High-Resolution Electron Microscopy of a Subgrain Boundary in Strontium Titanate Single Crystal

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The microstructure of subgrain boundaries in as-annealed non-doped SrTiO₃ single crystals was studied. When the crystal quality is good, it is difficult to observe lattice defects using only transmission electron microscopy (TEM). In such cases, pre-observation by X-ray topography is useful. Hence, the author used both TEM and X-ray topographic techniques. X-ray topographs showed the defect distribution throughout the crystals. [011]-Type crystals generally have subgrain textures. High-resolution transmission electron microscopy revealed that the subgrain boundaries were small-angle tilt boundaries formed by partial dislocations of $1/2\langle 110 \rangle$ Burgers vectors and there were no segregation of impurities.

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1. Introduction

The compounds of the perovskite family are important materials for future electric devices. The SrTiO₃ crystal has a perovskite structure with cubic symmetry. Thus, it is important to store the experimental data in order to reveal the nature of lattice defects in SrTiO₃. Various studies on lattice defects in SrTiO₃, using transmission electron microscopy (TEM), have been reported recently. Most of them were studies on dislocations. A detailed study on dislocations in SrTiO₃ crystals has been reported by Nishigaki *et al.*¹⁾ They observed many dislocations in SrTiO₃ indented at high temperature and determined the nature of the dislocations using a tilting and contrast experiment. There were two types of dislocations that had the $\langle 100 \rangle$ -type and the $\langle 110 \rangle$ -type Burgers vectors, respectively. Matsunaga and Saka observed dislocations in SrTiO₃ indented at room temperature using a tilting and contrast experiment.²⁾ They reported that almost all the dislocations had the $\langle 110 \rangle$ -type Burgers vectors. Mao and Knowles observed dislocations in SrTiO₃ grains of an experimental internal barrier layer capacitor.³⁾ They mainly used a weak beam method. They reported that the dislocations had $\langle 110 \rangle$ -type Burgers vectors. Partial dislocations were reported in the studies mentioned above, as observed by the weak beam method.^{1–3)} There are other studies on investigations of lattice defects in SrTiO₃: for example, studies on artificial boundaries,^{4,5)} grain boundaries in polycrystals,⁶⁾ and microstructure of thin films.^{7,8)}

When we consider the application of SrTiO₃ to substrates of superconducting oxide films, it is important to investigate the lattice defects in as-grown or as-annealed SrTiO₃ single crystals. However, it is difficult in general to observe lattice defects in bulk single crystals using only TEM when the crystal quality is good, particularly in the case of high-resolution electron microscopic observation. Hence there are few studies on observation of lattice defects in good-quality single crystals using high-resolution electron microscopy (HREM). X-ray topography is useful in these cases. The crystallographic perfection of as-annealed SrTiO₃ single crystals has been studied using X-ray topography.⁹⁾ Dislocation arrange-

ments due to heat treatment were also studied using X-ray topography.¹⁰⁾ However, the resolution of X-ray topography is not so good as that of TEM. Hence, the author and coworkers have observed as-grown SrTiO₃ using both TEM and X-ray topography to compensate for the weak points of each technique.^{11,12)} In these experiments, dislocations were mainly studied while subgrain boundaries were only partially studied. The observed dislocations had $\langle 100 \rangle$ -type Burgers vectors.

In this study, the author focused on the microstructure of subgrain boundaries in the SrTiO₃ single crystal. A technical characteristic of this study is to use TEM and X-ray topography together as in the author's previous studies.^{11,12)} The aim is to determine the character of the subgrain boundary on the HREM scale.

