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The Enhanced Penetration of Oxygen along the Grain Boundary in Semiconducting Barium Titanate

Akira HASEGAWA, Satoru FUJITSU¹, Kunihiro KOUMOTO
and Hiroaki YANAGIDA²

*Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
7-3-1, Hongo, Bunkyo-ku, Tokyo 113*

¹*Department of Materials Science and Ceramic Technology, Shonan Institute of Technology,
1-1-25, Tsujido-Nishikaigan, Fujisawa, Kanagawa 251*

²*Research Center for Advanced Science and Technology, The University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo 153*

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The characteristics of Positive Temperature Coefficient of Resistivity (PTCR) thermistors depend strongly on the atmosphere, especially oxygen, during the fabrication process. The PTCR jump decreases when the sample is heated in a reducing atmosphere, while it increases when the sample is heated in air. The behavior of oxygen which is important to improve the PTCR jump has been examined by a tracer (¹⁸O) method. The depth profile of the tracer has been determined by means of Secondary ion mass spectrometry (SIMS). The rate of penetration of oxygen into the grain boundary is very rapid and the PTCR jump depends on the amount of the oxygen penetrated into such a region.

KEYWORDS: semiconducting barium titanate, oxygen, PTCR effect, SIMS, diffusion

§1. Introduction

Pure barium titanate is a ferroelectric material with a perovskite structure whose Curie point is approximately 120°C. Barium titanate doped with a small amount of rare earth element (such as La, Nd, Sm and so on) shows n-type semiconducting properties. The resistivity of such a material increases drastically at its Curie point with heating, which is called the Positive Temperature Coefficient of Resistivity (PTCR) effect. The drastic change in the resistivity due to the PTCR effect is called a PTCR jump.

Since Haaijman *et al.*¹⁾ reported this phenomena, many scientific and industrial efforts²⁾ have been devoted to : (1) improving PTCR performance and (2) clarifying the PTCR mechanism.

The double-Schottky energy barrier model proposed by Heywang³⁾ is one of the most effective models by which to explain the mechanism of the PTCR effect. From this model, the double-Schottky type energy barrier is formed along the grain boundary and its barrier height determines the total conductivity. The height of the energy barrier, ϕ , is expressed as

$$\phi = (2eN_{ss}^2) / (\epsilon\epsilon_0 N_d), \quad (1)$$

where N_{ss} is the interface state density; N_d is the carrier density in grain bulk; and the other symbols have their usual meanings. The decrease in the dielectric constant, ϵ , with change from a ferroelectric to dielectric material in BaTiO₃ upon heating increases the barrier height, and then total resistivity increases. The acceptor type of interface state is required to form the Schottky-type energy barrier. The chemical and/or physical state playing a role as the interface state has not yet been determined.

It is well known that a large PTCR jump can be observed in the sample heated in an oxidizing atmosphere.⁴⁾ The samples heated in a reducing atmosphere or vacuum

do not show a good PTCR effect.

It is remarkable in porous material that the PTCR jump decreases with heating in a reducing atmosphere and increases with heating in an oxidizing atmosphere. We already determined the relation between the PTCR jump, the barrier height and the amount of chemisorbed oxygen.⁵⁾ The chemisorbed oxygen atom or molecule traps a conduction electron from the bulk to acquire a negative charge. Then, the Schottky-type of an energy barrier formed under the surface of the n-type semiconducting oxide such as BaTiO₃ is generated to compensate for the negative charge on the surface. The chemisorbed oxygen acts as an acceptor state in this case. Since the thickness of a surface energy barrier is very thin, its role as a barrier can be disregarded in a large polycrystalline sample with high density or in a large single crystal where the contribution from the surface on the total electrical properties is small. In the case of a porous body, however, the average neck radius connecting the grains is supposedly very small, and the effect of a barrier cannot be ignored. In ref. 5, we discovered that the height of the energy barrier determining the PTCR jump obeyed eq. (1), by applying the amount of chemisorbed oxygen to the interface state density. The interface state in porous BaTiO₃ is mainly formed by the chemisorbed oxygen.

