ESRF	**Experiment title:** **Investigation of non-conducting polar oxide interfaces by GXID measurements**	**Experiment number**: SI2029
Beamline:	**Date of experiment**: from: 12 May 2010 to: 18 May 2010	**Date of report**: 15.03.2011
Shifts: 18	**Local contact(s)**: Andrea Resta	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. GARIGLIO Stefano */ D.P.M.C., Université de Genève, 24 quai Ernest Ansermet, CH-1204 Genève, Switzerland / ++41-22-3796305 / ++41-22-3796869 / stefano.gariglio@physics.unige.ch
Dr. SALLUZZO Marco */ CNR-INFM Coherentia, Dipartimento di Fisica,Complesso Montesantangelo, I-80126 Napoli ++ 39 081 676318 / ++39 081 2391821 / Salluzzo@na.infn.it
Dr. RISTIC Zoran */ CNR-INFM Coherentia, Dipartimento di Fisica,Complesso Montesantangelo, I-80126 Napoli ++ 39 081 676318 / ++39 081 2391821 / ristic@na.infn.it
Dr. TORRELLES Xavier */ Institut de Ciència de Materials de Barcelona, Campus de la UAB, E-08193 Bellaterra, Spain 34 93 580 1853 ext. 307 / 34 93 580 5729 / xavier@icmab.es
Dr. FELICI Roberto */ E.S.R.F., 6 rue Jules Horowitz, B.P 220, F-38043 Grenoble Cedex, France +33 4 76 88 22 66 / +33 4 76 88 28 55 / felici@esrf.fr
Dr. CANCELLIERI Claudia */ D.P.M.C., Université de Genève, 24 quai Ernest Ansermet, CH-1204 Genève, Switzerland stefano.gariglio@physics.unige.ch

Report:

The discovery of a high-mobility quasi two-dimensional electron gas (q-2DEG) at the interface of polar $LaAlO_3$ and non-polar $SrTiO_3$ insulators [1] has motivated a wide research activity due their potential applications and for the very intriguing physical properties. The discovery of a 2D superconducting state [2] and its giant modulation by an electric field [3] testify the richness of this system.

Since its discovery, Othomo and Hwang proposed that the q-2DEG is realized due to the instability associated to the polar discontinuity at the interface. This topic has revived open questions on the surface stability of polar interfaces [4-7]. When a polar thin film is grown on top of a non-polar crystal, the electrostatic energy related to the dipole created by charged layers increases as function of the layer thickness and, at a critical thickness, the system has to rearrange to avoid the divergence of the electrical potential, i.e. the so called " polarization catastrophe" [4]. In semiconductors, this issue has been investigated in IV/III-V heterojunctions as Ge-GaAs due to their potential interest in applications [7]. These structures have proven difficult to fabricate with the desired electronic properties due to a transition region where ions rearrange over few atomic layers to compensate the electrostatic dipole [6].

In the case of oxide systems, different experimental evidences are worth to be mentioned. The q-2DEG occurs when a LaAlO3 thin film is grown onto a (001)-oriented TiO_2-terminated $SrTiO_3$ single crystal substrate, i.e. in the case of a LaO/TiO2 interface. Attempts to induce a q2DEG by using alternative material combinations, which theoretically should follow the same behavior, were rarely successful. While $LaVO_3$ on SrTiO3 is found to be conducting [8], well oxygenated $NdGaO_3$ and $DyScO_3$ films on STO do not form a 2DEG.

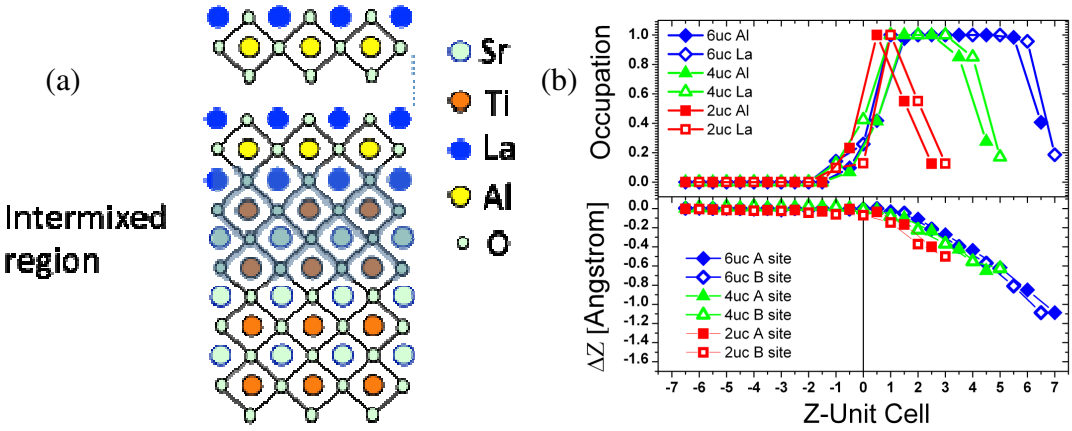

Fig.1: (a) The LAO/STO interface. The shaded region corresponds to the layers where intermixing is allowed in the model; b) upper panel Al and La occupation parameter and, bottom, cumulative displacements of 2 uc, 4uc and 6uc LAO/STO samples obtained from the fit of the GXID data.