2. Experimental Procedure

The experimental technique used in this study was similar to that used in the previous studies.^{11,12)} The starting samples were Verneuil-grown SrTiO₃ single-crystal plates supplied by Shinkosha Co. Ltd. Their lapped faces were (011), and their growth directions were [011]. Reflection X-ray topographies were obtained using a Lang camera with a conventional X-ray tube having a Cu anode. The tube voltage and current were 50 kV and 15 mA, respectively. Based on these X-ray topographic observations, the author selected one sample, which included many subgrain boundaries, for the TEM study. The sample was sectioned using a low speed diamond saw. The sectioned specimens were ground and lapped to less than 50 μm thickness, and further thinned by ion milling to obtain foils. TEM observation was conducted at an accelerating voltage of 200 kV using a JEOL JEM-2000FX-II microscope. The theoretical point resolution of this TEM, which is set up at Yamanashi University, is 0.28 nm. This resolution is insufficient to obtain high-resolution structural images but is sufficient to obtain high-resolution lattice images. It is possible to acquire useful information on subgrain boundaries from these lattice images.

Fig. 1 X-ray topograph of a (011) crystal plate taken with 033 reflection using $\text{Cu K}\alpha_1$ radiation.

3. Results and Discussion

The X-ray topographs obtained in previous studies revealed that subgrain textures were absent in (001) crystal plates but that some were present in (011) crystal plates.^{11,12} There was a tendency for the (011) crystal plates to have more defects than the (001) ones. A similar tendency was noted in this study.

Figure 1 shows a 033 reflection X-ray topograph of a (011) SrTiO_3 crystal plate. This crystal plate has a good quality compared to the general metallic crystals. X-ray topography is a very sensitive method for determining lattice defects and strained fields. We can observe the defects on a macroscopic scale (scale bar in the Fig. 1 is 1 mm). The mosaic-like image shows the subgrain textures. The dark gray and light gray contrast shows the macroscopic strain. This crystal plate had a relatively large number of subgrains compared to the other crystal plates examined. The upper left corner of the crystal plate, where the subgrains were fine, was sectioned for microscopic observation by TEM.

Figure 2 shows the selected-area electron diffraction pattern (SADP) from the area containing a subgrain boundary. Split spots, of which the tilt angle is approximately 3 degrees, appear in the SADP.

Figure 3 shows the HREM image corresponding to the

Fig. 2 Selected-area diffraction pattern from the area containing a subgrain boundary.

SADP shown in Fig. 2. A rectangle, shown on the lower left side of the micrograph, is the projection of a unit cell to the (011) plane. A subgrain boundary runs vertically through this micrograph. No segregation of impurities was observed around the subgrain boundary. The subgrain boundary is formed by the arrangement of dislocations. The letters A, B and C indicate the positions of the dislocation cores.

Fig. 3 High-resolution transmission electron micrograph of the subgrain boundary and neighboring area. A rectangle, shown on the lower left side of the micrograph, is the projection of a unit cell to the (011) plane. The letters A, B and C indicate the positions of dislocations.

Each dislocation shown in Fig. 3 is an edge type and has the $1/2[01\bar{1}]$ Burgers vector. The reason why the dislocations are partial cannot be discussed only by considering these results. However, this is not unusual since partial dislocations with $1/2\langle 110 \rangle$ Burgers vectors have been observed by the weak beam method in other studies.^{2,3)} In this study, partial dislocations were observed using the most reliable method, HREM. The distances among the dislocations range from 4.1 to 4.4 nm. The tilt angle, which is simply calculated from Burgers vectors and dislocation distances, is approximately 3.5 degrees. This is approximately equal to the experimental value of the SADP result shown in Fig. 2. These results show that this subgrain boundary is a small-angle tilt boundary without segregation of impurities. Of course, perfect crystal is the best for application to substrates. However, in the viewpoint of practical use, it may be impossible. Judging from the experimental results, SrTiO₃ is a feasible crystal to

use in practice. The dark gray and light gray contrast, which is seen throughout the micrograph, shows microscopic strain. This strain may be due to dislocations and oxygen vacancies.

4. Summary

In this study, the subgrain boundary of SrTiO₃ crystal-plates was observed. The Verneuil-grown (011) crystal plates showed the tendency to have subgrain textures. The subgrain boundary is a small-angle tilt boundary without segregation. The dislocations, which formed the small-angle tilt boundary, were partial dislocations with $1/2\langle 110 \rangle$ Burgers vectors. The author conducted the observations of small-angle tilt boundary and partial dislocations by the most reliable method, HREM. The key point of the experiment is pre-observation by X-ray topography.

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