Reconstruction of Alumina Grain Boundary Structure at Atomic Scale by Aberration-Corrected HAADF-STEM

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The development of aberration corrected HAADF-STEM (High Angle Annual Dark Field – Scanning Transmission Electron Microscopy) has enabled atomic scale resolution of ‘special’ grain boundaries [1], but to date there has been limited work on general grain boundaries. For this latter type of boundary, factors such as the non-planar boundary morphology and lack of a common zone axis for the adjoining grains present severe challenges to structural characterization at the atomic scale. Recently, work by Yu et al [2] elucidated the grain boundary segregation behavior of Hf ions in alumina doped with 500 ppm Hf. This study is an extension of that work to the complete reconstruction of a general boundary in this material system. Details of the powder processing and specimen preparation are given in ref. [3]. Because the depth of focus for our aberration corrected HAADF-STEM is ~10nm, this places an inherent limit on the depth resolution for probing the distribution of the Hf ions. For boundaries in the Hf-doped alumina, it was observed that in many cases one of the grain surfaces was facetted in a pseudo periodic manner. Under such conditions, reconstruction of the boundary surface can be achieved as described in the following.

1. The selected grain boundary should have an associated microstructural feature that will act as a marker to facilitate imaging of the same region of interest in both adjoining grains. In the present study, a spherical HfO₂ particle was used.
2. The grains on either side of the boundary are imaged at high resolution using HAADF-STEM, as shown in Figure 1(a-b). This is achieved by tilting the grain to the zone axis direction. If the grain surface is close to ‘edge on’ condition, focal series imaging of the boundary is also undertaken, as shown in Figure 1(c-f) for Grain 1.
3. Where feasible, the grain surface profile, together with the dopant ion distribution, is reconstructed from the ‘depth sectioning’ technique described in Step 2 above. As mentioned earlier, this is feasible only if the surface structure is quasi-periodic in the through thickness direction. Additionally, the grain surface must be ‘edge-on’ when the grain is viewed under zone-axis conditions. This is necessary because if the grain surface is inclined to the beam direction, focal series imaging will be unable to detect dopant atoms at single atom sensitivity. Because neither of these conditions was met by Grain 2, boundary reconstruction was completed using the following procedure.
4. Based on the identified grain surface profile of Grain 1 (which exhibited 2-D periodic faceting), the surface of Grain 2 was fitted to that of Grain 1 in the region of interest. The level of Hf ion segregation in Grain 2 was judged to be less than that of Grain 1; results of a more quantitative nature will be reported at a later date.

By using the reconstruction methodology as outlined above, it is hoped to elucidate the nature of the grain boundary complexion in Hf-doped alumina [4], and the mechanism by which additions of reactive elements such as Hf slow boundary transport processes in alumina [5].
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References:

Figure 1. (a) Atomic resolution imaging of the boundary at the left grain side (Grain 1) and right grain side (Grain 2) (b). These two images are taken at the same region of interested using the spherical HfO2 particle as the reference. Focal series images were recorded for the Grain 1 (c-f). The red circles indicate single Hf ions that are visible in the thinnest regions of the Grain 2.

Figure 2. Reconstructed 3D grain boundary structure at the atomic scale, showing periodic steps on both sides of the boundary, and the distribution of Hf dopant ions. Hf1 and Hf2 refer to Hf ions at different atomic levels in the through thickness (beam) direction.