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When X-Rays and Oxide Heterointerfaces Collide

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Abstract

The interface between $LaAlO_3$ (LAO) and TiO_2 terminated $SrTiO_3$ (STO) holds many interesting and unexpected properties. Both materials are non magnetic, wide bandgap perovskites with bandgaps of 5.6 and 3.2 eV, respectively. Yet at the interface not only conductivity emerges, but also magnetism, superconductivity and even the coexistence of the two. All this is caused by a high mobility 2-dimensional electron gas (2DEG), that for reasons which are subject to great debate manifests itself at the interface.

Many different mechanisms have been proposed over the years to explain the emergence of this 2DEG. Most of them are rooted in the same phenomenon: the polar catastrophe. STO and LAO are similar materials in many ways: they have the same structure, nearly the same lattice constant, both have a large electronic bandgap and are non-magnetic. But they are different in one crucial aspect: the SrO and TiO_2 layers of which STO consists are electrically neutral, whereas the LaO^+ and the AlO_2^- layers of the LAO are not. This causes the build-up of an internal potential which increases with every additional unit cell of LAO. The energy of this quickly diverging potential can be used by the system in various ways.

Perhaps the most popular model for explaining the 2DEG at the STO/LAO interface is that of electronic reconstruction. This model states that the polar catastrophe moves the LAO bands towards the Fermi level until the LAO valence band maximum overlaps with the STO conduction band minimum, i.e. the LAO bands traverse the STO bandgap. Once this occurs electrons can transfer from the LAO to the STO and in so doing cancel out the potential build-up in the LAO. The transfered electrons then form a 2DEG at the STO/LAO interface.

Another popular proposal involves oxygen vacancies. In bulk form both STO and LAO, are quite sensitive to oxygen vacancies, so it is not unreasonable to expect that they also play an important role in STO/LAO interfaces. Removing an oxygen ion dopes two electrons into the system which could alleviate the polar catastrophe in the same way as electrons brought into the system via electronic reconstruction.

Intermixing of ions around the interface has also been proposed but it must be emphasized that even though this mechanism allows for the formation of a metallic layer of for instance $La_{1-x}Sr_xAl_{1-y}Ti_yO_3$ or $Sr_{1-1.5x}La_xO$, it does not resolve the polar catastrophe. So even though it is still possible intermixing takes place, it cannot be the only effect.

Off-stoichiometry of the LAO layer, specifically La deficiency, has also been reported to be very important. Some groups have reported that only La deficient samples show conductivity. Such B-site vacancies offer the system a way to resolve the polar catastrophe without charge transfer.

In this thesis the properties of STO/LAO interfaces are investigated using X-ray spectroscopic techniques. In chapter four, which is dedicated to 'regular' STO/LAO heterostructures, it is shown that interfacial electronic charges are always present for any LAO thickness, despite the fact that in transport only samples with an LAO thickness of four unit cells or larger are conducting. The carriers do not show any strong confinement in our experiments, which means that if there is confinement, it is to a spatial region of certainly larger than 10 unit cells and more likely to a region of 20 unit cells thick.

The electronic reconstruction model predicts that the internal potential caused by the polar catastrophe builds up by 0.9 eV per unit cell, for as long as the LAO thickness remains below the critical thickness for conductivity (four unit cells). What is observed in the experiments, however, is but a fraction of the predicted potential build-up and also no sign of core level broadening is observed, also predicted by the electronic reconstruction model. A comparison to DFT calculations shows that oxygen vacancies provide the system with an alternative to electronic reconstruction, which would indeed result in the reduced potential build-up observed in the experiment. This does not mean that oxygen vacancies are the only possible solution. Other defect related explanations could still play a role.

In chapter five the effect of capping STO/LAO interfaces is investigated. In transport, a $SrCuO_2$/STO capping layer has a very strong effect on the interfacial properties. An increased electron mobility and a strongly reduced and temperature independent carrier concentration are the most striking improvements. The spectroscopic data underpin the hypothesis that this enhancement of the key properties is caused by a strongly reduced oxygen vacancy concentration. Oxygen vacancies not only provide the system with carriers, but are also scattering centers which reduce the interfacial electron mobility.

Another interesting effect found in these third generation samples is a strong increase of the valence band offset when compared to first generation samples. Valence band offsets up to 1 eV are observed for LAO thicknesses at or below the critical thickness for conductivity. When the LAO thickness places the system firmly in the metallic conducting regime, the valence band offset decreases dramatically to values also observed in first generation samples. This behavior is strongly reminiscent of what one would expect from electronic reconstruction except for two things: there is no layer-by-layer potential build-up, but rather a single energy offset at the STO/LAO interface and, secondly, the VBO is not large enough to bridge the STO bandgap. The values for the valence band offset observed for these samples are, however, the highest for STO/LAO-based interfaces reported to date.

The final chapter of this thesis deals with STO/LAO interfaces grown on $NdGaO_3$ (NGO) substrates. By growing the STO/LAO system on a substrate with a lattice parameter in between that of STO and LAO the strain at the STO/LAO interface is reduced. Additionally using a different substrate allows the variation of the STO thickness. In transport, strong localization is observed for STO thicknesses below eight unit cells and weak localization for thicker STO layers. Also an unusually high carrier concentration is reported which is confirmed by our spectroscopic experiments. The potential well to which the electrons at the STO/LAO interface are confined is probed with a clarity unprecedented for X-ray spectroscopic techniques in the field of oxide heterointerfaces. The transport active charge concentration observed at this interface approaches the value of 0.5 electrons per unit cell, which is the value required to avert the polar catastrophe.

A major difference between these samples and other STO/LAO interfaces is the fact that the lowest energy electron addition states are the Ti 3d xz and yz orbitals. In other STO/LAO interfaces these are the xy orbitals. Hence: the carriers dominating transport behavior in NGO/STO/LAO are of a different character than those in STO/LAO heterostructures. This orbital inversion is likely to be the cause for the different behavior observed in transport experiments.