a ratio of acac/Al = 5. Then, the Al solution was mixed with the Zn acetate solution. A quartz-glass substrate was dipped in the mixed solution. The substrate was kept in the solution for 1 min and withdrawn at 0.77 mm/s. The film was kept in methanol vapor for 3 min to prevent rapid drying. Then, the film was dried in air at 50°C for 1 min and calcined in air at 500°C for 7 min. The coating sequence was repeated 15–20 times to attain a certain thickness. Finally, the film was annealed at 500°C in air for 5 h.

In order to investigate the material conditions in different atmospheres, the films were treated in air, 0.5% H$_2$/N$_2$, 0.5% H$_2$/air and N$_2$ in a tubular furnace of quartz glass at 100–400°C. The optical and electric measurements were carried out after each treatment, where the films were withdrawn from the hot-zone of the furnace to the end of the tube to cool down to RT quickly. Then, the films were taken out of the furnace and characterized at RT in the open atmosphere. The optical characterization was carried out with a Xe short arc lamp (Ushio UI-501C, Japan) and a multi-channel spectral analyzer (Hamamatsu PMA-11, Japan) with a laboratory-made apparatus for the transmittance measurements. For the Hall effect measurements, the Au electrodes were formed on the films. Au was chosen because the sensitizing effects are relatively smaller than other noble metals such as Ag, Pt and Pd against hydrogen. Some papers have reported the sensitizing effect of Au to CO but it is not significant for hydrogen. The Hall effect measurements were carried out at RT under the atmospheric conditions (open air). The equipment was composed of an electromagnet (Echo Denshi EM-15055, Japan) with the strength of the magnetic field of 0.55 T; a dc voltage/current generator (Takeda Riken TR6141, Japan) and a digital multimeter (Agilent 34401A, USA).
Table 1. Electric conductivity ($\sigma$), carrier concentration ($n$) and Hall mobility ($\mu$) of a SnO$_2$ film of 380 nm thick after the treatment in different atmospheres. The values in the brackets are the factors of the enhancement compared to the values for ‘air’.

|                        | air           | N$_2$          | H$_2$/air      | H$_2$/N$_2$short | H$_2$/N$_2$ |
|------------------------|---------------|----------------|----------------|------------------|------------|
| $\sigma$ /S cm$^{-1}$  | 3.0 $\times$ 10$^{-1}$ [1] | 8.7 [29]       | 9.7 [32]       | 12 [40]         | 48 [160]  |
| $n$ /cm$^{-3}$         | 1.1 $\times$ 10$^{18}$ [1] | 6.9 $\times$ 10$^{18}$ [6.3] | 7.5 $\times$ 10$^{18}$ [6.8] | 9.6 $\times$ 10$^{18}$ [8.7] | 1.8 $\times$ 10$^{19}$ [16] |
| $\mu$ /cm$^2$V$^{-1}$s$^{-1}$ | 1.8 [1] | 7.9 [4.4]       | 8.1 [4.5]       | 7.8 [4.3] | 17 [9.4]   |

3. Results and discussion

3.1 Characterization of the films

The characteristics of the SnO$_2$ films prepared by the liquid phase deposition method were described in our previous paper in detail$^{[21]}$ and they are briefly reviewed here. The films were composed of nano-sized grains less than 15 nm and the relative density was ca. 50% which was evaluated by comparing the thickness optically determined with the peak-valley method and that directly determined by cross-sectional observation in SEM. As discussed later, the carrier concentration of a 380 nm-thick film was 1.1 $\times$ 10$^{18}$ cm$^{-3}$ (Table 1) after annealing in air at 800°C and, therefore, it was considered that a trace amount of fluorine was incorporated in the film as donors from the starting material (SnF$_2$). In the liquid phase deposition method, an oxide material is formed under the thermodynamically equilibrium conditions and, therefore, impurities are unlikely to be incorporated in the targeting material.$^{[28,29]}$ Although the F$^-$ contamination was suggested in the films, the contamination level was estimated to be as low as 0.02 at % to O$^{2-}$ suppose that all the carriers (1.1 $\times$ 10$^{18}$ cm$^{-3}$) originated in F$^-$. This value is high enough to influence the electric properties of a semiconductor but is still low for an additive as sensitizers are usually added at a few wt %. From the bases of, (1) the concentration of F$^-$ is quite low, if it exists, (2) it is dispersed over the material uniformly, and (3) it is not plausible that F$^-$ affects the adsorption properties of the molecules relating to gas-sensing at the surfaces, the effect of the F$^-$ contamination on the gas-sensing properties is considered to be limited. It might reduce $R_{w}$ (electric resistance in air) and, hence, the slight reduction of the magnitude of the response ($=R_{w}/R_{gas}$ with resistance in gas, $R_{gas}$).

