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Giant Piezoresistive Effects in Single Grain Boundaries of Semiconducting Barium Titanate Ceramics*

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Abstract. Extremely large piezoresistive effects with a gage factor (elastoresistance) of $> 1 \times 10^6$ in single grain boundaries of thin ceramic bars of semiconducting barium titanate have been observed at room temperature. Thin barium titanate ceramic bars with a diameter in the range of 10 to 20 μm were prepared to consist of single grains joined together in series. Large piezoresistive effects were observed for some of the single grain boundaries in the present samples under compressive stresses, but no distinct piezoresistance was observed in the grain bulk. A giant piezoresistive effect with a gage factor of 3×10^7 was observed for a single grain boundary which exhibited a saw-tooth type PTCR (positive temperature coefficient of resistivity) characteristic with a significantly large bias dependence of it. This demonstrates that the piezoresistive phenomenon may be interpreted in terms of the change of the potential barrier height due to the change of ferroelectric domain morphologies in the vicinity of grain boundaries under mechanical and electric stresses.

Keywords: piezoresistive effect, Barium titanate, single grain boundary, spontaneous polarization, domain morphology

1. Introduction

There have been many studies [1–5] on the piezoresistivity in doped semiconducting barium titanate ($BaTiO_3$) ceramics with an anomalous positive temperature coefficient of resistivity (PTCR) effect above the Curie point (around 120°C; corresponding to the onset temperature of the resistivity anomaly), and most of them reported that bulk $BaTiO_3$ ceramics exhibited large piezoresistive effects in a limited temperature range around their Curie point but only a small effect can be observed at room temperature. From the results obtained in previous studies it has been accepted that the piezoresistive effect in $BaTiO_3$ PTCR ceramics is one of the grain boundary properties that can be interpreted basically based on Heywang's grain-boundary barrier layer model [6], though no one has succeeded in interpreting quantitatively the sign and behavior of resistivity changes with application of stresses, which have not been observed to vary in a consistent manner for compositions and measuring systems used. In our recent study [7], however, we observed large piezoresistive effects in single grain boundaries of thin semiconducting $BaTiO_3$ ceramic bars at room temperature, and tentatively interpreted the nature of the piezoresistive effect in terms of the change of the potential barrier height due to the change of ferroelectric domain morphologies in the vicinity of grain boundaries under mechanical and electric stresses. The thin materials were successfully prepared to consist of single grains joined together in series using the method established by us [8]. The magnitude of the piezoresistive effect with a gage factor [3] (equivalent to the elastoresistance that is defined by the rate of

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change in resistance per strain) in the range of 10^3 to 10^4 has been normally observed in single grain boundaries of the materials prepared, but we found the fact that some grain boundaries exhibited an extremely large effect with a gage factor of $>10^6$ (the largest gage factor reached 3×10^7). This paper reports a typical example of extremely large piezoresistive effects newly observed in the present samples and presents a tentative model for explaining the effects.

2. Experimental

The details of the procedures used in this study for preparing thin ceramic bar samples and for measuring electrical properties of single grain boundaries in the materials have been described elsewhere [7, 8]. Only a brief description of the procedures is thus given here. By spinning first thin green strings from slurry made up of mixed powders, with the composition $Ba_{0.999}La_{0.001}TiO_3 + 0.4\,mol\,\%\,TiO_2$ (referred to as BTO, hereafter), of commercial high purity $BaTiO_3$, La_2O_3 and TiO_2, using polyvinyl butyral (PVB) as a binder, and then firing them at 1370°C in air, we obtained thin ceramic bar samples with a grain structure consisting of single grains joined together in series, with a diameter in the range of 10 to 20 μm. To a ceramic bar sample, glued onto a nylon line previously strained slightly (this state corresponds to the stress-free condition of the sample mounted on the nylon line), various tensile or compressive stresses to give them a range of strains were applied by pulling further the nylon line or releasing the pulling stress gradually to let it shrink. The magnitude of strain on a sample generated was evaluated by the equation $S = (L - L_0)/L_0$, where L and L_0 denote the lengths of the nylon line when the sample was stressed and stress-free, respectively. A positive value of S (positive stress; tension) thus denotes a tensile strain and a negative value of it (negative stress; compression) a compressive strain.

