Grain Boundary Atomic Structure of Asymmetric Σ3 Tilt Boundaries in $SrTiO_3$ Bicrystal

T. Yamamoto[1,2], A. Fukumoto[3], H. S. Lee[4], T. Mizoguchi[5], N. Shibata[4], Y. Sato[4] and Y. Ikuhara[2,4]

[1]Deaprtment of Quantum Engineering, Nagoya University, Nagoya, 464-8603, Japan
[2] Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
[3] Department of Advanced Materials Science, The University of Tokyo, Chiba, 277-8561, Japan
[4] Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
[5] Institution of Industrial Science, The University of Tokyo, Tokyo, 153-8505, Japan

Atomic structures at grain boundaries (GB) in polycrystalline materials show huge variation due to grain orientation relationship between adjacent grains. To control physical properties related to grain boundary phenomena, it is necessary to develop a technique controlling the GB atomic structures. So far, to know GB structure systematically, coincident site lattice (CSL) and unit structure concepts have been proposed. In these concepts, we roughly understand GB atomic structure from a viewpoint of the geometrical configuration. However, actual grain boundaries show variation due to experimental treatment such as annealing temperature, atmosphere, dopants and so on, even if the grain orientation relationship does not change. To clarify the GB structural change, systematic examination must be necessary. So far, in our research group, we have carried out GB structural analysis by using well-defined bicrystals prepared by a thermal joining technique of two single crystals. In this study, we focused GB facet/defacet transformation. For the purpose, we prepared asymmetric Σ3 boundaries of $SrTiO_3$ (STO) bicrystals, and investigated GB structural change due to oxygen activity with a special interest in the cation off- stoichiometry.

Asymmetric Σ3 boundary of $[1\bar{1}0]$ (114)//(110) was prepared by thermally joining STO single crystals whose surfaces for contacting were precisely polished. After joining, thin plates including the boundary were mechanically cut and used for annealing. The annealing was conducted at 1350°C for 5days in air and H_2. Thin foils for TEM observation were prepared by an ordinary technique including an ion-milling process. The grain boundary structures and the chemical compositions were investigated by a conventional TEM (CTEM, JEM-2010HC, JEOL Ltd.), a high resolution transmission electron microscope (HRTEM, JEM-4010, JEOL Ltd.) and Cs-corrected scanning TEM (STEM, JEM-2100F, JEOL Ltd.). The precise GB atomic structures and the GB energies were theoretically calculated by the first-principles calculation (VASP code).

The boundary was revealed to exhibit facetted GB in as-joint state. A typical example of GB is shown in Fig. 1. Fig. 1 is a HRTEM image taken from as-joint STO bicrystal. In the figure, GB can be seen as a zig-zag line. Similar faceting GB is often observed in other materials such as BTO, ZnO and so on[1]. The appearance of the facetted GB is sometimes discussed in terms of, what we call, Wullf's shape concept[2]. In the concept, a habit plane whose GB energy is low tends to appear. The habit planes generally vary with elevated temperature. In contrast, in case of STO, the faceting feature was found to depend on oxygen activity during annealing. Thus, we performed annealing the GB in air and H_2 atmosphere. The boundary annealed in air (hereafter,

air-boundary) exhibits clear faceted structure consisting of two habits of $(55\bar{2})_\alpha/(112)_\beta$ and $(\bar{1}\bar{1}5)_\alpha/(111)_\beta$, where α and β means respective crystals of the bicrystal. By annealing in air for long time, a facetted feature as seen in Fig. 1 becomes clearer. A corner of the two habits is very sharp. In addition, the two facet planes are close to the symmetric boundaries of Σ3. By annealing at lower oxygen activity (hereafter, H_2-boundary), another habit with $(114)_\alpha/(110)_\beta$ appears, which is similar boundary to the initial boundary used for contacting. The structural change induced by a variation of oxygen activity suggests GB energy of the $(114)_\alpha/(110)_\beta$ habit becomes lower at lower oxygen activity. Detail GB structural investigation gave an interesting structure configuration. High angle annular dark field (HAADF) STEM images have revealed that the facetted GB of H_2-boundary consists of three kinds of units named as A, B and C, respectively. $(55\bar{2})_\alpha/(112)_\beta$ habit consists of A and C units. In addition, the habit is formed by a periodical array of three A and one C units. $(\bar{1}\bar{1}5)_\alpha/(111)_\beta$ habit is formed with a periodical array of one B and one C units, and $(114)_\alpha/(110)_\beta$ habit with that of three A, one B and one C units. Here, A and B units are typical ones observed in a symmetric Σ3 boundary, suggesting that the inclination of the facet boundaries from a Σ3 symmetric boundary is adjusted by including C units. In addition, it was found that the appearance of C unit is closely related to cation (Sr/Ti) off-stoichiometry of GB. A cationic ratio of A and B units is stoichiometric as previous study[3]. In contrast, that of C unit is Ti-excess by theoretical calculation and EDS analysis performed in this study. The cation off- stoichiometry of C unit is a key to understand GB facet/defacet transformation in STO. At higher oxygen activity, off-stoichiometry at GB tends to become Ti-excess. Thus, the two habits of $(55\bar{2})_\alpha/(112)_\beta$ and $(\bar{1}\bar{1}5)_\alpha/(111)_\beta$, which includes C units, becomes stable, resulting clear facetted GB structure.

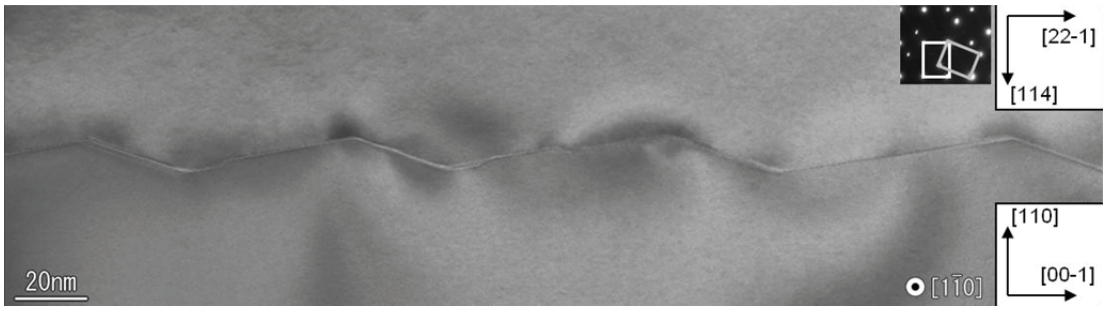

Fig. 1 HRTEM image obtained from as-joint asymmetric Σ3 boundaries. It's noted that GB shows a zig-zag feature, indicating that GB are facetted structure.

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