High Resolution Microscopy Study for [001] Symmetric Tilt Boundary with a Tilt Angle of 66° in Rutile-type TiO₂ Bicrystal

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In this study, the grain boundary structure of [001] symmetric tilt boundary with a tilt angle of 66° was investigated using a rutile-type TiO₂ bicrystal. The tilt angle of this boundary has a misfit angle of 1.7° from an exact Σ13 approaching to Σ17 relation. High-resolution transmission electron microscopy study (HRTEM) has revealed that the grain boundary was free from any secondary phases, and the two single crystals contact each other perfectly at an atomic scale. The boundary shows almost straight feature without any step structures whereas a part of the boundary forms facet structures consisting of low index planes such as {310} and {110}. On the other hand, it was found that the contrasts due to atomic structural analysis using HRTEM, the strain field results from a distorted Σ13 unit structure, which can be predicted from a rigid body model of Σ13 relation. This distorted unit structure has a similar structure of Σ17 relation. Namely, the boundary consists of a periodical array consisting mainly of Σ13 unit structures and partially Σ17-like unit structures. In other words, a misfit angle in this boundary was accommodated by not introducing secondary dislocations, but a transformation of basal unit structure.

Keywords: TiO₂, bicrystal, displacement shift complete dislocation, grain boundary structure, high-resolution transmission electron microscopy study

1. Introduction

In most of electroceramic devices, electrical properties are closely related to their grain boundary structures.¹,² For example, it is known that some of electrical anomalies such as varistive effect, positive temperature coefficient of resistivity (PTCR) effect and so on exhibit a grain orientation relationship dependency.³⁻⁶ These phenomena are considered to be due to a change in a height of potential barriers caused by a variation of grain boundary structure. Particularly, highly coherent boundaries such as sigma boundaries tend not to show such electrical anomaly.⁷ In order to understand a mechanism of an appearance of the electrical anomaly, therefore, it has important meaning to examine a transformation of grain boundary atomic structure when a grain orientation relationship shifts from an exact sigma relation.

TiO₂ is one of most useful materials that are often used for base materials of electroceramic devices. So far, several workers have examined grain boundary structure of several types of grain boundaries in this material.⁷⁻¹² D. J. Wallis et al. performed Z-contrast imaging analysis combined with electron energy-loss spectroscopy for Σ5(210) boundary. The boundary consists of a periodical array of unit structures obtained from Σ5 relation, however, oxygen ions at the boundary situate at three-fold coordination to titanium ions, which are similar to that in a bulk region. This result is consistent to the fact that highly coherent boundary does not exhibit clear electrical anomaly. As for the boundary including a small misfit, Dahmen et al. have examined for Σ5(210) boundary with a misfit angle of 2° from an exact Σ5 relation. They have reported that the boundary basically consists of an array of Σ5 unit structure, however, its misfit angle was accommodated by periodically including 1/5[210] DSC (displacement shift complete) dislocations. They also confirmed a formation of resulting step structures due to incorporating the DSC dislocations. On the other hand, Liu et al. have investigated atomic structures of [001] tilt type Σ5(210), Σ5(310), Σ13(320) and Σ17(410) boundaries by comparing with HRTEM images and simulated ones obtained from theoretical calculations.⁹ They also insisted that the respective boundaries include step structures caused by DSC dislocations to accommodate a small misfit from an exact Σ relation. According to these two reports, the boundaries including a small misfit angles generally tend to show a step feature due to DSC dislocations in the case of rutile type TiO₂.

In this study, we examined a tilt boundary having a large tilt angle of 66° in rutile-type TiO₂ bicrystal, which has not been investigated yet, from a viewpoint of accommodation mechanism of the misfit angle. This boundary has a small misfit angle of about 1.4° from Σ13(320) relation to a tilt direction of Σ17(530) relation.

2. Experimental Procedure

A commercially available rutile-TiO₂ single crystal blocks (Shinkosha Ltd., Tokyo, Japan) were used for preparation of bicrystals. After confirming a crystal orientation, a block was machined from a grown crystal with a size of 10 × 10 × 5 mm³. Broad faces were used for contacting planes. The planes used for contacting were precisely ground, polished finally using mechno-chemical treatment. A bicrystal was fabricated by annealing a staked pair of two obtained single crystals at 1600°C in air. The bicrystal has a boundary of [001] symmetric tilt type, which was prepared to have a tilt angle of 66°. The tilt angle has a small misfit angle about 1.4° from an exact Σ13 relation, i.e., 67.38° as shown in Table 1.
Specimen for transmission electron microscopy study (TEM) were prepared with ordinary thinning methods, including mechanical thinning and ion-beam milling using Ar ions. The investigations of the grain boundary structure were carried out by a high resolution electron microscope (HRTEM; EM-002B, TOPCON) and a conventional type TEM (JEM-2010HC, JEOL) operated at 200 kV.

