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# ISOE2019

## 5th International School of Oxide Electronics

Cargèse, France – June 25, July 5, 2019

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We would like to thank all our sponsors for their support.

# Abstracts of posters

# High-throughput quest for antiferroelectric perovskites

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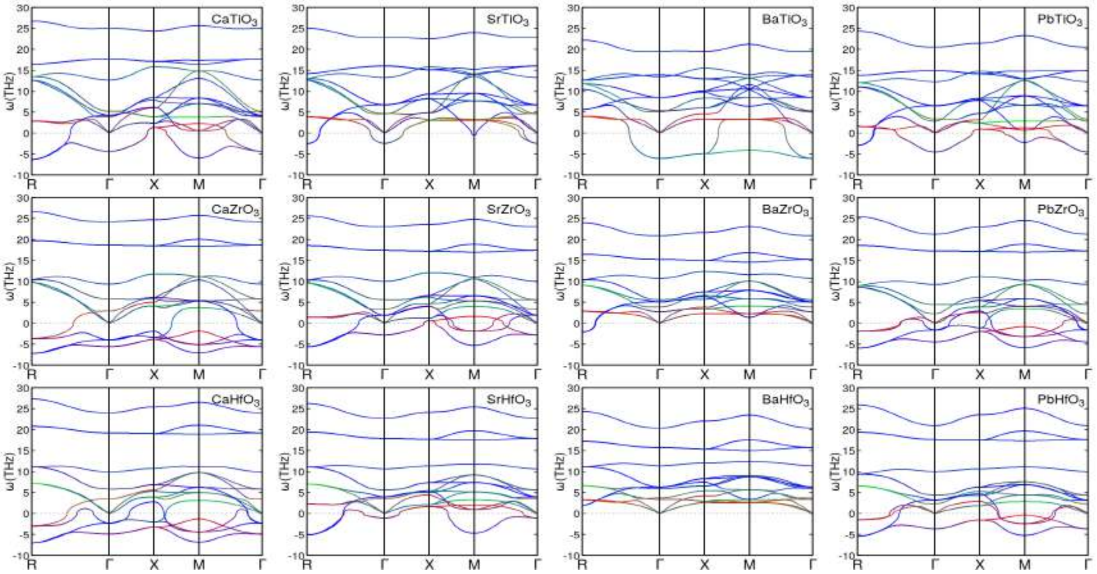
Up to now, there is no known displacive antiferroelectric perovskite oxide (but for maybe $PbZrO_3$). In this work we elucidate why perovskites undergo displacive ferroelectric, ferrodistortive and antiferrodistortive transitions, but never display a leading instability corresponding to an antiferroelectric mode. By means of first-principles calculations and second-principles models we carry out a high-throughput study of the vibrational spectrum of non-magnetic perovskite oxides ($ABO_3$), in order to look for possible new antiferroelectric materials (see Figure 1). The second-principles models [1,2] give us access to the hierarchy of atomic interactions in the materials, with which we can rationalize why in perovskites with an antiferroelectric instability there is always a different leading instability.

Figure 1:



Phonon spectra of some of the studied perovksites. The weight of the A, B and O atoms in each dynamical matrix eigenvector has been colour coded in red, green and blue, respectively.

[1] Jacek C. Wojdeł, Patrick Hermet, Mathias P. Ljungberg, Philippe Ghosez and Jorge Íñiguez, J. Phys. Condens. Matter 25, 305401 (2013).

[2] Carlos Escorihuela-Sayalero, Jacek C. Wojdeł and Jorge Íñiguez, Phys. Rev. B 95, 094115 (2017).

# Fatigue behavior of PZT thin films processed by Chemical Solution Deposition

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Over the past two decades, ferroelectric thin films have found their way into electrical and electronics applications such as micro actuators, micro sensors, memory devices, transducers and high frequency components. $Pb(Zr,Ti)O_3$ (PZT) is widely used for most of the above-mentioned applications. Thin films of PZT deposited on silicon offer effective integration into microelectronic systems as discrete integrated circuit (IC) components[1]. Chemical solution deposition (CSD) based on a sol-gel route is a cost effective and industrially viable method for producing electronic oxide thin films in general, and PZT in particular. It offers relatively a better freedom in choosing the substrate and electrode materials as per the application and requirements[2]. Although there are several constraints associated with the solution chemistry, processing temperature and environment, many research groups have successfully fabricated PZT thin films on silicon substrates, taking advantage of the CMOS compatibility. Textured films with [001] orientation were demonstrated for their better piezoelectric responses compared to the other randomly oriented films.

In this work, breakdown and fatigue behaviour of PZT thin films fabricated by CSD route in a metal-insulator-metal capacitor geometry were studied. Platinised silicon was the substrate of choice, with platinum as bottom electrode and lead titanate ($PbTiO_3$) as buffer layer to have [001] oriented films. The crystallization process was optimized to achieve perovskite phase purity, to have better ferroelectric properties. Platinum top electrodes of 100 nm thickness were sputtered on the PZT films following lift-off photolithography. Breakdown and fatigue tests were carried out on samples with different film thickness and top electrode size. Bipolar fatigue cycling was found to have more detrimental effect on switchable polarisation and permittivity compared to unipolar cycling. Similar behaviour for the bulk PZT samples was reported in the cited literature[3]. At the same time, loss of polarization during unipolar cycling could be recovered by applying electric field in the opposite direction. Experimental evidence was found to support the underlying phenomenon of polarization recovery in samples fatigued under unipolar cycling.

[1] Setter et al. J. Appl. Phys. 100, 051606 (2006).
[2] Bassiri-Gharb et al. Chem. Soc. Rev., 43, 2125-2140 (2014).
[3] C. Verdier et al. J. Eu. Ceram. Soc. 23, 1409–1415 (2003).

