A-site (La and Sr) and B-site (Mn) cations, which leads to the suppression of interface magnetism. The question then arises, how can the cation stoichiometry be modified, if we tune another main film growth parameter, oxygen pressure? In the vast available literature, the accepted selection of oxygen pressure during manganite film growth can be divided into two groups: films grown with oxygen pressure above 26 Pa, with or without post-annealing,[16] and films grown with oxygen pressure around 1 Pa, resulting in films with oxygen vacancies, followed by post-annealing to recover the oxygen stoichiometry.[17] It is worth considering that the tendency to neutralize the positive charges brought by oxygen vacancies during film growth may serve as a driving force for local cation nonstoichiometry which is difficult to recover by annealing. Fister et al. observed that the strontium surface segregation in $La_{0.7}Sr_{0.3}MnO_3$ thin films increases as oxygen partial pressure decreases, implying that oxygen vacancies are somehow involved in the cation nonstoichiometry.[18] In this study, detailed investigation is carried out to form a complete picture of the effects of oxygen vacancies during film growth, on the local cation stoichiometry, the variation of the Mn valence in the epitaixal films, and their impact on the electrical and magnetic properties.

2. Results and Discussion

2.1. Microstructure Analysis

Details on the growth conditions of the studied films are specified in the Experimental section. The two-dimensional layer-by-layer growth mode was monitored by intensity oscillations of the reflected high energy electron diffraction (RHEED) during pulsed laser deposition of $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) film, as described earlier.[19] High-resolution X-ray diffraction (HRXRD) reciprocal space mapping (RSM) directly measures the in-plane and out-of-plane lattice parameters, strain, as well as the mosaicity of the grown film. The reciprocal space mapping around the (103) plane of the as-grown film indicates its fully strained state. Additionally, an exceptionally low full-width at half maximum of 0.02° was measured by the thin film rocking curve, showing that the film is of high quality and low mosaicity. Based on the HRXRD measurements, the in-plane and out-of-plane spacing of the thin film are a = 0.3905 nm and c = 0.393 nm respectively.

Here, we present transmission electron microscopy (TEM) studies of the annealed thin film, demonstrating its monocrystallinity with high epitaxial quality and excluding the presence of grains/domains that can contribute to degradation in electrical and magnetic properties. **Figure 1**a shows a low magnification cross-sectional TEM image of the LSMO/STO couple. The micrograph was imaged with the specimen tilted to the [100] zone axis of STO. From the TEM images, there is no evidence for the formation of lamellae structures or domains, such as those discussed by Lebedev et al.[20] and Zhang et al.[21]. This point is further confirmed by the SAED pattern in Figure 1b, taken from the LSMO film. The diffraction spots of LSMO are sharp spots rather than curved, implying that the pseudocubic structures are not domain-oriented. High resolution TEM in

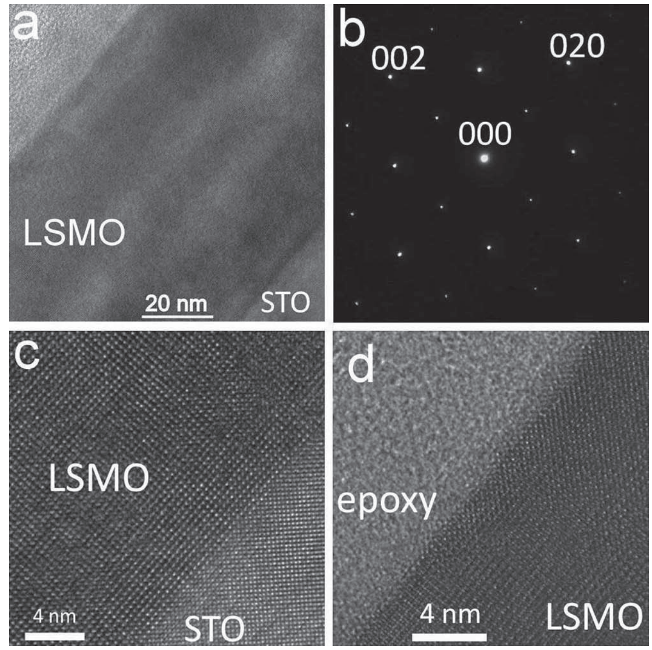

Figure 1. Morphology of the annealed LSMO thin film. a) An overview at low magnification. b) Selected-area electron diffraction pattern of the LSMO film at the [100] zone axis. c) HRTEM image of the interface of LSMO with the $SrTiO_3$ substrate. d) HRTEM image of the LSMO surface.

Figure 1c reveals that the interface between LSMO and STO substrate is atomically sharp, and nearly free of misfit dislocations, in agreement with RSM. Figure 1d shows that the high epitaxial quality is maintained throughout the film until the surface; no grain boundaries were found.

2.2. EELS Analysis of the Local Mn Valence and Chemical Composition

According to the phase diagram of $La_{1-x}Sr_xMnO_3$, its electrical and magnetic properties are strongly dependent on the Mn nominal valence, which is strongly correlated with the stoichiometry of each element.[1] Therefore, to study the effect of oxygen vacancies during film growth on the local cation stoichiometry, EELS line scans were used to characterize not only the cations content profiles but also the local Mn valence along the thickness of two LSMO films. Firstly, there is a reference sample, grown under high oxygen pressure (26 Pa). After high temperature oxygen annealing, there is no change in its electrical and magnetic properties, thus we can conclude that most of the oxygen vacancies were eliminated during growth. This sample shows bulk single crystal properties, and it is believed to have nearly ideal stoichiometry.[22] The second sample is a LSMO film grown under low oxygen pressure (1 Pa). The as-grown film and the one after oxygen annealing show completely different physical properties, suggesting the formation of oxygen vacancies during the film growth (more details in Section 2.4). To directly relate its Mn valence to the cation stoichiometry, the oxygen nonstoichiometry in the second sample