Atom-resolved Imaging of Grain Boundary Complex Superstructures in Oxides

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Doping oxide materials with impurity ions have been a widespread technique for altering the properties of materials. In many cases, a macroscopic change is apparently observed, but characterizing the changes of the structure of the materials on the atomic scale remains a difficult task. Particularly in the case of oxides, it is widely assumed that the dopants segregate to crystal defects (e.g. dislocations and grain boundaries (GBs)), as they are known to be sinks for impurity segregation. Recently, some studies have been performed on unraveling the atomic scale mechanism of dopant segregation to defects in GBs in oxides[1,2)]. But, these researches have been mainly performed for the simple model GB with isovalent dopants w.r.t. the grain matrix. Because the number of oxides and possible impurities are very large, a wide range of oxide systems must be characterized to fully understand the segregation behavior at GBs in oxides.

In this study, complex dopants systems with aliovalent dopants and co-dopant are quantitatively investigated by combining high resolution scanning transmission electron microscopy (STEM) characterization and first principles calculations. For the model GB with the aliovalent dopants, Zr^{4+} doped Al_2O_3 were are selected for the investigation. For the co-dopant system, Ca and Ti co-doped GB were characterized. It is interesting to confirm how the charge neutrality is compensated at the Gbs in such systems to relax the atomic structures. To accomplish this, two single crystals of Al_2O_3 and MgO were cut to have the suitable misorientation for Σ31 and Σ5 grain boundaries[1,3)],respectively. The two single crystals were joined using diffusion bonding. For characterization, Cs-corrected STEM (JEM-2100F, JEM-ARM200F, JEOL Co. Tokyo Japan) was used to acquire high-resolution high-angle annular dark-field (HAADF) STEM images.

Fig.1 (a) shows HAADF STEM image of the Zr doped Al_2O_3 Σ31 tilt grain boundary. It is found that periodic structural units formed along the grain boundary plane consist of a seven-membered ring of cation columns, as well as a deformed “peanut-shaped” unit, also consisting of seven cation columns (Fig.1(b)). As can be seen in (b), bright columns along the grain boundary plane correspond to Zr ions, and the dark sites indicated by black triangles may correspond to the Al vacancy sites. Using first principles for these calculations, the segregation energy was estimated by comparing the defect formation energy at the GB with that at the bulk. It was found that the segregation energy is relatively high for all cases without introducing vacancies as shown in Fig2 (b). Following these calculations, four key Zr segregation sites were picked to investigate the segregation energies of the Zr substitution with an associated Al vacancy defect pair by keeping each Zr substation site the same but changing the location of the neighboring Al vacancy. As seen in the figure, it is clearly seen that the segregation of Zr^{4+} is stabilized by associating V_{Al}^{3-}. In particular, the association of Zr^{4+} at site A and V_{Al}^{3-} at site c gives the lowest segregation energy, which is consistent to the STEM image in Fig.1 that the sites A and c are periodically bright and dark, respectively.

Fig.3(a) shows HAADF STEM image of Ca and Ti co-doped Σ5 GB in MgO. It can be seen that strong pair contrast is present along the GB, which is considered to correspond to Ca columns. It is also found that there are periodic spots with much weaker image contrast as indicated by the arrows. To understand this segregation behavior, first principles calculations were performed for the Ca and Ti segregated Σ5 GBs. It was found that the stability of the GB is enhanced by

introducing Ca and Ti simultaneously, which periodically segregate to the GB as shown in Fig.3 (b). To investigate whether Ti segregation and associated Mg vacancies can be responsible for the contrast variation, preferred sites for Ti were examined in all of its possible charge states. Geometrical investigation into the stable GB revealed a structural transformation: Ca ions in the left of pair spots relax laterally towards an interstitial sites indicated by the arrows in Fig. 3(b). The driving force for such a displacement is the adjacent Mg vacancies on both sides of GB plane, which frees up the space for Ca to relax into a more stable site, reducing substantially the GB free energy.

