

## Electron-Beam-Induced Antiphase Boundary Reconstructions in $\text{ZrO}_2\text{-La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ Pillar-Matrix Structures

Dan Zhou<sup>\*1</sup>, Wilfried Sigle<sup>1</sup>, Marion Kelsch<sup>1</sup>, Hanns-Ulrich Habermeier<sup>1</sup> and Peter A. van Aken<sup>1</sup>

<sup>1</sup> Stuttgart Center for Electron Microscopy, Max Planck Institute for Solid State Research, Heisenbergstrasse 1, Stuttgart, Germany

\* Current: Materials Science and Engineering, University of Wisconsin-Madison, 1509 University Avenue, Madison, WI USA

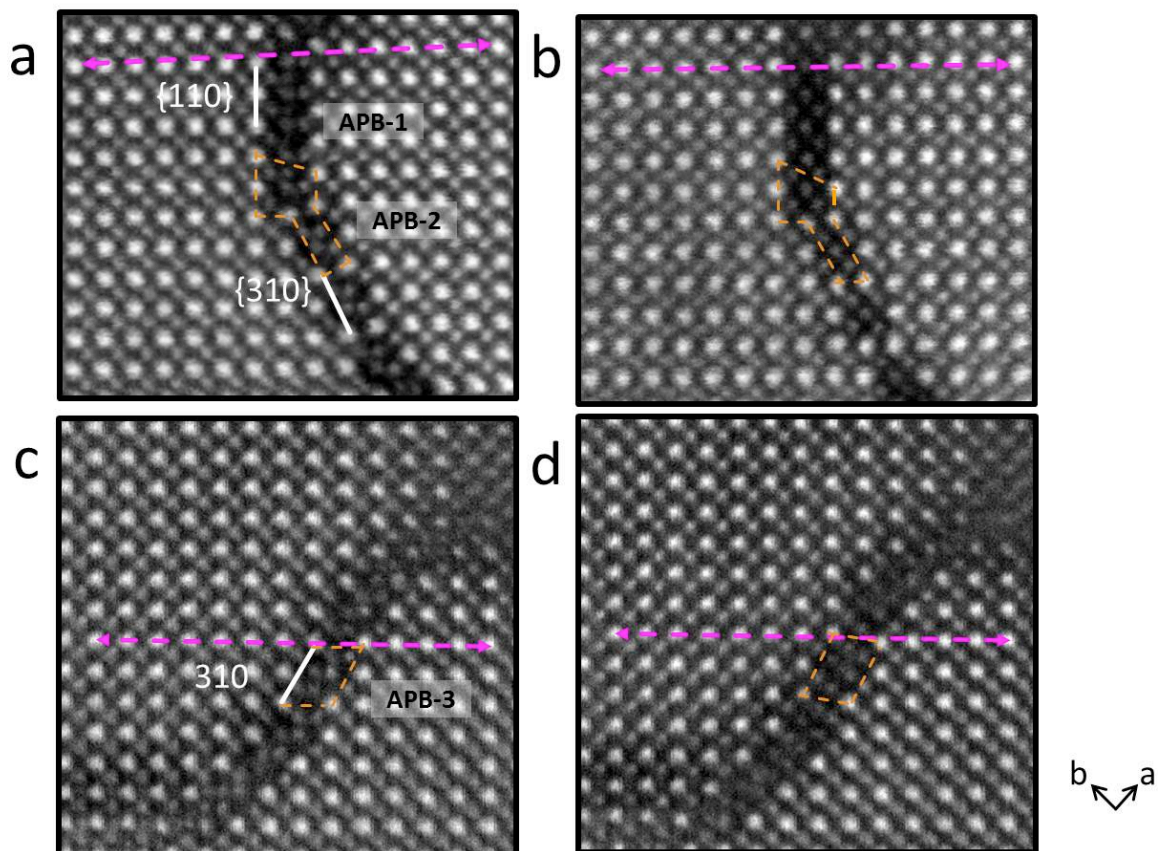
Electron irradiation effects in transmission electron microscopes (TEM) are usually thought to introduce undesirable disorder, and thus deteriorate the material. However, with controlled dose and beam energy, electron irradiation may have beneficial effects on nanostructured materials [1, 2]. Irradiation effects in TEM have attracted more and more interest due to the possibility of simultaneous structural and chemical modifications and characterizations down to the atomic-scale.

In a recent report we showed that the formation of antiphase boundaries (APB) provides a means for strain relaxation in a system composed of  $\text{ZrO}_2$  pillars in  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  thin films. Three types of APBs were observed and studied in detail [3]. In the course of this work, we report on electron-beam-induced reconstruction of these three types of APBs in a probe-aberration-corrected TEM as illustrated in Figure 1. With the utilization of high-angle annular dark-field scanning transmission electron microscopy (STEM), annular bright-field STEM and electron energy-loss spectroscopy, the motion of both heavy and light element columns under moderate electron beam irradiation are revealed at atomic resolution. Besides, Mn segregated in the APBs was observed to have reduced valence states which can be directly correlated with oxygen loss. Charge states of the APBs are finally discussed based on these experimental results. Finally, we discuss the reconstruction mechanism of the APBs in the context of radiation effects and electrostatic coupling at the boundaries.

This study provides support for the design of radiation-engineering solid-oxide fuel cell materials. [4]

### References:

- [1] J. Lee *et al*, Nat. Communications 2013, **4**, 1650.
- [2] Y.C. Lin *et al*, , *Nat Nanotechnol* 2014, **9**, (5), 391-396.
- [3] D. Zhou *et al*, Adv. Mater. Interfaces 2015, **2**, 1500377.
- [4] This work has been initiated by Prof. J. Zhang (Department of Physics, Shanghai University). Samples have been prepared by Dr. Y. Gao during his PhD work at Max Planck Institute for Solid State Research (MPI-FKF). The research leading to these results has received funding from the European Union Seventh Framework Program [FP/2007/2013] under grant agreement no 312483 (ESTEEM2). Dan Zhou would also like to thank her current advisor Prof. Paul M. Voyles for supporting her attendance of M&M 2016 to present her PhD work.



**Figure 1.** HAADF image of a plan-view 80 mol% LSMO-20 mol% ZrO<sub>2</sub> sample showing APB-1 and APB-2 (a) before and (b) after electron-beam-induced reconstruction, and APB-3 (c) before and (d) after electron-beam-induced reconstruction.