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Manganese Segregation at Antiphase Boundaries Connecting ZrO_2 Pillars in ZrO_2–$La_{2/3}Sr_{1/3}MnO_3$ Pillar–Matrix Structures

Dan Zhou[1], Wilfried Sigle[1], Marion Kelsch[1], Hanns-Ulrich Habermeier[2], and Peter A. van Aken[1]

[1.] Max Planck Institute for Intelligent Systems, Stuttgart Center for Electron Microscopy, Stuttgart, Germany
[2.] Max Planck Institute for Solid State Research, Stuttgart, Germany

Self-assembled vertically aligned nanocomposite thin films with two immiscible components hetero-epitaxially grown on single crystal substrates[1-4] have attracted tremendous research interest due to the advantages of utilizing both component functions and tuning material properties with high interface-to-volume ratio, hetero-epitaxial strain, or modifying the cation valence state. Anomalous magnetic anisotropy and modifications to the electric transport properties of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) has been reported to be achieved by introducing non-magnetic ZrO_2 pillars[5-7]. Whereas up to now, only macroscopic properties of ZrO_2–LSMO pillar-matrix systems (charge transport and magnetism) have been studied, microscopic properties at the atomic level were not studied at all.

Here we use high-angle annular dark-field (HAADF) imaging, annular bright-field (ABF) imaging and electron energy-loss spectroscopy (EELS) in aberration-corrected scanning transmission electron microscopy (STEM) to reveal the structure, composition and valence state at atomic resolution for the pillar–matrix interface region and antiphase boundaries (APB) connecting adjacent ZrO_2 pillars in ZrO_2–LSMO pillar–matrix structures with emphasis on the antiphase boundaries. Details about the pillar-matrix interface region can be found in our previous report.[8] Atomic resolution EEL spectrum imaging (SI) reveals the substantial interdiffusion at the ZrO_2-LSMO interface with Mn replacing Zr in ZrO_2 (thus stabilizing the cubic or tetragonal phase) and Zr replacing Mn atoms in LSMO. Charge balance requires the combination of Mn valence state change and oxygen vacancy formation which are observed to segregate at the interface.

As one way to relax the strain generated from the misfit of two components, three types of Mn segregated APBs were found connecting adjacent pillars. The crystal lattices on either side of the APB wall are displaced by an antiphase shift as can be seen in Figure 1, which includes two types of APBs. The Mn valence state in the channel was found to be the same as in the matrix. The APB wall planes are either {110} or {310}. The arrangement of heavy and light elements is revealed by simultaneously acquiring HAADF and ABF images, as shown in Figure 1c,d, and HAADF and EELS spectrum imaging. The role of the pillars and APBs regarding elastic strain and local electric fields will be discussed. The spin, charge, and orbital ordering in LSMO are extremely sensitive to local structural and elemental variations. Thus, our results provide a basis for understanding the origin of these properties.[9]

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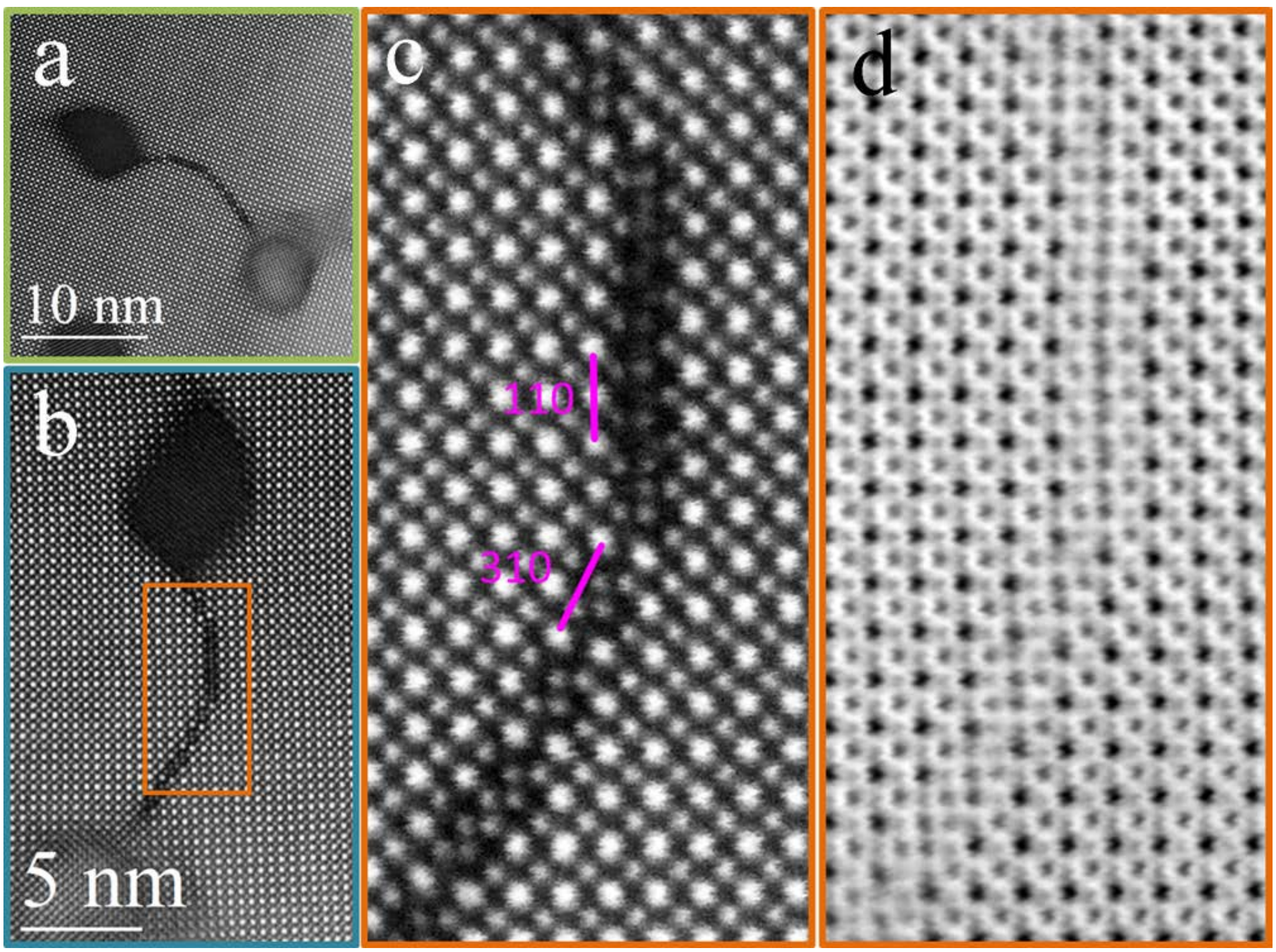

Figure 1 (a) HAADF image of a plan-view 80 mol% LSMO-20 mol% ZrO_2 sample showing two ZrO_2 pillars connected by boundaries. (b) Magnified image of the boundary region shown in (a). Simultaneously acquired HAADF image (c) and ABF image (d) of the orange marked region in (b) including APBs with {110} and {310} boundary planes, respectively.