# Stress in epitaxial functional oxides

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Functional oxides share the perovskite $ABO_3$ structure as a common crystal framework. Depending on the type of atoms occupying the A and B sites and potential dopants, they exhibit a wide range of physical properties such as ferromagnetism, ferroelectricity and superconductivity [1].

The realization of the MEMS structures based on epitaxial perovskite oxide requires (i) epitaxial growth of perovskite on Si template and (ii) to control the epitaxial and thermomechanical stresses that appear during the hetero-epitaxy. This stress plays a crucial role in the crystalline quality of the material but also its physical properties, those properties being directly linked with the crystal lattice that can be tuned by stress [2]. As a consequence, we performed a detailed study on the stress level in these materials integrated on Si by:

- Transmission Electron Microscopy that allows observing locally the overall quality and the presence of defects created to relax part of the stress. A typical image is shown in -Fig 1 (a)-.
- The temperature dependence of X-Ray Diffraction on different films, that allows to study the mechanical link between them, and to explain the changes that can take place during a heat treatment. An example of the temperature dependence of the lattice parameters of an LSMO film grown on Si is shown in -Fig 1 (b)-.

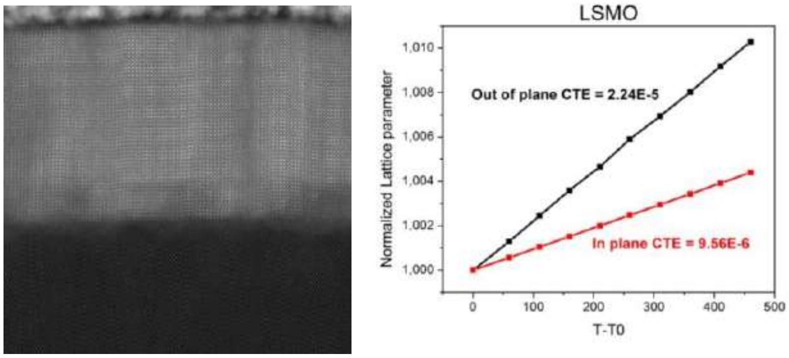

Figure 1. (a) TEM image of an LSMO film on Si, (b) The normalized mesh parameter in the plane and out of the plane as a function of LSMO film temperature.

[1] RE. Cohen, *Origin of ferroelectricity in perovskite oxides*, Nature **358**, 136-138 (1992).

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# Self-assembled networks of functional metal oxides

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We aim to fabricate and characterize self-assembled and dense networks of different metal oxides, including binary oxides ($AO_x$), perovskite ($ABO_3$), and spinel ($AB_2O_4$) structures, known to present memristive, ferroelectric or magnetic properties. These nanostructures are expected to have applications in adaptable electronics. This approach could lead to optimization of the connectivity of sub-micrometer memristive channels as well as of the number of accessible memory states.

Current techniques to fabricate nanopatterned structures, such as multiferroic nanocomposite thin films and crossbar array networks, involve expensive and complicated fabrication processes. As a method that is cheaper, more energy efficient and scalable to large-area production, we propose to use a chemical solution deposition approach based on polymer templating and imprinting (fig. 1). Polymer templating utilizes the self-assembly of block copolymers into complex structures, through solution-processable methods inorganic materials can be included in the polymer matrix. With this technique, well-defined, complex, and highly-interconnected networks of metal oxides can be fabricated.

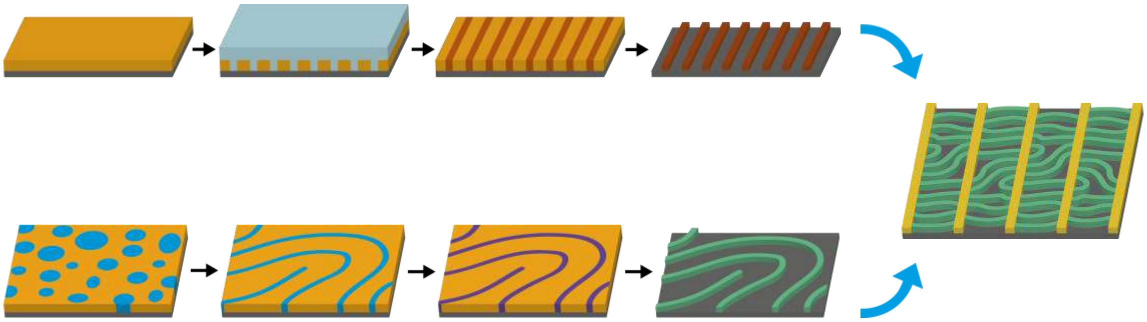

Fig. 1 Schematic representation of polymer imprinting (top) and polymer templating (bottom) to form the self-assembled networks of metal oxides (right). For polymer imprinting the pattern of a PDMS stamp is transferred to a polystyrene film, the pattern is then loaded with the metal oxide precursor solution by spin coating. Thermal treatment results in the formation of the inorganic structure. With polymer templating a block copolymer film self-assembles into a fingerprint pattern. Then, the metal oxide precursor solution is preferentially loaded into one block of the block copolymer. Thermal treatment results in crystallization of the inorganic structure and removal of the polymer. Combining the two techniques results in the networks of functional metal oxides.

