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High-precision stress mapping and defect characterization of thin films of $LaMnO_3$ grown on $DyScO_3$ substrate.

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$LaMnO_3$ (LMO) and related compounds have attracted significant attention as energy conversion materials for metal–air batteries and solid-oxide fuel-cell electrodes owing to their unique properties. Such applications and recent intriguing results showing a sharp transition from polar antiferromagnetic to ferromagnetic in very thin LMO grown on STO substrate [1] demands detailed structural analysis of thin LMO films grown on various substrates, which should include precise characterization of hetero-interfaces, stress relaxation of thin films, extended and point defect characterization. We have developed non- rigid registration and averaging of a series of STEM images, which enables sub-picometer precision in locating atomic column positions [2]. Highly precise, highly quantitative STEM imaging creates new possibilities for precise stress mapping in real space, and for detecting and characterizing point defects like vacancies, impurities, and point-defect complexes.

In this study, we investigated a $LaMnO_3$ film grown on a $DyScO_3$ (DSO) substrate by molecular beam epitaxy. Experiments were conducted on a probe-corrected FEI Titan STEM at 200 kV. HAADF and ABF STEM images were taken simultaneously with 24.5 mrad probe convergence semi-angle and detector collection angles are 84- 422 mrad and 8.5- 18.7 mrad, respectively. Series of typically 200 images were registered then averaged to produce the images for final analysis.

Although LMO has a good lattice match with DSO, the epitaxial structure is quite complex, containing domains rotated by 90° with respect to each other and the substrate. We do not observe interface misfit dislocations. We speculate that the rotated domains may form in order to relax the stress arising from differential thermal expansion of the film and substrate, combined with the transition in the LMO structure from high-temperature cubic to low-temperature orthorhombic structure. Different domains have different internal strain, which we can map by measuring atomic column distortions inside individual domains. Figure 1a shows an example HAADF image (post NRR and averaging) of a single LMO domain taken in [100] zone axis. Figures 1b and c show corresponding distortion maps in X and Y directions. These maps show that different parts of the same domain experience distortions in different directions. For example, there is a strain gradient in right- bottom corner, which can be explained by stress arising from the slight mismatch between [100] and [001] LMO domains and residual stress at the LMO/DSO interface.

NRR STEM can also be used to detect point defects in LMO such as vacancies and point defect complexes. Figure 2a and b shows NRR ABF and HAADF images of LMO film taken in [100] zone axis. Figure 2c and e (zoomed images from area shown on Fig 2a and b) demonstrate possible complex point defects in the stressed LMO film. The relatively low intensity of columns marked as 1, 2 and 4 may indicate that they contain vacancies of La, Mn and O respectively. The distortion of the oxygen column in ABF image marked as 3 may arise from an interstitial or anti-site defect, or it may represent an effective charge redistribution with the valence orbital of nearby oxygen atoms. The effect of residual strain on formation of such point defect complexes will be discussed. [3]

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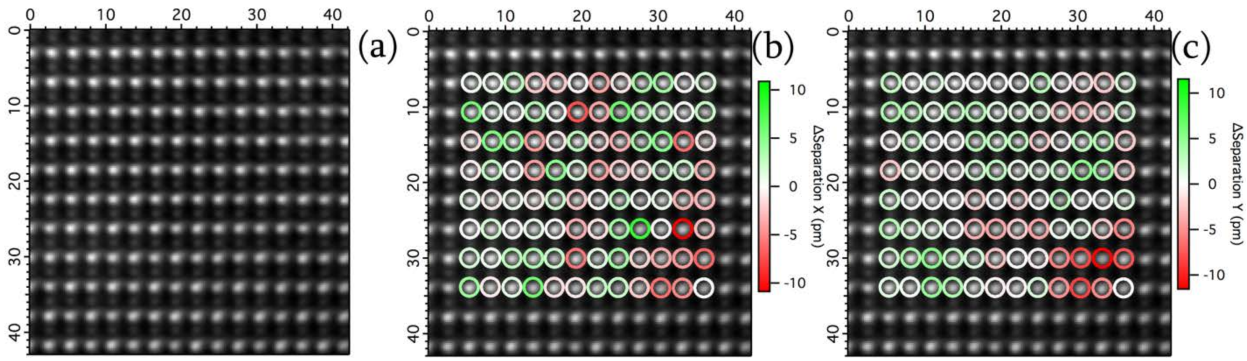

