Atomic-resolution 3D STEM characterization of individual dopant atoms in ceramic grain boundaries

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Control of crystal interfaces at atomic-scale is now actively being sought across a broad range of materials science and device engineering fields. Changing the local chemistry of an interface by doping foreign atoms has been shown to dramatically modify the atomic and electronic structure of the interface and hence its properties. However, understanding the fundamental role of the interfacial dopants is still a non-trivial task because it is extremely difficult to characterize the atomic-scale positioning of individual dopant atoms within the two-dimensional defects inside materials.

In recent years, Z-contrast scanning (S) TEM has become capable of directly imaging dopant atoms within the bulk and interfaces (Z in Z-contrast denotes the atomic number). In crystalline materials, strong electron channelling along atomic columns enhances imaging of the crystal structure, but may make determining the dopant atom positions along the atomic columns impossible [1]. It is therefore extremely difficult to identify the three-dimensional positions of interface dopant atoms by current cross-sectional imaging. On the other hand, the three-dimensional positioning of individual dopant atoms within an amorphous matrix can be directly probed by STEM depth sectioning [2], since without strong electron channelling one may more reliably focus the electron beam on single dopant atoms inside the matrix, maximizing their contribution whilst minimizing the contribution from the surroundings. Even in crystalline materials, it has been predicted that dopant atom positioning along the depth direction can be determined if the imaging is carried out from off-axis or weak channelling crystallographic orientations [1]. Thus it should be possible to selectively highlight individual dopant atoms within a buried crystalline interface if the electron beam probes the interface plane under very weak electron channelling conditions.

In the present study, we demonstrate Z-contrast STEM observation of an yttrium (Y) doped grain boundary in alumina (α-Al₂O₃) from the direction perpendicular to the interface plane [3,4]. In these observations, we focused a very fine electron beam onto the interface plane through the off-axis α-Al₂O₃ crystals, in order to probe and detect the individual Y atoms within the interface. We first fabricated a model Y doped α-Al₂O₃ grain boundary by diffusion bonding of two single crystals in the Σ13 orientation relationship [5]. Figure 1 shows typical atomic-resolution Z-contrast STEM images of the interface projected along the two orthogonal <1210> and <2021> directions. The doped Y atomic columns are clearly imaged with very strong contrast along the boundary, and form a monoatomic layer structure in the core of the boundary. Figure 2 shows the filtered plan-view STEM image viewed from the <5054> direction showing...
individual interface Y atoms [3]. We can clearly determine the two-dimensional positioning of the Y atom positions on the interface plane, and it proves to be consistent with our recent DFT calculations [6]. Thus, our study clearly demonstrates that Z-contrast STEM with off-axis illumination can be a very powerful method for directly imaging individual atoms within buried crystalline interfaces, bringing us a crucial step towards the full three-dimensional characterization of interface atomic structures inside materials.

References

FIG. 1. Typical atomic-resolution Z-contrast STEM images of the interface projected along the two orthogonal (a) <1210> and (b) <2021> directions.

FIG. 2. Filtered plan-view STEM image of the interface viewed from the <5054> direction. Bright spots correspond to the position of individual Y atoms on the interface.