3. Results

Figure 1 shows a TEM bright field image of the boundary. The inset is a selected area diffraction pattern taken from the two adjacent crystals. The boundary is free from any secondary phases such as amorphous phase and precipitate, indicating that the boundary was perfectly joined. On the other hand, a periodical array of particular contrasts can be seen along the boundary as indicated partially by the arrows. The periodical contrasts result from strain field as discussed later.

Figure 2 is a weak beam dark field image taken at \( g = \frac{0}{222} \). There can be seen bright lines due to strain fields on the grain boundary plane with a spacing of about 7.6 nm.

Figure 3 is HRTEM image of the boundary, which was taken at near Scherzer focus condition. In the figure, the boundary was set at an edge-on condition. The two single crystals were perfectly joined even at an atomic scale, and the boundary has no secondary phases. From lattice fringes of respective crystals, an actual tilt angle can be estimated to be 65.7°, indicating that the boundary has a misfit angle of 1.7° from an exact \( \Sigma 13 \) relation, i.e., 67.38°. On the other hand, a periodical structure exists at the boundary, indicating an array of unit structures. The grain boundary plane is likely straight, and has no step features in spite that the boundary has a misfit angle.

A part of the boundary exhibits a faceted feature as shown in Fig. 4. Figure 4 is a bright field image taken from a faceted region when the boundary is largely inclined. Along the boundary, the contours on the grain boundary exhibit a waving feature due to the faceting as in the figure (b). This feature appears periodically and its spacing is about 100 nm in a region where the facts exist.

4. Discussion

4.1 Rigid structure model

Figures 5(a) and (b) schematically show rigid body models of \( \Sigma 13 \) and \( \Sigma 17 \) boundaries. In \( \Sigma 13 \) model, a periodicity of a unit structure has a length of two and half unit cells as schematically shown in Fig. 5(a). In contrast, a unit structure of \( \Sigma 17 \) model is formed with a periodical array of a spacing of four unit cells as indicated by the arrow A in the figure (b), however, this unit structure can be separated into a smaller one with a half periodicity. Namely, a minimum periodical structure in \( \Sigma 17 \) model can be considered to consist of two unit cell length as shown with the arrow B in the figure (b). Comparing with these two unit structures in \( \Sigma 13 \) and \( \Sigma 17 \) boundaries, they have very similar structure each other in

<table>
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<tr>
<th>Boundary</th>
<th>Boundary plane</th>
<th>Tilt angle/°</th>
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<tbody>
<tr>
<td>( \Sigma 17 )</td>
<td>(530)</td>
<td>61.93</td>
</tr>
<tr>
<td>Present boundary</td>
<td>near (320)</td>
<td>66</td>
</tr>
<tr>
<td>( \Sigma 13 )</td>
<td>(320)</td>
<td>67.38</td>
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spite of different tilt angles. Figure 5(c) shows an overlapped illustration of $\Sigma_{13}$ and $\Sigma_{17}$ unit structures. As seen in the figure, the respective atomic columns become to be coincident each other only by a small distortion.

4.2 Strain field

In coincident site lattice (CSL) theory, a misfit angle from an exact $\Sigma$ relation is considered to be accommodated by an introduction of displacement shift complete (DSC) dislocations. At this time, the misfit angle can be expressed by the following equation,

$$\frac{|B|}{D} = \Delta \phi,$$

where $B$ is a component of DSC vector normal to a grain boundary plane, $\Delta \phi$ a misfit angle from an exact $\Sigma$ relation, and $D$ a spacing of DSC vectors. Figure 6 shows a DSC lattice obtained from an exact $\Sigma_{13}$ relation. In the schematic, three kinds of DSC vectors are presented, whose length is under second smallest length. The respective vectors are $a/13[320]$ in DSC1, $a/13[-230]$ in DSC2, and $a/26[1513]$ in DSC3, respectively, where $a$ is a lattice constant of a-axis in rutile type TiO$_2$. Among them, DSC1 is normal to a grain boundary plane, and have a length of 0.127 nm. In contrast, DSC3 is inclined at 45° to a grain boundary plane, and its length normal to a grain boundary plane is 0.0635 nm, which is half comparing with the other two DSC’s. As shown in
Fig. 2, the boundary had a periodical array of distorted contrasts, and the spacing was about 7.6 nm. If these contrasts result from DSC dislocations to accommodate a misfit angle of \( \frac{\pi}{C_1} \), a suitable magnitude of \( B \) can be estimated to be 0.22 nm from eq. (1), where \( \Delta \phi \) and \( D \) is 1.7° and 7.5 nm, respectively. The length of DSC dislocation necessary to accommodate a misfit angle of the boundary is almost the same value as that of a twice of DSC1, i.e., 0.254 nm.

