Growing oxide thin films in a low-energy electron microscope

Torren, A.J.H. van der

Author: Torren, Alexander J.H. van der
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Summary

The ongoing performance increase of electronics will reach its limit when Si-based devices reach the size of a few atoms only. As an alternative for Si, transition-metal oxides (TMOs) form an interesting materials group with new physical properties, which could be used for performance increase and novel devices. Research and development of TMO devices has long been held back by the difficulty to grow these materials. The development of pulsed laser deposition (PLD) and reflection high-energy electron diffraction (RHEED) made it possible to control growth up to unit cell precision. However, to really understand the growth process and the evolution in physical properties of the TMOs, it is important to further characterize the material during this growth process. Most of the common analysis techniques cannot be used in-situ due to the high growth temperatures and oxygen pressures. Hence, characterization of films is typically done afterwards when the full film has been grown. Here we use low-energy electron microscopy (LEEM) as a technique that cannot only work under these conditions and, when combined with PLD, control the thickness with sub-unit cell precision, but that can also directly monitor the structural and electronic properties during growth.

A very interesting phenomenon in TMOs is the presence of a two-dimensional electron gas (2-DEG) between the band insulators $LaAlO_3$ and $SrTiO_3$, which forms when at least four unit cells of $LaAlO_3$ are deposited on a $SrTiO_3$ substrate. Despite a considerable amount of research in the last years, there are many open questions around the formation of this electron gas. Our combination of LEEM and PLD allows us to study the layer by layer formation of this heterostructure in real time.

After a general introduction in chapter 1, chapter 2 provides a more detailed background on TMOs with the perovskite structure and especially the $LaAlO_3$/$SrTiO_3$ heterostructure. The two most important parameters for this thesis are bulk stoichiometry and surface termination. From literature it is known that the heterostructure only shows conductance when the $SrTiO_3$ substrate is TiO_2-terminated. Furthermore, it has been shown that the $LaAlO_3$ film has to be Al-rich, and that oxygen vacancies play an important role in the conductance.

I have used LEEM to study the properties and growth of $LaAlO_3$ and $SrTiO_3$. This technique is described in detail in chapter 3. Low-energy electrons used in LEEM make it a surface sensitive technique. Moreover, LEEM allows for real-time imaging at elevated temperatures up to 1500 °C with oxygen pressures up to 1×10^{-4} mbar. A combination of real space (LEEM) and diffraction (LEED) imaging results in complementary information about morphology and structure. Apertures allow to obtain this information on the nanometer scale. LEEM-IV (intensity versus voltage) curves can be used to probe the surface electronic structure. This can be

extended to a full band-structure map of the unoccupied bands by a new technique called angle-resolved reflection electron spectroscopy (ARRES). Here the energy dependence is not only measured for the specular reflection, but also for non-zero in-plane wave vectors, which makes it possible to obtain the dispersion of these bands. Chapter 3 describes how the resolution of this technique is extended by a combination of automation and extension of the dynamic range of the camera. Furthermore, spot-profile-analysis (SPA)-LEED is introduced. Film growth can be controlled with layer-by-layer precision by analyzing the width of the specular diffraction spot.

As a first set of results from using LEEM, chapter 4 describes the $LaAlO_3$ surface after high-temperature annealing. A mixed ordered surface of an unreconstructed AlO_2 surface and a reconstructed ($\sqrt{5}\times\sqrt{5}\,R26$) LaO surface is found, with the LaO fraction being about one third. These results are not different when the annealing is performed in UHV or air. The ordering of the surface termination can be imaged starting from small $\sqrt{5}\times\sqrt{5}\,R26$ islands until stripes in the middle of the terraces of AlO_2. Atomic force microscopy (AFM) shows the reconstructed LaO lies below the surrounding AlO_2 terraces. Furthermore, the IV-curves can be compared to a single AlO_2-terminated sample, confirming the terraces are AlO_2 with LaO strips.

Chapter 5 shows the first results from the combined PLD-LEEM system. I demonstrate its abilities by studying the growth of homo-epitaxial $SrTiO_3$. The combination allows for a unique possibility for in-situ growth analysis by SPA-LEED, real-space imaging and probing of the unoccupied band structure with ARRES. For the growth of homo-epitaxial $SrTiO_3$ we observe layer-by-layer growth, which changes slowly with thickness to a more three-dimensional growth. The electronic structure of the grown $SrTiO_3$ is different from the TiO_2-terminated $SrTiO_3$ substrate. This can be caused by oxygen vacancies due to the low oxygen pressure and by off-stoichiometric growth. The IV-curve shows the signature of a SrO termination, which can be restored to the IV-curve of the TiO_2-termination by buffered HF-etching (hydrofluoric acid) and annealing with the same parameters as the single termination procedure performed at new substrates. The conclusion is that our growth is Sr-rich.

In chapter 6 we use the combination of LEEM and PLD developed in the previous chapter to study the $LaAlO_3/SrTiO_3$ heterostructure. The electron reflectivity or ARRES maps give information about the electronic properties of the surface as it develops during growth, at the growth temperature. We make a connection between our measurements and the electronic properties of the $LaAlO_3/SrTiO_3$ interface by comparing samples that do and do not show a conducting interface. We find distinct signatures for the conducting versus non-conducting interfaces independent of their growth conditions. This, in principle, allows us to predict during growth whether a sample is going to show a conducting interface. From literature it is known that the two important ingredients related to the conducting interface are the surface termination of the $SrTiO_3$ and the stoichiometry of the $LaAlO_3$. We find that these same two ingredients are responsible for those distinct signatures. We demonstrate this by three samples, an TiO_2-terminated

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$SrTiO_3$ substrate with an Al-rich $LaAlO_3$ film, a SrO-terminated $SrTiO_3$ substrate with an Al-rich $LaAlO_3$ film, and a TiO_2-terminated $SrTiO_3$ sample with a La-rich $LaAlO_3$ film. Combining the results, we show that substrate B-site termination (TiO_2) together with Al-rich growth, leads to a B-site terminated surface (AlO_2) and a conducting interface. On the other hand A-site termination (SrO) or La-rich growth leads to an A-site terminated (LaO) surface and a non-conducting interface.

Finally in chapter 7 the various earlier observations and data come together. To overcome the limitations of the $SrTiO_3$ substrate onto which the $LaAlO_3/SrTiO_3$ heterostructure is grown, we use $Ca_2Nb_3O_{10}$-nanosheets in the form of micron-sized flakes as seed layers to grow the heterostructure on any substrate. In this chapter I show how LEEM can be used to investigate the growth on such flakes. We can image the $Ca_2Nb_3O_{10}$-nanosheets in LEEM and follow the growth on the flakes. Growth control on such small areas would be impossible by other techniques. We show that the first layers of $SrTiO_3$ do not grow in a layer-by-layer mode due to the imperfections in the nanosheets. The $SrTiO_3$ can only be grown at relative low temperatures, probably as a consequence of the low oxygen background pressure. At these temperatures we have imperfect $SrTiO_3$ growth as seen before in chapter 5. The $SrTiO_3$ can be improved by annealing. After annealing we find a TiO_2-terminated $SrTiO_3$ layer. Onto this, we can grow $LaAlO_3$ in a layer-by-layer mode. Such growth is very comparable to the growth on a $SrTiO_3$ substrate. The final ARRES map shows many similarities with the ARRES maps on the conducting interface in chapter 6, suggesting that also this interface is conducting. We could not verify this, however, with conductance measurements. The nanosheets bear promise to make devices of the $LaAlO_3/SrTiO_3$ heterostructure with thin $SrTiO_3$ bottom layer, allowing effective bottom gating.