# Magnetoelectric coupling in oxide heterostructures

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Voltage control of magnetism in oxide heterostructure has a broad playground with great potential to impact the magnetic data storage, spintronics and high-frequency magnetic devices. Most information storage device require high density current to read or write information in local variations in magnetization [2]. A structure in which one could manipulate magnetization using an applied electric field would significantly reduce switching power and energy dissipation. Since correlated complex oxides possess strong couplings between lattice, charge, spin and orbital degrees of freedom, one can use them to explore mechanisms of magnetoelectric coupling [1]. Here we study two systems : a heterostructure of ferroelectric $BaTiO_3$ and ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ on a Nb-doped $SrTiO_3$ substrate and a thin film of $La_{0.67}Sr_{0.33}MnO_3$ on a piezoelectric $0.7(Pb(Mg_{1/3}Nb_{2/3})O_3)$-$0.3(PbTiO_3)$ substrate. The samples are grown using Oxide Molecular Beam Epitaxy (OMBE) and High Oxygen Pressure Sputtering System (HOPSS). The systems are characterized structurally and magnetically in the laboratory. Interesting magnetoelectric coupling has been observed in the $La_{0.67}Sr_{0.33}MnO_3$/ $0.7(Pb\ (Mg_{1/3}Nb_{2/3})O_3)$-$0.3(PbTiO_3)$ heterostructure at room temperature and low temperature which requires further investigation. Atomically-resolved magnetism as a function of applied electric field is investigated using a combination of neutron scattering and advanced electron microscopy .

[1] Y. Tokura, et al., Orbital physics in transition-metal oxides, Correlated electron systems review, Science, Volume 288, 2000

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# Large area PLD of ferroelectric oxides on silicon for neuromorphic applications

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Inspired by the biological architecture of the brain and with the goal to mimic the processes underlying learning and memorization, we are developing memristive ferroelectric tunnel junctions (FTJs) for applications in neuromorphic computing, which allows for highly energy efficient and massively parallel data processing and storage.

FTJs are non-volatile memory devices with non-destructive readout whose resistance can be tuned by polarization reversal of a nanometer-thick ferroelectric layer sandwiched by two dissimilar metallic electrodes. Recently, several groups demonstrated the possibility to continuously tune the resistance of FTJs between the ON and OFF state [1,2]. Such memristive behavior is the key to mimic synaptic behavior in artificial neural networks and is realized through partial polarization switching of nanodomains within a single FTJ device [3].

For actual applications of complex oxides and industrial feasibility it is important to upscale sample fabrication processes from the millimeter to the wafer scale. To this end, a custom-made large area pulsed laser deposition (PLD) system is used to grow layers with atomically well-defined, sharp interfaces, which is a prerequisite for FTJs.

PLD parameters are optimized to grow ultrathin lead-free ferroelectric oxides, $BiFeO_3$ and $BaTiO_3$, and conducting $LaNiO_3$, $SrRuO_3$, and $La_{0.67}Sr_{0.33}MnO_3$ bottom electrode layers on 2 inch $SrTiO_3$ buffered Si wafers [4] and benchmark samples on single crystal $SrTiO_3$. AFM, XRR, and XRD are used to confirm the required flatness of less than 1 nm peak-to-peak roughness and epitaxy, respectively. PFM is used to investigate ferroelectricity in the ultrathin limit. Future work includes the fabrication of crossbar arrays and their integration with CMOS, eventually demonstrating machine learning capabilities such as pattern recognition in hardware and interfacing the system with complex signals such as the output of an event-based camera [5].

[1] Chanthbouala, A. et al. A ferroelectric memristor. Nat Mater 11, 860-864 (2012)
[2] Kim, D. J. et al. Ferroelectric tunnel memristor. Nano Lett. 12, 5697-5702 (2012)
[3] Boyn, S. et al. Learning through ferroelectric domain dynamics in solid-state synapses. Nat. Commun. 8, 14736 (2017)
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[5] http://www.ulpecproject.eu

# Phase transitions in ferroelectric domain patterns of strained $K_{0.9}Na_{0.1}NbO_3$ epitaxial films investigated by *in situ* X-ray diffraction

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A promising candidate for ferro-/piezoelectric applications is the perovskite-like material $K_xNa_{1-x}NbO_3$. Using liquid-delivery spin metal-organic vapor phase epitaxy (MOVPE), epitaxial thin films exhibiting highly regular ferroelectric domain patterns have been grown on lattice-mismatched substrates. Thereby various ferroelectric phases can be induced by different strain states, however, phase transitions among these phases are of particular interest since functional properties like the dielectric permittivity are often strongly enhanced in their vicinity. Ferroelectric phase transitions are accompanied by distinct changes in the crystal structure and the corresponding ferroelectric domain pattern and can thus be characterized very effectively by temperature dependent *in situ* X-ray diffraction.

In this study, we investigate ferroelectric $K_{0.9}Na_{0.1}NbO_3$ films grown on (110) $NdScO_3$, which show a characteristic herringbone domain pattern at room temperature resulting from the coexistence of the differently oriented monoclinic $a_1a_2$ and $M_C$ phases (Fig. 1a)[1]. This coexistence can also be identified in the corresponding grazing-incidence in-plane X-ray diffraction (GIXD) intensity distribution presented in Fig. 1b: P1 and P2 belong to monoclinic $a_1a_2$ cells and P3 to the monoclinic $M_C$ phase. Upon heating above 220 °C, a ferroelectric-to-ferroelectric phase transition to the orthorhombic $a_1/a_2$ phase is observed. Furthermore, we find an elastic relaxation that leads to a diagonal in-plane shearing of the orthorhombic unit cells that manifests itself as an in-plane peak splitting denoted as E1 and E2 in Fig.1c. Corresponding simulation (Fig.1d) and experiment (Fig.1c) are in good agreement. The fact that both diagonal branches are visible in the simulated GIXD image should be due to the fact that the individual structure factors of adjacent domains are presently not taken into account.