In general, when DSC dislocations are introduced in a boundary, a step structure is known to be formed. This is because lattice displacement takes place due to an introduction of DSC dislocations. However, such step structure could not be observed in the boundary as shown in Fig. 3. As for this discrepancy, we introduced a distortion structure of a unit structure as follows.

Figure 7 shows atomic columns lined to make \( \Sigma 13 \) relation rigidly. In the figure, \( \Sigma 13 \) unit structure is indicated with a solid line, and an atomic arrangement coincident to \( \Sigma 17 \) sub-unit structure is also shown with dashed lines, where a difference of tilt angle between the two sigma relations is ignored. As seen in the figure, \( \Sigma 13 \) unit structure is able to transform into \( \Sigma 17 \)-like unit structure by introducing a distortion corresponding to the arrow indicated in the figure. This distortion vector is similar to DSC1. In other words, the boundary has a distortion having a similar magnitude to that of DSC1, however, DSC dislocation itself is not incorporated. The strain field similar to a magnitude of the dislocation is introduced.

Figure 8 shows a HRTEM image of the boundary including a schematic of unit structures to match respective atomic columns in a sequence of their periodicity. As seen in the image, the boundary consists of three \( \Sigma 13 \) unit structures as shown by white lines and two of distorted \( \Sigma 13 \) unit structures (\( \Sigma 17 \)-like unit structures) as shown by black lines. The distorted \( \Sigma 13 \) unit structure is obtained from introducing a distortion vector into \( \Sigma 17 \) sub-unit structure as described above. In this model, two set of distorted unit structure exist in a unit of periodical series as indicated by the arrow. On the other hand, periodical contrasts due to a strain field could be seen in a grain boundary plane as shown in Fig. 2. The spacing of the contrast was about 7.6 nm, which is almost the same as that of a periodical unit as shown in Fig. 8. It is reasonable to consider that these strain contrasts are due to distorted \( \Sigma 13 \) unit structure. Namely, two set of the distorted unit structures can be seen as one lined contrasts because of a distance between them is too small to resolve by conventional TEM observation.

4.3 Facets

A part of the boundary was found to exhibit a faceting feature. Figure 9 shows HRTEM image taken from faceted region. The habit planes tend to have low index planes such as \{310\} and \{110\}. As for the formation of the faceting feature, it has been reported that grain boundary faceting is
due to a reconstruction of a grain boundary plane from an asymmetric boundary to a symmetric one. Namely, the asymmetry that exists initially in the grain boundary is accommodated by faceting. However, the habit planes observed in this boundary largely inclined from a symmetric relation. Recently, Shibata et al. have reported that even high coherent boundary sometimes exhibits to form faceted structures. They insisted that a distortion of unit structure gives a driving force to facet, and results in a reduction of grain boundary energy. In the case of the boundary examined in this study, similar interpretation may be adopted. As described, this boundary includes some distorted unit structures, resulting an appearance of an ununiform structure. This ununiformity possibly gives faceted features.

5. Conclusions

This study examined the grain boundary structure of TiO$_2$ [001] symmetric tilt boundary with a tilt angle of 66°, which has a misfit angle of 1.4° from an exact $\Sigma$13 relation. This misfit angle is tilted to $\Sigma$17 relation of 61.93°. Grain boundary was confirmed to be free from any secondary phases, and the two single crystals contact each other perfectly at an atomic scale. The boundary shows almost straight feature without any step structures whereas a part of the boundary forms facet structures consisting of low index planes such as {310} and {110}. Weak beam observation revealed that the contrasts due to strong strain fields existed on the grain boundary plane with a spacing of 7.6 nm. Comparing with atomic structural analysis using HRTEM, the strain field results from a distortion of $\Sigma$13 unit structure, which can be predicted from a rigid body model of $\Sigma$13 relation. In addition, the magnitude of the distortion is found to be almost the same as that of DSC dislocations. This distorted unit structure has a similar structure of $\Sigma$17 sub-unit structure, which could be considered to be introduced by a same distortion of DSC dislocations. Namely, the boundary consists of a periodical array consisting mainly of $\Sigma$13 unit structures and partially $\Sigma$17-like sub-unit structures. In other words, a small misfit angle from an exact $\Sigma$13 relation in this boundary was compensated by not an introducing secondary dislocations, but a transformation of basal unit structure.

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