ESRF	**Experiment title:** Study of the electric field induced metal-insulating transition at the $SrTiO_3/LaAlO_3$ interface by X-ray absorption spectroscopy and Resonant inelastic x-ray scattering	**Experiment number:** HE 2990
Beamline: ID08	**Date of experiment:** from: 15/7/2009 to: 21/7/2009	**Date of report:** 1/3/2010
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Names and affiliations of applicants (* indicates experimentalists):

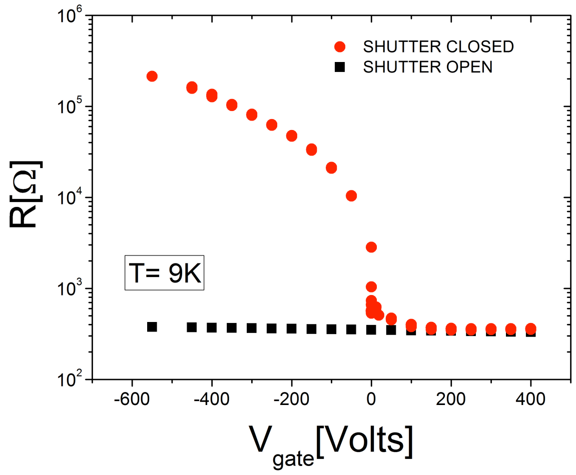
Dr BROOKES Nicholas / E.S.R.F.,
Dr. CRIGINSKI CEZAR Julio / E.S.R.F.,
BISOGNI Valentina / E.S.R.F
Prof. GHIRINGHELLI Giacomo/ Dipartimento di Fisica, Politecnico de Milano
MORETTI Marco/ Dipartimento di Fisica, Politecnico de Milano
PIOVERA Christian/ Dipartimento di Fisica, Politecnico de Milano
Dr. SALLUZZO Marco / CNR-INFM Coherentia
Dr. RISTIC Zoran / CNR-INFM Coherentia
Dr. DE LUCA Gabriella Maria / CNR-INFM Coherentia
GARIGLIO Stefano / D.P.M.C., Université de Genève
CANCELLIERI Claudia D.P.M.C., Université de Genève

Report:

The latest advancements in physical vapor deposition techniques have achieved an atomic control of oxides epitaxial heterostructures. New systems having novel functionalities have been artificially created. One of the most outstanding examples is the interface between metal transition oxides insulators.[1].

The LAO/STO interface becomes conducting when at least four monolayer of an $LaAlO_3$ thin film are deposited on the top of a TiO_2 terminated $SrTiO_3$. The electron gas is realized only when a perfect LaO/TiO_2 structure is created, yielding an *n*-type interface. Since both $LaAlO_3$, and $SrTiO_3$ are good insulators, with band gaps of 5.6 eV and 3.2 eV respectively, the realization of an electric field effect device based on this structure is natural. Indeed, the electronic properties of this system can be tuned by applying a sufficient large electric field through $SrTiO_3$, already demonstrated at room and low temperatures [2,3]. In particular an insulating to metal transition is achieved on samples composed by 3 unit cells (uc) of $LaAlO_3$. Very interestingly, the field effect transition in these particulars samples is metastable, since once the interface has become conducting, it remains in this state also when the electric field is switched off. Only an opposite electric field can effectively establish again the original insulating state.

Recently, by using X-ray absorption spectroscopy, we have investigated the electronic properties of the LAO/STO system as function of the LAO thickness (see report Experiment HE2688, ESRF Highlights 2009 page 71 and [6]). We have found that when the interface becomes conducting, i.e. above 3 uc of LAO, an orbital reconstruction takes place. Since the total electron yield (TEY) XAS spectra measured at the $L_{2,3}$ edge of titanium are very sensitive to the top STO layers, located at the LAO/STO interface, the electronic reconstruction occurs at or close to the interface. These results seem to confirm an intrinsic origin of the 2D electron gas, with respect to an oxygen vacancies mechanism. A possible explanation of these results is the occurrence of a ferro-distortive orbital ordering on the interfacial STO layer, creating $3d_{xy}$ sub-bands confined at the interface [4].