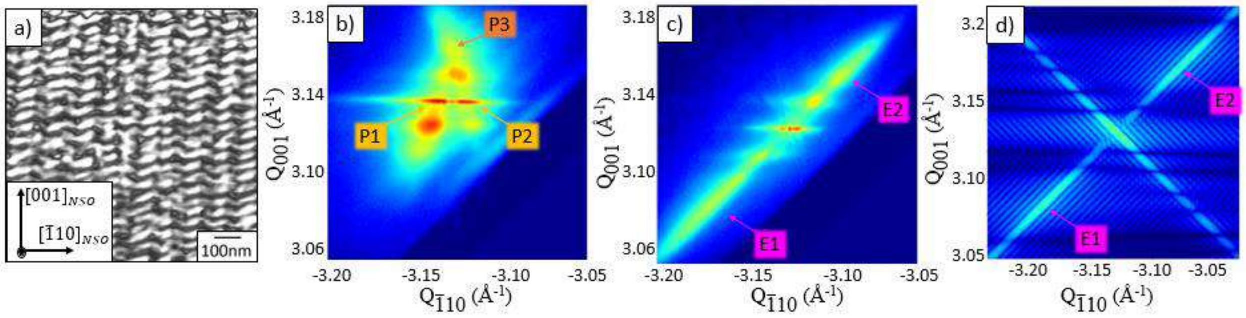

Fig 1. a) Room temperature lateral piezoresponse force amplitude microscopy image of a 38 nm $K_{0.9}Na_{0.1}NbO_3$ thin film on $NdScO_3$ and corresponding GIXD in-plane intensity distribution around the $2\bar{2}4$ substrate Bragg reflection recorded at b) 25 °C and c) 340 °C along with d) corresponding simulation.

[1] M. Schmidbauer et al., Nanotechnology 28, 24LT02 (2017)

# The formation of a rocksalt structure to overcome the large lattice mismatch between $BaBiO_3$ and $SrTiO_3$

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Complex oxides form a material class in which a wide range of properties is observed. The large tunability and high level of control during the growth process are important advantages of this material class and make it possible to influence the electronic and magnetic properties. Different material compositions can be stacked as heterostructures of thin films [1]. However, when subsequent layers have a too large lattice mismatch, the growth cannot continue epitaxially and the crystal quality of the film decreases. To overcome large lattice mismatches, buffer layers are widely adapted [2]. In this work stoichiometric, single oriented $BaBiO_3$ thin films are grown on a $SrTiO_3$ substrate without the use of a buffer layer, even though a 12% lattice mismatch is present. With high resolution scanning transmission electron microscopy (HRSTEM) and geometric phase analysis it is visualized that the large lattice mismatch between $BaBiO_3$ and $SrTiO_3$ is accommodated by a rocksalt structure that forms between the two perovskite compounds. The dislocation that appears every ninth unit cell is consistent with the 12% lattice mismatch [3]. Since the lattice constant of $BaBiO_3$ is quite large for a perovskite crystal phase ($a$ = 4.35 Å), this complex oxide itself is also suitable to function as a template for other perovskite structures. In the same article [3], we show that by using $BaBiO_3$ as a buffer layer material, the Y-Bi-O system is stabilized in the perovskite structure while this is not the most energetically favourable crystal phase.

[1] M. O'Sullivan *et al*., Nat Chem. 8(4), 292-4 (2016)
[2] G.H. Lee *et al*., APL Materials 4, 126106 (2016)
[3] R.L. Bouwmeester *et al.*, Phys. Status Solidi RRL, 201800679 (2019)

# Magnetic textures due to non collinear quasi particles in ultrathin LSMO on a strained interfaces

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Magnetic textures in thin films of strongly correlated oxides are being increasingly studied for the observation of new non-collinear magnetic textures such as conical, cycloidal and skyrmions. These magnetic states have a potential for applications in magnetic memory. Most investigations have been done with surface sensitive techniques such as STM [1] or MOKE [2] in heterostructures that comprises of thin magnetic films and a layer of material with large spin-orbit coupling. By varying the thickness of the heavy metal layer, the ideal thickness for the observation of non-collinear spin states can be determined.
In our work [3] we focus on the study of new magnetization textures in thin films of ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) by studying spin transport with varying magnetic field applied at different angles to the film normal, using a Hall bar geometry. Magnetic textures in thin films of LSMO are known to have different behavior under the influence of strain. Bulk LSMO for instance, is an in-plane easy axis ferromagnetic material with a Curie temperature of 360 K. Compressive strain induced by a substrate such as $LaAlO_3$ (LAO) changes the material properties. Thin films of LSMO with a large strain can become antiferromagnetic and further due to the coupling between charge and magnetization, become insulating. In this work we have tuned the interfacial strain such that LSMO films undergo a magnetic phase transition between antiferromagnetic insulating to ferromagnetic metallic state and probe this using magnetotransport studies in applied magnetic fields. The systematic study of this interplay is characterized by variations in the applied magnetic field, temperature, and the angle between the applied magnetic field and the current. We find that the ferromagnetic metallic state is induced from the antiferromagnetic state both by field and temperature. By measuring the longitudinal resistivity with respect to angle, the easy axis of such thin films can be determined and we find that both the antiferromagnetic as well as the ferromagnetic states have their easy axis in-plane.

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# Local Control of Strain in $La_{0,7}Sr_{0,3}MnO_3$ Thin Films – Application to MEMS

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The wide range of physical properties belonging to oxide perovskites have put these compounds in high demand for sensing applications. This includes the $La_{1-x}Sr_xMnO_3$ half-metallic manganite, a room temperature ferromagnetic metal (FM) with Curie temperature around 370K [1]. Our objective is to fabricate Micro-Electro-Mechanical Systems (MEMS) structures making use of the effect of strain on the electrical and magnetic properties of LSMO. With high interest in using a silicon-based technology, $SrTiO_3$ (STO) peroviskite with cubic unit cell of 0.3905 nm, chosen based on its structural and chemical compatibility with silicon, is to be grown on top of a Silicon-On-Insulator (SOI) substrate. SOI substrates are chosen to give the possibility to take advantage of the top Si layer as a part of the suspended structure, making it more robust, hence, less prone to breakage. Silicon-On-Sapphire (SOS) subtrates were also used with the same fabrication technology for comparison reasons.

