

## Grain Boundary Complexions in TiO<sub>2</sub> Bicrystals Doped with CuO

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The kinetic properties of grain boundaries play a crucial role in determining the processing, properties and performance of crystalline materials. A new concept of grain boundary complexions that relates the kinetic properties and structures of grain boundaries has recently been proposed [1, 2]. With increasing temperature or doping activity, a grain boundary (GB) can undergo coupled structural and chemical transitions, producing a series of discrete “interfacial phases”. These thermodynamically stable (or metastable) interfacial phases are termed as “GB complexions” [1, 2].

Our preliminary experimental results suggest a drastic increase in grain growth kinetics of CuO-doped TiO<sub>2</sub> as compared to identically prepared undoped TiO<sub>2</sub>, indicating the existence of different GB complexions in the doped material. To elucidate the associated GB complexions, several well-controlled model experiments have been conducted on undoped and CuO-doped TiO<sub>2</sub> rutile bicrystal sandwich structures. The TiO<sub>2</sub> bicrystal samples were annealed at 850 °C for 24 hours (which is below the eutectic temperature of 919 °C [3]) and then air quenched. As shown in Fig. 1, discontinuous nanoscale amorphous films were observed at this TiO<sub>2</sub> bicrystal GB penetrated by CuO. With the aid of HRTEM and aberration corrected STEM imaging, several structurally distinct GB complexions and their abrupt transitions were also revealed to co-exist along the same GB in between the amorphous films. The presence of these GB complexions and their very abrupt transitions in this CuO-TiO<sub>2</sub> bicrystal GB is believed to result from the dewetting of a CuO intergranular film during cooling.

STEM images in Figs. 2a and 2b show an amorphous film with a thickness of ~ 5nm at this CuO-TiO<sub>2</sub> bicrystal GB. EELS analysis of this amorphous film and the adjacent grain in Fig. 2c indicates a significant intensity reduction of the Ti L peaks at the GB. Since the intensity changes observed for the corresponding O peaks are much smaller (Fig. 2c), the reduction of the Ti peak intensity is not primarily due to thickness differences. Comparison of the simulated EELS signals for crystalline and amorphous rutile suggests the mean signal is unchanged in the crystalline and amorphous areas, as shown in Fig. 3. The observed reduction in Ti L shell signal is hence not due to different channeling conditions. Therefore, it is proposed that most of the Ti atoms at the GB are replaced by Cu atoms or other impurity atoms. The modified O EELS fine structure observed at the GB, as compared with the bulk grain (Fig. 2c), indicates a lowering of the coordination number at the GB [4].

### References

- [1] S.J. Dillon et al., *Acta Materialia* **55** (2007) 6208.
- [2] M.P. Harmer, *J. Am. Ceram. Soc.* **93** (2010) 301.

- [3] F. Lu et al., *J. Eur. Ceram. Soc.* **21** (2001) 1093.  
 [4] C. Hébert et al., *Eur. Phys. J. B* **28**, (2002) 407.  
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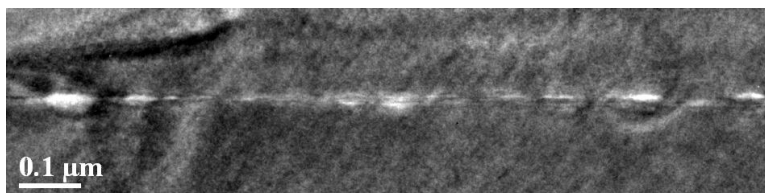


FIG. 1. A TEM micrograph of a TiO<sub>2</sub> bicrystal GB penetrated by CuO, showing discontinuous nanoscale amorphous films along the GB.

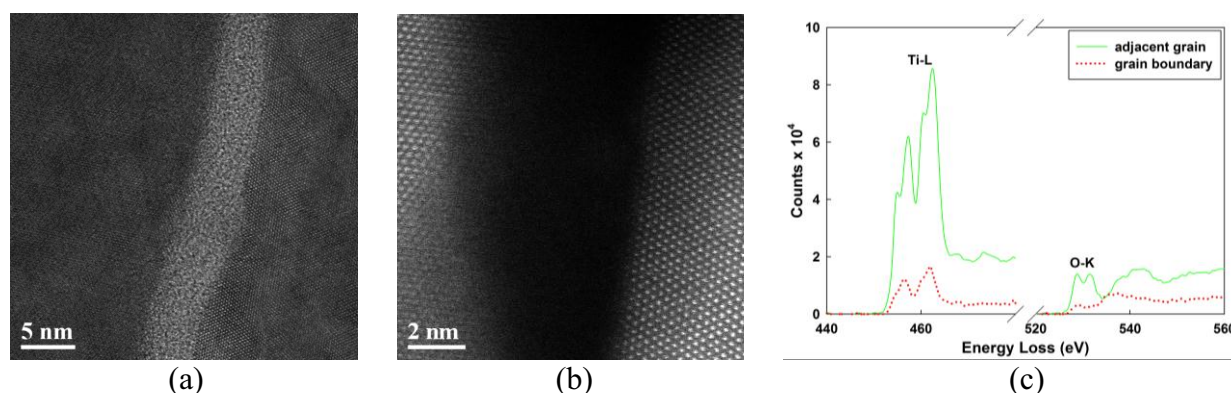


FIG. 2. BF-STEM (a) and HAADF-STEM (b) images of a nanoscale amorphous film at the GB in Fig. 1; EELS spectra (c) of the GB and the adjacent grain, indicating a significant reduction of the Ti peak intensity and a change of the O fine structure at the GB.

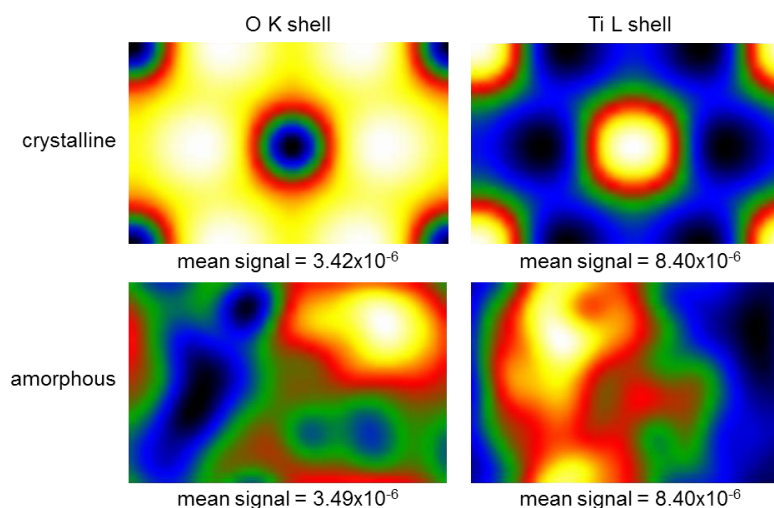


FIG. 3. Comparison of the simulated EELS signals for crystalline and amorphous rutile.