Polar-nonpolar oxide interfaces charge dynamics investigated by a single Pump - double Probe experiment

In this project, a single THz-Pump and double THz-Ellipsometry / Second-Harmonic Probe experimental setup will be built in order to investigate the polarization and the charge dynamics of polar-nonpolar oxide interfaces under an intense transient electric field. This new experimental approach will be applied to a prototype oxide interface: $LaAlO_3$/$SrTiO_3$. The main goal of the project is to disentangle the contribution from trapped and free charges to the interface electronic reconstruction that lead to the insulator-to-metal transition and the onset of 2D-conductivity in these systems.

1. Introduction:

The discovery of a high-mobility 2-dimensional electron liquid (2DEL) at the interface between $LaAlO_3$ and $SrTiO_3$ (LAO/STO), two insulating perovskites [1], is perhaps one of the most recent and fascinating examples of interface-related phenomena. Because of both its interest in the field of fundamental Solid State Physics and a possible massive impact on technological applications, the discovery of this effect attracted a large interest in the scientific community. It was shown that the 2DEL appears when a minimum thickness (n=4 monolayers) of LAO is deposited on the STO substrate. Across this threshold, the sheet resistivity decreases by several orders of magnitude. In addition, the insulator-to-metal transition can be reversibly induced by an external electric field in the n=3 samples [2]. Moreover, samples grown on SrO terminated substrates are found to be insulating [1], the charge carriers are found to be localized within few nanometers from the interface [3] and, below 200 mK, they give rise to 2D-superconductivity [4]. Despite all the experimental effort, a complete agreement about the inmost nature of the charge injection mechanism has not been reached yet. The main difficulty is to disentangle extrinsic and intrinsic effects. On one hand, it is clear that extrinsic doping cannot be alone responsible for the observed phenomenon [3]. On the other hand, an interpretation based on purely intrinsic effects, such as the so-called "polar catastrophe" model [5], is still too qualitative, and does not account for important observations, such as the striking difference between the predicted 2D electron density ($\sim10^{14}cm^{-2}$) and the one observed by Hall effect ($\sim10^{13}cm^{-2}$). It is clear that either the predicted value is wrong, or not all the electrons at the interface are mobile [6,7]. In addition, more investigations on the charge dynamics, in particular the insulator-to-metal transition minimum switching time, is strongly required in view of a possible industrial exploitation of these findings. To address this task, it would be highly desirable to drive the system out of its equilibrium by means of an intense ultrafast transient electric field, while monitoring the system by two ultrafast techniques, to probe separately the different charge carrier states: 2D mobile charges and non-mobile surface-trapped ones. Here we propose to use the synergy between Surface-enhanced Second Harmonic Generation (SSHG) and Terahertz Time-domain Ellipsometry (TTE) to address this challenge. The final goal of the project is to build the experimental setup and to test its performances on the LAO/STO interfaces. The samples that we plan to investigate will be provided by the CNR-SPIN MODA Lab, a PLD growing facility that has already a long-lasting collaboration with the proponent on the base of previous projects. Therefore, the entire project will be carried out within CNR-SPIN.

2. Surface Second Harmonic Generation:

SSHG has been recently applied with success on LAO/STO interfaces [6-7]. The SSHG signal is extremely interface-sensitive, due to a strong suppression of the background contribution to the signal because of symmetry-breaking at the interface: since the SSHG signal vanishes in bulk centrosymmetric materials, such as both LAO and STO are, only the air-LAO and the LAO-STO interfaces, where the bulk symmetry is broken, can contribute to the signal. Phase- and frequency-resolved SSHG measurements demonstrated that the SSHG signal comes entirely from the STO side of the LAO-STO interface in the range of 3-4 eV and that it couples with the formation of a so-called “precursor” of the 2DEL, resulting into a strong enhancement of the polar rearrangement of the interface at n=3. Since no change in SSHG is found across n=4, the signal was proved not to couple directly with the mobile charges. Since SSHG can probe the interfacial polarization on the time-scale of a laser pulse (<100 fs), it is an ideal tool to study the time-evolution of the system upon excitation.