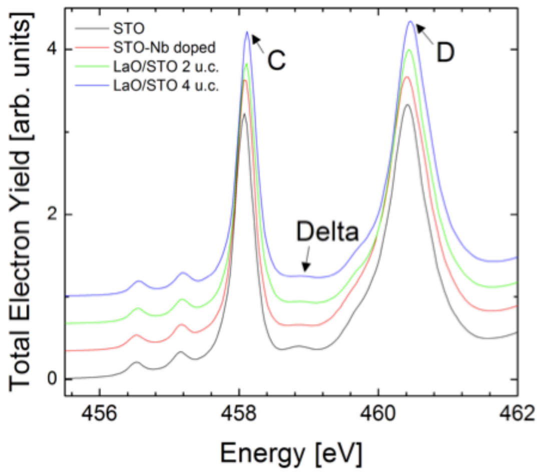


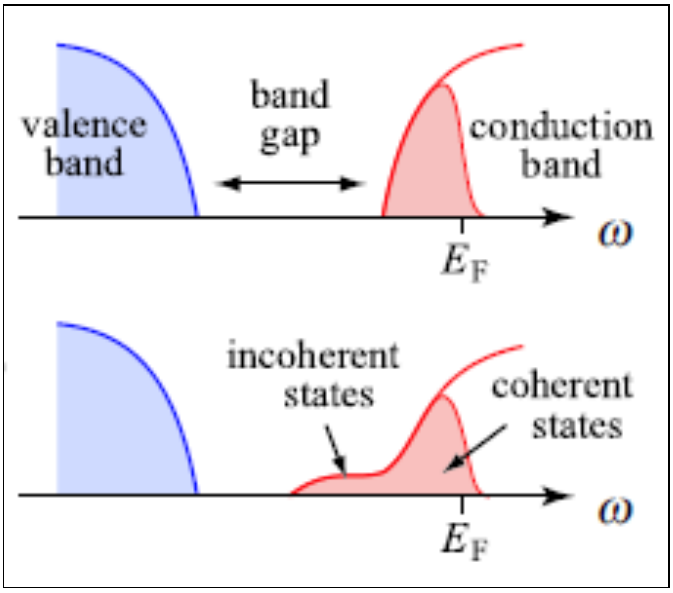
FIGURE 1 (left) and FIGURE 2 (right). Fig 1. The effect of the x-ray beam on the resistivity of the LAO/STO interface: the photoconductivity kills totally the field induced metal-insulator transition. Fig. 2. Example of TI $L_{2,3}$ XAS spectra

An important issue to be investigated is the effective role of electron correlations, which determine the interface conductivity. Theoretical the $3d_{xy}$ sub-bands should be partially filled by electrons. Resonant inelastic x-ray scattering is an ideal technique to probe possibly existing Ti $3d^1$ states in STO: the normal Ti^{4+} of STO is $3d^0$, thus no d-d excitations are possible in that case. But as recently shown on $LaTiO_3$, d-d excitations are very well detected in a Ti^{3+} system [7]. Our purpose was to probe the possible presence of Ti^{3+} states by looking at d-d excitations at the Ti L_3 edge. Therefore studying the differences among insulating and metallic LAO/STO interface using combined XAS and RIXS experiment could definitively answer many of those questions.

In the Experiment HE2990 in particular, we tried to induce a metal-insulator transition by applying an electric field using a bottom gate configuration. In fig. 1 the resistance vs. gate voltage measured on a 10 uc LAO/STO field effect device at 9 K is shown, demonstrating a complete switching from the metallic to the insulating state by applying negative gate voltages. The measurements were performed in the XAS measurement chamber but without the x-ray beam (shutter closed). The same trans-characteristic with the beam on (shutter open) on the contrary, shows very little changes of the conductivity with the gate voltage, which remains at the value corresponding to the conducting state. <u>This result shows that the LAO/STO interface is extremely sensitive to photo-doping, and that in this case, the switching from a conducting to an insulating state cannot be studied using X-rays.</u> Unfortunately, even starting from an insulating state, the resistance very quickly drops to the low resistivity values even with high negative voltages applied, and therefore it was impossible to study this evolution using TEY. Fluorescence Yield, on the other hand, is not interface sensitive and cannot be usefully used to measure XAS from the interface. The issue of photo-doping has to be investigated in details to understand the electronic properties of this system. However, very interestingly, the XAS and linear dichroism data measured as function of the LAO thickness shows an abrupt change between 2 uc and 4 uc, suggesting that the photocarriers do not have any role in this transition. <u>The latter result enforces the idea that photodoping and electronic reconstruction (occurring when at least 4 uc of LAO are deposited on the top of STO) are different and rather independent phenomena</u>. This issue is particularly interesting and should be investigated by using probes that are not perturbing the system.

