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Report

The discovery that a conducting electron gas with extraordinary properties is realized at the interface between insulating oxides, namely in the $LaAlO_3$ (100)/ $SrTiO_3$ (100) system (LAO/STO), have raised strong interest in the material science community. It has been speculated that a 2D electron gas, with extraordinary high mobility, is created at the n-type TiO_2/LaO interface. The physical mechanism explaining the creation of the 2D gas and their physical properties are a strongly debated issues in the community. The "polarization catastrophe" occurring at the $LaAlO_3$ thickness of only 4 unit cells, is considered one possible origin of the phenomena. This is related to the fact that alternating (100) layers of AlO_2^- and LaO^+ gradually increase the electrostatic energy of the $LaAlO_3$ film, in such a way that at a given thickness the system tries to reduce this energy by transferring ½ electrons per unit cell to the interface.

The phenomenon is believed to be due to an 'electronic reconstruction' occurring at the interface, which seems very general to the class of metal transition oxides. Other examples of 'electronic reconstruction' effects are the realization of ferromagnetic interfaces in the case of $LaMnO_3/SrMnO_3$ (Antiferromagnetic/ Antiferromagnetic) multilayer, and high-Tc superconducting interfaces in $LaCuO_4/La_{1.55}Sr_{0.55}CuO_4$ metal/insulating bilayer [1]. Interface 'electronic reconstruction' promises to become a general method to create novel concept devices based on oxides, where functionalities can be added by interface engineering.

However, even in the case of the most studied $LaAlO_3/SrTiO_3$ system, there is not yet a demonstration that a truly intrinsic 'electronic reconstruction' is taking place. Moreover, the mechanism leading to such phenomena is still unclear.

Table 1: List of samples studied during the HE2688 Experiment.

Sample	Number of unit cells	Supplier	Characteristics
STO (100) etched TiO_2	--	Crystec (checked by AFM)	Insulating
STO (100) Nb doped (1%wt) etched TiO_2	--	Crystec (checked by STM-AFM)	Conducting
$LaAlO_3$ (100)	--	Crystec	Insulating
$LaTiO_3$ (100)	--	Single Crystal	Mott Insulator
STO/LAO	2 u.c.	Augsburg	Insulating
STO/LAO	4 u.c.	Augsburg	Conducting
STO/LAO	4 u.c.	Twente	Conducting
STO/LAO	8 u.c.	Augsburg	Conducting
STO/LAO	10 u.c.	Twente	Conducting
STO/LAO	12 u.c.	Augsburg	Conducting

Other groups, have indeed shed doubts about the "polarization catastrophe mechanism", i.e. an intrinsic phenomena related to the concept of "interface electronic reconstruction". The main criticisms can be summarized in two categories, and are related to purely extrinsic effect, at odds with the other category of "intrinsic" "electronic reconstruction" concept. More precisely the formation of conducting system is interpreted as result of a) formation of oxygen vacancies within more than one layer of STO at the interface [2 and references therein] and/or b) cation substitution among La and Sr, and possibly Ti and Al, occurring some nm inside the STO and the LAO layers [3]-[4]. In both scenarios the deposition process has an important role, in particular the oxygen partial pressure used during the deposition (the use of an additional oxygenation step) and the energy and/or diffusion of the species during the pulsed laser deposition process. In case a) the electronic properties of the STO layers at interface with LAO should resemble strongly those of STO and Nb doped STO, while in case b) the formation of $La_{1-x}Sr_xTiO_3$ solid solution is expected (for some composition also $La_{1-x}Sr_xTiO_3$ can be superconducting).

In this experiment we have tried to establish if an effective electronic reconstruction is taking place in the $LaAlO_3/SrTiO_3$ interface when it becomes conducting. To this purpose we have used X-ray Absorption Spectroscopy (XAS) at the Ti $L_{2,3}$-edge of LAO/STO films deposited by Pulsed Laser Deposition. The samples have been deposited at University of Augsburg and at the Mesa+ Institute, in Twente, using different deposition conditions, which gives low temperature superconducting and weakly ferromagnetic interfaces, as shown in [5] and [6] respectively. After the deposition the samples are annealed in situ at high oxygen pressure and high temperature. The annealing step is essential to fill the oxygen vacancies in the $SrTiO_3$ single crystal and in the $LaAlO_3$ film, resulting in a conducting layer close to the interface [7].

In order to have bulk and mainly interface sensitive XAS signal, we have used simultaneously the total electron yield (TEY) and Fluorescence Yield (FY) methods. Finally we used mainly grazing incidence conditions, with the x-ray beam having an angle of 70 degree with the surface normal, and the linear polarization of the x-ray to get spectra with the electric field E parallel (Iab) and perpendicular (Ic) to the interface.

In Tab. 1 there is a summary of the samples studied during the HE2688 experiment. We have studied films characterized by a thickness of the $LaAlO_3$ varying from zero (bare TiO_2 terminated STO and Nb-doped STO) to 12 unit cells (uc). It is well established that there is a metal-insulating crossover when the LAO thickness is above 3 uc. The comparison between the insulating and conducting samples, consequently, gives interesting information about the evolution of the system. Data have been also compared to $LaTiO_3$ single crystal (a prototype $3d^1$ system).