3. Time-Domain THz Ellipsometry:

For a complete description of the Time-domain THz Spectroscopy (TTS) technique, see e.g. Refs 8-10. Due to the very high optical density in the FIR region of the samples that we plan to investigate, it is necessary to measure the reflection rather than the transmission coefficients. TTS is not by itself a surface-specific technique, although it has been already employed with success to the study of 2D-electron gas in semiconductors [11]. Although the penetration length in the Far Infrared (FIR) spectral region is quite small (µm), it is anyway much larger than the interface layer itself (nm). Nonetheless, it is possible to study sub-wavelength thin-films by exploiting the polarization changes of the reflected light. In particular on LAO/STO, the FIR Ellipsometry has been found to be a suitable tool to observe the Drude contribution to the dielectric constant [12]. Anyway, this technique is model-dependent and not suitable to investigate the charge dynamics. The experimental approach here proposed is based on the synergy between TTS, conventional Ellipsometry and magneto-optical Kerr spectroscopy. Let us note that TTS measures the amplitude and phase of the electric field oscillations and thus the dielectric constant of the material can be inferred with no need of the Kramers-Kronig relations [13]. In addition, it is possible to disentangle the response of the free carriers from the rest by measuring the off-diagonal components of the dielectric function by polar Kerr effect [14]. It is possible to regard this technique as an ultrafast high-frequency contactless Hall-probe. This technique is able to deduce the effective mass, scattering time, density, and type (n or p) of free carriers independently [15]. In addition, by exploiting the short duration (~1 ps) of a THz pulse, it is possible to access their dynamics. Since trapped charges cannot affect the Hall conductivity, they cannot contribute to the TTS magneto-optical signal: SSHG and TTE are two complementary techniques, that allow to have a complete characterization of both the trapped and mobile charge dynamics independently, on a sub-picosecond time-scale.

4. Pump excitation sources:

As mentioned before, the insulator-to-metal transition can be triggered by applying a static electric field along the normal direction. It is then straightforward to investigate the behaviour of the system once it is perturbed by a strong electric transient. A large literature is available about the generation of very strong electric fields by Non-linear Optical Rectification, either by exploiting high power laser fluence on very large nonlinear crystals [16], or by some more refined techniques [17]. The electric field peak that can be generated using this novel techniques can be as high as 250 KV/cm [18], while the static field required to achieve the switching between the insulating and the metal state at n=3 is about 1 KV/cm [2]. Additionally, the spectral region of the Pump THz pulse lies mainly in the range below the TO soft phonon (~3 THz), which is the lowest FIR excitation of bulk STO, and therefore a direct resonant excitation of the substrate is not expected. On the contrary, a different source of THz radiation can be employed to investigate the 0.1 eV (~24 THz) band splitting that has been observed by SSHG spectroscopy [7]. For that purpose, it is necessary to use a different nonlinear crystal, namely the Gallium Selenide (GaSe), that can generate a broad band THz spectrum, ranging from 5 to 50 THz.

