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Exploring the Atomic Scale Structure and Properties of Grain Boundary in $SrTiO_3$ by Electron Beam Imaging and Spectroscopy

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Most important crystalline materials are polycrystalline and consist of grain boundaries which are interfaces between pairs of contiguous, but differently oriented grains. Many physical and mechanical properties of polycrystals are influenced by the structure and properties of grain boundaries. Thus, one effective approach for tailoring materials properties is through grain boundary engineering by exploitation of grain boundary structure-property relationships to control the structure, composition, atomic arrangements, and crystallographic distribution of grain boundaries.

We carried out a systematic study of a 10° tilt bicrystal grain boundary of strontium titanate ($SrTiO_3$). $SrTiO_3$ has attracted significant attention of researchers in recent years because of unique structure and properties. It is also a model system for studies of a large family of perovskite oxide materials. High resolution scanning transmission electron microscopy (STEM) has shown the existence of periodic dislocation cores at this type of bicrystal boundary. The cores are separated by “bridges” that resembles $SrTiO_3$ crystal lattice. This periodicity is speculated to be a result of the 10° tilt around the in-beam direction. The periodicity has been measured to be 2.1 nm and the diameter of the dislocation core to be 1 nm.

In this work we use STEM imaging and electron energy loss spectroscopy (EELS) techniques to investigate the structure and properties of the 10° tilt grain boundary. We are interested in how the composition change at the GB and how does this influence its thermal properties. This information can be revealed by investigating different energy ranges on EELS from the cores. Core-loss EELS analysis of change in L_3 t_{2g}-L_3 e_g peaks shows a reduction of peak splitting, reminiscent of the merging of the two peaks seen in Ti^{3+} [3], indicating the valance state of titanium has changed to +3 from +4 which is its default valence state within the bulk STO material (Fig. 1d). We can also see using line scan measurement that peak splitting reduction occur at elemental vacancies (Fig. 1e). These findings are evidence of a change in composition and valence state which cannot be easily revealed using EDS mapping. This reduction in valance state is likely caused by oxygen deficiency resulted from strain around the dislocation cores [2]. Vibrational EELS, on the other hand, shows decreased overall vibrational signal at the cores (Fig. 2c). The background subtracted phonon signal show two peaks, one at 60 meV corresponding to O-Ti vibration, another at 100 meV corresponding to pure oxygen vibration (Fig. 2b). When the ratio of these two peaks is mapped (Fig. 2d), we see a decrease in the peak ratio corresponding oxygen vibration at 100 meV, consistent with previous reports of oxygen vacancies and increased Ti/O ratio at the cores [2, 3, 4]. The difficulty for the electron beam to produce phonons at the GB indicate that phonon form one grain may be inhibited from propagating to the other grain. Further, an altered Ti to O ration indicate the presence of excess charges which serve as an additional barrier to phonon propagation and thus heat transfer. Therefore, our findings indicate that the grain boundary inhibit heat transfer within the material.

Many other investigation avenues can be applied to this model system. For example, the fine structures of the GB can be studied using EELS since Ti peak splitting is very sensitive to picometer variation in bond length[5]. In addition, vibrational EELS can be applied to understand the changes in thermal properties of the material due to the GB scattering. We believe understanding the composition, valence state, and vibrational properties of defect cause by GB are very important for understanding its effect on electronic and thermal properties on a material [6].

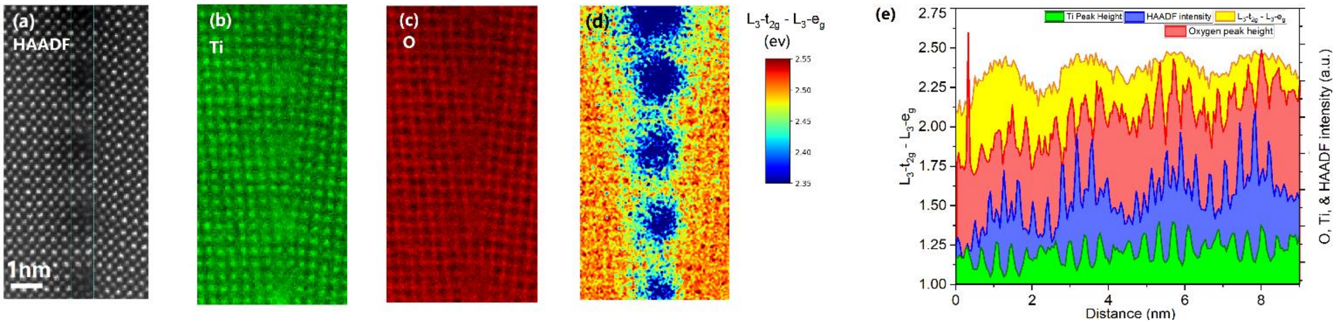

Figure 1. (a) HAADF image showing both the primary and secondary cores. The blue box indicates the line scan region. (b) EELS elemental mapping of titanium. (c) EELS elemental mapping of oxygen. (d) Mapping of titanium L_3-t_{2g} - L_3-e_g peak splitting. (e) Line scan comparing HAADF, Ti, O, and L2-L3 peak splitting.

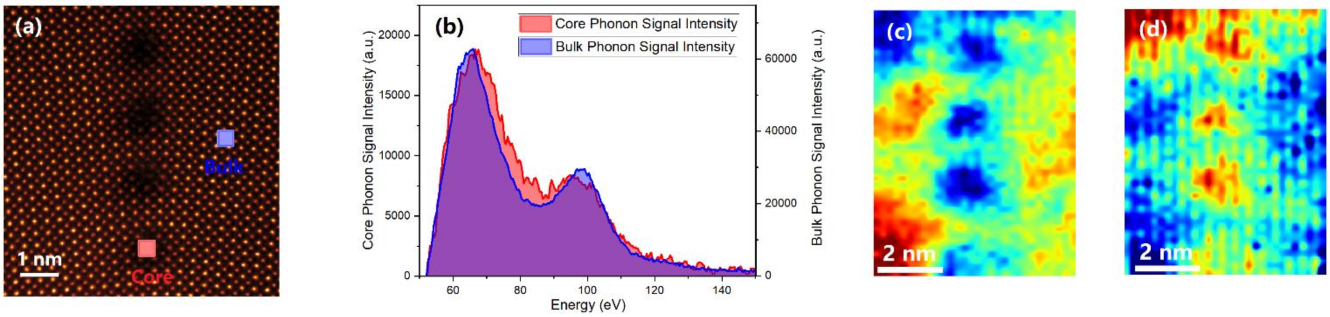

Figure 2. (a) HAADF image showing core structure and location which phonon signals are measured. (b) Background subtracted phonon energy loss signal at bulk and core. (c) Phonon signal intensity mapping at the GB. (d) Map of the peak ratio of the 60 meV and 100 meV peaks.

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