Current–Voltage Characteristics Across Small Angle Symmetric Tilt Boundaries in Nb-Doped SrTiO₃ Bicrystals

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Grain boundary structure and current–voltage (I–V) characteristics were investigated for Nb-doped SrTiO₃ bicrystals having small angle tilt boundaries with misorientation angles of 2° and 4° against [001]. The bicrystals were fabricated by using hot-joining technique at 1400°C for 10 h under a pressure of 0.4 MPa. High resolution transmission electron microscopy study revealed that the joined boundaries are free from any secondary phases such as amorphous phases even on an atomic scale. The structures of the two boundaries are composed of edge type dislocations whose Burgers vector is [010]. But the density of boundary dislocations differs between the two boundaries. They exist at an interval of 10 nm in the 2°-boundary and 5.2 nm in the 4°-boundary. On the other hand, it was found that non-linearity in I–V relation across the boundary increases with an increase in the misorientation angle. This result clearly indicates that the potential barrier height is closely related to the density of boundary dislocations in the case of small angle type boundaries.

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1. Introduction

Electrical properties of electroceramic materials such as thermistors, varistors and boundary layer capacitors are closely related to those of potential barriers such as double Schottky barriers formed at grain boundaries.¹–³ These grain boundary phenomena are known to have a dependency on grain boundary orientation relationship.⁴–⁹ For example, Hayashi et al. have revealed that PTCR (positive temperature coefficient of resistivity) effects vary with a coherency of grain boundaries using unique sintered materials.⁵ According to their results, high coherent boundaries such as coincident site lattice or small angle boundaries do not exhibit clear resistivity jumps around ferroelectric Curie temperature while large resistivity jumps appear in random boundaries. Their results clearly suggest the existence of a relationship between electrical properties and grain boundary structure. However, it has not been clarified yet why electron transport changes with a variation of grain orientation relationship. Generally, potential barriers are generated when conductive electrons in the vicinity of grain boundaries are trapped at interface states which operate as acceptors.¹⁰ Therefore, it must be necessary to reveal the nature of interface states in order to understand the dependency of electrical properties on grain boundary structure.

As for the origin of interface states, two mechanisms can be considered, i.e., atomic configuration at grain boundaries or charging-up of point defects.¹¹–¹³ As these two mechanisms have a dependency of grain orientation relationship between adjacent grains, it may be difficult to clear which mechanism is dominant for the electrical property across grain boundaries. In order to clarify this point, it must be necessary to use model boundary such as bicrystals. Yamamoto et al. have recently reported that atomic structure itself at grain boundary has not so much influence on the current–voltage behaviour across small angle type grain boundaries using Nb–SrTiO₃ bicrystals.¹⁴,¹⁵ In addition, they suggested the possibility that acceptor type defects accumulated around grain boundary dislocations give the formation of potential barriers. To obtain further interpretation, it needs to bridge the dislocation structure at grain boundary to the electrical properties across the boundaries.

In this study, the grain boundary structure and the electrical properties in Nb-doped SrTiO₃ bicrystals were examined with a viewpoint of boundary dislocations using small angle boundaries.

2. Experimental Procedure

Commercial SrTiO₃ single crystals doped with 0.2 at%Nb (Earth Chemical Co. Ltd.) were used for the preparation of bicrystals. The size of the single crystals were 10 × 10 × 5 mm³. In the present study, the boundaries of 2° and 4° symmetric [001] tilt type were fabricated as in Fig. 1. For comparison, a boundary without a misfit angle was also prepared.

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$\Delta \theta = 0^\circ$. They are classified into a small angle boundary. Hereafter these three boundaries will be noted as $2^\circ$, $4^\circ$, and $\Sigma 1$ boundaries, respectively. The contact planes were ground and polished to a mirror state finally with $0.25 \mu m$ diamond slurry. Then the two single crystals were joined by hot-pressing method at $1400^\circ C \cdot 10$ h under a pressure of $0.4$ MPa in air with heating or cooling rates of $200^\circ C/h$. After joining, thin plates of $1 \times 10 \times 10$ mm$^2$ were cut parallel to (001) plane from as-joint bicrystals (see Fig. 1). Then they were annealed again at $1400^\circ C$ for 1 h. On this annealing process, a cooling rate of $50^\circ C/h$ was applied down to $900^\circ C$ and the furnace was switched off at $900^\circ C$. Fixing Ag-Ohmic paste as electrodes at $500^\circ C$ for 0.5 h, the plates were used for electrical measurement, current–voltage ($I–V$) characteristics were measured by a computerized system consisting of a current source (Keithley, model 220) and a voltage meter (Keithley, model 2010) with a four probe method. After measurement of electrical properties, the boundary structure in the thin plates were examined by a high-resolution transmission electron microscope (HRTEM) with a field emission type gun (TOPCON, EM-002BF) or a conventional high-angle type microscope (JEOL, 2010HC), which were operated at 200 kV.

Specimens for TEM observation were prepared by a conventional ion-milling method using Ar ion beam milling machine (GATAN, duo-mill model 666).