In Fig. 2 we show the typical absorption spectra at the Ti 3d edge measured on STO (insulating), Nb-doped STO (conducting) and 4 uc LAO/STO conducting sample. The main differences consist in a shift toward higher energy of the main absorption peaks of Ti^{4+} (peak C and D), and in the appearance of an anisotropy between in plane and out of plane polarizations. Small differences can be also detected at the point delta, which is also the energy where excitations due to Ti^{3+} ions are expected.

We performed also measurements on trilayers, where a thin film of STO (001) composed by a controlled number of unit cells is deposited between the LaO film and the TiO2 terminated STO single crystal. These samples show that that the conductivity at the interface is crucially dependent on the number of layers, which compose the STO film. The analysis of these data is in progress.



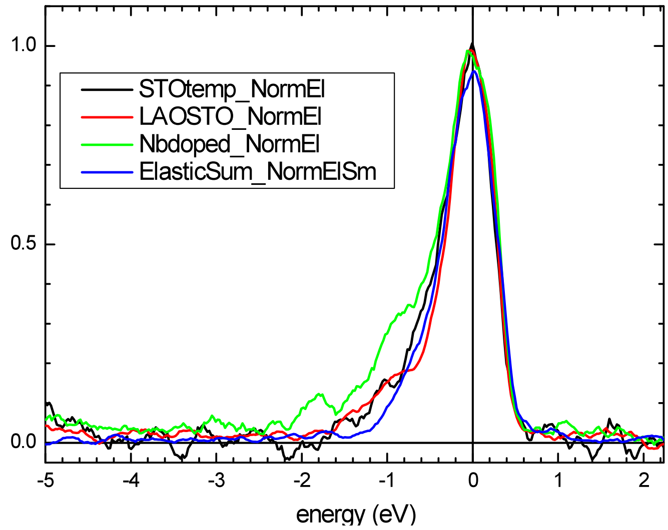


FIGURE 3 (left) and FIGURE 4 (right). Fig 3. The in-gap states in Nb:STO as presented in ref [8]. Fig. 4: The comparison of RIXS spectra measured on pure STO (black), Nb:STO (green) and LAO/STO (red). The Nb:STO shows extra intensity in the low energy region, across 1 eV energy loss. The other two samples appear to have very similar spectral shape in that range of energy, but a difference might appear in a better experiment with narrower linewidth (here about 0.5 eV) and higher statistical quality.

Finally, we performed Resonant Inelastic x-ray scattering measurements on LAO/STO samples, and in particular we compared data acquired on 4 uc LAO/STO and those measured on STO (insulating) and Nb-doped STO (Nb:STO, conducting). RIXS data have been acquired using the AXES + Polifemo, end station with Vertical polarization and close to specular geometry. RIXS data were acquired at the points C , D and delta on each sample. The RIXS spectra are very similar for the three samples. No clear d-d excitation peak is detectable (expected around 2 eV in analogy to the case of $LaTiO_3$). In Nb:STO the dopant acting as a donor provides in-gap states that can be found in RIXS spectra around 1.0 – 1.5 eV (ref [8] and figure 3). The measurement on the LAO/STO interface does not show clearly the signature of similar states (see figure 4) although the relatively poor statistical quality of the RIXS spectra does not allow us to exclude that a weak spectral weight is present in LAO/STO and not in pure STO. In all cases the RIXS spectra seem to indicate that no genuine $3d^1$ states are present, because at 2 eV the spectra of LAO/STO do not show any intensity difference to the pure STO case. These results deserve to be confirmed by better quality data (both in energy resolution and statistics) in the future. After the upgrade of AXES at ID08 the combined resolution at Ti L3 is around 130 meV and the count rate has improved by a factor of 2 with respect to the experiment reported here. This means that in the future the RIXS experiment on LAO/STO will be tried again in order to come to firmer conclusions on the nature of in-gap states formed at the interface.

References

[1] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).
[2] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, J. Mannhart, Science **313**, 1942 (2006).
[3] A. D. Caviglia et al. , Nature 456, 624-627 (2008).
[4] Satoshi Okamoto, Andrew J. Millis, and Nicola A. Spaldin, Phys. Rev. Lett. **97**, 056802 1-4 (2006)
[5] M. Abbate et al. Phys. Rev. B **44**, 5419 (1991).
[6] M. Salluzzo et al., Phys. Rev. Lett. **100,** 056810 (2008).
[7] C. Ulrich et al Phys. Rev. Lett. **103**, 107205 (2009)
[8] Y. Ishida et al, Phys. Rev. Lett . **100**, 056401 (2009)