Once LSMO properties are sensitive to strain, the LSMO/STO/(SOI or SOS) heterostrucures, patterned as bridges and cantilevers, are to be used for the realization of devices making use of strain effect in the LSMO film, induced by the electrostatically or magnetically actuated MEMS. To facilitate the fabrication process, the local static strain in the clamped edges of the suspended structures can be applied through lateral gates as fabricated in Biasotti et al., 2013 [2], through the application of a Lorentz force, by defining different sizes or geometries or, still, by an external Atomic Force Microscopy (AFM) tip. This configuration was simulated in COMSOL leading to an estimation of the displacement.

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[2] Michele Biasotti, Luca Pellegrino, Renato Buzio, Emilio Bellingeri, Cristina Bernini, Antonio Sergio Siri, and Daniele Marre. Fabrication and electromechanical actuation of epitaxial SrTiO3(001) microcantilevers. Journal of Micromechanics and Microengineering, 23(3):035031, feb 2013.

# Tunable Two-dimensional Electron System At (110) surface of SnO2

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Tin oxide ($SnO_2$) is an important transparent binary oxide widely used as a gas sensor material and believed to remain insulating even in the presence of oxygen vacancies[1]. We report the discovery of a metallic two-dimensional electron system (2DES), see Figure 1, at the (110) surface of the transparent bulk insulator $SnO_2$, with the exciting possibility to tune its carrier density at will by means of external parameters[2]. We characterize its electronic structure using angle resolved photoemission spectroscopy (ARPES), and show that it is formed out of the bulk s-like conduction band minimum of $SnO_2$ confined at the surface. This 2DES is robust with respect to surface preparation, insensitive to surface reconstructions, and exhibits clear signatures of electron phonon coupling.

Furthermore, our experimental data show that the emergence of the metallic 2DES is related to the presence of surface oxygen vacancies, providing crucial input to the possible origin of n-type conductivity in $SnO_2$ that is at the basis of a wide range of technological applications. Taken together with previous results on other oxide templates[3], our study proves that the emergence of a 2DES depends on the delicate interplay of the crystal structure and the orbital origin of the conduction electrons.

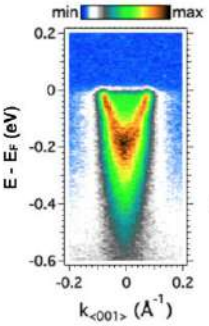

**Figure 1: Energy-momentum ARPES intensity map at the $SnO_2(110)$ surface, along the in plane $k_{<001>}$ direction. The measurement temperature is T = 15 K.**

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[2] J. Dai, et al., submitted to PRL.

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# Atomic control of disorder in PZT and epitaxial integration on GaN for high-power devices

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Due to its physical properties gallium-nitride (GaN) is gaining a lot of attention as an emerging semiconductor material in the field of high-power and high-frequency electronics applications. Therefore, the improvement in the performance and/or perhaps even extension in functionality of GaN based devices would be highly desirable. The integration of ferroelectric materials such as lead–zirconate–titanate ($PbZr_xTi_{1-x}O_3$, PZT) with GaN has a strong potential to offer such an improvement. However, the large lattice mismatch (9%) between PZT and GaN makes the epitaxial growth of on GaN a formidable challenge. Our starting point is based on previous work, which introduced a novel strain relaxation mechanism observed when MgO is used as a buffer layer, with thicknesses down to a single unit cell, inducing epitaxial growth of high crystallinity (PZT) thin films [1].

Here, we will discuss the large dielectric constant of PZT, of technological interest in transistors, and our attempt to control it by tailoring PZT structure at the atomic scale. More precisely, the amount of disorder in the system is tuned by growing epitaxial layers of $PbZr_xTi_{1-x}O_3$ with alternating tetragonal and rhombohedral order, inducing large strain and interface effects in the superlattices. Among its technological interest, this work sheds light on fundamental properties of disorder in systems showing a morphotropic phase boundary.

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# Epitaxial double perovskite $La_2NiMnO_6$ films grown by off-axis RF magnetron sputtering

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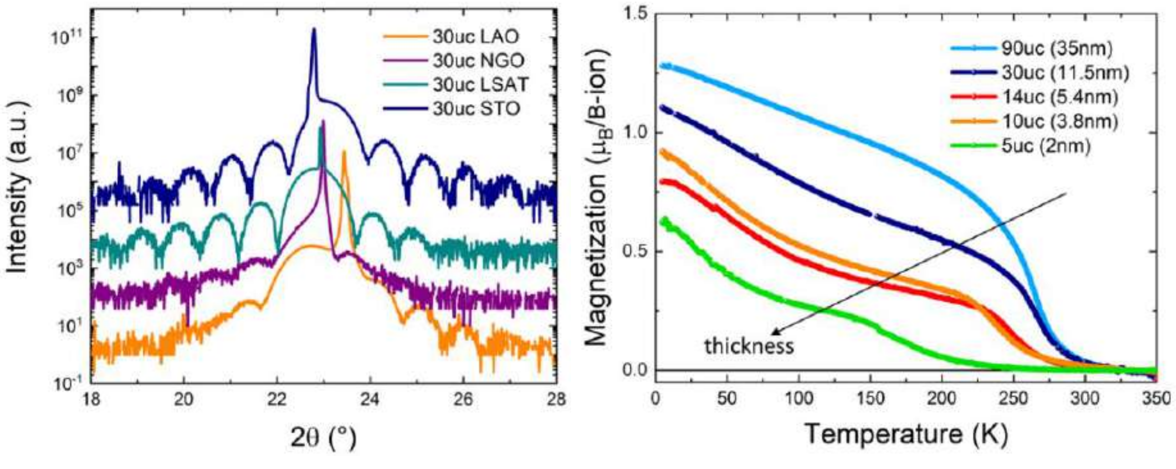
Double perovskite oxides ($A_2BB'O_6$) retain the prototypical perovskite structure complemented by a rock-salt ordering of the B and B' cations. Bulk $La_2NiMnO_6$ (LNMO) attracted some attention since it has a very high ferromagnetic Curie temperature (≈ 280K) paired with semiconducting behavior. This unusual property combination is driven by the oxygen-mediated super exchange interaction between the long-range ordered $Ni^{2+}$ and $Mn^{4+}$ ions. Next-generation spintronic devices would hugely benefit from the integration of an insulating ferromagnet in a multilayer geometry but only a few attempts of growing epitaxial LNMO ultrathin films are reported in literature.