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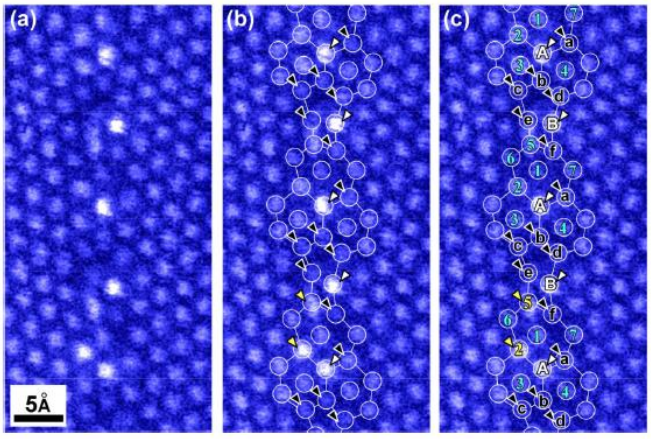

Fig.1: a) shows HAADF STEM image of the Zr doped Σ31 tilt grain boundary. b) shows the same image with an overlay indicating the structural units along the grain boundary. c) shows the same image with an overlay indicating the name of sites.

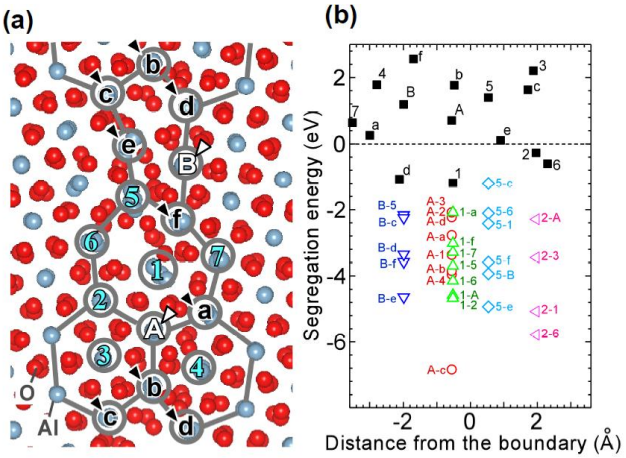

Fig.2: a) Schematic of the relaxed supercell used in the static lattice calculations. b) Plot of the segregation energies for Zr to various sites (without associated Al vacances (black squares) and for Zr to various sites with an associated Al vacancy (open symbols).

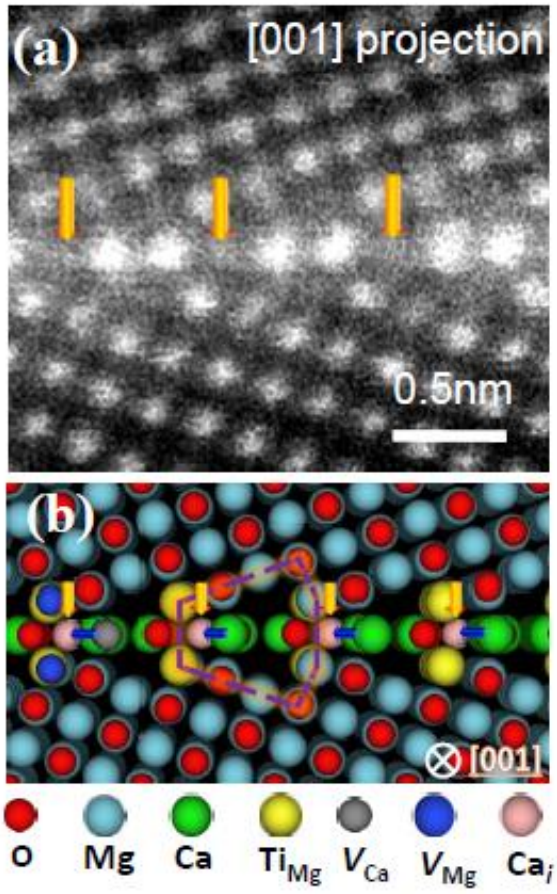

Fig.3: (a) HAADF STEM image of the Σ5 GB viewed from the [001] directions, indicating that there are the weak spots in addition to the two strong spots of Ca columns. (b) Most stable grain boundary atomic structures calculated for for Ca and Ti segregation, in which the GB structural unit is highlighted by a polygon. The dots with weak image contrast in (a) are recognized as Ca interstitials, as marked by arrows.