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Assessing electron beam sensitivity for $SrTiO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ using electron energy loss spectroscopy

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ABSTRACT

Thresholds for beam damage have been assessed for $La_{0.7}Sr_{0.3}MnO_3$ and $SrTiO_3$ as a function of electron probe current and exposure time at 80 and 200 kV acceleration voltage. The materials were exposed to an intense electron probe by aberration corrected scanning transmission electron microscopy (STEM) with simultaneous acquisition of electron energy loss spectroscopy (EELS) data. Electron beam damage was identified by changes of the core loss fine structure after quantification by a refined and improved model based approach. At 200 kV acceleration voltage, damage in $SrTiO_3$ was identified by changes both in the EEL fine structure and by contrast changes in the STEM images. However, the changes in the STEM image contrast as introduced by minor damage can be difficult to detect under several common experimental conditions. No damage was observed in $SrTiO_3$ at 80 kV acceleration voltage, independent of probe current and exposure time. In $La_{0.7}Sr_{0.3}MnO_3$, beam damage was observed at both 80 and 200 kV acceleration voltages. This damage was observed by large changes in the EEL fine structure, but not by any detectable changes in the STEM images. The typical method to validate if damage has been introduced during acquisitions is to compare STEM images prior to and after spectroscopy. Quantifications in this work show that this method possibly can result in misinterpretation of beam damage as changes of material properties.

1. Introduction

Perovskite oxide materials have received a great deal of interest due to their magnetic and electronic properties [1,2]. In bulk form they exhibit a wide range of functional properties, such as ferroelectricity [3], ferromagnetism [4], dielectric properties, and colossal magnetoresistance [4]. These range of properties are enabled by strong structure–function coupling, where small variations in structural parameters can result in large changes in functional response. In recent years there has been a resurgence of interest in these materials due to advances in thin film synthesis methods such as molecular beam epitaxy and pulsed laser deposition (PLD), where epitaxial growth can be controlled down to single monolayers [3]. By epitaxial growth and correct substrate use it is possible to control the structure, opening for new avenues for fine tuning functional properties.

One such control parameter is chemical substitution of the A- or B-cations. For example, by replacing La with Sr in $La_{1-x}Sr_xMnO_3$ the magnetic response can be tuned, and at $x \approx 0.3$ maximum in colossal magnetoresistance is observed [5]. Strain engineering is another control parameter, by changing the in-plane lattice constant of the substrate the thin film's in-plane lattice spacings can be locked to the substrate's. This clamping can modify the crystal structure of the film, for example through biaxial strain and suppression of oxygen octahedral rotations [6,7]. Oxygen vacancies constitute an important control parameter. It has been reported that by growing oxygen deficient $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ on substrates with different lattice parameters, the oxygen vacancies can order in specific crystal directions [8]. Oxygen vacancies can also affect the conductivity of a material, for example turning the insulating $SrTiO_3$ into a conductor through charge transfer from the vacancy to the titanium atom [9]. In $La_{0.7}Sr_{0.3}MnO_3$, the presence of oxygen vacancies can lead to breakdown of the ferromagnetic order by suppressing the double-exchange mechanism [10]. Lastly, crystal orientation of the substrate adds another control parameter. As materials often are anisotropic, growing films in different crystal orientations is paramount. The most studied substrate orientation has been the (100) orientation, however recently (111) oriented

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thin film systems have been realized [11,12]. By relying on the discussed control parameters, it should be possible to fine tune functional properties and to tailor-make devices. However, the complex interplay between the different parameters makes it challenging to understand and characterize the relationship between structure and properties, generating a demand for high resolution spatial techniques.

Transmission electron microscopy (TEM) is one of the most used tools to study perovskite oxides [7,12–17], and in particular embedded parts of the materials. In the latter years, the development of sub-Å resolution scanning TEM [18,19] (STEM) combined with high energy resolution electron energy loss spectroscopy (EELS) has turned the combination of STEM and EELS into one of the most powerful tools to characterize the structure and electronic properties of perovskite oxides with atomic resolution [13,14]. EEL spectra are now used to collect information about chemical composition including cation diffusion [20], cation oxidation state [21,22], crystal structure modifications [23], and vacancies [15,16]. These are all parameters that the functional properties are extremely sensitive to. However, a correct interpretation of structure–property relations relies on several sensitive steps in the characterization scheme: (a) the high energy and flux of the electron beam used in modern TEMs can possibly modify the materials due to beam damage [17,24–27], (b) the interpretation of the fine structure information of the EEL core loss spectra rely on a correct handling of the plasmon background and modelling of the various features in the spectra, and (c) the TEM sample preparation can possibly alter the inherent structure and properties of the materials.

