Atomic-scale structure relaxation, chemistry and charge distribution of dislocation cores in SrTiO$_3$

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ABSTRACT

By using the state-of-the-art microscopy and spectroscopy in aberration-corrected scanning transmission electron microscopes, we determine the atomic arrangements, occupancy, elemental distribution, and the electronic structures of dislocation cores in the 10° tilted SrTiO$_3$ bicrystal. We identify that there are two different types of oxygen deficient dislocation cores, i.e., the SrO plane terminated Sr$_{0.82}$Ti$_{0.85}$O$_{3-x}$ (Ti$^{3.67+}$, $0.48 \leq x \leq 0.91$) and TiO$_2$ plane terminated Sr$_{0.63}$Ti$_{0.90}$O$_{3-y}$ (Ti$^{3.60+}$, $0.57 \leq y \leq 1$). They have the same Burgers vector of **a**[100] but different atomic arrangements and chemical properties. Besides the oxygen vacancies, Sr vacancies and rocksalt-like titanium oxide reconstruction are also identified in the dislocation core with TiO$_2$ plane termination. Our atomic-scale study reveals the true atomic structures and chemistry of individual dislocation cores, providing useful insights into understanding the properties of dislocations and grain boundaries.

1. Introduction

Dislocations and grain boundaries are ubiquitous in the crystal materials. These defects can have very different atomic arrangement and/or chemistry from the bulk matrix [1–5], which strongly influences on the physical and chemical properties (e.g. the ionic and electrical conductivities) or even dominates the entire response of devices that are in nanometer scale. In electroceramic SrTiO$_3$ (STO, a model perovskite oxide), on the basis of the electrical and ionic transport measurements the dislocations are usually assumed to be non-stoichiometric [3] due to the presence of charged defects [6–9]. However, it's still unclear as to what type and amount of charged defects is and how these defects distribute in the dislocations, *i.e.*, whether they are localized in the very core region or spread over the surrounding dislocation area. The atomic arrangements of dislocation cores particularly for the oxygen configuration have been rarely reported [10] mainly due to the experimental limitations and structural complexity of STO and thus a deterministic correlation of the chemical properties

to the microstructure for a specific dislocation core has not been achieved.

The knowledge of the local atomic structure and chemistry of the dislocations indeed is extremely difficult to be extracted by the bulk-based characterization techniques such as the electrical measurements [3]. Despite a lot of microscopy efforts [6,9–16] have also been devoted to reveal the microstructure of dislocations, high-angle annular dark-field (HAADF) [9,12–14] is insensitive to oxygen, and the conventional TEM [6,16] and exit surface wave function reconstruction in the negative C_s imaging [10] are unable to distinguish the localized structural reconstruction which commonly exist in the dislocation cores [8,9,13,17]. In contrast, the recent advancements of annular bright-field (ABF) imaging in aberration-corrected scanning transmission electron microscope (STEM) not only enables us to simultaneously visualize both heavier cation and relatively lighter oxygen columns [18] but also is more robust for determining the atomic arrangements in the vicinity of the defects which usually show poor contrast in the HAADF images [19]. In addition, it is also convenient to combine atomic-resolution imaging and spectroscopy such as energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) in the STEM mode, allowing us to precisely determine the atomic arrangements, occupancy, elemental distribution, and electronic structures.

Here, by employing these complementary imaging and spectroscopy techniques, we reveal both the cation and anion arrangements in the dislocation cores in STO and identify that the atomic structure of dislocations in STO bicrystal is dominated by the terminated atomic layer on the core, that is, SrO plane terminated core A–$Sr_{0.82}Ti_{0.85}O_{3-x}$ ($Ti^{3.67+}$, $0.48 \leq x \leq 0.91$), and TiO_2 plane terminated core B–$Sr_{0.63}Ti_{0.90}O_{3-y}$ ($Ti^{3.60+}$, $0.57 \leq y \leq 1$). Both of them are oxygen deficient and have the same Burgers vector of $\mathbf{a}$[100], while they are distinct in the atomic arrangements and chemical properties. The core B contains high density of Sr vacancies and rocksalt-like reconstruction in the tensile strain zone. Oxygen deficiency in the core A is caused by removal of anions in the confined core zone due to the strong Coulomb repulsive interaction, whereas in the core B the oxygen deficiency mainly originates from the Ti-O polyhedral connection change from the corner sharing in the perovskite to edge sharing octahedrons in the rocksalt-like reconstruction, leading to an increase in the Ti/O ratio (reduced Ti ions). Our study precisely determines the atomic structure and chemistry of non-stoichiometric dislocation cores in $SrTiO_3$. These findings unambiguously clarify a long-standing question on the type and distribution of defects in the dislocations and thus can not only help us to explain the past experiments but also provide essential information for space charge zone calculation and the atomistic simulation for dislocations. The demonstrated methodology by combining the state-of-the-art microscopy and spectroscopy provides unprecedented opportunity to explore the defect properties in complex ceramics.

2. Experiments

Bi-crystal fabrication: The STO bi-crystal with a [001]/(100) 10° mistilt grain boundary was fabricated by the thermal diffusion bonding of two STO single crystals. First, 5° off (100) surfaces of the single crystals were polished to a mirror-like state. Then, the surface was cleaned with ethanol and propanol to remove contaminants. Subsequently, one crystal was set on the other to create a 10° tilt grain boundary bi-crystal. Under the uniaxial load of ~0.2 MPa, the two crystals were heat-treated at 700 °C for 20 h at the rate of 20 °C/h in air for bonding. Post annealing was carried out to obtain larger bonded area. Heat treatments were performed at 1000 °C for 80 h in total and subsequently at 700 °C for 14 h.

