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The Oxidation State of Antimony and Electrical Properties in Antimony-Doped Rutile

N. MORITA, T. ENDO, T. SATO, AND M. SHIMADA*

Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai, Miyagi 980, Japan

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The reaction of TiO_2 with Sb_2O_4 for temperatures in the range of 650 to 1000°C indicates that Sb can dissolve in rutile up to the proportion of 7 mole% in an Sb_2O_4 equivalent. With increasing content of Sb, the unit cell volume increased gradually. From the results on the binding energies of 530.6 eV for $Sb(3d_{3/2})$ and 540.1 eV for $Sb(3d_{5/2})$, it is expected that Sb was substituted as Sb^{3+} ion for Ti^{4+} in the rutile structure. The *ac* resistivities of rutile with Sb are in the range of 10^2 to 10^5 ohm · m at room temperature. The frequency and temperature dependencies of the dielectric constant can be elucidated by the ionic polarization model coupling Sb with oxygen vacancy. The activation energy, giving a loss maximum, was determined to be 0.15–0.17 eV over a frequency range of 10^4 to 10^7 Hz.

Introduction

Many works have been devoted to nonstoichiometric rutile, TiO_2, in relation to its electrical properties (*1*). The rutile structure is able to tolerate a certain amount of oxygen deficiency and the doping of foreign elements (*2*). Since it is considered that an oxygen vacancy was readily created by Ti^{3+} and a conducting electron for preserving the electroneutrality of the Ti^{4+} site of rutile, an increase of electrical conductivity could be found occasionally in the sample prepared at high temperature under a reducing atmosphere. Also, the introduction of Ti^{3+} was established by doping with the pentavalent state foreign cations. On the other hand, the replacement of Ti^{4+} ion by foreign trivalent ions may impart electronic conduction to insulating rutile.

On the basis of the above-mentioned ideas, it is expected that trivalent and/or pentavalent antimony is one of the elements suitable for doping into rutile. Krause *et al.* (*3*) and Sheinkman *et al.* (*4*) reported formation of a solid solution with TiO_2 rutile in the concentrations up to 15 mole% Sb_2O_3, and consisting of Sb^{3+} and Sb^{5+} simultaneously for ensuring electroneutrality. The present study is conducted to determine the oxidation state of Sb by using of electron spectroscopy for chemical analysis (ESCA) and to examine the effects of Sb ions and oxygen vacancies on the electrical properties of rutile.

Experimental

The Synthesis of Sb-Doped Rutile

TiO_2 (rutile) was obtained by firing TiO_2 (anatase) at 1050°C in air for 24 hr. Sb_2O_4

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* To whom all correspondence should be addressed.

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was prepared using the method reported by Miyayama *et al.* (*5*). Both materials obtained in this way were intimately mixed with acetone using an agate mortar and dried in air. The mixtures were formed into disks at 200 MPa and fired at 1000°C for 24 hr in air; then the sample was quenched to room temperature.

The Characterization of Sb-Doped Rutile

In order to determine the chemical composition, the samples were placed in a Pt crucible and decomposed by molten Na_2CO_3 at 1000°C for 1 hr. After dissolving the product in a hot diluted HCl solution, the molar ratio of Sb/Ti in rutile was determined with a conventional atomic absorption spectrophotometer. The phase of sample was identified by X-ray powder diffraction with the Cu$K\alpha$ radiation. Accurate lattice parameters for the samples were determined using Si as a standard material and were calculated by a least-squares method.

The apparent densities of the sintered samples were measured by the Archimedes method. The microstructure was observed with a scanning electron microscope (JEOL JTM-T20).

The binding energies of Sb, Ti, and O were measured at room temperature by using ESCA (Shimadzu 750). The oxidation states of Sb in rutile were evaluated by comparison with the binding energies of Sb compounds observed in compounds such as Sb_2O_3, Sb_2O_4, and $VSbO_4$. The energy was calibrated against the C(1*s*) peak resulting from usual contamination.

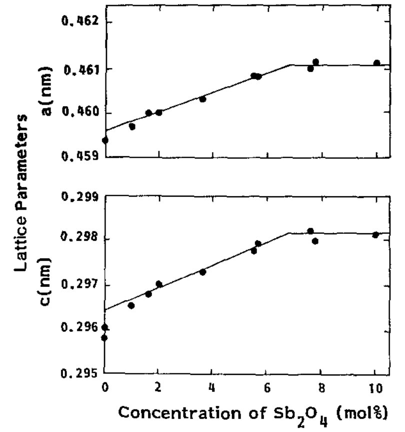

FIG. 1. The change of lattice parameters depending on the concentration of Sb_2O_4.