On the other hand, it is impossible to apply the chemisorbed oxygen state to the acceptor state along the grain boundary in a dense sample. But the importance of oxygen to develop the PTCR effect leads us to believe that a similar state such as chemisorbed oxygen (i.e., excess ionized oxygen) exists as an acceptor state in the grain boundary. The decrease in the PTCR jump by heating in a reducing atmosphere is also observed in the dense sample. Furthermore, such a PTCR effect is restored by heating in an oxidizing atmosphere.

In this study, the penetration of oxygen into the reduced semiconducting BaTiO₃ was measured by the tracer

(^{18}O) method to clarify the role of the oxygen in the dense sample.

§2. Experimental Procedure

2.1 Sample preparation

Nominally pure BaCO_3 (from Soekawa Chemical Co., Ltd.), TiO_2 (from Fuji Titanate Co., Ltd.), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (from Kanto Chemical Co., Inc.), MnSO_4 (from Shuzui's Pure chemicals Co., Ltd.) and SiO_2 (from Kanto Chemical Co., Inc.) were employed as starting materials. The starting powders were mixed in ethanol. The composition of the product was $\text{BaO}:\text{TiO}_2:\text{LaO}_{1.5}:\text{MnO}:\text{SiO}_2 = 99.7:101:0.3:0.07:2$. Lanthanum oxide was doped to change the BaTiO_3 into a semiconductor, and the doping of MnO and SiO_2 improved the PTCR performance.⁶⁾ The mixed powder was calcined at 1150°C for 1 h in air. After filtering (#400), the powder was pelletized in a steel die, and then pressed isostatically under the pressure of 2.6×10^7 Pa. This pellet was sintered at 1350°C for 1 h in air and was cooled with a constant rate of $100^\circ\text{C}/\text{h}$. The density and the average grain size of the sample obtained by this process were $5.97 \text{ g}/\text{cm}^3$ and $10 \mu\text{m}$, respectively.

2.2 Reduction and reoxidation

The obtained sample was heated at 1000°C for 24 h in the atmosphere with low-oxygen partial pressure of 10^{-12} atm. This sample was reoxidized in air or 0.2 atm of O_2 containing 20 vol% ^{18}O for 0.01 to 6 h at 600 to 1000°C , and then quenched to room temperature.

The resistivity of the sample was measured by using a DC resistivity meter (Advantest TR8652) at 20 to 250°C in air. An In-Ga alloy was painted on both sides of the sample as an electrode.

2.3 Penetration of oxygen

The depth profile of ^{18}O was measured by using Secondary ion mass spectrometry (SIMS) (Hitachi Ltd., IMA-2A) under the following conditions; primary ion $^{40}\text{Ar}^+$, primary ion energy 15 keV, primary ion current 6×10^{-8} A, probe size $200 \mu\text{m}$ in diameter, secondary ion accelerating voltage 3 kV and residual gas pressure $< 10^{-5}$ Pa. Since this probe size of SIMS was large enough as compared to the grain size of the measured samples, it was judged that the average amount of ^{18}O existing in a grain and grain boundary was obtained. The depth of the ion-etched crater was measured with a profilometer (Talystep, Rank Precision Industries, Ltd.). Under this condition, a flat-bottomed crater was formed, confirming a reliable depth profile.

§3. Results and Discussion

3.1 Change in the PTCR jump by reduction and reoxidation

The PTCR jump and the resistivity at 20°C of the as-obtained sample were 5 orders of magnitude and 50 to $100 \Omega\text{cm}$, respectively (see Fig. 1). When the sample was reduced, the PTCR jump disappeared and the resistivity at 20°C decreased to $< 10 \Omega\text{cm}$. While the PTCR jump and the resistivity increased by heating this reduced sample in air. Figure 1 shows the temperature dependence of

resistivity of the sample reoxidized for 1 h at a prescribed temperature.

Two types of processes are possible by which to explain such phenomena: (1) increase by reduction and decrease by reoxidation in the carrier density, and (2) decrease by reduction and increase by reoxidation in the interface state density. From the result of the resistivity measurement, it cannot be determined which type of process, (1) or (2) dominates the change in the PTCR jump and resistivity that resulted from heating in various gases.

