

Nonstoichiometry and the atomic structures of grain boundaries in SrTiO₃

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SrTiO₃ is one of the most important electroceramic materials used for capacitors and low-voltage varistor. In this material, nonstoichiometry such as Ti/Sr and Ti/O ratio change in the vicinity of the grain boundary (GB) is related to GB electronic properties necessary for devices. Thus, an understanding of the chemical compositions at the GB core is essential for improving the properties.

In this study, the defect energetics in three SrTiO₃ symmetric tilt GBs, [110](111) Σ 3, [001](210) Σ 5 and [001](510) Σ 13, were theoretically studied with a first-principles calculation to understand the nonstoichiometry at the GB core. In addition, the GB core structures were characterized with high angular annular dark field (HAADF)-scanning transmission electron microscope (STEM) observations and the cation chemical composition in the vicinity of the GB was measured by an energy dispersive X-ray spectroscopy (EDS).

A first-principles projector augmented wave (PAW) calculations within Generalized Gradient Approximation (GGA) were performed using VASP code to calculate the defect energetics at the GB core. To obtain the stable atomic structure of each GB, rigid body translation was considered. With the stable atomic structures, vacancy formation energies were systematically calculated for 32 sites in [110](111) Σ 3 GB, 28 sites in [001](210) Σ 5 GB, and 38 sites in [001](510) Σ 13GB. The difference of the vacancy formation energies at the GBs from that in the bulk-area was estimated by the following equation:

$$\Delta E_f = E_f^{\text{defect at GB core}} - E_f^{\text{defect at bulk-area}}$$

In order to characterize the atomic structures of the GB core and measure the cation ratio in the vicinity of the GB, SrTiO₃ bicrystals with Σ 3, Σ 5 and Σ 13 GBs were fabricated by joining two single crystals with 78.4°, 53.2° and 22.6° misorientations, respectively. TEM specimens were fabricated by a conventional method and those specimens were observed by an aberration corrected STEM (JEOL-2100F) and the Ti/Sr ratios were measured by STEM-EDS. Detail procedures were described elsewhere [1].

Figure 1 shows the most stable calculated structure and the HAADF-STEM image of $[001](210)\Sigma 5$ GB. Since the intensity of the image is approximately proportional to the square of atomic number (Z), the brighter and darker columns correspond to Sr and Ti-O columns, respectively in the HAADF-STEM image. The calculated atomic positions of Sr and Ti-O columns of $[001](210)\Sigma 5$ GB were also shown as white circles in Fig. 1(b), respectively. In a similar manner, other two grain boundaries, $[110](111)\Sigma 3$, and $[001](510)\Sigma 13$ were examined experimentally and theoretically.

Nonstoichiometry at the GB core in SrTiO_3 must be explained with the species and the amount of the vacancies at the GB core. To estimate the total amount of the defects, the differences of the vacancy formation energy at the site which shows the lowest formation energy were considered. Figure 2 shows the plots for the lowest Sr vacancy formation energy at Ti-rich oxidizing condition versus GB energy and the average Ti/Sr ratios for each GB. It was found that the Sr vacancy formation energy was lower and the Ti/Sr ratio was also increased when the GB energy is higher.

In this paper, the atomic structures of SrTiO_3 grain boundaries were systematically investigated and the relationships between the nonstoichiometry and the defect energetics at the GB will be discussed.

[1] M. Imaeda et al., Physical Review B 78, 245320(2008)

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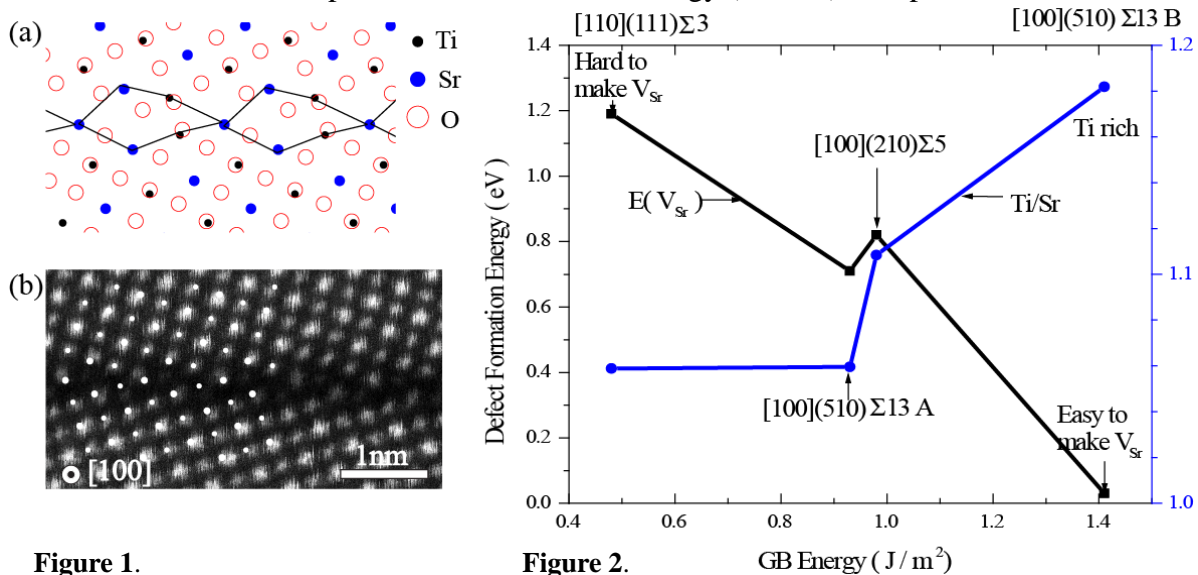


Figure 1.
(a) Most stable atomic structures obtained by the theoretical calculation, and (b) the HAADF-STEM image of $[001](210)\Sigma 5$ GB.

Figure 2.
The plot of the lowest Sr vacancy formation energy at Ti rich oxidizing condition and Ti/Sr ratio measured by STEM-EDS versus GB energy