3. Results & Discussion

Figure 2 shows bright field images taken in the $2^\circ$-boundary. In the figure (a), the electron beam direction is nearly parallel to [001] of both crystals. The two single crystal contacts each other perfectly and its boundary is free from large voids or precipitates. The boundary can be seen as a smooth and straight line, which means the boundary migration did not take place macroscopically by annealing during joining process used in this study. This fact was also confirmed by observation using an optical microscope. On the other hand, the particular contrast can be seen along the boundary. These contrasts are due to boundary dislocations as seen in the following photographs. The Fig. 2(b) and (c) show the boundary dislocation structure taken with different diffraction vectors, i.e., $g = 110$ in (b) and $g = 200$ in (c), respectively. These photographs were taken by inclining the boundaries at about $30^\circ$ against the electron beam direction. The contrast showing boundary dislocations can be clearly seen on the boundary plane as in the figure (b). The boundary dislocations are situated at an interval of about a few nm and they exist parallel each other. On the contrary, their contrast disappears under $g = 200$ condition as in (c). Namely, the Burgers vectors of the boundary dislocations are at least normal to [200] from the set of $g \cdot b$ criterion.

Figure 3 is a HRTEM image taken in the vicinity of the $2^\circ$-boundary. In the image, the electron beam is parallel to [001] direction of respective crystals and the boundary is set at the edge-on condition. The both crystals were joined without any secondary phases even at an atomic scale by the hot-pressing condition used in this study. The diffraction pattern inset in the image is a SAD pattern including adjacent crystals. From both the SAD pattern and the lattice fringes, the misorientation angle between both crystals is confirmed to be $2^\circ$ tilt rotation against [001] as expected. On the other hand, contrasts caused by distortions appear periodically along the boundary as indicated with the arrows in the photograph. These contrasts result from boundary dislocations introduced in order to accommodate the misorientation angle between adjacent crystals. The interval of the contrasts, i.e., boundary dislocations, is 10 nm. This value is almost the same one as that obtained in the bright field image as in Fig. 2(b).

Figure 4 shows a magnified high resolution image around the boundary dislocation as indicated with the arrow A in Fig. 3. An unit cell and a Burgers circuit are schematically shown in the image. As seen in the circuit, the interval of a start and a finish points of the Burgers circuit appears clearly. From the interval, the length of the Burgers vector of the boundary dislocation projected to (001) can be estimated to be equal to a lattice constant of an unit cell, i.e., $0.3904$ nm. And therefore, it is reasonable to consider that the Burgers vector of the boundary dislocation, $b$, is [010]. This agrees with the result obtained from $g \cdot b$ criterion carried out in Fig. 2 showing that the contrast of the boundary dislocations disappears under $g = 200$. In addition, the direction of the boundary dislocations is normal to $b$ so that they are considered to be edge type dislocations.

Figure 5 is a HRTEM image taken from the $4^\circ$-boundary. This boundary is also free from any secondary phases and the two crystals contact each other on an atomic scale as seen in the $2^\circ$-boundary. In addition, contrasts showing boundary dislocations are also observed in this boundary. But their interval is narrower than that of the $2^\circ$-boundary, i.e., $5.2$ nm in
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Fig. 3 A HRTEM image in the vicinity of the 2$^\circ$-boundary. The diffraction pattern inset in the image is SAD pattern including both crystals. Note that contrasts caused by distortions can be seen along the boundary. The area indicated by the arrow A will be described in Fig. 4.

Fig. 4 A schematic of a Burgers circuit around a boundary dislocation as indicated by the arrow A in Fig. 3. An unit cell is also shown in the image. The letters of S and F indicate a start and a finish point in the Burgers circuit.

Fig. 5 A HRTEM image of the 4$^\circ$-boundary. The arrow indicates a dislocation contrast.

the 4$^\circ$-boundary while 10 nm in the 2$^\circ$-boundary. By drawing a Burgers circuit as carrying out in Fig. 4, the projected length of the boundary dislocations in the 4$^\circ$-boundary is similar to that of the 2$^\circ$-boundary. As the number of boundary dislocations are so many in the case of the 4$^\circ$-boundary that the boundary dislocation image can not be clearly observed by an inclined-image technique. But it is reasonable to consider that the Burgers vectors of the boundary dislocations in the 4$^\circ$-boundary is similar to that of the 2$^\circ$-boundary as described below.

The interval of boundary dislocations has a function of a misorientation angle between adjacent crystals. According to Frank’s equation,\textsuperscript{16} a misorientation angle of a symmetric tilt boundary can be written as

\[ d = \frac{|b|}{2} \sin(\Delta\theta/2), \]

where $d$ is a spacing between adjacent boundary dislocations, $|b|$ magnitude of a Burgers vector of a boundary dislocation projected to a normal plane against a tilt rotation axis, and $\Delta\theta$ a misorientation angle, respectively. As mentioned above, the intervals of boundary dislocations in respective boundaries are 10 nm in the 2$^\circ$-boundary and 5.2 nm in the 4$^\circ$-boundary.