The conductivities of the samples were measured over the frequency range 50 kHz to 10 MHz and 76 to 350 K by a Q-meter (YHP Model QM-102B).

Experimental Results and Discussion

The Synthesis of a Solid Solution in the Ti–Sb–O System

According to the chemical analysis of products with rutile-type structure, the maximum Sb concentration in rutile was about 7 mole% in an Sb_2O_4 equivalent.

Figure 1 shows the dependence of lattice parameters on the Sb_2O_4 concentration. The unit cell parameters increased linearly with increasing Sb concentration and reached the constant values of $a = 0.46112 \pm 0.00002$ nm and $c = 0.29810 \pm 0.00003$ nm up to the concentration limit of Sb. The present results are in good agreement with those reported by Sheinkman *et al.* (*4*).

From the extrapolation of the compositional dependence of lattice parameters shown in Fig. 1, the apparent lattice parameters of a sample with 0 mole% Sb can be evaluated as $a = 0.4596$ nm, and $c = 0.29645$ nm. By comparing with the lattice parameters of rutile, $a = 0.4594$ nm and $c = 0.2959$ nm, it was found that the c parameter increased by a factor of 1.018 and that the a parameter changed little. The change of the c parameter seems to be due primarily to oxygen vacancies that belong to the shared edges of TiO_6 octahedra along the c direction. This consideration would be verified by the results in which the c/a ratio gradually increased with increasing content

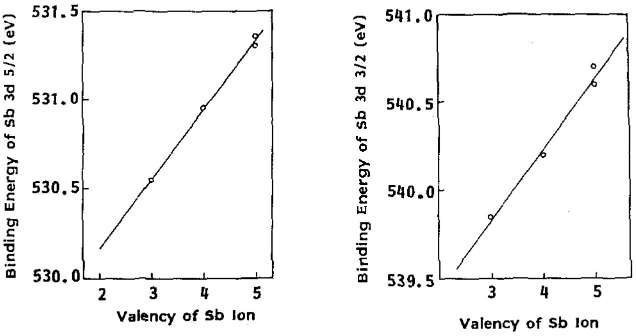

FIG. 2. The relationship between the binding energies of Sb($3d_{3/2}$) and Sb($3d_{5/2}$) and the valency state of the Sb ion.

of Sb. Above 7 mole% of Sb_2O_4, trace products of $Sb_3Ti_2O_{10}$ and Sb_2O_4 were observed on the inner wall of the alumina crucible.

Determination of the Oxidation State of Sb in Rutile

For determining the valence state of Sb in rutile, Sb_2O_3, Sb_2O_4, and $VSbO_4$ were used as reference materials. According to the data reported by Birchall and Sleight (*6*), $VSbO_4$ is represented to be $V^{3+}Sb^{5+}O_4$.

Sb_2O_4 can be estimated to be $Sb^{3+}Sb^{5+}O_4$ because Birchall *et al.* (*7*) observed the separated peaks arising from Sb^{3+} and Sb^{5+} ions in the ESCA spectrum. In the present experiments, the binding energy of Sb in Sb_2O_4 was obtained as the mean value of Sb^{3+} and Sb^{5+} ions.

The relation between the binding energies and the valency state of Sb in Sb_2O_3, Sb_2O_4, and $VSbO_4$ is shown in Fig. 2. As shown in this figure, a linear correlation was found. This fact indicates that the binding energy should increase when the interaction between cation and anion is intensified due to the ionic size and valency state of cation.

Figure 3 shows the binding energy of Sb($3d_{3/2}$) and Sb($3d_{5/2}$) as the function of the Sb concentration in rutile. When the Sb concentration increases and approaches the solubility limit, the binding energies of Sb($3d_{5/2}$) and Sb($3d_{3/2}$) increase and gradually reach the values of 540.1 and 530.6 eV, respectively. The reason the binding energies increase with increasing concentration of Sb in antimony-doped rutile solid solution is not yet clear. Since the mean values of binding energies for Sb($3d_{5/2}$) and Sb($3d_{3/2}$) closely correspond to those of Sb^{3+}, the valence state of in rutile was considered to be trivalent state.

