Aberration corrected STEM of defects in epitaxial n=4 Ruddlesden-Popper phase Ca$_{n+1}$Mn$_n$O$_{3n+1}$

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Abstract. Defects in Ruddlesden-Popper phase CaO•[(CaMnO$_3$)$_4$]$_4$, epitaxial films grown on SrTiO$_3$ (001) by pulsed laser deposition have been investigated using high angle annular dark field imaging in an aberration-corrected STEM. The stacking faults perpendicular and parallel to the substrate formed during the growth are discussed in detail. The desired n = 4 RP phase is imaged and chemically analyzed at the atomic scale using electron energy loss spectroscopy.

1. Introduction

The Ruddlesden-Popper (RP) perovskite-like manganites [AO•(A′BO$_3$)$_n$] (n = 1, 2, 3) and [A′BO$_3$] (n = ∞) have recently become subjects of interest due to their complex magnetic and electrical transport properties and colossal magnetoresistance (CMR). The RP structure, [AO•(A′BO$_3$)$_n$] has n-octahedra thick perovskite-like blocks [(A′BO$_3$)$_n$] separated by one (AO) layer of the rock salt structure. The presence of such rock-salt planar blocks defines the thickness of MnO$_2$ planes incorporated in the perovskite block, influences the value of the exchange constant in that direction and modifies the magnetic and transport properties compared with the [A′BO$_3$] perovskite [1]. Hence, changes in the structure, composition and bonding occurring around the (AO) layer can have a significant impact on the desired macroscopic properties. This provides the motivation to characterize the structure and local composition around the (AO) layer on the atomic scale. In principle, the value of n could be arbitrary, but conventional solid-state synthesis methods typically only produce oxides with n up to 3 under high pressure. The n = 4 (CaO•[(CaMnO$_3$)$_4$])$_4$ phase separates into n = 3 (CaO•[(CaMnO$_3$)$_3$]) and n = ∞ (CaMnO$_3$) in classical high temperature synthesis [2]. The inaccessibility of higher n members in the RP manganates is a significant limitation, because higher n values are expected to increase the magnetic ordering temperature for tunneling magnetoresistance [3]. Recently, molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) which can control the atom-by-atom construction of materials have been exploited as a versatile route to inter-growing unit cells with different metal compositions [4]. These approaches of layer-by-layer assembly make it feasible to synthesis the n = 4 member of the Ca$_{n+1}$Mn$_n$O$_{3n+1}$ RP series [2].
In order to obtain an insight into the physical properties of RP series, a number of analytical transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) studies have been carried out using both energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) to characterize the structure and composition \[5\]. STEM with high-angle annular dark field (HAADF) imaging is one of the most powerful tools for the visualization of interface and defects at atomic resolution \[6\]. These images are known as Z-contrast images and can often be directly interpreted. Recent developments in correcting the aberrations of the lenses in the electron microscope have pushed the resolution of HAADF imaging to an unprecedented level. Simultaneously, EELS can be recorded at the electron probe positions with atomic precision. EELS is able to provide an insight on the local elemental composition, electronic states, bonding, and coordination. This means the structure (from the image), and the composition (from the spectra) can be correlated at atomic spatial resolution.

In previous work, the epitaxial growth of n = 4, 5, 6 RP phases CaO\([(\text{CaMnO}_3)]_n\) on SrTiO\(_3\) (001) substrate by PLD and the dislocations incorporated at the interface/substrate have been studied \[2\]. In this work, we focus our studies on the structure and chemical composition of the CaO rock salt blocks in the n = 4 RP phase at the atomic scale using HAADF imaging EELS in the aberration-corrected STEM.

2. Experiments

The epitaxial film of RP phase CaO\([(\text{CaMnO}_3)]_4\) was grown by pulse laser deposition (PLD) on a SrTiO\(_3\) (100) substrate \[2\]. The cross-sectional specimen for STEM was provided by Electron Microscopy for Material Science, University of Antwerp. The thinned sample was examined using an aberration-corrected STEM at the SuperSTEM Laboratory. This instrument is based on a 100 keV VG HB501 with a cold-field emission source and the Nion Mark II spherical aberration equipped with a Gatan Enfina parallel EELS system.

3. Results And Discussion

A atomic resolution HAADF image of the epitaxial growth of the n = 4 RP phase CaO\([(\text{CaMnO}_3)]_4\) along [001] is shown in figure 1. The HAADF detector has an angular range from 70 to 210 mrad and high-angle incoherently scattered electrons are detected. Since high-angle scattering of the electrons is strongly dependent on the atomic number (Z) of elemental species present, the output images are called incoherent Z-contrast images. A resolution of 0.118 nm has been achieved in the images, which is indicated by the Fourier power spectrum from the SrTiO\(_3\) substrate shown on the bottom left-hand corner in figure 1. In the HAADF image the heavy metal atomic columns of the perovskite lattice are resolved as white dots of different intensities. As the intensity is proportional to the atomic number (Z), SrTiO\(_3\) shows the brighter Sr (38) and the less bright Ti+O (22) column. Figure 2 is a contrast-enhanced and noise-filtered image of figure 1 for revealing lattice contrast of the epitaxial film, which shows the brighter Mn+O (Z = (25/2+8/2)\(1/2\) = 26.25) and the less bright Ca (20) column, while the O columns are not visible, and the CaO layer appears as a stripe of lower intensity.