3.2 Penetration of oxygen

Figure 2 shows the depth profile of ^{18}O annealed at 1000°C for 1 h after reduction. The ^{18}O concentration at the surface was in agreement with that in the gas phase for all the measurements, which indicated that the exchanging reaction at the surface takes place rapidly enough to neglect the reaction time. The concentration decreased remarkably in the shallow region and very

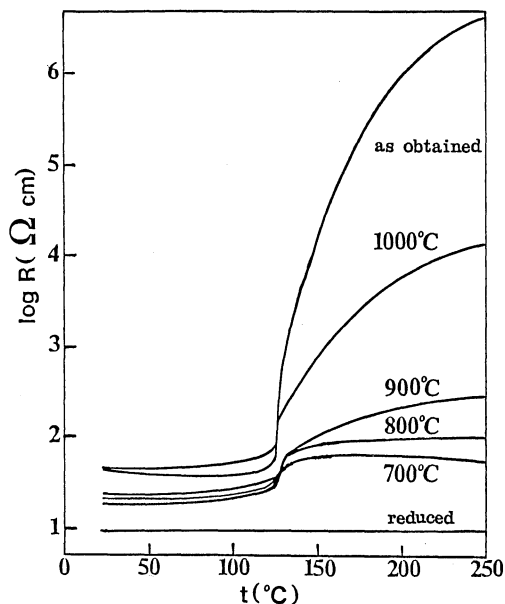


Fig. 1. Resistivity versus temperature of barium titanate specimens annealed at different temperatures in air atmosphere for 1 h.

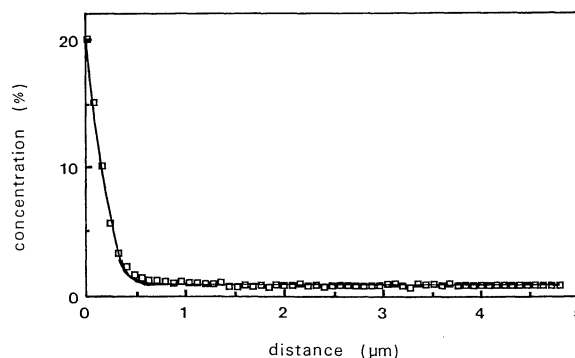


Fig. 2. Diffusion profile of ^{18}O tracer. Sample was heated at 1000°C for 1 h in 20 vol% $^{18}\text{O}_2$. Concentration means $^{18}\text{O}/^{18}\text{O} + ^{16}\text{O}$.

slowly in the deep region. The concentration in the deep region (2 to 4 μm) seems to be constant.

Assuming that the tracer diffusion is in a homogeneous medium with a constant surface concentration, the equation that calculates the depth profile is⁷⁾

$$(C - C_0)/(C_s - C_0) = \text{erfc}(x/2\sqrt{Dt}), \quad (3)$$

where C represents the concentration of the tracer at the distance (x) from the surface, C_s denotes the concentration at the surface, D is the diffusion coefficient, t stands for the annealing time and C_0 is the basic concentration of the tracer which is the natural abundance in an ordinary diffusion measurement. This measurement for the reduced sample is different from an ordinary tracer diffusion measurement in which the sample is annealed in a tracer atmosphere after attaining the equilibrium condition. However, eq. (3) could approximately express the obtained depth profile by applying the constant concentration of the tracer deep region to C_0 . The solid line in Fig. 2 shows the calculated result by using the values of $D = 6.2 \times 10^{-14} \text{ cm}^2/\text{s}$ and $C_0 = 1.1\%$.

The temperature dependence of diffusion coefficients estimated by the method above is shown in Fig. 3. The volume diffusion coefficient reported by Shirasaki *et al.*⁸⁾ is also shown in this figure. The obtained data are lower than those reported. Since the oxygen penetration into the reduced sample was measured in this experiment, it is expected that the higher diffusion coefficient should be estimated. Though the reason of this difference has not been clarified, some impurities doped in the present sample such as MnO , SiO_2 and/or La_2O_3 should affect the diffusion behavior of oxygen.

