Electron energy-loss spectroscopy study of a \((\text{LaMnO}_3)_8(\text{SrMnO}_3)_4\) heterostructure

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An epitaxially grown heterostructure consisting of alternating layers of \(\text{LaMnO}_3\) (8 unit cells) and \(\text{SrMnO}_3\) (4 unit cells) on a \(\text{SrTiO}_3\) substrate has been studied by a combination of electron energy-loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM) on an atomic scale. Excitation edges of all elements are captured with subnanometer spatial accuracy, and parametrized to obtain chemical profiles. The fine-edge structure of \(\text{O} K\) and \(\text{Mn} L_{2,3}\) edges are interpreted as signatures of the local electronic structure and show a spatial modulation of the concentration of holes with \(\text{O} 2p\) character. The chemical concentration is found to be different for the bottom and top interface of a \(\text{SrMnO}_3\) layer. HRTEM complements the EELS results and confirms the asymmetry of the interfaces. © 2001 American Institute of Physics.

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Studies on perovskite-based bulk materials of the type \((\text{Ln}_{\text{e}}\text{A}_{\text{e}})\text{MnO}_3\) have shown that three parameters are most important for the control of the magnetic and electronic properties: (a) the valence of the manganese which is determined by the ratio between the lanthanide and the rare-earth cations, (b) the average \(A\)-site cationic radius, and (c) the difference in size between the \(A\)-site cations. A-site ordering of bulk \(\text{LaBaMn}_2\text{O}_6\) increases the metal-to-insulator transition temperature and the Curie temperature. However, such an ordered bulk material is difficult to synthesize using the classical solid-state synthesis methods. Thin-film laser molecular-beam epitaxy (laser-MBE) growth methods offer the possibility, utilizing a multitarget deposition process, to directly control the location of the different cations in an artificial superlattice.

In the present contribution, the superlattice is grown in a reflective high-energy electron diffraction (RHEED) monitored laser-MBE system from two targets, \(\text{LaMnO}_3\) and \(\text{SrMnO}_3\), with a nominal average composition of \(\text{La}_{0.66}\text{Sr}_{0.33}\text{Mn}_2\text{O}_6\) and an ideal sequence \((\text{LaMnO}_3)_8(\text{SrMnO}_3)_4\).

The possibilities to obtain information on the electronic structure of a material by using a combination of scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) on an atomic scale have already been shown for \(\text{Si}–\text{O}\) gate oxide. Combining this technique with fitting methods to interpret the spectra gives an opportunity to investigate the chemistry of the present heterostructure on a unit cell (0.4 nm) scale. The detailed shape of the spectra contains information on the electronic structure. Combination with more conventional techniques such as high-resolution transmission electron microscopy (HRTEM), enables us to complement and compare the EELS data with structural and contrast information.

The RHEED-monitored laser-MBE system has been described elsewhere. A \([001]\)-SrTiO\(_3\) (STO) substrate is treated for good surface quality to enable step-flow-mode growth. Deposition of the superlattice is carried out at 535 °C in a dynamic vacuum of \(5 \times 10^{-3}\) mbar of 94% oxygen and 6% ozone to ensure a complete oxidation of the superlattice. After deposition the superlattice is cooled to 300 °C under the same pressure and atmosphere. Between 300 and 200 °C, the ozone production is stopped but the pressure is held constant. Below 200 °C the superlattice is cooled under low pressure (<\(5 \times 10^{-7}\) mbar).

Sample preparation for TEM and HRTEM was done using a standard TEM cross-section technique, and mechanical wedge polishing for STEM.

Cross-section high-resolution TEM images were recorded on a JEOL 4000EX operating at 400 keV and having a point resolution of 0.17 nm.

For EELS experiments, use was made of the Cornell VG HB501A STEM operating at 100 keV with a cold field-emission electron gun having a probe diameter of 0.2 nm and energy spread of 0.6 eV. Each EELS spectrum is recorded by automatically scanning the STEM probe over a region of 15.7 nm, parallel to the layers to average out possible interface roughness or surface contamination. The probe is manually repositioned after each acquisition to consecutively capture data in different perpendicular positions of the layers. A total set of 36 spectra contains information starting from the
bottom of LMO layer 4 going trough SMO layer 4 and ending at the top of LMO layer 5.

EEL spectra are collected in four different energy ranges: the low loss (−60.2 eV/241.6 eV), the Mn L2,3 and O K (~439.7 eV/741.6 eV), the La M4.5 (~739.7 eV/1041.6 eV), and the Sr L2,3 range (1839.7 eV/2141.6 eV).

Recorded spectra are analyzed using a spectrum-fitting technique. Considering the low signal-to-noise ratio in the Sr spectrum, the Sr intensity is taken as the intensity of the Sr L1 white line, since this feature is about an order of magnitude stronger than the excitations to the continuum. All other edges are fitted to a Hartree–Fock model for excitations to the continuum.

The fitted-edge intensities serve as an estimation of the total chemical concentration with an estimated error of 10%. The results are corrected for thickness changes in the sample as well as for changes in bright-field intensity due to different elastic scatterings in the two types of materials through dividing by relative thickness and bright-field signal. The STEM probe is calculated to spread from 0.2 nm at the entrance plane to around 0.32 nm at the exit plane of the specimen (diameter containing 80% intensity, thickness 25 nm, multislice simulation), which gives an indication on the expected blurring of the chemical profiles caused by electron scattering. The error on the probe position is on the order of 0.2 nm.