XAS results

The XAS spectra measured on STO and Nb-doped STO and LatiO3 are consistent with data published in literature. The spectra can be perfectly reproduced by using the Missing Scientific software, based on the Cowan's code calculations in single ion model with point charge crystal field. While FY data are substantially identical among the samples listed in table 1, the TEY data are slightly different and moreover they acquire a dependence on the polarization which is not present in the FY data. This result is explained by the fact that the FY method has a probing depth larger than 50 nm at the 500 eV energy used, so it is a bulk probe for the system. On the contrary, the sampling depth of the TEY method is much lower, between 1 and 3 nm, which are estimates based on data taken in literature on similar oxides (TiO_2) and on the calibration perfomed during our experiment. Consequently, in the TEY mode we are quite sensitive to the interface states. An estimation of the sensitivity to the interface effects is given by comparing TEY XAS spectra acquired on LAO/STO sample (4 uc) and simulation obtained by combining the spectra measured on $LaTiO_3$ and $SrTiO_3$, using the TEY formula valid for a bilayer. As shown in fig. 1, there is no possibility to reproduce the data by supposing that a monolayer of $LaTiO_3$ is realized at the interface.

The most interesting result of the experiment comes from the linear dichroism. In fig. 2 we plot the comparison between the linear dichroism of a bare STO and STO-Nb doped, and the linear dichroism measured on the LAO/STO interface composed of 4 uc, i.e. being conducting. The small dichroism observed in the STO samples is due to some symmetry breaking occurring at the TiO_2 surface, which usually is reconstructed. It corresponds to an elongation of the TiO_6 octahedra along the surface normal. Consequently the 3d level of Ti at the surface in the STO system are split, with the out of plane orbital being the lowest energy states.

On the contrary in the conducting interface the opposite is realized, i.e. the splitting is opposite, much larger (involves more than one monolayer at the interface (less than 5 monolayers)) and corresponds to 3dxy states with energy below the (3dxz, 3dyz) levels. In the 2 uc sample the dichroism is very small, confirming that the change in the splitting occurs at the transition from insulating to conducting.

The changes in the linear dichroism demonstrate that there are important structural modifications at the interfaces, which alter the electronic characteristics of the system. This is a possible experimetnal proof of an orbital reconstruction occurring at the LAO/STO interface.

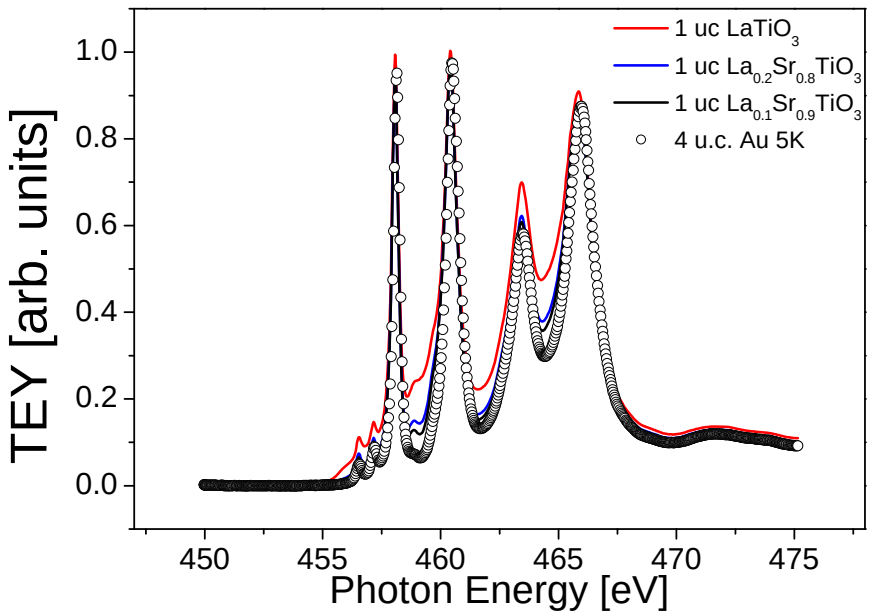

Fig. 1:TEY XAS spectra near the L_{23} Ti edge (open cicles) of LAO/STO interface and comparison with a simulated spectra representing the combination of an $La_{1-x}Sr_xTiO_3$ monolayer and an STO bulk.

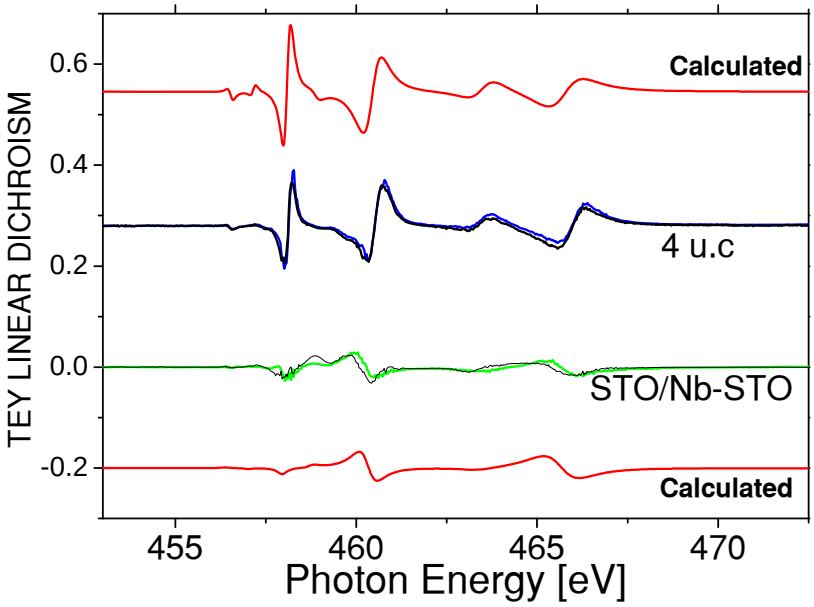

Fig. 2: TEY XAS linear dichroism at the L_{23} Ti edge of LAO/STO 4 uc interface compared to bare STO (black line) and Nb-doped STO (red line). The data are shofted for clarity. In red the calculated linear dichroism is shown for opposite 3d level splitting.

References

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