Valence Band Analysis of LaAlO$_3$/SrTiO$_3$ Oxide Heterostructures using Hard X-ray Photoelectron Spectroscopy

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The origin of the 2DEG at the interface of the LaAlO$_3$/SrTiO$_3$ oxide heterostructure (LAO/STO) is a heavily discussed topic in both theory and experiment [1, 2, 3, 4]. Apart from possible influences of oxygen defects recent experimental and theoretical works suggest an electronic reconstruction as the driving mechanism for the high conductivity of the interface. In this simplified ionic picture half an electron is transferred from the surface to the interface due to an electric potential gradient across the polar LAO overlayers. Such a gradient is also consistently found by DFT calculations [5].

By hard x-ray photoelectron spectroscopy (HAXPES) the potential gradient should be observable as a significant broadening of the Al 1s core level. Moreover, due to the electron transfer the valence band of the topmost LAO layer should cross the chemical potential.

![Figure 1: Comparison between expected spectra predicted from theory (grey shaded) and the experimental data: (a) The measured valence band show a large gap between chemical potential and the VBM. (b) The Al 1s core level exhibits no potential gradient as predicted from theory. (c) A simplified sketch show the band behavior of both the valence band and the core levels. The valence band can be modeled by an superposition of the valence bands measured on bulk components.](image)

We performed HAXPES measurements at beamline P09 of PETRA III on several samples with different overlayer thicknesses. The samples were grown by pulsed laser deposition as described in Ref. [3]. As references we used Nb doped STO (0.05%wt.) and a 50nm thick LAO film grown on Nb doped STO by PLD. To compare our measured data with theory, we introduced a model: One generates the sum of each layer including the shift and multiplied with the damping factor $e^{-z/\lambda}$ to include the depth sensitivity of photoelectron spectroscopy, where $z$ is depth from where the photoelectrons are emitted and $\lambda$ the inelastic mean free path of the photo-electrons. The underlying...
spectra for one layer is a spectrum measured on the reference sample. However, in our data none of the predicted signatures are observed, which indicates a flat band behavior in the LAO overlayer (see Fig.1). This result is consistent with other XPS studies [6].

<table>
<thead>
<tr>
<th>VB offset (eV)</th>
<th>4 uc</th>
<th>5 uc</th>
<th>6 uc</th>
<th>mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.41</td>
<td>-0.33</td>
<td>-0.37</td>
<td>-0.36</td>
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Table 1: Values for valence band offsets determined from valence band analysis. Because no dependency on the LAO overlayer thickness can be observed, a mean value can be quoted.

Furthermore, the DFT calculations give an estimation for the band offset between both band insulators LAO and STO, where the valence band maximum (VBM) of STO is above the VBM of LAO. We determined the band offsets of LAO and STO at the interface using a valence band analysis. For that, we measured the valence band of both bulk components for reference. These spectra were then shifted and weighted in such an adequate way, that the superposition of both spectra fits the measured data. Fig. 2 show a valence band analysis for a 4uc and 6uc sample. It can be clearly seen, that the VBM of LAO is above the VBM of STO. The resulting value for the band offset is summarized in Tab. 1. From our data the valence band offset is independent from the LAO overlayer thickness.

![Figure 2: Valence band analysis of a (a) 4uc and (b) 6uc LAO/STO sample.](image)

References