Photoelectron diffraction on LaAlO$_3$/SrTiO$_3$ heterostructures by using hard x-rays

F. Pfaff$^1$, L. Dudy$^1$, A. Gloskovskii$^2$, W. Drube$^2$, M. Sing$^1$ and R. Claessen$^1$

$^1$Physikalisches Institut and Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

$^2$DESY Photon Science, Deutsches Elektronen-Synchrotron, Notkestrasse 85, D-22603 Hamburg, Germany

The oxides of transition metals exhibit a wide range of different physical properties due to the interplay of charge, orbital, spin and/or lattice degrees of freedom. By designing heterostructures which consist of layers of different transition metal oxides, it becomes possible to tune these properties. The most prominent example of such a tuning is the formation of a two dimensional electron system (2DES) at the interface between the two wide-gap band insulators LaAlO$_3$ (LAO) and SrTiO$_3$ (STO). The 2DES-formation occurs when the LAO film exceeds a thickness of 3 unit cells (uc) [1,2]. Despite intensive studies, the mechanism leading to the conducting interface is still under debate. Although the 2DES is buried, it can be probed by hard x-ray photoelectron spectroscopy (HAXPES) as demonstrated by Sing et al. [3]. Thereby, it was found that Ti sites of the STO at the interface change the valency from former Ti$^{4+}$ to Ti$^{3+}$ due to a charge transfer from the sample surface to the interface, visible by a chemical shift in the photoemission spectra. Probing the change in the Ti$^{4+}$/Ti$^{3+}$ ratio under variation of the detection angle in such a photoemission experiment, allows for a non-destructive depth profiling and, therefore, can be used to measure the extension of the 2DES. However, the photoemission intensity can be strongly influenced by the surrounding atoms, at which the photoelectrons are scattered. These photoelectron diffraction (XPD) effects can lead to intensity modulations of the photoelectron intensity depending on the orientation of the sample. As a consequence for the depth profiling, electrons ascribed to Ti$^{4+}$ ions can originate from the complete accessible probing depth of the sample (depending also on the used photon energy), whereas photoelectrons from Ti$^{3+}$ ions emanate only from the interface. These electrons can merely be scattered by the atoms of the LAO film while electrons from Ti$^{4+}$ ions will also be scattered by the atoms of the substrate. Hence, the XPD pattern for the two Ti valences in LAO/STO heterostructures could be different and therefore the Ti$^{4+}$/Ti$^{3+}$ ratio in HAXPES

Figure 1: Left: Ti 2p$^{3/2}$ HAXPES spectra of a 6uc LAO/STO sample. The integrated region for generating the Ti$^{4+}$ XPD pattern is marked by the blue area. Right: Ti$^{4+}$ XPD pattern. The strong intensity modulations under change of the samples’ orientation are well observable.
experiments could be distorted for certain polar angles. Furthermore, it has been demonstrated for silicon oxide on a silicon substrate, that XPD patterns for different valences due to the presence of different oxygen bonds can be different. By using comparative model structure simulations one is able to determine the local atomic structure at the interface [4].

In order to elucidate such differences and to analyse the interface structure in more detail, we performed HAXPES measurements on 6uc LAO/STO heterostructures and measured the Ti2p core level spectra for a wide polar and azimuthal range. The photon energy was set to 3.5 keV to increase the interface sensitivity. Due to the fourfold symmetry of the perovskite structure, it is sufficient to record only a 90° section of the full azimuthal range. Here, we measured an azimuthal range over 110° to verify the symmetry for both oxidation states. The polar range covered 5° to 45°. The total acquisition time was 4 x 24h. For generating the Ti4+ XPD pattern a linear background has been subtracted and the intensity of the blue marked area in Fig. 1 left has been integrated for every photoemission spectrum. As it can be seen on the Ti4+ XPD pattern on the right hand side of Fig. 1 one can observe a strong modulation of the photoemission intensity when changing the polar and azimuthal angle. Additionally, as shown in Fig. 2, one can clearly observe a change in the Ti4+/Ti3+ ratio when varying the azimuthal angle of the sample, while keeping the polar angle constant. These results already indicate that there might be a considerable effect of photoelectron diffraction influencing the Ti4+/Ti3+ ratio, which can distort the results from depth profiling using HAXPES. As the 2DES is strongly confined to a very narrow region at the interface the Ti3+ contribution to the spectrum is very small. Therefore, it is very challenging to extract a proper Ti3+ XPD pattern from the measured spectra. Thus, beside these interesting results, additional data processing and detailed calculations of the diffraction patterns for the bare STO surface and the relaxed and strained heterostructure, which are already in progress, are needed to arrive at definite conclusions.

References