The piezoresistivity in single grain boundaries in the present samples was evaluated from their current (I)-voltage (V) characteristics, which were obtained at room temperature under various stresses using a programmable pA-meter (HP-4140B) by a two-probe method with In-Ga microelectrodes. We measured resistivity (ρ)-temperature (T) characteristics at temperatures between 25 and 210°C for single grain boundaries in the materials that were placed on glass plates. (The resistivity was calculated using the values of the distance between the electrodes and the diameter of a ceramic bar sample examined.) Unfortunately, both data of the piezoresistivity and resistivity-temperature characteristics could not be obtained simultaneously for the same sample because of the thermal stability problem of nylon lines used for the piezoresistivity measurements. Only one example of the resistivity-temperature characteristics for a single grain boundary that exhibited an extremely large piezoresistive effect, which was obtained prior to the piezoresistivity measurement, is presented in this paper. The measuring system was fully automatically controlled using a personal computer except for operation for loading stresses. Pulsed biases (according to the user's guide of the instrument used) were used in the electrical measurements. The grain structures of ceramic bar samples were examined by a scanning electron microscope (SEM). Figure 1 shows a typical SEM grain structure of thin $BaTiO_3$ ceramic bars produced in the present study.

3. Results and Discussion

Figure 2 shows the *I-V* characteristics obtained for a single grain boundary in a BTO sample at room temperature under various stresses that yielded compressive strains within a range of $< -3.3 \times 10^{-4}$ and tensile strains of $< 8.7 \times 10^{-4}$. The measurements were performed first under compressive stresses and then under tensile stresses successively, as in the order of strains with S (from the top) listed in the inset. Although we measured the *I-V* characteristics under both positive and negative biases (the sign of biases used has no physical meaning here) and found that they showed considerably asymmetric behavior [7], only the *I-V*

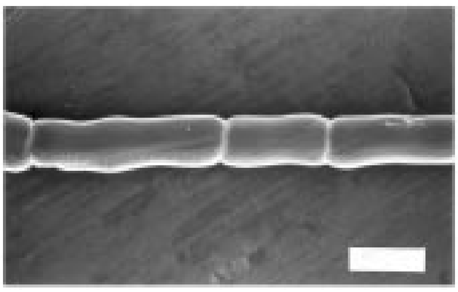

Fig. 1. SEM photograph of a semiconducting $BaTiO_3$ ceramic bar produced in this study. Bar = 20 μm.

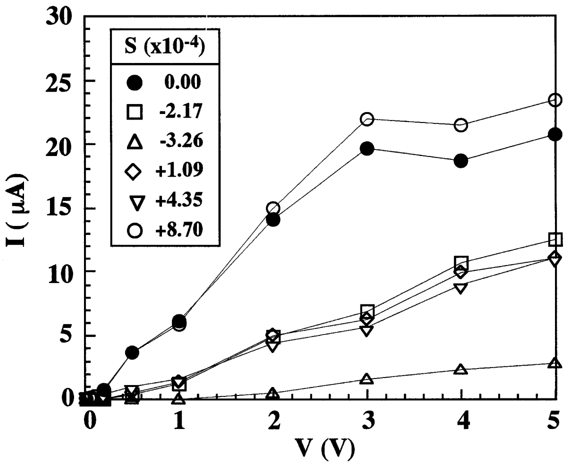

Fig. 2. I-V characteristics of a single grain boundary in a thin $BaTiO_3$ ceramic bar under various compressive and tensile stresses; *S* denotes strain. Sample diameter: 18.6 μm. Distance between electrodes: 4.1 μm.

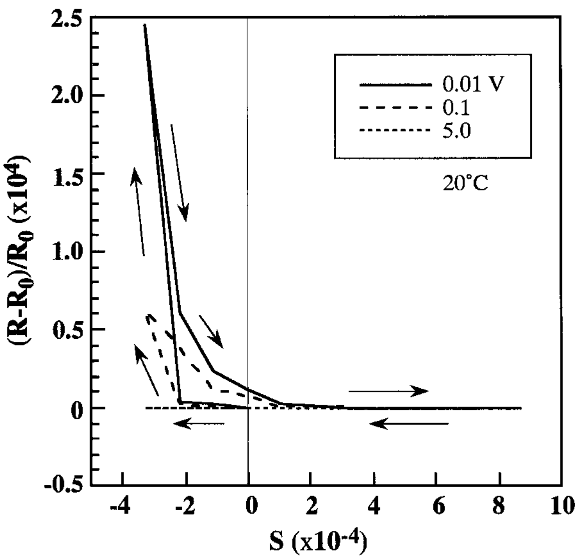

Fig. 3. Changes of resistance with strain obtained for the single grain boundary at biases of 0.01, 0.1 and 5.0 V at room temperature, which were obtained from the *I-V* characteristics shown in Fig. 2. Arrows on the curves indicate the direction of the measurements during single loading cycle of stress.