The ZnO films prepared in this work were also polycrystalline without any preferred orientation. Figure 2 shows the XRD patterns of the dip-coated ZnO films with different Al concentrations. All the peaks were assigned to wurtzite-type ZnO (JCPDS #36-1451) and the XRD patterns confirmed the formation of polycrystalline ZnO on the glass substrates regardless of the Al concentration. Figure 3 shows the surface morphologies of a ZnO (Al/Zn = 0) film observed by SEM (Fig. 3(a)) and SPM (Fig. 3(b)). The SEM image in Fig. 3(a) exhibits the flat surface without cracks, voids and abnormally-grown grains. The SPM image [Fig. 3(b)] shows that the film is composed of closely packing, spherical grains of ca. 200 nm in size. From the cross-sectional observation, the thickness of the 20-time-coated film was 220 nm. Therefore, the increment of the thickness by each coating was about 10 nm. The relative density was estimated to be 94% to the ideal value of ZnO (5.7 g/cm$^3$), which was derived in the same way as the SnO$_2$ films.
The conductance of the film was about $1.0 \times 10^{-8}$ S in air and it jumped up to $6.0 \times 10^{-8}$ S when the film was exposed to $0.5\%$ H$_2$/air [Fig. 4(a)] and it reached a plateau promptly. A ratio of the electric conductance between in gas ($C_{\text{gas}}$) and in air ($C_{\text{air}}$), $C_{\text{gas}}/C_{\text{air}}$ ($=R_{\text{air}}/R_{\text{gas}}$), was 6 for $0.5\%$ H$_2$/air. This value is not very high for a SnO$_2$ gas sensor but it is reasonable because any sensitizers were not added. On the other hand for $0.5\%$ H$_2$/N$_2$ [Fig. 4(b)], two types of responses are recognized, namely 'quick response' and 'slow response'. The conductance jumped to $3.5 \times 10^{-7}$ S [quick response, A $\rightarrow$ B in Fig. 4(b)] as the film was exposed to the gas and the conductance continued to increase gradually up to $3.1 \times 10^{-6}$ S (slow response, B $\rightarrow$ C). For $0.5\%$ H$_2$/N$_2$, $C_{\text{gas}}/C_{\text{air}}$ is about 35 for the quick response and it gradually increased during the slow response to 310 at Point C.

Figure 5(a) compares the optical absorption spectra of a SnO$_2$ thin-film of 380 nm thick after the treatments in air, $0.5\%$ H$_2$/N$_2$ and $0.5\%$ H$_2$/air for 4 h at 300°C. As described in Experimental section, the absorption spectra were measured in open-air under the atmospheric conditions after each treatment. Here, the difference between the spectra should be noted because the oscillation itself in each spectrum is due to the interference of the light between the surfaces of the thin-film and the substrate. Figure 5(b) is the differential absorbance spectrum between $0.5\%$ H$_2$/N$_2$ and air to cancel out the interference oscillation. The absorption decreases below 340 nm because of the Burstein–Moss effect and increases between 340 and 800 nm with the maximum around 380 nm. Figure 5 clearly shows that the optical absorption was enhanced specifically when the film was treated in H$_2$/N$_2$. This absorption enhancement in H$_2$/N$_2$ reversibly disappeared when the film was treated in air again.
that the spectra were unchanged from that of ‘air’. Again, the spectral change was characteristic for the treatment in 0.5% H2/N2 after a certain period of treatment time [after Point C in Fig. 4(b)].

The electric conductivity (σ) was 3.0 × 10⁻¹¹ S cm⁻¹ for the SnO2 film treated in air with n = 1.1 × 10¹⁹ cm⁻³ and μ = 1.8 cm² V⁻¹ s⁻¹. σ increased in the other atmospheres and it became 8.7, 9.7, 12 and 48 S cm⁻¹ for N2, H2/air, H2/N2-short and H2/N2-long respectively. They increased by the factors of 2.9, 3.2, 40 and 160 compared to σ in air. n changed from 1.1 × 10¹⁸ cm⁻³ for air to 6.9 × 10¹⁸, 7.5 × 10¹⁸, 9.6 × 10¹⁸ and 1.8 × 10¹⁹ cm⁻³ for N2, H2/air, H2/N2-short and H2/N2-long respectively. They increased by the factors of 6.3, 6.8, 8.7 and 16 compared to n in air. σ is proportional to n×μ and the enhancement of σ is not explained only by n. Therefore, the enhancement of σ is a consequence of the increase in both n and μ. The electric properties of the SnO2 film are similar to each other for N2, H2/air and H2/N2-short. σ and μ are near 10 S cm⁻¹ and 8 cm² V⁻¹ s⁻¹, respectively, and n is between 7 × 10¹⁸ and 1 × 10¹⁹ cm⁻³. The interaction with these atmospheres was inferred to be basically similar. The treatment in H2/N2 further increased n and μ twice during the slow response [B → C in Fig. 4(b)], leading to the enhancement of the optical absorption.

