**Polarity-driven nickel oxide precipitation in nickelate superlattices**

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Multilayer systems of transition metal oxides (TMOs) have recently come to the fore due to their ability to form correlated electron interfaces \([1]\). In addition to the chemical composition, their electronic and magnetic properties can be affected by the substrate material by means of an input of strain \([2]\) or by varying the layer thicknesses \([3]\). Because of its strongly correlated conduction electrons, LaNiO\(_3\) is a promising candidate as one component of such superlattices. Separated by an insulating layer, as LaAlO\(_3\), superconductivity is predicted to emerge if the electronic dimensionality and the orbital polarization are correctly controlled \([4]\).

One important condition for the exact control of the properties of such heterostructures is a high accuracy of their growth because even minor irregularities can have a significant impact on their properties. However, a “perfect” structure is energetically instable if polar and non-polar TMOs are combined because an electric potential builds up at such a polar discontinuity \([1]\). This so called polar catastrophe can be avoided e.g. by interdiffusion or electronic reconstruction. In the case of a LaNiO\(_3\)–SrTiO\(_3\) (LNO–STO) hetero-interface, the formation of an interfacial LNO layer with divalent Ni was proposed based of the measurement of a Ni\(^{2+}\) valence state signal in addition to the trivalent state of bulk LNO \([5]\).

We characterize here LaNiO\(_3\)/LaAlO\(_3\) superlattices (LNO/LAO SLs) by means of transmission electron microscopy (TEM) in combination with electron energy-loss spectroscopy (EELS). The microstructure of films which were grown on polar (La,Sr)AlO\(_4\) (LSAO) or non-polar STO substrates is compared in order to study the influence of the polarity of the substrate.

In the high-angle annular dark field (HAADF) image in Figure 1a La, Ni, and Al atoms are resolved showing well-defined single layers which demonstrates the high precision of the SL. This is confirmed by an EELS linescan in growth direction from the bottom to the top of Figure 1a. The integrated intensities of the Ni L\(_2\) and Al K edges are plotted in Figure 1b. The profiles indicate that the LNO–LAO interface is more abrupt than the LAO–LNO interface.

In contrast to the SLs grown on LSAO, nanometer-sized precipitates are visible directly at the interface to the substrate in films on STO as the HAADF image in Figure 2a shows. The elemental EELS map in Figure 2b is an overlay of La (blue), Ni (green), and Al (red) signals and shows 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 fine structure of the O K absorption edge and the lattice parameter which was determined with an atomically resolved image. Since NiO precipitates were found only in films on STO and not in films on LSAO, they are no general product of the growth process but rather a consequence of the polar mismatch between LNO and STO \([6]\).

The high quality of LNO/LAO SLs was proven by HAADF images and elemental EELS maps which also show that the LNO–LAO interface is sharper than the LAO–LNO interface. The formation of NiO precipitates triggered by the polar discontinuity illustrates that in general the precipitation of secondary phases should be considered as consequence of a polar mismatch because such precipitates can dramatically affect the properties of the entire SL. The exclusion of these phases can be very difficult with standard techniques. Here we show that TEM in combination with EELS is excellently suited for the detection of nanometre-sized secondary phases.
References


Figure 1. a) HAADF images of a LNO/LAO superlattice with 4 u.c. thick single layers: the brightest spots are the La columns, in between weaker Ni and Al columns are visible. b) Integrated EELS linescan over the horizontal width of image a) from the bottom to the top: the profiles of the normalized intensities of the Ni $L_2$ (blue) and Al $K$ (red) edges are plotted.

Figure 2. a) HAADF image of a NiO precipitate which forms directly at the interface to the SrTiO$_3$ substrate. b) Elemental EELS map of La (blue), Ni (green) and Al (red) showing the in the SL embedded precipitate.