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Study of the Atomic Structures of $Si_3N_4/CeO_{2-\delta}$ and Si_3N_4/SiO_2 Interfaces Using STEM and First-Principles Methods

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Interest in silicon nitride ceramics results from their physical and mechanical properties suitable for many high temperature and pressure applications. The widespread use and reliability of Si_3N_4 as structural components are, however, limited by its brittleness [1]. Rare-earth oxides (REOs), when included in Si_3N_4, can promote the formation of a reinforced toughened microstructure and thus enhance mechanical properties of the ceramic. Studies aimed at achieving an understanding of the atomic composition and local bonding at the interface of Si_3N_4 and the integranular film (IGF) formed by REO are, therefore, of both fundamental and technological interests.

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 density functional theory calculations, we examine the atomic and electronic structures at the interface between β-Si_3N_4 $(10\bar{1}0)$ grain surfaces and $CeO_{2-\delta}$ IGF as well as between β-Si_3N_4 $(10\bar{1}0)$ grain surfaces and SiO_2 IGF. The experimental Z-contrast images and EELS spectra were acquired with a JEOL 2010F equipped with a Schottky field-emission gun operated at 200 kV as well as an aberration-corrected FEI Titan operated at 300kV.

Figure 1 shows the interface between $CeO_{2-\delta}$ IGF and a Si_3N_4 grain in the [0001] orientation with the open ring termination [2]. The Ce atoms (circled) in the nominally amorphous IGF, ~1.2 ± 0.3nm in thickness, 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 inset of the figure shows the arrangement of Ce atoms in films wider than ~3.0 nm.

Figure 2 shows the interface between Si_3N_4 and the IGF composed of SiO_2 only. Even in the absence of a rare-earth element, the open ring termination of Si_3N_4 is observed as can be seen in the figure.

Figure 3a shows the O K and the Ce M-edges signals from EELS line-scan integrated over a 50eV window and plotted as a function of position across the Si_3N_4 / $CeO_{2-\delta}$ interface. Figure 3b shows the normalized O and Ce signal fits using two Gaussians revealing that the onset of the O signal occurs before that of Ce. This suggests that the Si_3N_4 open ring surface is in direct contact with oxygen.

Figure 4 shows the O and N concentration profiles across the Si_3N_4 / SiO_2 interface, showing appreciable O concentration at the interface where the N signal starts to go down. This indicates that oxygen replaces nitrogen in Si_3N_4 at the interface.

The underlying mechanisms for the observed preferential segregation of the Ce atoms and the electronic structure of the Si_3N_4/IGF interfaces will be discussed in detail in conjunction with the theoretical results focusing, in particular, on the role of oxygen in stabilizing the Si_3N_4 $(10\bar{1}0)$ open-ring surface [3].

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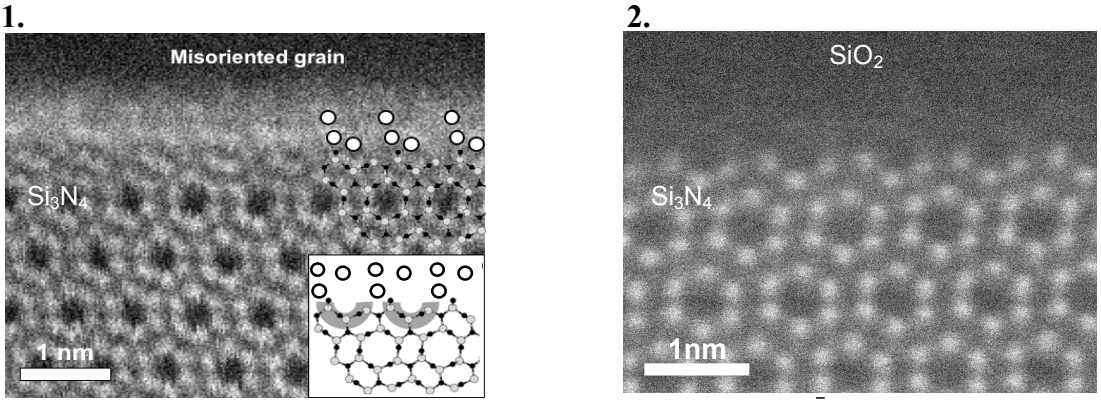

Figure 1: High-resolution Z-contrast image of the Si_3N_4 $(10\bar{1}0)$ interface with the $CeO_{2-\delta}$ IGF. The inset shows a schematic representation of the interfacial structure as found in thicker films [3]. **Figure 2**: The interface between Si_3N_4 / SiO_2 IGF.

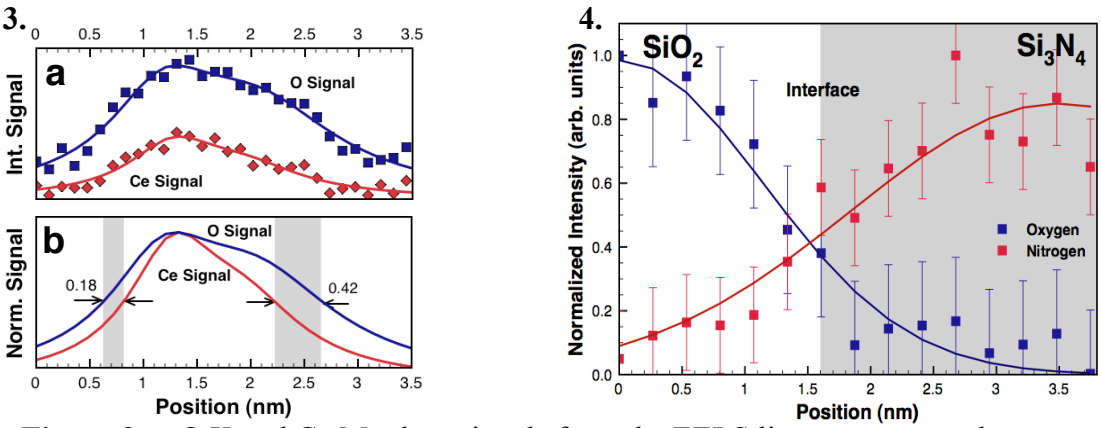

Figure 3a: O K and Ce M-edges signals from the EELS line-scan across the $Si_3N_4/CeO_{2-\delta}$ interface [3]. **Figure 3b:** Normalized signals [3]. **Figure 4:** N and O concentration profiles across the Si_3N_4 / SiO_2 interface.

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