characteristics that showed a larger dependence on strain (that is, the data of Fig. 2) is presented in this paper. It is obvious from this figure that the single grain boundary examined exhibited a significantly large stress dependence of resistance, that is piezoresistance (here, given by $(R - R_0)/R_0$; where R and R_0 are the resistances at $S \neq 0$ and $S = 0$, respectively). Although piezoresistance (or piezoresistivity) is usually evaluated by the magnitude of its coefficient expressed in m^2/N from the equation $d(R/R_0)/dX$, where X[N/cm^2] is the stress applied, the piezoresistance in the present materials is given simply by the change in resistance with S, since we cannot know the precise value of the stress applied on the materials by the loading method used in this study. Figure 3 shows the $(R - R_0)/R_0$ versus S characteristics obtained from the *I-V* characteristics of Fig. 2. In the figure are shown the data obtained at biases of 0.01, 0.1 and 5.0 V. One can see from this figure that the resistance at 0.01 V extremely increased under compressive stresses giving strains $|S| > 2 \times 10^{-4}$ to yield its change of more than four orders of magnitude; this corresponds to piezoresistance with a gage factor (given by $(R - R_0)/R_0S$) of $> 1 \times 10^7$, though the piezoresistance drastically decreased with increasing bias voltage and finally a distinct piezoresistance could not be observed any more at 5.0 V. Under tensile stresses, on the other hand, the resistance showed only a very small stress dependence in the whole bias range used, as seen from the data of Figs. 2 and 3; the behavior of its piezoresistance is found to be completely different from that under compressive stresses. Moreover, a significant hysteresis is seen to be involved in the $(R - R_0)/R_0$ versus S characteristic.

The extremely large piezoresistive effect with a gage factor of $> 1 \times 10^7$ newly observed in this study may be called ''giant piezoresistance (GPR)'' from its magnitude. From piezoresistive measurements on the grain bulk in some of the present BTO samples (the data are not shown in this paper) it has been confirmed that no appreciable piezoresistive effect was observed in the grain bulk, and that the GPR phenomenon is definitely a grain boundary property. So, to understand the mechanism of the GPR phenomenon observed for a single grain boundary in a thin BTO sample, it may be useful to know the correlation between the piezoresistive effect and the PTCR characteristics the grain boundary exhibited. The ρ-T characteristics obtained for the grain boundary that exhibited the piezoresistive characteristics of Fig. 3 under various biases are shown in Fig. 4. The PTCR characteristics shown in this figure are of typical saw-tooth type, [8] as clearly seen under low applied biases of < 0.2 V, and one may recognize that the PTCR characteristics have several features of particular interest. First, the

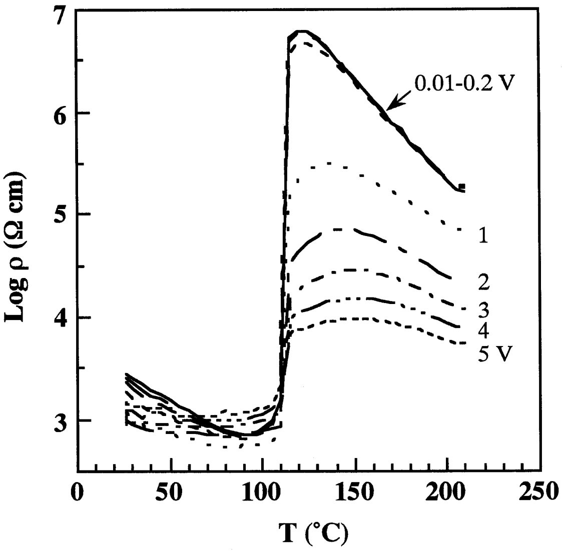

Fig. 4. Resistivity-temperature characteristics for the single grain boundary that exhibited the piezoresistive characteristics of Fig. 3 under various electric biases, which are shown on the curves.