Figure 1 (a) HAADF image of single LMO domain taken in [100] zone axis by NRR method; (b) Distortion map in X direction (left-right), (c) Distortion map in Y direction (up-down). The distortion is indicated by the color scale and calibrated in pm. The scales on all images are shown in Å.

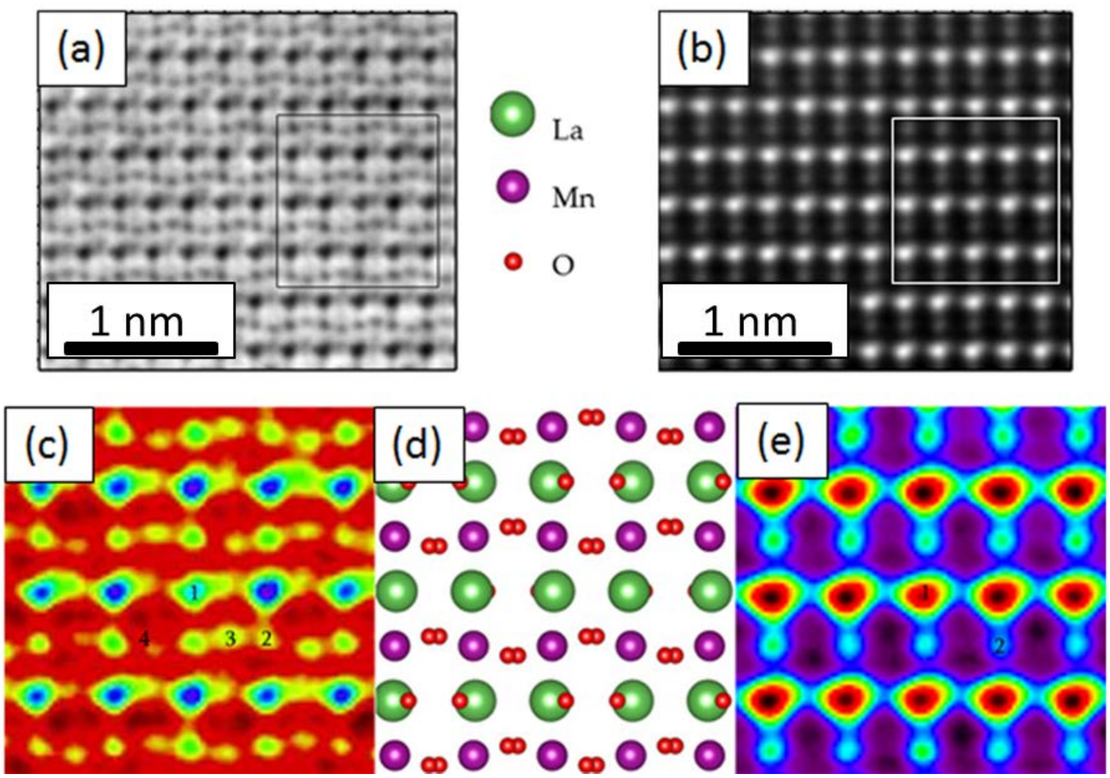

Figure 2. STEM images of possible point defect complexes in a LMO film in [100] zone axis. (a) NRR ABF image; (b) NRR HAADF image of the same area; (c) Expanded area of the ABF image as marked in (a); (d) Positions of La, Mn and O atomic columns in this zone axis; (e) Expanded area of the HAADF image as marked on (b). A possible point defect complex is shown in (c) and (e), marked with labels 1-4.

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