5. Experimental layout:

The proposed experimental approach will be then implemented as depicted in Fig 1. An intense Pump pulse from a amplified Ti:Sa laser (3.5 mJ per pulse, 35 fs, 1 KHz rep rate) generates a strong electric pulse in the nonlinear crystal (NL). The pulse is collimated and then focused on the sample surface and its arrival-time sets the t=0. Three weak beams are splitted off the main one before the NL. One will be sent onto the sample to generate the SSHG signal ("SSHG-probe"), the second will be collimated along the Pump direction trough the NL ("THz-probe") and the third ("Gate") will be sent to the detection crystal (DC). A Si-wafer can be used to remove the residual visible light from the Pump pulse and to couple a second, delayed and weaker 800 nm pulse, into the THz beam direction. A Si-wafer will then reflect the visible SSHG signal (at 400nm) and the remaining visible light, through the SSHG detection line, and it will couple the Gate pulse into the THz beam path. The system is excited by the strong THz pump pulse at t=0. At adjustable delays, the weak THz pulse will probe the mobile charge carrier state, and the visible 800 nm pulse will probe the trapped charge state through SSHG. The reflected SSHG-probe is then spectrally filtered and revealed. The THz-probe and the SSHG-probe pulses are synchronized, while the THz-Pump arrival time can be adjusted with a remote controlled delay-stage (DS1). The Gate pulse is delayed periodically (DS2) across the THz-probe for Electro-Optical sampling, measured by a retardation plate, a Wollaston Prism (WP) and two balanced photodetectors (PhD1,2). Within this scheme, a measurement of the THz-Pump alone is possible at t=0 to check the spectral and time profile of the excitation source, but an independent measurement of the THz-probe alone is not possible within about ±0.5 ps from the Pump, because both Pump and Probe pulses will be read in the DC. Furthermore, at t=0 both Pump and Probe will be generated in the NL, and this will result in unwanted interference between them. On the contrary, the SSHG-probe will be able to probe the system during the excitation pulse with a fs time resolution. If the dynamics is much longer than the THz-Pump duration, the proposed "Scheme 1" will be able to detect it. Anyway, in case of a sub ps dynamics, it will still be possible to measure it by turning to a slightly more complex geometry ("Scheme 2"): a different THz-probe will be generated in a second NL, and then sent parallel to the THz-Pump, but displaced by some mm, into the focusing parabolic mirror. The two beams are both reflected by the sample and spatially filtered, so that the THz-probe can be focused on DC and detected alone. The Pump pulse will be modulated by a chopper, while the THz-probe waveform and the SSHG intensity will be recorded for two subsequent Pump-ON and Pump-OFF pulses. Their relative difference will give the dynamical change of the two signals.

6. Time and Financial plan of the project:

Three steps are foreseen in order to achieve the final results. First of all, the THz setup already present in the CNR-SPIN Nonlinear Spectroscopy (NLS) Lab has to be updated to work in a reflection geometry, according to Fig 1. Some commercial semiconductor samples and n-doped STO will be purchased to characterize our TTE setup in static measurement by reproducing the existing measurements in literature and to extend those results to oxides. To this purpose, we plan to buy the WG polarizers and some strong (electro-)magnets. In the second step, the SSHG line will be added in the setup, a full characterization of the static TTE, SSHG response and the possible correlation effects will be done. If present, these effects have to be suppressed by a shutter system, and an appropriate software control. Therefore we will buy remote-controlled shutters and some general electronic instrument that can help at this stage. In the third step, the THz-pump beam will be generated, and different generation schemes will be tested in order to achieve the desired pump requirements. We plan to buy large-area ZnTe and GaSe with different size and thicknesses, in order to maximize the low-frequency electric peak amplitude and spectral weight and to generate high frequency THz pulses. In addition, we will need to buy a THz camera to measure and optimize the THz focus, which is a very important parameter to achieve a large local field, and a second remote-controlled delay stage. At this point, we will be able to run a Pump&Probe measurement and test the setup performances. The estimated duration of every step is about 4 months, and a detailed time-plan is depicted in the Gantt chart in Fig 2. The resources of the project will be allocated in two distinct sections: 1) all instrumental items that are needed but not present in the current equipment of the NLS Lab, 2) Expenses concerning scientific dissemination. The total sum requested to carry out the project is 20.000 €. Additional economical resources will be allocated through current projects as specified in Table 1.

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Description of the Principal Investigator’s scientific activity.

