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Cation stoichiometry, microstructure and properties tuned by oxygen vacancies in epitaxial manganite and manganite-based heterostructures

Z. Li¹, M. Bosman², W. Zhu³, Z.-L. Dong¹

¹Nanyang Technological University, Materials Science and Engineering, Singapore, Singapore

²Institute of Materials Research and Engineering, Singapore, Singapore

³Nanyang Technological University, Singapore, Singapore

zldong@ntu.edu.sg

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$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is viewed as one of the key building blocks of oxide spintronics devices due to its rich physical properties. However, when manganite and other materials are engineered together, the induced interfacial dead layer can reduce the device performance such as the tunneling current or magnetoelectric coupling effect. In this study, transmission electron microscopy and synchrotron-based spectroscopic techniques were used to demonstrate that the oxygen vacancies during film growth can serve as a critical factor in tuning the cation stoichiometry in pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films. When the oxygen vacancies are induced, A-site cations (La/Sr) are in excess near film/substrate interface [1]. Simultaneously, SrO rocksalt monolayer is formed due to the migration of the Sr cations. Consequently, a gradient of Mn nominal valence is observed along the film growth direction according to the electron energy loss spectroscopy results. Figure 1 shows the comparison of Mn $L_{2,3}$ edge spectrums near film/substrate interface and film surface. The lattice image of the manganite film was shown in Figure 2, indicating good crystalline quality. This finding suggests that the oxygen pressure serves as one extrinsic tuning parameter for the interfacial dead layer and hence control over device properties. Furthermore, we studied the oxygen pressure-mediated microstructure and multiferroic properties of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ superlattices. By atomic-resolution electron microscopy, piezoelectric force microscopy and magnetic properties measurements, we demonstrated that the degradation of multiferroic properties in the superlattices is strongly correlated to the local strain fields and cation off-stoichiometry induced by cation defects. When the defects which include pure edge dislocations and planar defects are eliminated by increasing oxygen pressure during growth, near bulk ferroelectric and ferromagnetic properties can be achieved. In summary, our work suggests that controlling the oxygen pressure during growth is crucial to achieving better interfaces, surfaces and microstructures, paving the way for the fabrication of complex oxide devices with high performance.

1. Z. P. Li, M. Bosman, Z. Yang, P. Ren, L. Wang, L. Cao, X. J. Yu, C. Ke, M. B. H. Breese, A. Rusydi, W. G. Zhu, Z. L. Dong, and Y. L. Foo, *Advanced Functional Materials*, 22 (2012), p 4312.
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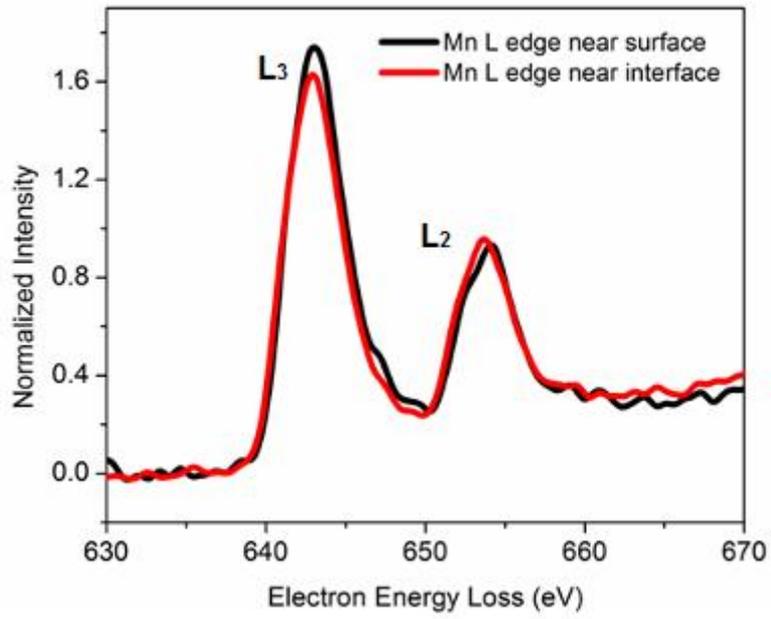


Figure 1. The EELS profiles of Mn L_{2,3} edges taken near the La_{0.8}Sr_{0.2}MnO₃/SrTiO₃ interface and near LSMO surface of the sample grown under low oxygen pressure.

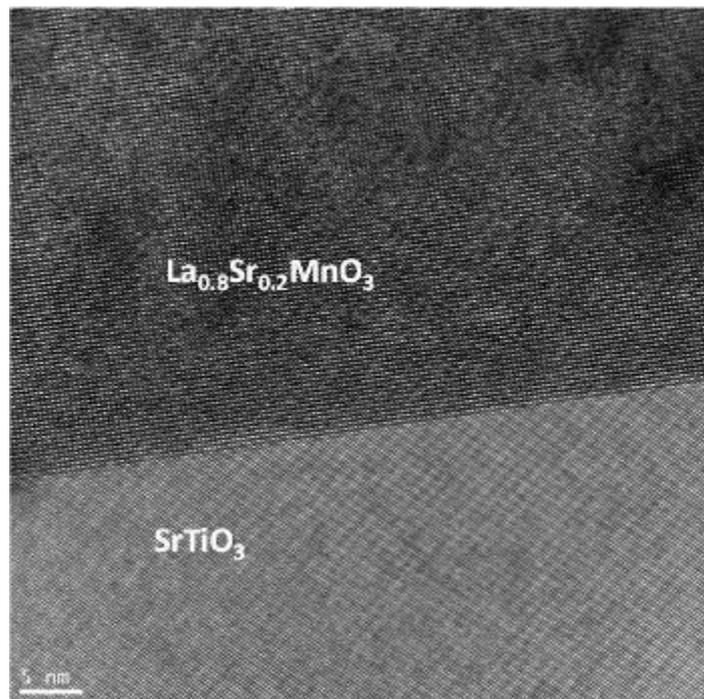


Figure 2. The high resolution TEM image of the interface between La_{0.8}Sr_{0.2}MnO₃/SrTiO₃.