

Combined Electron Channeling Contrast Imaging (ECCI) and Transmission Electron Microscopy (TEM) Studies of Coherent Domain Boundaries in Strained $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) Epitaxial Thin Films

Miaolei Yan¹, Yoosuf N. Picard¹ and Paul A. Salvador¹

¹ Dept. of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA, USA

Electronic, magnetic, electrochemical properties of functional oxide materials depend critically on the presence of extended defects [1]. In addition to traditional techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD), recent developments in electron channeling contrast imaging (ECCI) have enabled non-destructive analysis of extended defects on the mesoscale [2,3]. Combining these techniques offer unique advantages to further understanding extended defect generation and their potential impacts on functional properties in oxide materials.

The perovskite oxide $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is widely adopted as a solid oxide fuel cell (SOFC) cathode material, due to its excellent high temperature catalytic properties towards the oxygen reduction reaction. In this study, extended defects in coherent, epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) thin films were studied using combined ECCI, TEM and XRD techniques. The 600 nm LSM film was deposited via pulsed laser deposition (PLD) on a $(100)_o$ -oriented NdGaO_3 (NGO) substrate (subscript “o” denotes an orthorhombic structure). X-ray reciprocal space maps revealed that the LSM film also adopts an orthorhombic structure. Despite being beyond the critical thickness to relax the overall compressive strain induced by the substrate, the film remained coherently strained to the substrate. The film exhibited an exceptional crystalline quality, with the rocking curve FWHM value of the $(200)_o$ LSM peak being 8 arcseconds, among the lowest value reported for perovskite oxide thin films.

Defect analysis using ECCI under various g conditions are presented in **Figure 1**. While almost no threading dislocations were discovered (consistent with X-ray data), a high density of stripe features oriented along the $[001]_o$ direction were present in all images. The stripes have two contrast variants, exhibiting either dark or bright contrast with respect to the film matrix. On one side of the stripe, regions with weaker diffusive contrast were observed, suggesting these defects may be slanted with respect to film normal. In addition, the stripe contrast inverts upon the inversion of g vectors, suggesting the crystallographic nature of these defects. Cross-sectional dark field TEM images are presented in **Figure 2** and **Figure 3**. Two domains variants slanted at ca. $\pm 45^\circ$ with respect the film normal are clearly visible. They originate from the film-substrate interface and have well-defined boundaries. In addition, contrast levels from domains and their boundaries are both dependent on the g vector, suggesting that the defects have associated displacement vectors. According to X-ray data, the overall LSM film is under uniform coherent strain induced by the substrate. Interestingly, TEM images reveal that strong local contrast exists near the intersection of the slanted domain boundary with the film-substrate interface and the film-Pt interface, likely due to residual non-uniform local strain. Such local strain likely reflects distortions in crystal symmetry or oxygen octahedral tilt patterns, potentially caused by the substrate-induced lattice mismatch. Combining nondestructive and destructive techniques improves our understanding for the defect generation in functional oxide materials and provides opportunities for local structure-property relationship determination.

References:

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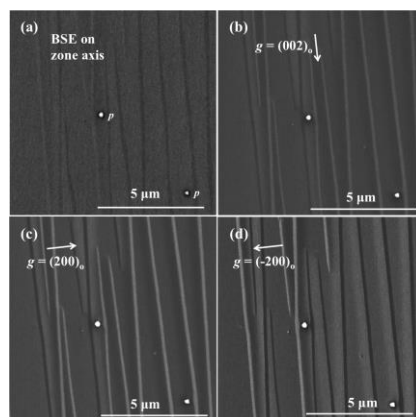


Figure 1. Electron channeling contrast micrographs (plan view) on the same location of a 600 nm strained $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) film grown on $(100)_o$ -NdGaO₃ (NGO) substrate. Images were collected under: (a) $\langle 100 \rangle_o$ zone axis; (b) $\mathbf{g} = (002)_o$; (c) $\mathbf{g} = (200)_o$ and (d) $\mathbf{g} = (-200)_o$. Surface particles are labeled “*p*”. The film exhibits extremely low density of dislocations (consistent with X-ray data). The most significant defects are stripe features oriented along $[001]_o$ direction. They exhibit either dark or bright contrast, with diffusive contrast regions on the side suggesting they may be slanted with respect to film normal. Stripe contrast invert upon inversion of \mathbf{g} vectors (c-d), suggesting the crystallographic nature of such defects.

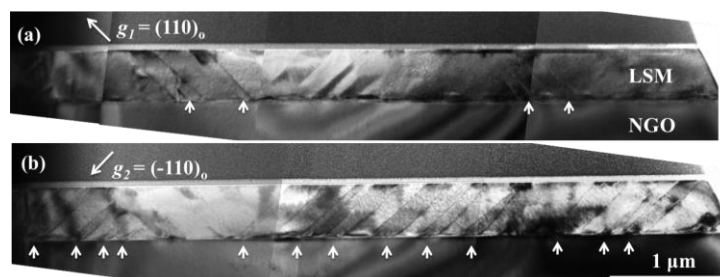


Figure 2. Cross-sectional TEM images of the same LSM film on NGO substrate. Sample is viewed near the $\langle 001 \rangle_o$ zone axis under (a) $\mathbf{g}_1 = (110)_o$ and (b) $\mathbf{g}_2 = (-110)_o$. Contrast from domains slanted at ca. $\pm 45^\circ$ with respect the film normal are labeled with white arrows. Such domains exhibit a darker contrast than the rest of the film. In addition, their contrast is clearly \mathbf{g} - dependent, being invisible when \mathbf{g} is perpendicular to the domain orientation. This suggests that the displacement vector (\mathbf{R}) of such defects is parallel to the domain tilt direction ($[\pm 110]_o$).

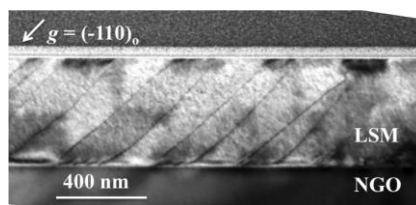


Figure 3. Higher magnification cross-sectional TEM images of LSM film under the same condition as **Figure 2(b)**. The slanted domains are bound by well defined boundaries on both sides. In addition, the film-substrate interface and film-Pt interface exhibit strong contrast, indicating residual strain exist in such regions.