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Investigation of the Atomic Structures of $Si_3N_4/CeO_{2-\delta}$ Interfaces using Atomic Resolution Z-contrast Imaging and EELS combined with First-Principles Methods

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Silicon nitride is an extensively studied ceramics material due to its desirable physical and mechanical properties for many high temperature and pressure applications. Good resistance to oxidation, low coefficient of friction, negligible creep, and high decomposition temperatures are some of these important properties. The widespread use of silicon nitride as a structural component is, however, limited by its brittleness [1]. It has been empirically shown that rare-earth oxides (REO), when included in the sintering process of Si_3N_4, can help overcome this problem by forming an intergranular film (IGF) surrounding the matrix grains of the ceramic. Studies aimed at achieving a microscopic understanding of the atomic composition and local bonding at the Si_3N_4 / REO interface are, therefore, of both fundamental and technological interest.

Using a combination of atomic-resolution Z-contrast imaging and electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) as well as first-principles calculations, we examine the atomic and electronic structures at the interface between β-Si_3N_4 $(10\bar{1}0)$ and $CeO_{2-\delta}$ inter-granular film (IGF). The experimental Z-contrast images and EELS spectra were acquired with a JEOL 2010F operated at 200 kV, and an aberration-corrected VG 603 operated at 300 kV.

Figure 1 shows the interface between $CeO_{2-\delta}$ IGF and a Si_3N_4 grain in the [0001] orientation of sample prepared with 2 wt% MgO. The Ce atoms (circled) in the nominally amorphous IGF are visible as bright spots segregated to the interface in a two-layer periodic arrangement. The superimposed atomic structure shows Si and N atoms with light and dark circles, respectively. The observed structure is significantly different from the one reported in a previous study shown in the inset of the figure. [2] We have further studied the diffusion of Si and N into the ceria IGF by performing atomic-resolved EELS line-scans across two Si_3N_4 grains with the ceria IGF in between (see Figure 2a). We observe that while the N concentration decreases significantly when going across the Si_3N_4/CeO_2 interface, the Si concentration remains nearly constant. This indicates that a significant amount of Si diffuses from the Si_3N_4 grain into the IGF and as such, Si cannot be ignored in atomistic modeling of the IGF film. Finally, we have studied the valence state of Ce atoms across the IGF. Figure 2b shows Ce $M_{4,5}$ edge intensities and edge onset for the spectra taken at the center of the IGF and at the interface with the Si_3N_4 grain. Comparing the M_4/M_5 intensity ratios and the onset energy for the two spectra with reference spectra (see inset), we find that the valence state of Ce is close to Ce^{3+} at the interface and close to Ce^{4+} in the middle of the IGF. [3]

The atomic scale structure-property relationships of the Si_3N_4/ceria IGF interface will be discussed in the context of atomic-column resolved EELS, Z-contrast imaging in an aberration-corrected STEM, and in conjunction with first-principles calculations. [4]

References

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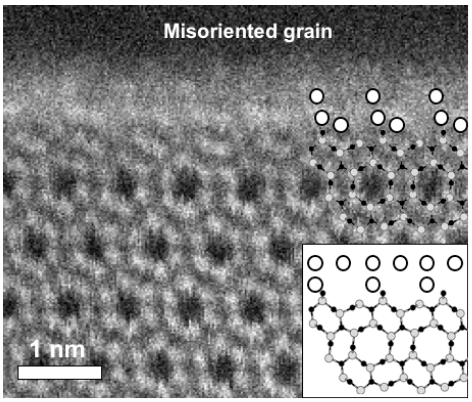

Figure 1: High-resolution Z-contrast image of the Si_3N_4 $(10\bar{1}0)$ interface with the $CeO_{2-\delta}$ IGF. The inset shows a schematic representation of the interfacial structure as found in a previous studied sample prepared with 1 wt% Al_2O_3.[2]

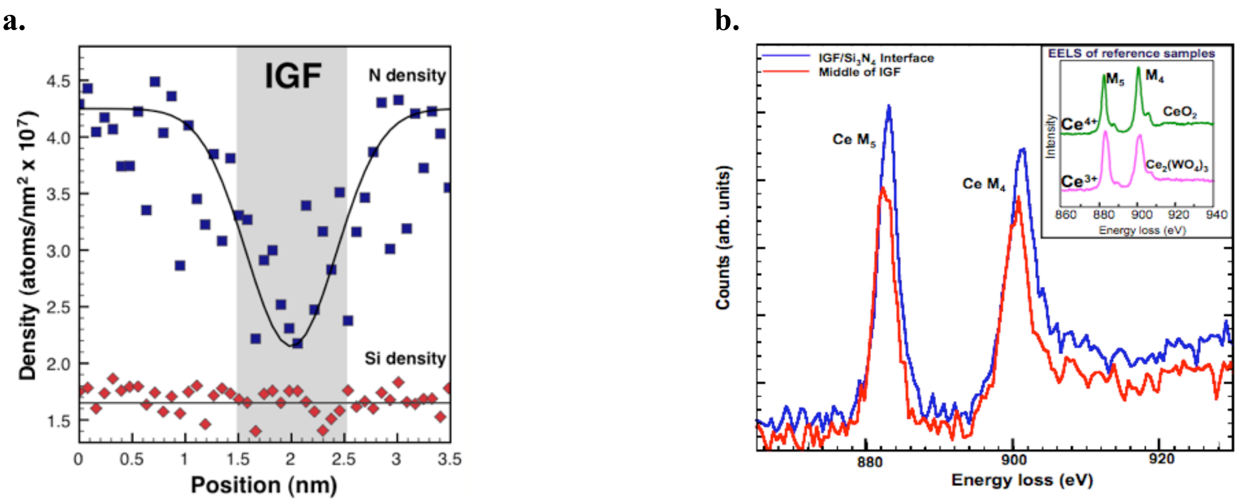

Figure 2: (a) Si and N concentration profiles across the $Si_3N_4/CeO_{2-\delta}$ interface extracted from an EELS line-scan. In each background-subtracted spectrum, the spectrum intensity under the Si L and the N K-edges was integrated over a 40 eV window and multiplied by the corresponding scattering cross-sections. (b) Near edge fine-structure of the Ce M-edge taken from the middle and at the interface of the Si_3N_4/IGF. The insert shows reference spectra (from Ref. [3]) obtained for CeO_2 and $Ce_2(WO_4)_3$, corresponding to valences of Ce^{4+} and Ce^{3+}, respectively.