From these values and the Burgers vector, $b$, the misorientation angles are estimated to be 2.0$^\circ$ in the 2$^\circ$ and 4.3$^\circ$ in the 4$^\circ$-boundaries, respectively. These angles are almost the same values as experimentally expected.

Figure 6 shows I–V characteristics across the 2$^\circ$- and the 4$^\circ$-boundaries as shown in Fig. 3 and Fig. 5, respectively. For
comparison, $I$–$V$ behavior obtained from the $\Sigma 1$ boundary is also shown in the figure. The $\Sigma 1$ boundary exhibits clear Ohmic relation, i.e., $\alpha = 1$, where the non-linearity coefficient $\alpha$ is defined as $\partial \log(I)/\partial \log(V)$. The behavior of $\Sigma 1$ boundary is similar to that obtained in the single crystal. On the other hand, $I$–$V$ behavior clearly turns from linear to non-linear relationship over the voltage in the $2^\circ$- and the $4^\circ$-boundaries. However, the value of $\alpha$ is different among the two boundaries. It increases with an increase in a misorientation angle, i.e., about 1.2 in the $2^\circ$-boundary and about 1.7 in the $4^\circ$-boundary, respectively. This fact strongly suggests that non-linearity in $I$–$V$ relation across a boundary depends on its misorientation angle in the case of a small angle type boundary.

Non-linear electron transport behavior across grain boundaries in semiconductive electroceramic materials has been often discussed in terms of potential barriers such as double Schottky barrier (DSB).\textsuperscript{1–3} The barriers are considered to be generated by trapping electrons at acceptor states in a band gap. Recently, it is experimentally pointed out that the origin of the acceptor states is closely related to the charging-up of cation type point defects accumulated in the vicinity of grain boundaries in the case of semiconductive SrTiO$_3$ materials.\textsuperscript{14} Figure 7 shows a typical result reported in their report. In the figure, the $I$–$V$ behaviors across small angle boundaries are shown when a cooling rate was changed each other. In spite of the same boundary, non-linearity increases with a decrease in a cooling rate. As obtained also in this study, a small angle boundary has dislocation structure as its grain boundary structure. This type of the boundary structure can be considered not to change by a variation of a cooling rate. Namely, the change in $I$–$V$ behavior is not due to the change of atomic configuration such as dangling bonds at boundaries. This means the origin of interface states is possibly attributed to the accumulation and charging-up of point defects.

Meanwhile, this study revealed that the non-linearity of $I$–$V$ curve differs with a misorientation angle of small angle boundaries. Namely, it is reasonable to consider that the increment of dislocation density gives the increment of the non-linearity in $I$–$V$ relation. Figure 8 shows schematic illustrations for a relation between a boundary dislocation and a defect accumulation. The accumulation of point defects depends on the generation/recover process of point defects during annealing and cooling. SrTiO$_3$ structure is known to be Schottky type defects as follows,

\begin{equation*}
\text{NULL} \leftrightarrow V_{\text{Sr}} + V_{\text{Ti}} + 3V_{\text{O}}
\end{equation*}

This type of the defects is considered to generate or sink at distorted areas such as dislocations, surfaces, grain boundaries and so on because the reaction of this type needs the generation or the diminishment of excess vacant sites.\textsuperscript{12} During annealing, a flow of point defects takes place from kink area to grain interior, while vice verse during cooling. However, the process depends on a kind and a type of point defects kinetically. In the case of SrTiO$_3$, the diffusivity of oxygen is considered to be faster than that of cation. So, acceptor type point defects such as $V_{\text{Sr}}$ and $V_{\text{Ti}}$ have a tendency to segregate in the vicinity of grain boundaries (see Fig. 8(b)). As a result, cation type defects accumulate to the vicinity of boundaries as seen in Fig. 8(a). If these acceptor type defects charge up, they can trap electrons, which gives a band-bending. As the non-linearity is described as a function of the amount of acceptor type defects, more dislocations give larger non-linearity. In order to reveal this point, more detail examination must be necessary from a viewpoint of electrical properties of defects.
4. Conclusions

The present study examined boundary structures of 2°- and 4°-small angle tilt boundaries by transmission electron microscopy study. In addition, the relationship between the dislocation structure and the electrical properties across small angle boundaries were investigated. The following conclusions could be obtained.

(1) The two single crystals contact each other under an annealing condition at 1400°C for 10 h under a pressure of 0.4 MPa in air. The obtained boundaries are free from any secondary phases such as amorphous films or precipitates even on an atomic scale.

(2) The boundary structure in a small angle boundaries are composed with edge type boundary dislocations whose Burgers vector is [010]. The density of the boundary dislocations increases with an increase in the misorientation angle.

(3) The I–V behavior exhibits non-linearity in the both small angle boundaries. The non-linearity coefficient is 1.2 in the 2°- and 1.7 in the 4°-boundaries, respectively.

(4) It was revealed that the non-linearity increases with a dislocation density. This suggests that the origin of interface states is due to an accumulation and charging-up of defects which generates around boundary dislocations.

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