These findings rise the question whether the formation of a q-2DEG is due to compositional changes (oxygen vacancies, cation intermixing), complex structural rearrangements at the interface due to the large lattice mismatch between these oxides, or is due to the polar discontinuity occurring at the interface between oxides of different polarity.

In the SI2029 experiment we have carefully investigated these issues. In particular we compared the measurements obtained from this experiment on conducting 6uc LAO/STO and insulating 4uc $NdGaO_3$/STO with those derived from SI1853 experiment on 2uc and 4uc LAO/STO interfaces.

A complete structural refinement have been obtained by measuring Crystal Truncation Rods (CTRs) of the STO surface substrate. These reflections contain information on the structure of both the film grown on top of the substrate and the interface between them. The CTRs have been complemented by HK and HL reciprocal space maps, which can give possible hints on the appearance of surface/interface structural reconstructions.

$LaAlO_3$ and $NdGaO_3$ thin films were realized by RHEED assisted Pulsed Laser Deposition in oxygen pressures above 10-5 mbar at high temperature exceeding 800°C. Both the film deposited and the STO single crystals used as substrates have been specifically characterized by Atomic Force microscopy and x-ray diffraction to confirm the high structural properties and to complement the GXID data for the analysis.

The structural refinement of the investigated interfaces were obtained by simultaneously fitting up to 15 inequivalent (H, K) crystal truncation rods for each sample, i.e. by fitting the structure factor F_{hkl} (q) measured by the GXID technique as function of L . Here, (H, K) are the Miller index corresponding to the in plane reciprocal lattice units (r.l.u.), while L is the Miller index for the out of plane r.l.u. The same 1x1 structural model (P4mm symmetry), which includes a bulk STO unit cell and a surface model composed by 6 STO uc and a number n+1 of LAO uc (with n=2, 4 and 6), was employed for each of the samples analyzed [Fig. 1a]. The relative large number of fitting parameters required the acquisition of large data sets, which in the case of the 6 uc sample included more than 3600 inequivalent structure factors. The refinement was performed using a modified version of the ROD software program. The parameters of the fit, which represent also the outcomes of the GXID experiments, are the out of plane displacements of each ion, the independent occupancies of the LAO layers, and finally the La/Sr and Ti/Al substitution in the first 2 unit cells belonging to STO and in the first unit cell of the LAO film close to the interface.
In Fig.1b we show some of the results of the structural refinement.

In agreement with the AFM measurements, the topmost layers of all the samples investigated are incomplete, with both LaO and AlO_2 partially exposed at the surface. However, the main (85%-100%) termination of the films is AlO_2, in agreement with the expected growth sequence imposed by TiO_2 termination of
the STO substrate. We can notice that while a 2uc LAO/STO is characterized by a chemically abrupt LaO/TiO_2 interface, La/Sr intermixing in the first LaO layer of the LAO film determined the creation of chemical rough interface in the case of 4uc and 6uc LAO/STO. Additionally, not shown, we found that the position of the ions in the LaAlO3 film, and in particular those belonging to the layers above the fourth atomic plane