TEM sample preparation, images acquisition and analysis: The TEM specimens were prepared by the mechanical polishing followed by the argon ion milling (Precision Ion Polishing System, Gatan). At the final stage of ion milling, the voltage was set at 0.2 kV for about 5 min to remove the surface amorphous layer and minimize the damage. HAADF and ABF images were recorded at 300 kV in a JEM ARM300CF (JEOL Ltd.) with spatial resolutions up to 45 pm. The convergence semi-angle for imaging is 24 mrad, the collection semi-angles snap is 12 to 24 mrad for the ABF imaging and 65 to 240 mrad for the HAADF imaging. During imaging, we also deliberately minimized the electron dose by using small aperture, small beam current and short scanning time. Typical HAADF and ABF images are shown in Fig. 1a and b respectively. Two different dislocation cores are visiable, which are labeled as core-A and core-B. To determine the occupancy of individual atomic columns in the dislocation cores, the intensity ratio of each atomic column in the cores to that in the bulk is calculated. We use the relation $I^{1.7}$ for HAADF and $I^{1/3}$ for contrast inverted ABF images to estimate the occupancy, where I is the normalized intensity of the columns in the dislocation cores. For those columns in the dislocation core B with mixed Sr and Ti, both Sr and Ti signal is normalized to the columns in the bulk based on the EDS counts and thus the ratio of Sr to Ti is determined.

EDS mapping: The EDS experiments were carried out in a 200 kV JEM-ARM200F (cold-FEG) equipped with dual-SDD EDS de-

tectors (JEOL Ltd.). The convergence semi-angle for imaging is 22 mrad. The total solid angle of EDS detectors is 1.7 sr. Typical net count EDS maps for Sr, Ti and O are shown in Fig. 2a–c. No principal component analysis is used to process the data. To estimate the elemental occupancy of the dislocation cores, linear approximation method was employed to calculate the average occupancy for cationic columns. A selected core region of 20 × 30 pixels is integrated to calculate the average net count. The bulk region is integrated from all over the entire image with the grain boundary region being excluded. The total pixels for bulk calculation are 256 × 216 pixels. The net count in the cores is normalized to the bulk, *i.e.*, both Sr and Ti are assumed to be 1 in the bulk matrix. The calculated values are 0.82(±0.02) for Sr and 0.85(±0.03) for Ti in the core A compared to the bulk. The error is the standard deviation when averaging the three cores. From two B-type cores, the calculated values are 0.63(±0.04) for Sr and 0.90(±0.01) for Ti compared to the bulk.

EELS mapping: The EELS experiments were carried out in a JEM ARM200CF (JEOL Ltd.) equipped with dual Enfinium camera (Gatan). All the spectra were recorded at 200 kV. The electron beam was slightly spreaded and the acquisition time is 0.1 s/pixel to minimize possible damage to the core structures. The convergence semi-angle is 24 mrad, and the collection angle is 53 mrad. Spectrum image is recorded from 400 ~ 600 eV with energy dispersion 0.1 eV. The size of mapped region is ~16 × 16 nm^2 with 100 × 100 pixels. Three 7 × 5 pixels rectangles are added up as one spectrum to represent the core A. Six 7 × 5 pixels rectangles are added up as one spectrum to represent the gap between two dislocation cores. Three 7 × 5 pixels rectangles are added up as one spectrum to represent the core B. The rest of regions are used to calculate the spectrum of the grain matrix.

3. Results and discussion

3.1. ABF image analysis

Fig. 1a is a HAADF (*Z*-contrast; *Z* is atomic number) image of a 10° tilted grain boundary in STO bi-crystal that consists of two types of edge dislocations [6,14,15,20]. The core A is SrO plane terminated and core B is TiO_2 layer terminated (indicated by the dashed-line arrows in Fig. 1a). These two types of dislocations alternately sit along the grain boundary. The distance between two cores is about six unit cells, which is in good agreement with Frank's theory for 10° tilted boundary [21]. Although both core A and B have the same Burgers vector of $\mathbf{a}$[100], they show very different contrast, *i.e.*, core B is darker and wider than core A. The ABF image in Fig. 1b enables all the columns including oxygen in the dislocation cores to be visible, indicating the ABF is more robust than the HAADF for imaging the defects [19]. Judging from the contrast in the HAADF and ABF images, a substantial decrease in the occupancy occurs in the oxygen column No.11 in the core A in Fig. 3a and b, and another oxygen column No.12 at the symmetrical side of column No.11 is almost unoccupied. The contrast of Sr columns (No. 8, 9, and 10), however, decreases subtly, suggesting the core A is deficient in oxygen. Given the estimated unoccupied numbers of 0.45 for the No.11 (O), 1 for the No.12 (O), 0.2 for the No.8 (Sr), 0.09 for the No.9 (Sr), and 0.12 for the No.10 (Sr) columns, we conclude that approximately one oxygen column is missing in the core A (see details in the Experiments section). In the core B in Fig. 3c and d, some columns appear diffuse (*e.g.* No.13, No.21, No.22 and No.23) or split (No.16), indicating local structural inhomogeneity. Therefore, to precisely identify the structure of dislocation core B, the elemental information is also needed.