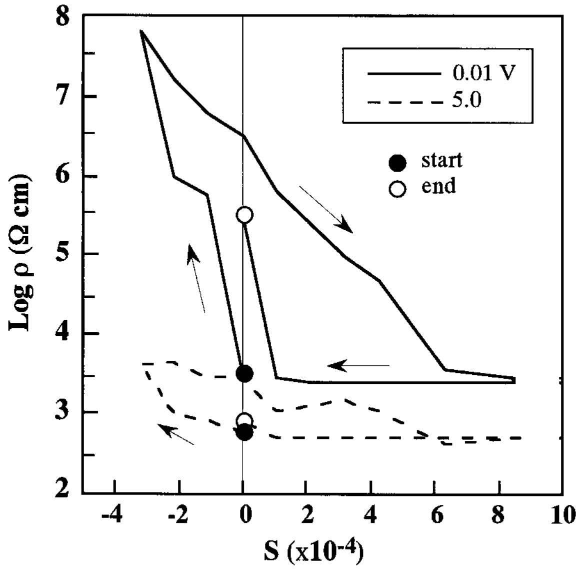

Fig. 5. Log ρ versus S plots of the data of Fig. 3 except for the characteristic obtained at 0.1 V. The resistance is given in the form of resistivity for the sake of convenience in comparing the data of this figure with those of Fig. 3.

saw-tooth type PTCR characteristics are characterized by a very large increase in resistivity of nearly four orders of magnitude at the Curie point (this is the largest resistivity jump at the Curie point ever observed for single grain boundaries of semiconducting barium titanates). Secondly, the resistivity above the Curie point showed a significant dependence on applied bias and the PTCR effect decreased remarkably to fall in the level of less than one order of magnitude. This indicates that the *I-V* characteristics above the Curie point showed a significantly large nonlinearity above a voltage around 0.2 V (per boundary); similar behavior of the characteristics was observed in the previous study [8]. Thirdly, unusual behavior of resistivity in the ρ-T characteristics below the Curie point, indicating the existence of an interesting phenomenon that can be described by a differential negative resistance (DNR). The DNR phenomenon below the Curie point has hardly been observed for bulk PTCR ceramics, but it has been reported for single grain boundaries in the previous paper [7].

Comparison between the PTCR characteristics of Fig. 4 and the piezoresistance of Fig. 3 further provides essential information about the mechanism of the PTCR effect as well as the mechanism of the GPR effect. For the sake of convenience in comparing the piezoresistive characteristics with the PTCR characteristics, the data of Fig. 3 (except for the characteristic obtained at 0.1 V) are given in log ρ versus S plots, as shown in Fig. 5. This figure clearly demonstrates that the resistivity under compressive stresses giving strains $|S| > 2.5 \times 10^{-4}$ (at room temperature) increased to a value exceeding the maximum resistivity on the PTCR characteristic curves above the Curie point. Obviously, this phenomenon is hardly interpreted in terms of the change of the grain-boundary potential barrier height due to the stress dependence of dielectric constant based on the Heywang model, because it cannot be considered that the dielectric constant showed such a stress dependence that yielded the rather discontinuous piezoresistive response seen in Fig. 3. It may thus be reasonable to conclude that the occurrence of the GPR phenomenon is attributed to the change in the degree of surface charge compensation by spontaneous polarization (according to Jonker's model [9]) resulting from changes of the domain structure morphologies in the vicinity of the grain boundary under mechanical and electric stresses. A closer investigation of the correlation between the changes of the ferroelectric domain structure and the resistance at many single grain boundaries in thin BTO samples under various stresses is now underway using a polarizing microscope. Based on this model, the mechanism of the PTCR characteristics are to be interpreted by the loss of surface charge compensation by spontaneous polarization above the Curie point. To confirm this, we need evidence for the existence of spontaneous polarization or strain still remaining in the PTCR temperature range above the Curie point.

4. Conclusion

Thin, semiconducting $BaTiO_3$ ceramic bars with a diameter of 10 to 20 μm, consisting of single grains joined together in series, were prepared in this study. Some single grain boundaries in the ceramic bars produced exhibited a GPR at room temperature. Although we cannot interpret precisely the mechanism of the GPR phenomenon at present, it is certain from a comparison of it with the PTCR characteristics that this phenomenon is hardly interpreted in terms of the change of the grain-boundary potential barrier height due to the stress dependence of dielectric constant based on the Heywang model. It may be reasonable to conclude that the mechanisms of the piezoresistive effect and the PTCR effect in grain boundaries of semiconducting barium titanates are both closely connected with the morphological change of the ferroelectric domain structure in the vicinity of the grain boundaries.

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