Here we show that the epitaxial growth of highly-ordered LNMO ultrathin films can be accomplished with off-axis RF magnetron sputtering. Surface microscopy suggests that a layer-by-layer growth is stabilized for moderate strain conditions, while Laue fringes certifies the high crystalline quality of the films (left figure). Transport measurements confirm the insulating nature of the compound. The expected ferromagnetic behavior has been measured by SQUID magnetometry resulting in a bulk-like Curie temperature of ≈ 280K and low-temperature saturation magnetization/formula unit approaching the theoretical value of 5 $\mu_B$. A reduction in both Curie temperature and saturation magnetization is observed for reducing film thickness, but the ferromagnetic character of the film is retained at least down to 2nm (right figure). The ferromagnetic properties of the LNMO films are very robust with respect to epitaxial strain, somehow certifying the absence of competing $Ni^{3+}$-$Mn^{3+}$ antiferromagnetic interactions. X-ray absorption spectroscopy measured at the Mn/Ni $L_{2,3}$ edges supports the electronic state inferred from the magnetic properties.

These results illustrate the preparation of epitaxially-strained LNMO films with high crystalline quality and minimal degree of antisite disorder. The preservation of the magnetic properties down to 2nm is the first step towards the implementation of ultrathin LNMO films in multilayer structures to be routinely grown with off-axis RF magnetron sputtering. Moreover, the demonstrated capability of sputtering epitaxial double perovskite oxides thin films naturally broadens the range of systems to be explored in the quest to obtain all-oxide-based functional properties.



*Left*. X-ray diffraction scan around the $(001)_{pc}$ LSMO for films with the same nominal thickness grown on different substrates. *Right*. Magnetization/B-ion vs temperature for films with reducing thickness grown on $SrTiO_3$.

# Magnetoresistance effects in ferromagnetic metallic systems

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We investigate systematically the electronic transport in the ferromagnetic and metallic $SrRuO_3$ thin films and its correlation with the magnetic domain structure. Our work is mainly focused on the negative and positive magnetoresistance response in this ferromagnetic system, which has an itinerant exchange mechanism, as being dependent on the orientation of the magnetic domain walls. The interpretation of our experimental results brings into discussion the weak localisation theory, spin-orbit coupling effects and domain wall resistivity.

The $SrRuO_3$ thin films were grown epitaxially on slightly-miscut (~0.2°) $SrTiO_3(001)$ substrates using the Pulsed Laser Deposition technique and have thicknesses between 3 and 15nm. We conducted the low-temperature magnetoresistance and Hall effect measurements in various current-field configurations using patterned Hall bar devices with widths 70µm and lengths 800µm. The magnetic structure was analysed by MFM (Magnetic Force Microscopy).

# First-principles Investigation of Ferroelectricity in $HfO_2$-based Materials

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Abstract:

Hafnia ($HfO_2$) is attracting attention due to its empirical ferroelectric behaviour for the past few decades. It has various applications in ferroelectric field effect transistor, energy storage, electro caloric device and non volatile memory, etc. There are many experimental and theoretical studies on $HfO_2$ present in literature. However, the origin of its surprising ferroelectric behaviour is still an open question. Hence, our main goal is to investigate the origin of the ferroelectricity and optimize its ferroelectric and piezoelectric properties. In this present study, we have used first-principles methods to check the relative stability of all reported polymorphs and analysed their distortions. We have selected the polar polymorphs to study how their stability and electromechanical responses vary as a function of chemical doping. In this poster I will present our preliminary results.

# Photoinduced effects in cuprates superconductors: Ordering vs doping effects

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Complex oxides are characterized by an extremely rich phase diagram, in which the transitions between very different ground states can be triggered by small changes of the charge carrier density. One finds that interplay between these two mechanisms –and the resulting ground states– can be externally manipulated by illumination. Despite the amount of work performed in the last two decades on cuprate high Tc superconductors, a clear picture of the mechanisms governing photo-induced effects has not emerged yet. In particular the role played by doping, ordering effects or both has not been settled. Here we investigate this issue by studying light illumination effects in oxygen deficient $YBa_2Cu_3O_{7-x}$ thin films grown epitaxially on STO (001) in which different degrees of disorder are intentionally induced through i) changes in the growth conditions ("quenching") and ii) ion irradiation. Generally, we observe an increase in the superconducting critical temperature and in the carrier density coupled to a decrease in the normal state resistivity after illumination. However differences in the response to light of quenched and irradiated samples have been observed, which suggests that light-induced ordering may play an important role in the photoinduced effects.