On the other hand, eq. (3) cannot express the slow decrease in the tracer concentration in the deep region. This result suggests the inhomogeneity of the diffusion path. It is known that the oxygen diffusion in BaTiO_3 is enhanced by the grain boundary.⁹⁾ Figure 4 shows the depth profiles of different grain size samples (1 μm and 10 μm) which were heated at 1000°C for 1 h. The tracer concentrations in the deep region (2 μm in this experiment) of the samples with a fine grain size (1 μm) and a

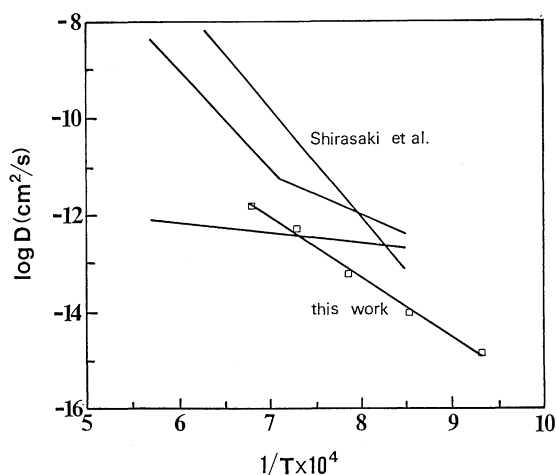


Fig. 3. Arrhenius plots of volume diffusion coefficients. Volume diffusion coefficients were estimated from the diffusion profile near the surface.

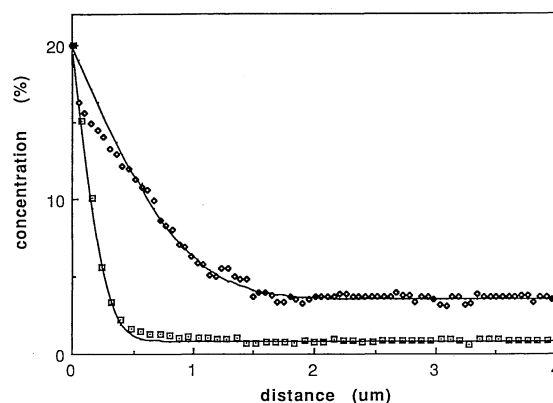


Fig. 4. Diffusion profiles of large grain sample and small grain sample. Samples were heated at 1000°C for 1 h in 20 vol% $^{18}\text{O}_2$.

coarse grain size (10 μm) were 3.5 and 1.1%, respectively. When the samples with different grain sizes prepared by varying the sintering time were annealed under the same conditions, the D of the nearest surface was independent of and the C_0 depended on the grain size. The C_0 of the sample with the fine grain size was higher than that with the coarse grain size. From this result, it is suggested that the estimated D of the nearest surface is the diffusion (or penetration) coefficient of oxygen into the grain bulk, and the slow change in the tracer concentration in the deep region (seems to be flat) is due to the extremely rapid penetration of the oxygen through the grain boundary.¹⁰⁾ In the deep region, the penetrated oxygen exists in the grain boundary and its vicinity. Hence, the C_0 is determined by the amount of penetrated oxygen into the grain boundary and its vicinity. It is judged that oxygen concentration in the grain boundary region is in excess as compared with that in the grain bulk in this reoxidized sample, which resulted from the extremely rapid penetration of oxygen into the grain boundary.

3.3 Oxygen penetration and PTCR effect

As shown in Fig. 1, oxygen plays an important role in the development of the PTCR effect. When the reduced sample was reoxidized in air, its PTCR jump and resistivity increased with increasing reoxidizing temperature. In high temperature, the penetration of oxygen is remarkable. Not only the D but also the C_0 increased with increasing reoxidizing temperature (see Fig. 5). In this study, the tracer concentration at 2 μm of depth was applied to C_0 . In all measured depth profiles, the tracer concentration seems to be constant at 2 μm of depth. Since the value of C_0 is determined by the amount of tracer in the grain boundary and its vicinity in the samples with same grain size, the large C_0 was observed in the samples annealed at high temperature where oxygen penetrates into the samples rapidly.

The increase in the PTCR jump and resistivity of the reduced sample depends not only on the reoxidizing temperature, but also on the time. As shown in Fig. 6, the PTCR jump and resistivity increased with increasing reoxidizing time at 1000°C. Similar results were obtained in the samples reoxidized at the other temperatures.

