Atomically Resolved Structure characterization of TiO_2 Grain Boundaries

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Polycrystalline TiO_2 finds numerous technological applications where its grain boundaries (GBs) are known to influence the functionality. Light sensitive photovoltaics, oxygen transfer catalysts and host for semiconductor spintronics are just a few important examples. Grain boundaries in these systems can be both beneficial and harmful to applications and have been the subject of intensive researches. To date, many studies using methods such as the transmission electron microscopy (TEM), the x-ray diffraction and radioactive tracer diffusion have provided convincing evidence that GBs in TiO_2 can act as sinks for defects and impurities and also can offer shortcut pathways for their diffusion[1,2]. However, an issue that has not been addressed so far is that defects segregated to GBs *via* external stimuli such as thermal annealing may induce a structural transformation of the GBs, which significantly modifies their properties and affects the applications of TiO_2. A detailed understanding of such an effect requires a spatial resolution and chemical identification of all the atoms at GBs, which has so far been a nontrivial task.

Here, we fabricate the pristine (112)$[1\bar{1}0]$ symmetric tilt model GBs of TiO_2 using the bicrystal techniques. The two pristine single crystals were joined at 1773 K for 10 h in air. The samples were then annealed at 1023 K at a mixed atmosphere of 5% H_2 and 95% Ar for 3 h. Specimens for TEM and Scanning TEM (STEM) observations were prepared by cutting, mechanical grinding and argon ion-beam thinning process. The high-angle annular-dark-field (HAADF) STEM and annular bright-field (ABF) STEM images were taken with a 200 kV STEM (JEM-ARM200F) equipped with an aberration corrector, which provides an unprecedented opportunity to probe structures with a Sub-Å resolution. The electron energy-loss spectroscopy (EELS) spectra were recorded using a Gatan ENFINA system equipped on STEM with an energy resolution, at a full-width of half-maximum, of ~0.5 eV.

Figure 1(a) shows low magnification TEM image of the tilt GB before annealing viewed along the $[1\bar{1}0]$ direction. The GB is flat without any secondary phase and amorphous area. Figure 1(b) shows the diffraction pattern taken around the GB, which reveals that the GB has a tilt angle of 49.1°, consistent with the near-Σ3 relationship. From high-resolution TEM (HRTEM) image of the GB, one can see that the two single crystals are well bonded even at an atomic scale. A special structure unit is formed along the GB. To probe the exactly atomic arrangement along the GB, we apply the HAADF STEM imaging of the GB(Figure 2).Since intensity of an atomic column in the HAADF-STEM imaging mode is proportional to $Z^{1.7}$ (where the Z is atomic number), lighter spots in the image represent the normal Ti columns, whereas the brighter ones indicate the columns with mixed Ti and O. The GB is structurally symmetric with one atomic array of alternating image contrast precisely on the mirror plane, which corresponds to the periodic distribution of the Ti-only and mixed atomic columns. Such an atomic arrangement is confirmed in the ABF STEM image, in which columns of oxygen can be unambiguously visualized. The GB structure is found to be modified significantly after annealing, since in contrast to the one array, there are two atomic arrays with alternating image contrast on the mirror plane, although the symmetry across the mirror plane is maintained. Such structural transformation should be associated with shift in electronic states of the GBs, which plays an important role in affecting properties of polycrystalline TiO_2.

References:
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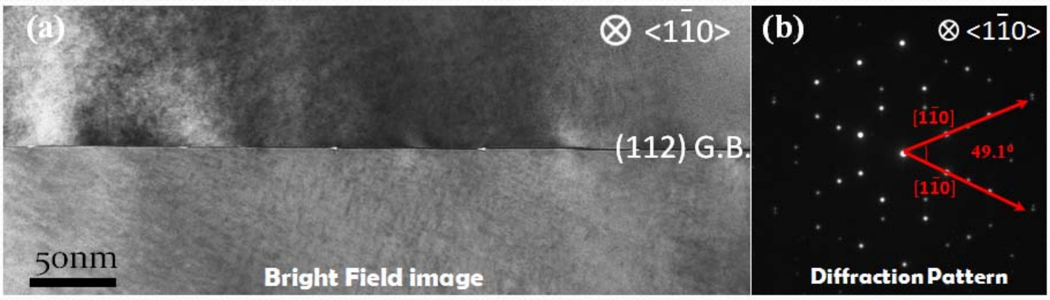

Fig. 1. (a) Bright-field image of the (112)[1$\bar{1}$0] Σ3 GB of TiO_2. (b) Diffraction pattern taken at the GB area.

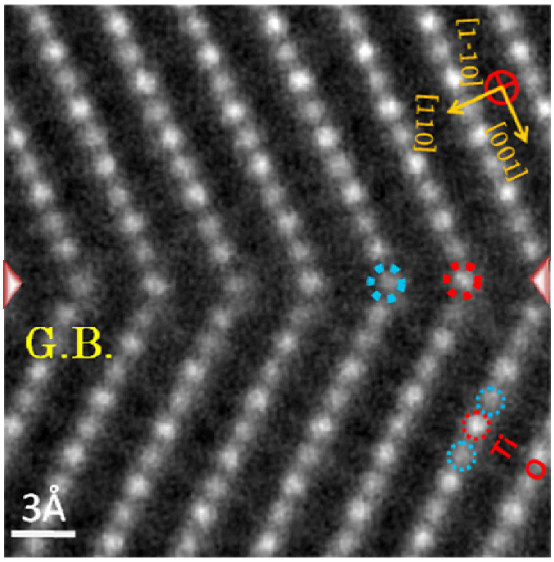

Fig. 2. High angle annular STEM image of the GB.

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