Electrical Properties of Sb-Doped Rutile

The electrical conductivity as a function of frequency range in the temperature range from 76 to 350 K was measured using the sintered body of a Sb-doped rutile. Figure 4 shows the SEM photograph of the fracture

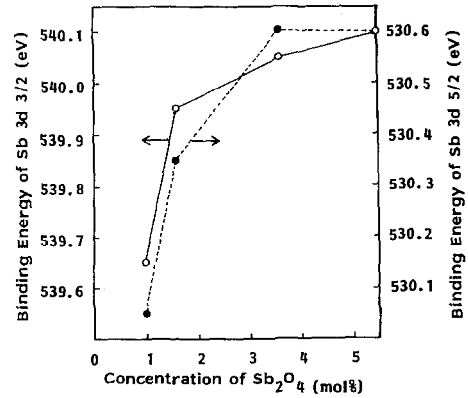

FIG. 3. The binding energies of Sb($3d_{3/2}$) and Sb($3d_{5/2}$) as a function of the Sb_2O_4 concentration in the rutile-type structure.

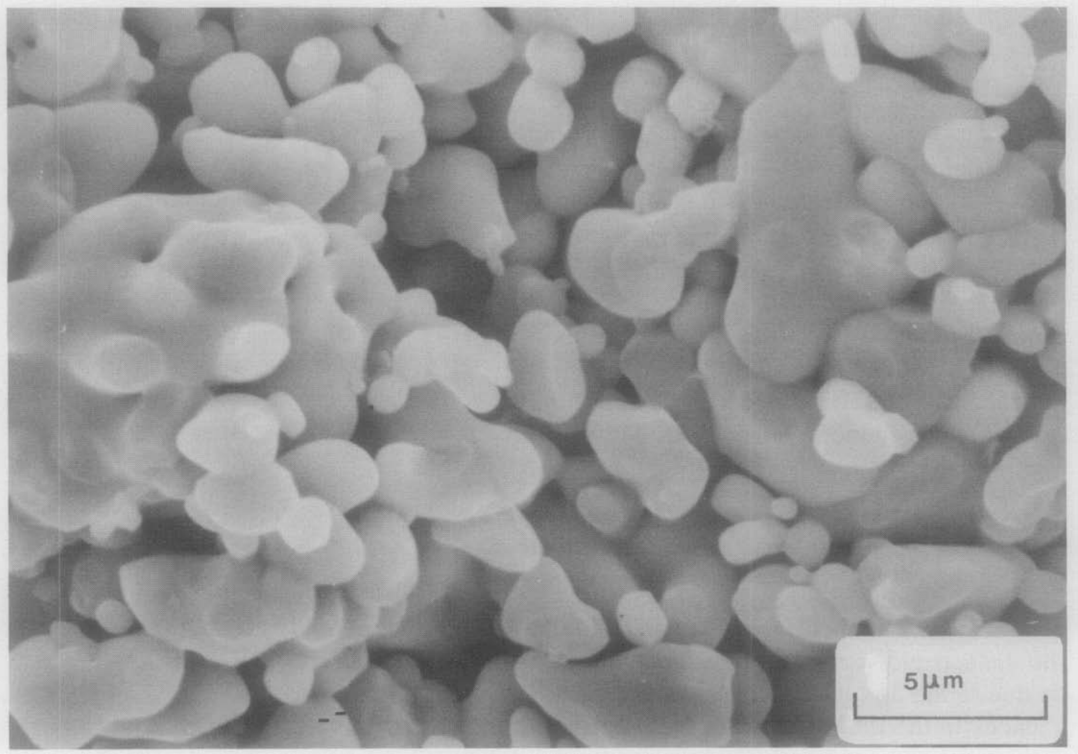

FIG. 4. The SEM photograph of the fracture surface of rutile with 12 atm.% of Sb.

surface of rutile with 12 atm.% of Sb. The grains were irregular and frequently coagulated, with sizes in the range of 0.6 to 10 μm. The relative density of the sintered body was determined to be about 75% by the water displacement method.