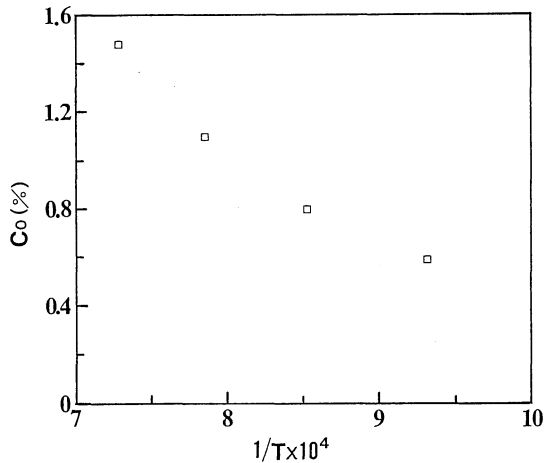


Fig. 5. The relation between C_0 and temperature. C_0 levels were derived from eq. (3) applying diffusion profile.

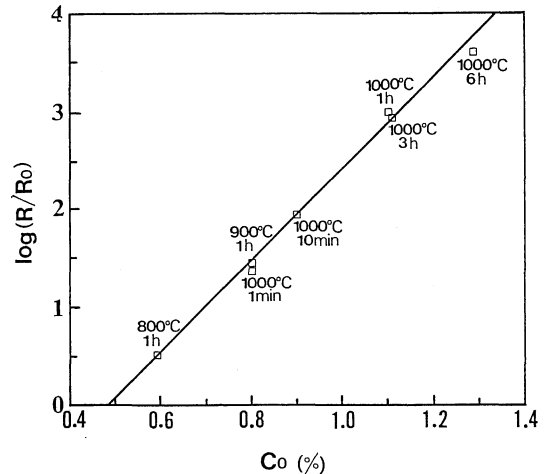


Fig. 7. The relation between the magnitude of PTC effect $\log(R/R_0)$ and C_0 .

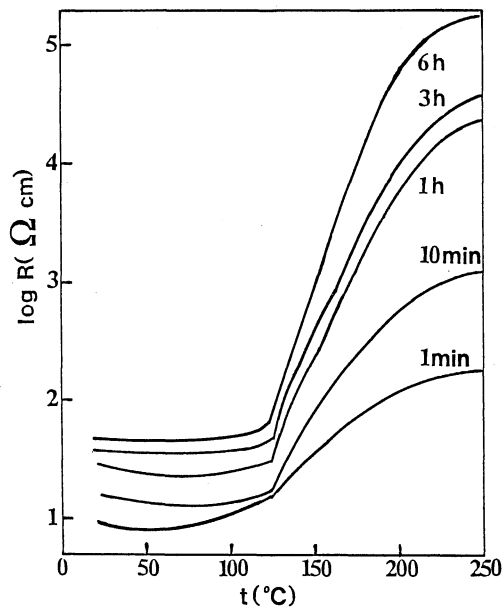


Fig. 6. Resistivity versus temperature of barium titanate specimens annealed at different temperatures in air atmosphere for different times.

When the samples were annealed for various reoxidizing times, their depth profiles indicated that D was independent of and C_0 depended on the time.

The PTCR jump of the reoxidized sample and its C_0 are shown in Fig. 7. As shown in this figure, it is judged that the PTCR jump depends on the C_0 , which is determined by the amount of penetrated oxygen into the grain boundary region, rather than the reoxidizing conditions such as temperature and time. A similar relationship was also observed when the tracer concentration at a point in the deep region other than $2\text{ }\mu\text{m}$ was applied to C_0 .

If the excess oxygen ion exists along the grain boundary, the double-Schottky-type of energy barrier should be formed along the grain boundary to compensate for its negative charge. The excess oxygen ion in the grain boundary can form the acceptor type of an interface state

as the chemisorbed oxygen on the surface.

The oxygen penetrated into the reduced sample in the present case. Therefore, it is considered that the existence of an excess oxygen ion in the grain boundary was achieved by the rapid penetration through the grain boundary. It cannot be determined that such an excess state of an oxygen ion is still maintained in the sample annealed for a long time, thus achieving the equilibrium condition. If the oxygen ion penetrates into the gap in the grain boundary formed by the mismatching of the lattice, it is possible to maintain the excess state of the oxygen ion.

However, it is clear that the reappearance of the PTCR effect in the reduced sample in the present case mainly results from the formation of the acceptor type of an interface state (i.e., the excess oxygen ion) along the grain boundary. This is because: (1) the penetration into the grain bulk is very slow and that into the grain boundary is extremely rapid, and (2) the reappearance of the PTCR jump depends on the amount of oxygen that has penetrated into the grain boundary.

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