The Principal Investigator (PI) A. Rubano got his PhD in “Fundamental and Applied Physics” in the University of Naples Federico II, in 2008. The scientific activity of the PI was devoted to a wide class of materials named “strongly correlated electron systems” (SCES) by means of Linear and Nonlinear Optics. During the first period of his PhD work, the PI focused on the field of High Tc Superconductors (HTCS). He investigated the low-energy excitations of HTCS by means of a third-order nonlinear optical technique named Coherent Raman Scattering (CRS) and he measured the CRS spectrum (**3**) of one of the most representative material of this class, $YBa_2Cu_3O_7$. CRS can measure the phase of each single resonance with respect of the non-resonant electronic background and allow a selective excitation of a single resonance and, thus, the observation of the relaxation dynamics of system, in a Pump&Probe scheme. During the second period of his PhD work, the PI moved his interest to one of the most studied perovskite, the strontium titanate $SrTiO_3$ (STO). He investigated the spectral and dynamical behaviour of the STO luminescence under intense UV-light. This intensive study (**1,2,4,5**) shed light both on basic issues regarding the nature of charge carriers in STO, as for instance the possible presence of self trapped polarons, and on some technologically relevant issues (switching speed, optical bandwidth, etc.). Since March 2008 up to December 2010, the PI has worked as post-doc at the University of Bonn, in the group of prof. M. Fiebig, one of the leading European groups in nonlinear Optics on Solid State systems. There, he gave his contribution to the study of the dynamical properties of the antiferromagnetic (AFM) order parameter in nickel oxide (NiO). By means of the optical Second Harmonic Generation technique (SHG), he has measured the AFM order parameter in a wide dynamical range. He demonstrated that an intense pulse of light (Pump) generates a coherent superposition of different spin states having different orientations. In addition, he clarified the coupling between the Pump-pulse duration and the order parameter reorientation, showing that a fully reversible and three-dimensional switching of the NiO AFM state is possible (**6**). In the second interval of his post-doc period, the scientific activity of the PI was devoted to the investigation of oxide interfaces, which is still currently his main research field. Some of his main results on this topic have been already mentioned in the main body of the project (**7**). The PI also investigated the spectral changes at low temperature, the spatial profile of polar domains along the interface plane and the interface polarization dynamics. These last three topics will be published in a close future. In January 2011 the PI has been awarded a Max Planck Fellowship at the Fritz Haber Institut von der Max Planck Gesellschaft, in Berlin, in the Nonlinear Optics group of Prof. Martin Wolf. He has built a Time Domain THz Spectroscopy (TDTS) setup and he is currently studying the low-frequency response of Nb-doped $SrTiO_3$.

1. **A. Rubano**, D. Paparo, F. Miletto, U. Scotti di Uccio and L. Marrucci “Recombination kinetics of a dense electron-hole plasma in strontium titanate” Physical Review B **76**, 125115 (2007).
2. **A. Rubano**, D. Paparo, M. Radovic, A. Sambri, F. Miletto Granozio, U. Scotti di Uccio and L. Marrucci “Time-resolved photoluminescence of n-doped $SrTiO_3$ ” Applied Physics Letters **92**, 021102 (2008).
3. **A. Rubano**, D. Paparo, F. Miletto Granozio, U. Scotti di Uccio and L. Marrucci “Coherent Raman Spectroscopy of $YBa_2Cu_3O_7$” Optics Express **16**, No. 12, 90549 (2008).
4. **A. Rubano**, F. Ciccullo, D. Paparo, F. Miletto Granozio, U. Scotti di Uccio and L. Marrucci “Photoluminescence dynamics in strontium titanate” Journal of Luminescence **129** 1923–1926 (2009).
5. **A. Rubano**, D. Paparo, F. Miletto Granozio, U. Scotti di Uccio and L. Marrucci “Blue luminescence of SrTiO3 under intense optical excitation” Journal of Applied Physics **106** 103515 (2009).
6. **A. Rubano**, T. Satoh, A. Kimel, , A. Kirilyuk, T. Rasing, M. Fiebig “Influence of laser pulse shaping on the ultrafast dynamics in antiferromagnetic NiO” Physical Rev. B **82** 174431 (2010).
7. **A. Rubano**, D. Paparo, A. Marino, D. Maccariello, F. Miletto Granozio, U. Scotti di Uccio, C. Richter, S. Paetel, J. Mannhart, L. Marrucci and M. Fiebig “Spectral and spatial distribution of polarization at the $LaAlO_3/SrTiO_3$ interface” Phys. Rev. B. **83** 155405 (2011).

Since March 2008 to Dec 2010 the PI was Exercise Lecturer of the Solid State Physics course of Prof. R. Vianden, Helmholtz-Institut für Strahlen- und Kernphysik, Bonn, Germany. He has been the supervisor of a Master student during his PhD and two PhD students during his post-doc period. The PI has been chosen as referee for App. Phys. Lett.

Description of the research team, environment and resources.