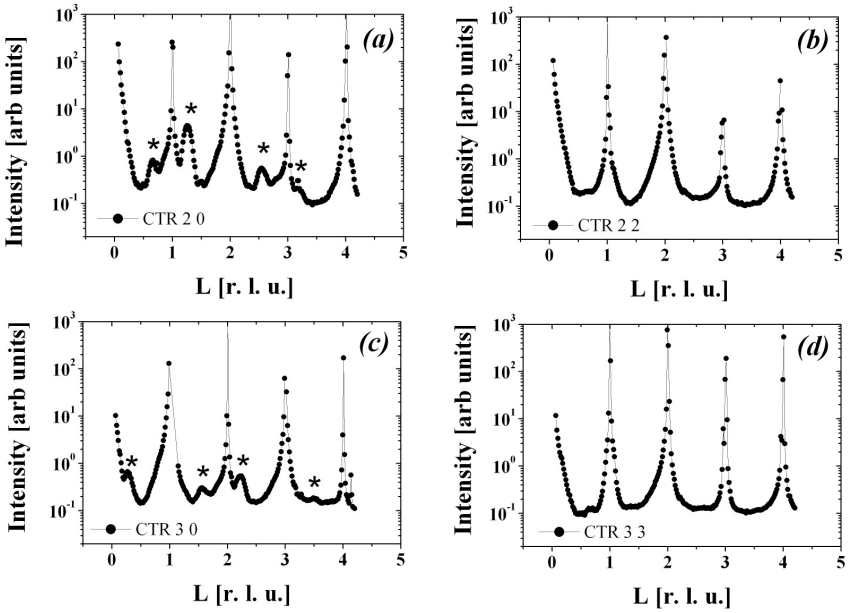

Fig. 2: (H, 0) and (H, K) l-scans (H=K =2, 3) of a 4uc $NdGaO_3/SrTiO_3$ heterostructure. The asterisk in the (2 0) and (3 0) l-scans ((a) and (c)) indicate peaks associated uniquely to the $NdGaO_3$ film. These peaks are absent for (2 2) and (3 3) reflections.

from the interface, are very close to the expected position for a completely strained LAO film on STO single crystal. These results do not hold for the first 2 LAO uc, and in particular for 2uc thick LAO/STO films, which are insulating. The large cation displacements, and consequent rumpling of the LAO layers, before the realization of the 2DEG, is expected and predicted by DFT calculations [9]. Indeed, the presence of polar layers and the accumulation of electrostatic potential can be partially compensated by the ionic polarizability of the LAO film. However, this compensation mechanism is no more convenient above 4 uc, so that the system rearrange electronically and structurally in order to create a 2DEG. It seems, however, that the intermixing in the first LAO layer is a consequence of this structural and electronic rearrangement.

The second part of the experiment was dedicated to the structural study of an insulating interface, the $NdGaO_3/SrTiO_3$, where the polar catastrophe is expected to play an important role as-well. $NdGaO_3$ has an orthorhombic structure similar to the classical $GdFeO_3$ antiferrodistorted structure, characterized by GaO_6 octahedra which are tilted and rotated one respect to the other, giving rise to a superstructure and thus to a reduction of the *P4mm* symmetry to *Pbmn*. However, in pseudocubic units, $NdGaO_3$ is characterize by lattice parameters which are relatively close to the ones of STO, and in particular $a_{pc}=b_{pc}=3.86$ Å, $c_{pc}=3.85$ Å. A cube on cube growth can be expected as in the case of $LaAlO_3$ on $SrTiO_3$.

Surprisingly, the structure of a thin 4uc (in pseudo-cubic units) $NdGaO_3$ is very different from the one of a $LaAlO_3$ sample with a similar thickness. As shown in Fig.2, additional pronounced peaks in the (H, 0) and (0, K) l-scans, which are displaced from the Bragg peaks at 0.33 and 0.66 r.l.u. in L, are present. On the other hand, these peaks are not present in (H, K) reflection with H=K. Additionally, not shown, we observed diffraction at fractional order rods, and in particular at (3/2, 1/2, L) and at (0.77, K, L). A complete refinement of the structure is under way.

[1] A. Ohtomo and H. Y. Hwang, A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface. *Nature* **427**, 423 (2004).
[2] N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, J. Mannhart, Superconducting Interfaces Between Insulating Oxides. *Science* **317**, 1196 (2007).
[3] A. D. Caviglia, S. Gariglio, N. Reyren, D. Jaccard, T. Schneider, M. Gabay, S. Thiel, G. Hammerl, J. Mannhart, J.-M. Triscone, Electric field control of the $LaAlO_3/SrTiO_3$ interface ground state. *Nature* **456**, 624 (2008).
[4] P W Tasker, The stability of ionic crystal surfaces. *J. Phys. C: Solid State Phys.* **12**, 4977 (1979).
[5] W. A. Harrison, E. A. Kraut, J. R. Waldrop and R. W. Grant, Polar heterojunction interfaces. Phys. Rev. B **18**, 4402 (1978)
[6] C. Noguera, Polar oxide surfaces. *J. Phys.: Condens. Matter* **12**, R367–R410 (2000).
[7] J. Goniakowski, F. Finocchi and C. Noguera, Polarity of oxide surfaces and nanostructures. *Rep. Prog. Phys.* **71**, 016501 (2008).
[8] Y. Hotta, T. Susaki, and H.Y. Hwang, Polar Discontinuity Doping of the $LaVO_3/SrTiO_3$ Interface, *Phys. Rev. Lett.* **99**, 236805 (2007).
[9] R. Pentcheva and W. Pickett, Avoiding the Polarization Catastrophe in $LaAlO_3$ Overlayers on $SrTiO_3$ (001) through Polar Distortion, *Phys. Rev. Lett.* **102**, 107602 (2009).