**Work supported by the ERC grant Nº 647100 "SUSPINTRONICS" and French ANR grant ANR-15-CE24-0008-01 "SUPERTRONICS"**

# Spin to charge conversion at 2-D interface states

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Spintronics relies on the discrimination of spin up and down carriers originally generated by charge currents in metallic ferromagnets. Recent developments aim to get rid of this source of dissipation by manipulating pure spin currents without the charge counterpart. One convenient way of producing pure spincurrents is to use the spin-orbit coupling (SOC) interaction in a non-magnetic heavy metal like Pt. The interaction relies on a preferential directional scattering of electrons of different spins by SOC resulting in the generation of a spin current transverse to a charge current. This is the Spin Hall Effect (SHE) first introduced in the seventies[i]. As signals should eventually be read as voltages, it is important to efficiently convert spin into charge. This can also be done using the inverse Spin Hall effect converting a spin current into a transverse charge current. Very recently, another SOC effect based on the Rashba interaction has been shown to be more efficient[ii]. The effect stems from the joint action of the SOC and built-in electric potentials in two-dimensional electron gases existing at surfaces, interfaces or semiconductor quantum wells[iii]. In these systems, charge and spin currents are coupled through the Rashba Hamiltonian:

$$H_R = \alpha_R(\vec{k} \times \vec{z}).\sigma$$

Where $\sigma$ is the spin Pauli matrix, k the momentum of charge carriers, z the coordinate normal to the interface and $\alpha_R$ the Rashba coefficient, proportional to the induced internal electric field.

Recently, the Inverse (Rashba) Edelstein Effect (IEE) has been measured in the Ag/Bi interface[iv,v]. In the experiment, spin currents are generated by spin pumping using ferromagnetic resonance (FMR) in an adjacent ferromagnet[vi]. The Bi/Ag system is a particularly good one where the strong asymmetrical potential at the interface is responsible for generating the transverse electrical current stemming from the flow of angular momentum. Thus, interfaces with a strong Rashba splitting are good candidates as spin to charge convertors.

In these lines, other systems of a slightly different nature can also give rise to spin to charge conversion, like the 2D electron liquid appearing at the interface between two insulators as in the $LaAlO_3/SrTiO_3$ system[vii,viii]. When $LaAlO_3$ is epitaxially grown on $TiO_2$-terminated $SrTiO_3$ along the (001) direction, electrons are transferred to the interface to compensate for the polar discontinuity present between the two materials[ix]. The electrons are confined in $SrTiO_3$ within few nm far from the interface[x]. This system is characterized by some interesting properties as it undergoes a superconducting transition below ~ 300 mK [xi] and it has a strong Rashba spin-orbit interaction raising from the breaking of inversion symmetry[xii,xiii,xiv]. Both phenomena are tunable by applying an external electric field.

Spin to charge conversion in these Rashba split interfaces is still not fully understood, in particular in the LAO/STO system where we have shown that there is an in-plane dependence of the effect that probably reflects the non-isotropic Fermi surface inducing either an angular dependence of the Rashba field or a direction dependent scattering time[vii] , as shown in the figure below. This could be linked to the symmetry of the relevant in-plane d-orbitals, but this is not yet clear. In this respect the Ag/Bi interface seems simpler as no angular dependence has been demonstrated. In all cases, time-resolved measurements would be highly desirable in order to elucidate carrier lifetime effects. However, this is a very hard task as present measurements rely on spin pumping by ferromagnetic resonance, a technique intrinsically limited to the nanosecond range.

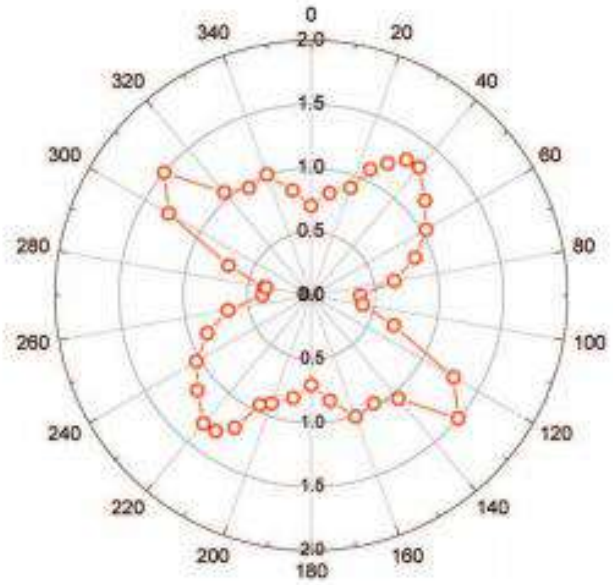

**Figure:** Angular dependence of the DC IEE length for a 4-monolayer-thick LAO at 77K.

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# Rotational Polarization Nanotopologies in $BaTiO_3/SrTiO_3$ Superlattices

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Some nanoscale ferroelectrics have demonstrated a high capability to exhibit non-trivial or exotic polarization configurations under the proper electrostatic and elastic conditions. These polar states may exhibit emerging properties not present in the bulk compounds and are potentially promising for technological applications. Here, using Cs-corrected scanning transmission electron microscopy, we report the observation of rotational polarization topologies at the nanoscale in $BaTiO_3/SrTiO_3$ superlattices grown on $SrTiO_3$. More specifically, we have observed the transition from a highly homogeneous polarization state to the formation of rotational nanodomains when increasing the superlattices period from a short one to a longer one. Such rotational nanodomains manifest despite the superlattice high anisotropy that is produced by the compressive clamping to the substrate. The nanodomains reveal nanometric dipole topologies such as vortices or waves, never before reported in $BaTiO_3$.