In the present paper we have used STEM–EELS to systematically study an epitaxial heterostructure with two of the most studied perovskite oxides: $La_{0.7}Sr_{0.3}MnO_3$ (henceforth LSMO) grown on $SrTiO_3$ (STO) along the [111] direction. A refined and improved model based approach for processing of EELS spectra in order to correctly interpret the fine structure of the core loss is presented. From this we have established thresholds for beam current and exposure times, beyond which beam damage is introduced. One very important observation is that for LSMO the onset of beam damage, both as a function of beam current and exposure time, sets in before any damage can be seen directly in the STEM image. For STO, changes in the STEM image occur simultaneously with the onset of beam damage as deduced from EELS, however some of these subtle changes can be missed under common experimental conditions.

2. Materials and method

2.1. Experiment

The beam exposure experiments were performed on LSMO/STO:Nb-(111) and LSMO/$LaFeO_3$ (LFO)/STO-(111) samples grown by PLD [11]. Cross section TEM lamellas were prepared by focused ion beam (FIB), on a FEI Helios Nanolab DualBeam FIB, using standard lift-out technique. Prior to starting the FIB preparation, a 10 nm Pt/Pd layer was sputter coated on top of the wafer. In the FIB an additional 80 nm Pt protection layer was deposited by electron beam assisted deposition, before adding a 3 µm carbon protection layer by ion beam assisted deposition. The coarse ion beam thinning was done at 30 kV. Final thinning was performed with 5 and 2 kV ion beam acceleration voltages. After FIB preparation, the TEM samples were milled for 20 s on each side with Ar-ions at 100 eV using a Gatan PIPS II. The TEM experiments were done on a double-corrected Jeol ARM200CF equipped with a Gatan Quantum ER, using an energy dispersion of 0.25 eV/channel and a collection semi-angle of 66 mrad. Low and core loss EEL spectra

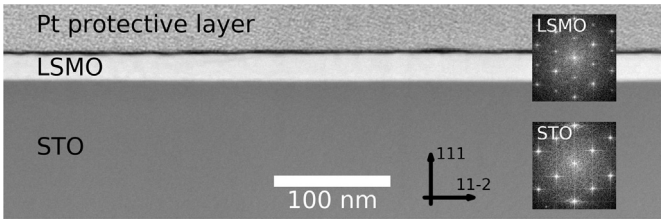

Fig. 1. HAADF STEM overview of the LSMO film, STO substrate and the FIB deposited Pt protection layer. Insets show FFTs from HRTEM images acquired on the same sample.

were acquired quasi-simultaneously using the DualEELS functionality on the Gatan Quantum. All STEM-high angle annular dark field (HAADF) data were acquired with inner and outer collection angles of 118–471 mrad. A HAADF-STEM overview of the LSMO/STO sample is shown in Fig. 1.

The beam exposure experiments were performed by acquiring a STEM-HAADF image of the area, then positioning the STEM probe inside this area while simultaneously acquiring an EEL spectrum every 0.1 s. The probe remained at this position for up to 3.3 min. After the exposure experiment was finished, another STEM-HAADF image was acquired for comparison and to estimate the sample drift. The sample drift was estimated by using some landmark features in the field of view, for example an inhomogeneity in the Pt-protective layer for the experiments done on the LSMO film. For the STO substrate, which has no inherent identifiable features, a marker was created by leaving the electron probe for a sufficient time to change the HAADF intensity, like in Fig. 3. This procedure was repeated for different acceleration voltages, spot sizes and condenser apertures on both the LSMO film, and the STO substrate. The properties of the different probes are shown in Table 1. For the LSMO film, all the exposure experiments were done in the middle of the cross section film: about 10 nm from the interface. The STO substrate exposures were performed about 100 nm away from the interface. The TEM foil thickness in the analyzed regions was approximately 0.5λ (λ = inelastic mean free path) at 200 kV, and 0.6λ at 80 kV.

2.2. EELS modelling

To extract physical relevant parameters from the EELS fine structure data, the model based approach was utilized [28] using the open source software HyperSpy [29]. This approach works by fitting several components to an experimental spectrum, and the sum of these components is the model. These components are distributions or functions such as Gaussians or Hartree–Slater core loss ionization edges [30]. For modelling the titanium-$L_{2,3}$ core loss edge (transitions between $2p^{1/2}$ and $2p^{3/2}$ to 3d), four Gaussians were used (one for each peak), and two Hartree–Slater edges

Table 1
Properties for electron beams used in the exposure experiments. Probe currents were measured using the Gatan Quantum ER.

Acceleration voltage (kV)	Probe	Aperture (µm)	Current (pA)	Size (Å)	Convergence semi-angle (mrad)
200	3C	50	646	1.2	34.2
200	3C	30	223	1.1	20.4
200	5C	50	177	0.9	34.2
200	5C	30	63	0.9	20.4
80	3C	50	631	2.2	34.2
80	3C	30	215	1.9	20.4
80	5C	50	167	1.6	34.2
80	5C	30	58	1.4	20.4