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doi:10.1017/S143192761901153X
Microsc. Microanal. 25 (Suppl 2), 2019

Transmission Electron Microscopy Study of Epitaxial Li-Mn-O Films Grown by Pulsed Laser Deposition: The Effect of Temperature on Formation of Phases

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We demonstrate the thin film epitaxial growth of two phases, orthorhombic o-$LiMnO_2$ and monoclinicm-Li_2MnO_3 on $SrRuO_3$/$SrTiO_3$ substrates with selected orientations at different temperatures [1]; Detailed high-resolution scanning transmission electron microscopy (HRSTEM) of cross-sections has determined the unique orientation relationship for both phases. These epitaxial films are designed to study Li-Mn-O (LMO) structural changes occurring at electrode/electrolyte interfaces, which was previously applied on $LiCoO_2$ films [2,3].

High-resolution HAADF-STEM images of the LMO film grown at 600 °C shows coherent growth with layered structure on the SRO/STO(111) substrate (Fig. 1a,b). Furthermore, there are regions in the film that can be interpreted as belonging to $Li_{0.5}MnO_2$ spinel structure (marked as S in Fig, 1a,b). In some regions, the (001) layers are coherently switching their orientation and forming an orientation variant confined to a lath with parallel coherent interfaces; The nature of the layered structure was better revealed when the TEM samples were prepared with [-112]STO direction normal to the cutting plane (Fig. 1c). The image shows a contrast corresponding to a sequence along the layers of two manganese columns (two bright dots) and one lithium column (no contrast), which is of the Li--2Mn layers of m-Li_2MnO_3 structure. Such contrast was shown in other microscopy studies of bulk m-Li_2MnO_3 [4, 5]. Stacking of the layers is not uniform and creates three alternating 60°-rotational variants of m-Li_2MnO_3, which appears as having [110], [1-10] and [100] zone axes in Fig. 1d; this interruption of long range order is due to low-energy mistakes in packing sequence. For all three variants, assuming the same octahedral coordination of Li and Mn by oxygen, there is a common oxygen sublattice of near-close packed a-b-c-sequence, the same as for the monoclinic phase.

The HAADF-STEM image of LMO film grown on SRO/STO(001) at 800 °C has a prominent zig-zagging contrast of the bright Mn columns arrangement, which cannot be explained by the m-Li_2MnO_3 structure (Fig. 2a,d,e). In contrary, the pattern fits well to the structural projection of the orthorhombic o-$LiMnO_2$ structure in [001] direction [6]. The (100) plane of o-LiMnO2 is parallel to (110) of the STO substrate. HAADF image in Fig. 2d shows in more details the arrangement of Mn columns for the [001] orientation (compare to the projected structural arrangement of Mn in inset). An enlarged image taken from defective regions is recognized as intergrowth of thin layers of the m-Li_2MnO_3 phase, with predominately flat interphase interfaces parallel to (100)STO surface (Fig. 2e).

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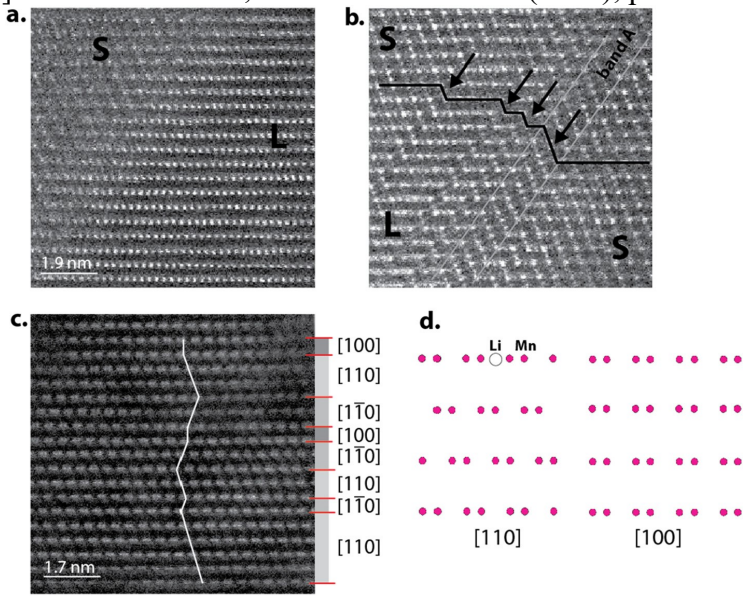