The main part of the experimental work will be carried on in the Nonlinear Spectroscopy Lab (NLS) of Prof. Lorenzo Marrucci and Dr. Domenico Paparo. The NLS Lab has a long-standing experience in applying nonlinear optical spectroscopies to the investigation of different materials in topical fields ranging from soft-matter to solid-state physics. In the last five years major efforts have been devoted to the study of SSHG from metal-oxides polar-nonpolar interfaces. Very recently the NLS laboratory has been equipped with a new Ti:Sa laser system thanks to the financial support of the European Community under grant agreement N.264098-MAMA. This laser system delivers pulses having 35 fs time duration, 3.5 mJ energy and 1 kHz repetition rate. By exploiting this new light source, a Time-domain THz spectrometer has been recently built up. Standard-size ZnTe crystals are available together with a $LiNbO_3$ crystal to generate high-intensity THz. Standard optical and electronic equipments are available for the present project. The scientific managers of the NLS Lab are responsible of a PRIN and an EU FET-open project. The first of these projects and some additional support from the University Department of Physical Sciences will provide additional economical resources needed for guaranteeing the full realization of the project. In particular, a one-year (possibly renewable) fellowship for supporting the PI during the work proposed in this project will be obtained from these funds. In the following, a brief overview on the two scientific managers background is given. Lorenzo Marrucci is associate professor at the University of Naples Federico II and associated scientist with SPIN-CNR. He graduated from Naples University (PhD 1993) and completed his training as a post-doc for two years in the University of California at Berkeley, before returning to Naples as a researcher (1995-2001) and associate professor (2001-now). His research activities are in nonlinear and quantum optics, with a focus on the interaction between light and complex materials such as liquid crystals and transition-metal oxides, and on the angular momentum of light. In 2006 Marrucci invented the *q-plate* (international patent pending), a device for controlling the orbital angular momentum of light by means of its coupling with light polarization. Marrucci authored or co-authored about 100 papers (80 in the ISI database), which have received almost 1300 citations to date, and three patents. He has been a member of the board of directors of the European Laboratory for Nonlinear Spectroscopy (LENS) in Florence (2007-2010) and is presently the international coordinator of a FET-Open European research project (PHORBITECH), which involves groups from Roma-Sapienza, ICFO-Barcelona, Glasgow University, Bristol University, and Leiden University. Domenico Paparo is a permanent staff member of SPIN-CNR Institute since 2005, where he is the scientific responsible of the research activity *‘Growth and characterization of epitaxial and nanostructured films, and interfaces: pulsed laser deposition, in-situ analysis, optical, magnetic and transport properties’*, with seventeen SPIN researchers contributing. His research activity is located at the intersection between Optics and Condensed Matter physics. He is author of about 50 communications to conferences, more than 40 papers (40 in the ISI database, 3 invited chapters of books). The 40 ISI works have been cited about 700 times (one recent PRL paper cited more than 100 times in the last five years), with an H-index of 14. He is the Scientific Responsible of different projects. Two of these have been financed by INFM, an international one by the Ministry for Foreign Affairs, and recently he was the CNR responsible for a PRIN 2008. Recently, he was awarded by a Marie Curie fellowship to be trained on Time-Domain THz Spectroscopy at the FOM-Amolf Institute in Amsterdam. His scientific collaborations spread among several international groups, as for instance Prof. J.-M. Triscone (Univ. of Geneve), Prof. M. Fiebig (ETH Zurich), Prof. Mannhart (Max Planck Inst. Stuttgart), Prof. M. Bonn (Max Planck Inst. Mainz).

Selected publications of the group:

1. A. Rubano, D. Paparo, A. Marino, D. Maccariello, F. Miletto Granozio, U. Scotti di Uccio, C. Richter, S. Paetel, J. Mannhart, L. Marrucci and M. Fiebig “Spectral and spatial distribution of polarization at the $LaAlO_3$/$SrTiO_3$ interface” **Phys. Rev. B.** 83 155405 (2011).
2. G. Tosi, F. M. Marchetti, D. Sanvitto, C. Antón, M. H. Szymańska, A. Bercenau, C. Tejedor, L. Marrucci, A. Lemaître, J. Bloch, L. Viña, ‘‘Onset and dynamics of vortex-antivortex pairs in polariton optical parametric oscillator superfluids’’ **Phys. Rev. Lett.** 107, 036401 (2011).
3. E. Nagali, D. Giovannini, L. Marrucci, S. Slussarenko, E. Santamato, F. Sciarrino, ‘‘Experimental optimal cloning of four-dimensional quantum states of photons’’ **Phys. Rev. Lett.** 105, 073602 (2010).
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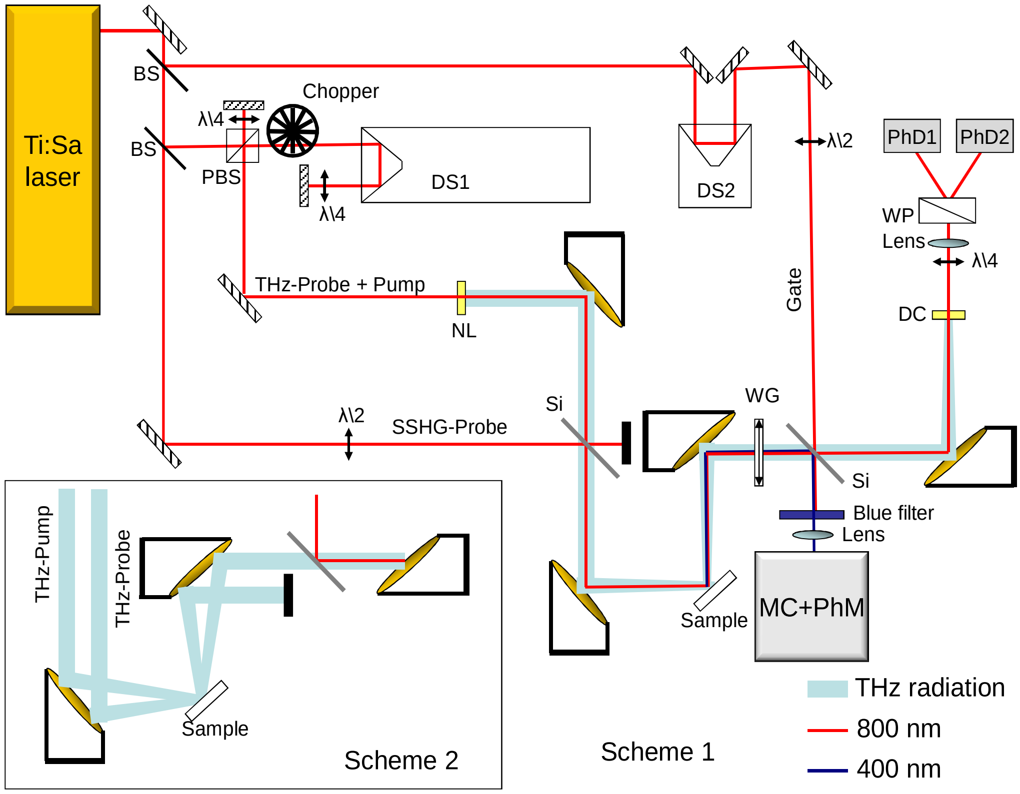

Fig1: Experimental layout.

Activity:	Month:	01	02	03	04	05	06	07	08	09	10	11	12
Purchasing			■	■	■								
Planning		■											
THz setup update			■	■									
TTE characterization					■	■	■						
Sample preparation		■	■	■	■								
SSHG measurements							■	■	■				
TTE-SSHG corr. effects									■				
High THz generation										■	■		
LAO\STO experiments												■	■
Results analysis and dissemination												■	■

Fig2: Gantt chart of the tasks timing.

Nonlinear crystals	4000 €
High frequency triggered chopper	2000 €
Permanent(-Electro)magnet, High Voltage power supply	4000 €
Wire Grid THz Polarizers	3000 €
Commercial samples and substrates	3000 €
Optical shutters, Filters, Delayline and Diverse Electronics	4000 €
THz camera	5000 €
Scientific Dissemination	2000 €
Total	27000 €
Co-funding from other projects	7000 €
Requested to SEED-SPIN	**20.000 €**

Table 1: Details of the financial plan.