A HRTEM image of the initial layers on the STO substrate is shown in Fig. 1. The image shows perfect epitaxial growth. No structural evidence of stress relaxation was observed during the growth of the first layers of LMO on a 30 s exposure time. Careful inspection of the spectra over time, showed no changes in the ELNES spectra at exposure times up to 120 s. This is taken as an indication that no significant beam damage effects occurred during the acquisition of the ELNES spectra.

The spectral data are treated with a standard background removal method and the high frequency noise is removed by convolution with a Gaussian profile of 0.3 eV full width at half maximum. Two spectra represent the middle part of a LMO and SMO layer. The energy resolution of this experiment is estimated around 0.65 eV by a Lorentz fit to the experimental zero-loss peak.

A HRTEM image of the interfaces between two LMO layers is shown in Fig. 1. The image shows perfect epitaxial growth. No structural evidence of stress relaxation was observed. The contrast at the interfaces between the layers shows a sharper onset at the bottom interface (LMO/SMO) of a SMO layer compared to the top interface (SMO/LMO) of that layer. Image simulations show that the white dots in the STO and the SMO correspond to the cation sublattice, while in the LMO they correspond to the Mn sublattice.

The contrast of the HRTEM also indicates that the further away from the substrate, the less sharp the LMO–SMO interfaces are. A more detailed structural paper will follow.

Figure 2 shows a plot of the result of the fitting and correction process for all chemical elements in the sample. The plot shows a relatively constant Mn signal and the expected complementary La/Sr signal. A slight asymmetry is observed in the La signal as a sharper drop of La signal at the bottom compared to the top SMO interface. The O intensity shows a significant drop centered around the top of the SMO layer. This behavior was also observed in a similar (LMO)12(SMO)6 heterostructure, studied by energy-filtered TEM (EFTEM) methods.

A possible explanation for both asymmetric interfaces is the stress induced by lattice mismatch. During deposition of the layers, the situation for starting a SMO layer on LMO can be quite different from starting a LMO layer on SMO. Three types of stress can be distinguished: lattice mismatch between substrate and film, lattice mismatch between LMO and SMO layers, and stress caused by the fact that cubic perovskite-like SMO is a phase which is not stabilized in a cubic form as a bulk or single thin-film material in such an oxidizing atmosphere. The fact that SMO can exist in this phase is because of stabilization by spatial confinement between two LMO layers. One of the simple explanations is that stress during the growth of the first layers of LMO on a SMO layer makes these layers heavily oxygen-deficient, cre-

FIG. 1. HRTEM image of the STO substrate and the first LMO and SMO layers. The arrow indicates the approximate direction and extent of the STEM scan.

FIG. 2. Edge intensities corrected for thickness and bright-field intensity changes for all chemical elements. Sr L1 scaled to the right axis, all other elements relative to the left axis. The gray region indicates the position of the SMO layer.
ating an oxygen-depleted region around the top of the SMO layer, consequently inducing an O drop in the top interface of the SMO layer. A more detailed study will test these assumptions taking into account the complex stress situation.

The ELNES results are shown in Fig. 3. The O K edge shows three peaks marked (a), (b), and (c). These peaks have been attributed as excitations from the O 1s state to the partially filled O 2p state hybridized with Mn 3d (a), La 5d or Sr 4d (b), and Mn 4sp (c) states. The most remarkable changes are the rise in peak (a) and a shift of peak (b). These changes are in qualitative agreement with x-ray absorption spectroscopy (XAS) results of bulk material, and indicate a spatial modulation of the amount of holes with O 2p character showing a higher concentration of holes in the SMO layers as compared to the LMO layers.

The Mn L2,3 edge shows very little change apart from a change in the L3 white line shape. In a simple ionic picture, a change in the filling of the 3d band is expected when going from LMO to SMO. It was found both experimentally and theoretically that the Mn fine structure shows a clear change when changing the 3d band filling in a number of ionic compounds. The expected changes include a drop in the total white line intensity, a rise in the white line L3/L2 intensity ratio, and a negative chemical shift of the white lines on the order of 1 eV on increased filling of the Mn 3d band. This chemical shift is attributed to an increased Coulombic repulsion of the Mn 3d electrons inside the O octahedra when filling the 3d band.

The discrepancy between the present study and the results from ionic Mn compounds seems to support the hypothesis that the studied materials require a more accurate model for the bonding, as shown also in calculations and XAS experiments of La1−xSrxMnO3 and La1−xSrxFeO3 in Ref. 16 and for EELS experiments on La1−xSr1−yMnxRu1−yO3+δ in Ref. 22. Moreover, the very existence of peak a in the O K ELNES indicates the existence of hybridized states with partial O 2p character, and thus shows that simple Mn valence considerations may not be applicable. The observed O nonstoichiometry as well as the structural parameters affect the electronic structure and will be included in a more detailed study.

The experimental results clearly show the possibility of getting accurate chemical and electronic data on a subnanometer scale, even for heterostructures. A chemical and structural difference between the LMO/SMO and SMO/LMO interface was observed with EELS and HRTEM. The La profile is shown to be steeper at the LMO/SMO interface compared to the SMO/LMO interface. The SMO/LMO interface also shows a remarkable drop in oxygen concentration. Both effects can be tentatively explained by stress effects during deposition of the heterostructure.

The interpretation of the ELNES features in the ELNES spectra shows that comparison with a simple ionic model does not hold, although there is evidence for spatial modulation of holes with O 2p character in the O K ELNES. A more detailed study of the ELNES spectra will require theoretical calculations of the electronic structure, taking into account structural, chemical, and bonding effects.

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