Figure 1. Atomic resolved HAADF-STEM images of the LMO film grown on the SRO/STO(111) substrate at 600 °C . (a, b) LMO images alone the [110]STO showing two orientational variants of the Layered phase (L) arrange in alternating bands with parallel coherent interfaces of spinel structure (S). (c) Similar STEM image from [-112]STO zone axis showing a contrast typical for the Li--2Mn layers of m-Li2MnO3. (d) structural projections of Mn columns alone [110] and [100] of m-Li2MnO3 structure.

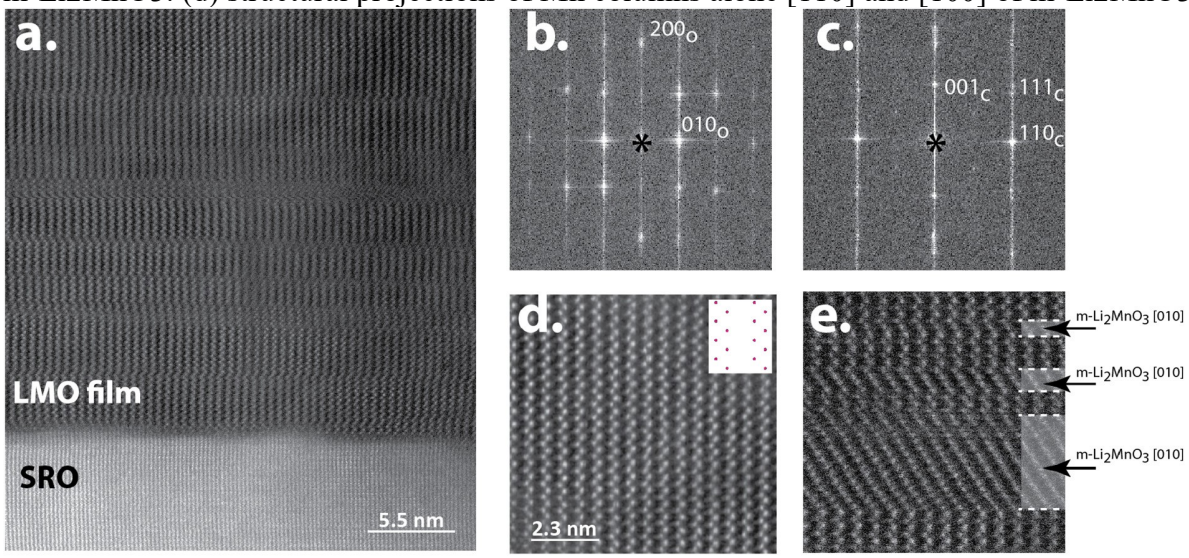

Figure 2. (a) STEM image of the LMO film grown on the SRO/STO(001) substrate at 800 °C; (b, c) FFT patterns taken from the film (b) and SRO/STO substrate (c) confirm the o-LiMnO2 phase in [001] zone axis and STO in [-110] zone axis, accordingly, and (100) plane of o-LiMnO2 parallel to (110) of the substrate; (d) the region of single crystal o-LiMnO2 showing in more details a characteristic zig-zag contrast; (e) a region with defects recognized as intergrowth between o-LiMnO2 and m-Li2MnO3 phase in [010] zone axis.

https://doi.org/10.1017/S143192761901153X Published online by Cambridge University Press