As described above, the response to H2/N2 is divided into the quick and slow responses. The quick response is a common feature to semiconductor-type gas-sensors, which has been considered to be based on the detachment of chemisorbed oxygen. The slow response is proposed to relate to the oxygen vacancies from SnO2.1) It excludes the possibility of the formation of the low-valence oxide (SnO) in the film because the conversion between SnO2 and SnO is not topotactic. If SnO is formed in each reducing cycle, the in-plane oxygen vacancies brought the surface conductivity, leading to the occupied state (by the defect levels) distributed in the band-gap below the conduction-band-minimum. Our results on the optical absorption [Fig. 5(b)] indicate rather wide distribution of the defect levels in the visible-light region. Such wide distribution seems to be a common feature in spectral approaches as shown also in UPS,17) although S. Samson estimated the value of 150 meV for the second ionization level of oxygen vacancies in SnO2.1)

Figure 7 schematically illustrates the image of the above discussion about the two responses.

3.3 Responses of ZnO

A typical response of the ZnO (Al/Zn = 0) film to 0.5% H2/air at 300°C is shown in Fig. 8. The thickness was ca. 30 nm. The conductance of this film is 1.0 × 10⁻¹¹ S in air at 300°C. Cgas/Cair in this case is 8.4 to 0.5% H2/air. The response to the gas is somewhat slower than that of the SnO2 film in Fig. 4(a).

It was found that the ZnO films treated in air were highly resistive for the electric measurements at RT and that made it difficult to evaluate the electric properties for some ZnO films properly. Therefore, in order to characterize the responses of ZnO, (1) the elevated temperatures.17) They classified the surface oxygen on a nearly-ideal SnO2 (1 1 0) surface into ‘bridging’ and ‘in-plane’ oxygen atoms. The former is the outermost oxygen atoms bridging between the tin atoms underneath and the latter is the oxygen atoms in the second layer aligned with the tin atoms. They suggested that the vacancies of the bridging oxygen were rather acceptor-like and they did not significantly enhance the surface conductivity. The in-plane oxygen vacancies brought the surface conductivity, leading to the occupied state (by the defect levels) distributed in the band-gap below the conduction-band-minimum. Our results on the optical absorption [Fig. 5(b)] indicate rather wide distribution of the defect levels in the visible-light region. Such wide distribution seems to be a common feature in spectral approaches as shown also in UPS,17) although S. Samson estimated the value of 150 meV for the second ionization level of oxygen vacancies in SnO2.1)
electric conductivity of the ZnO films was enhanced by Al-doping and (2) the degrading phenomena of the electric conductivity were examined instead of measuring the conductivity at a constant temperature. There, the Al-ZnO films were initially treated in 0.5% H$_2$/N$_2$ at 200°C for 3 h to enhance the electric conductivity and, then, the films were treated in air at a temperature from 100 to 200°C with a 5 or 10°C step. The electric properties were measured after each treatment in air. Hereafter, they were discussed based on the ‘initial carrier concentration ($n_{\text{init}}$), which is the carrier concentration after the treatment in 0.5% H$_2$/N$_2$ at 200°C, instead of indicating the Al concentration nominally. For example, $n = 1 \times 10^{19}$ cm$^{-3}$ indicates that Al$^{3+}$ effectively replaces 0.041% of the Zn$^{2+}$ sites as active donors [Eq. (2)].

$$\text{AlZn}^{2+} \rightarrow \text{AlZn}^+ + e^- \quad \text{(2)}$$

Figure 9 compares the optical absorption spectra after the treatments in air and 0.5% H$_2$/N$_2$, of an Al-ZnO film of 210 nm thick with $n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$. In contrast to the SnO$_2$ film in Fig. 5, the enhancement of the optical absorption did not occur for the Al-ZnO film, although the electric conductivity varied with the atmosphere as discussed later. No change in the optical spectra was confirmed with the different Al concentrations including non-doped ZnO up to 400°C in 0.5% H$_2$/N$_2$.

A typical degradation behavior is shown in Fig. 10 for a $n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$ film. There, the initial conductivity (after the treatment in H$_2$/N$_2$ at 200°C) is indicated with a broken line. The treatment in air at 100°C did not bring a significant change in $\sigma$ and it was 1.3 S cm$^{-1}$. $\sigma$ began to drop at 140°C and it decreased to $3.8 \times 10^{-1}$ S cm$^{-1}$ at 170°C. A remarkable point is that the change of $n$ is limited from $1.7 \times 10^{19}$ to $8.8 \times 10^{18}$ cm$^{-3}$ between 100 and 170°C, whereas $\mu$ drastically changes nearly two orders of magnitude from $9.1 \times 10^-4$ to $2.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 170°C. $\sigma$ seems to follow the change of $\mu$ rather than $n$ and, therefore, the degradation of the conductivity in air at the elevated temperatures is attributed to the decrease of the mobility for the $n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$ film. It depicts a figure that the electric properties of the film are governed by the change of the nature of the grain boundaries (or inter-grain regions) with the unchanged inner-grain properties, and this agrees with the grain-boundary-controlled model (Fig. 11).\(^{(9,10)}\)

