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Analytical TEM Study of the Microstructure of $LaNiO_3/LaAlO_3$ Superlattices

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Heterostructures of transition metal oxides show intriguing phenomena such as the ordering of charge, spin and orbitals which can give rise to multiferroicity or superconductivity and makes them interesting candidates for future electronic devices [1]. Among them, $LaNiO_3$ (LNO) is a promising representative due to its strongly correlated conduction electrons. It was reported that in ultrathin LNO films or LNO-based superlattices (SLs) the phase behaviour and the transport properties depend on the thickness of the films or the single layers of the SL [2]. We have used transmission electron microscopy (TEM) in combination with electron energy-loss spectroscopy (EELS) to study the microstructure of $LaNiO_3/LaAlO_3$ (LNO/LAO) superlattices in dependence of the used substrates which differ in their polarity and the strain they induce.

LNO/LAO SLs were epitaxially grown by pulsed laser deposition on three different substrates: $SrTiO_3$ (STO), $(La,Sr)AlO_4$ (LSAO), and $DyScO_3$ (DSO). Due to their lattice misfit tensile strain in the case of STO and DSO and compressive strain in films on LSAO are induced, respectively. Furthermore, the polarity of the substrate materials is different resulting in a polar discontinuity between STO and SL if the initial SL layer is LNO. A C_s-corrected Nion UltraSTEM operated at 100 kV acceleration voltage was used to record atomically resolved high-angle annular dark field (HAADF) images and EELS spectra.

Particularly with regard to the macroscopic material properties, the microstructure of the complete film has to be considered. Especially, a polar discontinuity, as in the case of the SLs on STO, can lead to any kind of reconstruction, e.g. interdiffusion, the formation of oxygen vacancies or electronic reconstruction [3]. In LNO/STO heterostructures, a Ni 2+ valence state has been reported besides trivalent Ni of bulk LNO concluding the formation of an interfacial LNO layer with a Ni valence state of 2+ which hinders the polar catastrophe [4].

Films grown on STO contain nanometer-sized precipitates which are located directly at the interface of the substrate (Fig. 1a). The elemental EELS maps (Fig. 1b) show that the particle is Ni-rich and La- and Al-deficient. Oxygen is homogeneously distributed so that the precipitates can be specified as NiO which is in accordance with the O K-edge fine structure and the lattice parameter which has been determined from an atomically resolved image. In contrast to the SLs on STO, no precipitates were found in films grown on LSAO or DSO so that they are no general product of the growth process. In fact, the polar mismatch between the initial LNO layer and STO, and not the strain, is the decisive parameter for the formation of NiO precipitates [5]. Although there is indeed Ni 2+ in these films, our study shows that it is not homogenously distributed along the interface but rather locally agglomerated in precipitates. The formation of these precipitates can be prevented by starting the SL deposition with an LAO layer.

Extended planar defects which can be classified as Ruddlesden-Popper (RP) faults exist in SLs grown on LSAO substrates. The HAADF image in Figure 2a shows that the atomic planes from both sides of the defect are shifted against each other and that one NiO_2 plane along the defect is missing. This arrangement which is characteristic for RP faults is confirmed by the elemental EELS map in Figure 2b. The growth of these planar RP faults is triggered by the surface steps of LSAO which can be always found underneath the defects [6]. Furthermore 3D RP faults of nanometre scale exist in the films due to the formation of local stacking faults during film growth [7].

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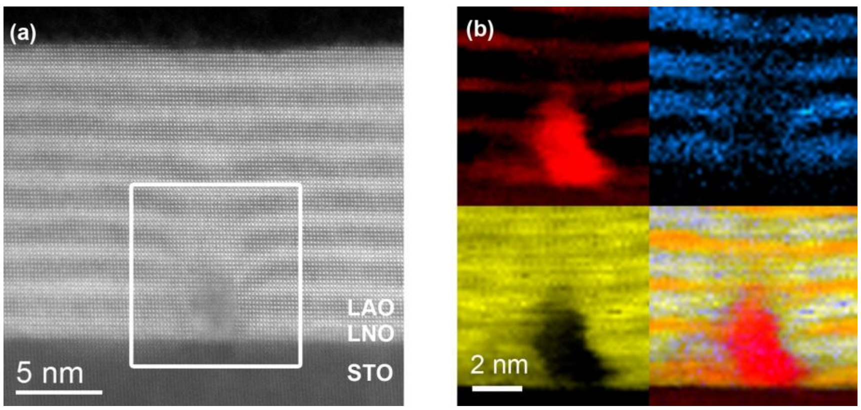

Figure 1. a) HAADF image of a SL containing a NiO precipitate. b) Elemental maps of Ni (red, upper left), Al (blue, upper right) and La (yellow, lower left) recorded within the marked rectangular area marked in (a) and the overlay of the elemental maps (lower right) shows the Ni enrichment within the precipitate.

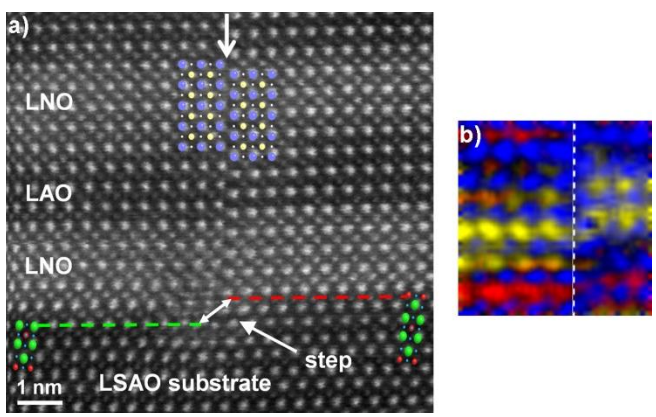

Figure 2. a) HAADF image of a planar RP fault in an LNO/LAO superlattice on LSAO (marked by the upper arrow). The unit cells of LNO and LSAO are overlaid. b) Elemental EELS map of the overlapped La (blue), Ni (yellow) and Al (red) signals (size of the image: 2.56 x 2.56 nm²).

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