Chemical and Defect Analysis in a ZrO$_2$/LSMO Pillar-Matrix System

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Recently there has been tremendous research on self-assembled vertically aligned nanocomposite thin films with two immiscible components hetero-epitaxially grown on single crystal substrates [1-4]. These structures have 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.

Here we report about the characterization of self-assembled vertically aligned non-magnetic zirconium oxide (ZrO$_2$) and ferromagnetic perovskite lanthanum strontium manganese oxide (La$_{2/3}$Sr$_{1/3}$MnO$_3$, LSMO) pillar-matrix nanostructures, which are epitaxially grown on (001) single-crystalline lanthanum aluminum oxide (LaAlO$_3$, LAO) substrate by pulsed laser deposition. Scanning transmission electron microscopy in combination with electron energy-loss spectroscopy (EELS) is used to study the elemental distribution and the defect structure on the atomic scale.

ZrO$_2$ remains in the LSMO matrix as vertical pillars (~5 nm in diameter) up to a volume fraction smaller than the one calculated from the sample preparation recipe. Atomic resolution EEL spectrum imaging (SI) of the matrix region confirms the existence of Zr in the matrix region. Atomic-resolved EEL SI at the interface region shows that the elemental concentrations of La and Mn increase and Sr and Zr decrease when going from the matrix to the pillar, as shown in Figure 1. Accompanying the non-homogeneous elemental distribution, the Mn valence state in the matrix was found to decrease when approaching the interface.

In addition, Mn-rich walls were found connecting adjacent pillars. The crystal lattices on either side of the wall are displaced by an antiphase shift as can be seen in Figure 2. The Mn valence state in the channel was found to be decreased compared to the matrix. The wall plane is $\{110\}$ or $\{130\}$. The role of the pillars and walls 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, these results provide the basis for understanding the origin of the anomalous magnetic anisotropy and modifications to the electric transport properties of LSMO by introducing non-magnetic ZrO$_2$ pillars [5-8].

References:
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\begin{figure}[h]
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\includegraphics[width=0.75\textwidth]{figure1.png}
\caption{Annular dark-field and elemental distribution images extracted from EELS spectrum images.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.75\textwidth]{figure2.png}
\caption{Left: HAADF image of ZrO$_2$ pillars and LSMO matrix. Right: Enlargement of a Mn-rich wall with annotations of the wall plane.}
\end{figure}