The further investigation exhibited a dependence of the response on the carrier concentration. Figures 12(a)–12(c) compares the degradation phenomena of the Al–ZnO films with different carrier concentrations. The deduced features are as follows. (1) $\sigma$ decreases with treatment temperature [Fig. 12(a)], $\sigma$ of the $n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$ film constantly decreases from 110°C, whereas $\sigma$ of $n_{\text{init}} = 1 \times 10^{21}$ cm$^{-3}$ film begins to drop around 170°C and it is rather sudden. The tendency of $n_{\text{init}} = 1 \times 10^{20}$ cm$^{-3}$ film is intermediate between the $n_{\text{init}} = 1 \times 10^{19}$ and $1 \times 10^{21}$ cm$^{-3}$ films. (2) The declining slopes of $n$ for all the films are similar to each other up to 160°C [Fig. 12(b)]. (3) For lower carrier concentration ($n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$), the conductivity follows the change of $\mu$. $\mu$ of the $n_{\text{init}} = 1 \times 10^{19}$ cm$^{-3}$ film steeply decreased with the treatment temperature in air, whereas the change of $\mu$ becomes smaller at higher $n$ [Fig. 12(c)]. The decrease of $n$ seems to be responsible for the degradation of the electric conductivity for the $n_{\text{init}} = 1 \times 10^{21}$ cm$^{-3}$ film rather than $\mu$. There, $\mu$ is between 1 and 10 cm$^2$ V$^{-1}$ s$^{-1}$ and a clear tendency is not recognized on $\mu$ against the temperature. The detailed mechanism is still unclear that the Al–ZnO films showed such mode change in the response depending on the carrier concentration.

### 3.4 Comparison between SnO$_2$ and ZnO

The difference between the SnO$_2$ and ZnO films is noticeable when the changes are compared at a similar carrier concentration level of $1 \times 10^{19}$ cm$^{-3}$. The further increase or decrease of $\sigma$ of the SnO$_2$ film in H$_2$/N$_2$ or air was attributed to both $n$ and $\mu$ (Fig. 6), whereas $\sigma$ of the ZnO film was largely dominated by $\mu$ (Fig. 10). It means that the nature of the grain-boundaries and/or boundary phases determines the conductivity of the polycrystalline ZnO film (Fig. 11).

The oxygen vacancies were strongly indicated to be dynamically involved in the response of SnO$_2$ to 0.5% H$_2$/N$_2$ even at
the moderately heated conditions of 300°C. On the other hand, a
detectable change related to oxygen vacancies was not observed
for ZnO and Al–ZnO, although a certain amount of oxygen
vacancies should be intrinsically contained as well as general
oxide materials. The difference can be explained by the possible
oxidation states of Sn and Zn. Sn allows the oxidation states of
Sn⁴⁺ and Sn⁵⁺ while Zn has only one oxidation state of Zn²⁺.
The change from Sn⁴⁺ to Sn⁵⁺ can compensate the reduction of
the negative charge with the formation of the oxygen vacancies,
while ZnO needs an extrinsic charge compensator against the
formation of the oxygen vacancies.

4. Summary

In this work, the responses of SnO₂ and ZnO to several gases
were investigated with optical absorption spectroscopy and Hall
effect measurements. The SnO₂ film showed two types of the
responses. The quick response was one typically observed in
semiconductor-type gas-sensors. The slow response was specific
to H₂/N₂ gas and it enhanced the optical absorption of the films
in the visible-light region. The enhanced absorption reversibly
disappeared by the treatment in air and it strongly suggested
the oxygen vacancies in the bulk-grains involved in the slow
response at the moderately heated conditions.

The ZnO and Al–ZnO films did not show any evidence relating
to oxygen vacancies. Rather, the drastic change of the mobility
at lower n and the mode change in the response at higher n were
the characteristics of the polycrystalline Al–ZnO. At lower carrier
concentration (1 × 10¹⁹ cm⁻³), μ dominated the conductivity.
The existence of the grain boundaries and/or the boundary
phases was assumed, which affected the mobility and, hence, the
electric properties of ZnO. The clear tendency of μ became
ambiguous at higher n (1 × 10²¹ cm⁻³) and, there, the conduc-
tivity seemed to be dominantly influenced by the change of
n with the atmosphere.

There is still ambiguity in the detailed mechanism of the surface
phenomena but this work revealed the difference of these
semiconductive oxides in the response against the gases.

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