Figure 2 shows the epitaxy is apparent with SrTiO\(_3\) (001) || CaO\([(\text{CaMnO}_3)]_4\) (001). The SrTiO\(_3\) substrate has a mismatch of 4.5% with CaMnO\(_3\) (\(a_{\text{SrTiO}_3}\) = 3.905 Å; \(a_{\text{CaMnO}_3}\) = 3.73 Å) while the rock-salt structure CaO (\(a_{\text{CaO}}\) = 4.815 Å) has a Ca-O bond length mismatch of 12.8% with the Sr-O distance in the SrTiO\(_3\) substrate. In order to decrease the mismatch between the substrate and the epitaxial film, the strategy here is to introduce a buffer CaMnO\(_3\) layer before the first CaO layer by starting the growth of the target n = 4 RP structure with the deposition of four unit cells of CaMnO\(_3\) on the SrTiO\(_3\) (100) substrate. Ideally, the first CaO layer should form a horizontal block parallel to the substrate on top of this first unit cell of CaMnO\(_3\). However, figure 2 shows the first rock salt layer rather than forming the desired horizontal AO units on top of this first block parallel to the substrate, instead nucleates extra CaO layers perpendicular to the substrate, which appear as dark stripes starting after the first module. These layers have the character of a misfit-like dislocation.
As the film thickness increases, the elastic energy stored within the film increase due to the large mismatch. When the film reaches a certain thickness, it becomes energetically favourable to relieve the misfit strain by the formation of dislocations at or near the substrate/film interface \cite{7}. The buffer CaMnO$_3$ layer is deposited without the required excess of CaO for the n = 4 phase, so the major defects in this partially relaxed film are edge dislocations with the Burgers vectors $<010>$ and $\frac{1}{2}<01\bar{1}>$ which has been discussed previously \cite{2} and are indicated by the red $\perp$ symbols in figure 2. Once the CaO excess is available, in addition to these edge dislocations, the non-perovskite misfit-like fault appears (marked in figure 2). This misfit-like fault has an atomic arrangement similar to a rock salt structure and appears as a dark line in the enhanced contrast image. The desired RP structure only starts to re-establish after the deposition of a CaO layer followed by the second block of [CaMnO$_3$]$_4$, as indicated by white arrows (AO) in figure 2. After subsequent cycles of CaO•[CaMnO$_3$]$_4$ the desired RP film structure becomes apparent with the c-axis orientation normal to the substrate. However, n = 3 phases are observed occasionally in the film structure at the intersection of the vertical (AO) rock salt dislocations and horizontal CaO units within the RP structure (A in figure 2). At regions such as point A (figure 2), the RP structure becomes misaligned by one perovskite unit cell which might be due to surface steps formed during the growth. Brighter atomic columns around the step are highlighted by pink circles, showing the misalignment of horizontal RP faults accompanying the transit from n = 3 to n = 4 phase near the step. Lower intensities of atomic columns at the point A and larger spacings in the structure suggests that Rock-salt CaO structure might be formed to balance further growth of CaMnO$_3$ layers at the region of the steps.

The region indicated in the white dashed frame in figure 2, shows the single series of the target n = 4 RP structure. The atomic columns of the perovskite lattice are resolved and the mixed atomic columns of Mn and O are brighter than the Ca columns, while the rock salt CaO layer appears as a stripe of lower intensity. Two line profiles across two neighbouring atomic planes along [001] direction indicated the white doted lines in the region in figure 2 are shown in figure 3. The modulations of the HAADF intensities at the Mn+O and Ca columns match the n = 4 RP superlattice. The c-axis lattice parameter of CaO•[CaMnO$_3$]$_4$ is 3.443 ± 0.015 nm which is expected to be smaller than the value of 3.465 nm for the structure in the absence of strain, due to an out-of-plane compression along c-axis \cite{2}. The distance of Ca and O in the rock-salt structure is 0.190 ± 0.015 nm.

**Figure 1.** shows a high-resolution Z-contrast image illustrating epitaxial growth of the n = 4 RP phase Ca$_5$Mn$_4$O$_{13}$ along [001]. Overlaid is Fourier power spectrum from the SrTiO$_3$ substrate.

**Figure 2.** shows a noise-filtered and contrast-enhanced image of illustrating lattice contrast in the epitaxial film. The (AO) designations represent the presence of a CaO layer.
The HAADF signal in the profiles across atomic columns in the [001] direction along the dotted upper line (filled) and lower (line) in the white dashed frame in figure 2 shows the difference in the contrast between Mn+O and Ca atomic columns in the n = 4 RP superlattice.

In order to confirm the composition of the phase CaO•[(CaMnO$_3$)$_4$, high spatial resolved EELS studies were carried out using line scans across a lattice plane in the superlattice along the [001] direction at 0.024 nm intervals with the 0.118 nm probe, as shown by the red line in figure 1. Ca and Mn concentrations can be qualitatively represented by the signal integrals of Ca-L$_{2,3}$ and Mn-L$_{2,3}$ edges extracted from background subtracted spectra, as shown in figure 4. The Ca and Mn concentrations peak at their corresponding atomic columns matches the HAADF intensity and Ca concentration is strongly peaked at the CaO rock salt layers in agreement with the target n = 4 RP phase.

4. Conclusion
Pulsed laser deposition of epitaxial RP phase CaO•[(CaMnO$_3$)$_4$ on SrTiO$_3$ (001) has been studied by combining HAADF imaging with electron energy loss spectroscopy in the aberration-corrected STEM. The vertical misfit-like dislocations of a rock salt character are incorporated in the perovskite buffer layer contributing to misfit relaxation of the highly strained buffer layer. CaO•[(CaMnO$_3$)$_3$ (n = 3) phases occur at the intersection of these misfit-like dislocations and the CaO units within the RP structure. The superlattice structure of the target n = 4 RP phase is characterized by HAADF imaging at atomic resolution and the composition of the phase is confirmed by the high spatial-resolved EELS investigation.

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