The temperature dependence of the *ac* conductivity at 500 kHz is shown in Fig. 5. As shown in this figure, all curves are convex. When the Sb concentration is increased, the position of the maximum shifts to the higher temperature and higher conductivity sides. Moreover, when the applied frequency is increased, the position of the maximum also shifts to the higher temperature side. The conductivities of all these samples were magnified as compared with the conductivity of rutile, with values in the range of 10^{-1} to 10^{-3} Ω^{-1} m^{-1}.

In the present system of Ti–Sb–O, it was experimentally found that the valency state of a doped Sb ion is trivalent. Since the Sb ion seems to interact strongly with an oxygen vacancy, it is believed that the two free electrons introduced by an oxygen vacancy

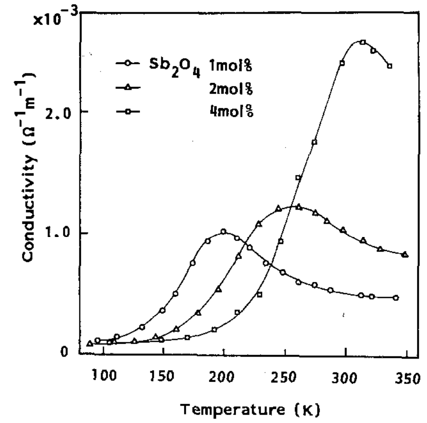

FIG. 5. The temperature dependence of the conductivity at 500 kHz.

participate in the determination of the valency state of Sb ion and are localized around Sb ions. It is likely that such electrons excited onto the Sb^{3+} acceptor level result simultaneously in formation of electron holes in the valence band. In fact, the thermoelectric power data indicated that the sample is *p*-type semiconductor.

In Fig. 6, the frequency dependence of dielectric loss factor ε'' derived from Langevin–Debye's equation was plotted as a function of temperature for rutile doped 1 mole% in Sb_2O_4. This figure implies that the relaxation frequency f_m increases with increasing temperature. Also, it was found that f_m shifts to the higher frequency side when the Sb concentration is decreased.

In Fig. 7, the significant relationship between the logarithm of relaxation frequency and reciprocal temperature is shown. When the dielectric dispersion loss is believed to be due to the Sb^{3+} coupled with the oxygen vacancy in the rutile structure, the value of activation energy ΔE is found to range from 0.15 to 0.17 eV, according to the expression

$$f_m = A \exp(-\Delta E/kT),$$

where A is the period of the atomic vibration.

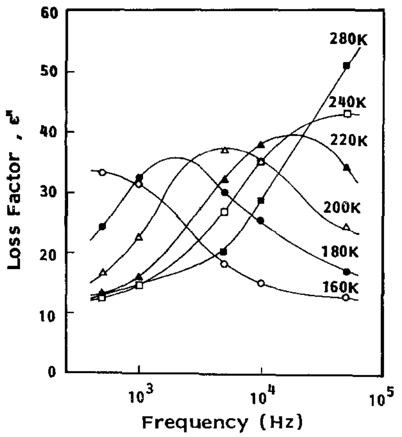

FIG. 6. The frequency dependence of the dielectric loss factor as a function of temperature for rutile doped 1 mole% in Sb_2O_4.

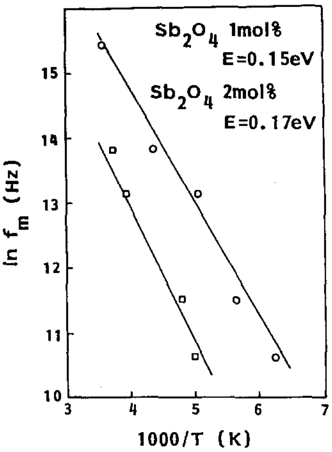

FIG. 7. The relationship between the logarithm of relaxation frequency and the reciprocal temperature.

The value obtained in this way is smaller than the value for ionic migration process, which is the order of 0.7 eV (*8*), and corresponds substantially to the relaxation time of the polarization of the Sb^{3+} oxygen vacancy.

Summary

The ESCA and X-ray diffraction data could provide evidence that Ti^{4+} ions in the rutile structure are partially replaced by Sb^{3+} ions up to the proportion of 7 mole% in an Sb_2O_4 equivalent. The suggestion that oxygen vacancies couple formally with the Sb^{3+} ions was verified by the results of the dielectric dispersion loss, with an activation energy of about 0.16 eV.

Acknowledgment

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