# Electrical characterization and analysis of Energy Efficient Embedded Non-volatile Memory based on Ferroelectric materials

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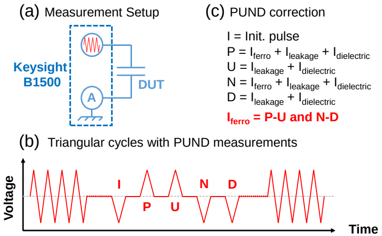
Ferroelectric materials are currently showing a novel appeal for microelectronic applications, especially for non-volatile memory devices. While several materials (PZT/SBT...) have been widely studied in the past decades, their poor scalability and poor compatibility with industrial CMOS processes have limited the rise of ferro-based devices. Since 2000's, $HfO_2$-based dielectrics are commonly used for CMOS applications because of their high permittivity. They are now part of conventional process routes for 28nm node platforms and beyond. Recent findings have shown that when submitted to proper process conditions (doping for instance), $HfO_2$-based dielectrics exhibit a ferroelectric crystalline phase, i.e. with a spontaneous, switchable and controllable electrical polarization [1]. This opens the way towards highly scalable and CMOS-compatible memory devices, such as FeRAM or FeFET.

As a first step towards memory devices, a material analysis is mandatory to establish the best process conditions to achieve ferroelectric $HfO_2$ layers. Firstly, state of the art ferroelectric characterization have been developed, cf. Fig. 1. Ferroelectricity can be evaluated by mean of Positive Up Negative Down (PUND) [2] method in order to extract pure ferroelectric contributions [3].



I = Init. pulse
$P = I_{ferro} + I_{leakage} + I_{dielectric}$
$U = I_{leakage} + I_{dielectric}$
$N = I_{ferro} + I_{leakage} + I_{dielectric}$
$D = I_{leakage} + I_{dielectric}$
$I_{ferro}$ = P-U and N-D

*Figure 1: State of the art ferroelectric characterization.*

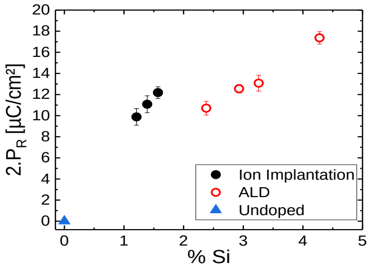


*Figure 2: Remnant polarization as a function of %Si.*

While Atomic Layer Deposition (ALD) is the most commonly used doping technique, ion implantation would allow a more precise control of the doping. Hence, Si ion implantation's efficiency to induce ferroelectricity in $HfO_2$ layers has been demonstrated through a wide range of %Si [4]. Moreover, a clear benchmark with ALD has been established, demonstrating similar ferroelectric characteristics, cf. Fig. 2, and cycling capabilities between both techniques [5].

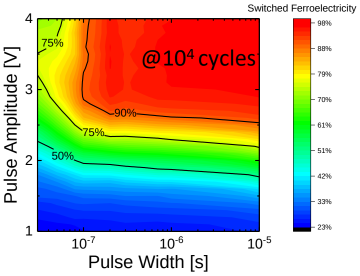


*Figure 3: Switching efficiency map.*

Finally, to make the bridge between material analysis and memory-like performance, the triangular cycling signal has to be replaced by a square cycling signal, i.e. the typical signal delivered by memory circuits. Thus, the switching efficiency of square pulses has been evaluated (Fig. 3) by mean of a dedicated electrical sequence [5]. Furthermore, 30ns switching speed is demonstrated, suitable for fast NVM operations.

To conclude, state of the art electrical characterization has been applied to extract ferroelectric parameters and reliably compare the ion implantation technique to ALD technique. First steps toward memory-like performance have been done, latter allowing to benchmark FeRAM performance with respect to other Non-Volatile Memories (OxRAMs, STT-MRAMs…) in future FeRAM bitcells in 1T-1C 16kb-array environment.

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# Photoinduced strain in devices based on ferroelectric oxide thin films

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Due to their large number of properties, such as switchable ferroelectric polarization, piezoelectricity or optical absorption, ferroelectrics are particularly promising in order to develop the next generation of electronic microdevices. Among ferroelectrics, lead zirconate titanate (PZT) has been widely studied for its high electromechanical properties. Ferroelectrics have been investigated for their potential to generate deformation under continuous illumination and more recently through ultrafast light excitation [2]. This mechanism, commonly named photostriction, combines photovoltaic and converse piezoelectric effects, but remains not fully understood.

The main goal of our recent study is to investigate ultrafast photostriction in PZT epitaxial thin films, in particular the interplay between electric polarization and optically induced deformation [2]. For this purpose, the temporal response of the out-of-plane lattice parameter of PZT integrated in capacitor geometry was measured by time-resolved X-ray diffraction after UV pulse illumination.

Tuning in situ the polarization state in PZT has revealed that both magnitude and sign of the ultrafast photostriction strongly depend on the transient photoinduced change of the internal electric field. These results also demonstrate that two distinct remanent photostrictive responses can be achieved by changing the pre-poling direction of the material [3].

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# Electro-mechanical control of ferroelectric domains and domain walls with AFM

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Controlling ferroelectric domains and domain walls appears as a promising new approach for enhancing the performance of electronic devices due to their unique electrical properties at the nanoscale. Recently, several orders of magnitude of resistivity difference have been measured between conducting domain walls and the bulk of the domains on selected ferroelectric materials [1-4]. These results may open the path to a new generation of memories or transistors taking advantage of such variations of electrical conductivity at the nanoscale [5].

Indeed, conduction in domain walls depends on different factors, including intrinsic ones such as the nature and configuration of the domains and domain walls, and extrinsic ones as the environmental conditions or point defects. Moreover, the creation, movement and stability of domain walls strongly depend on the presence of defects in the material. Our work is placed in this framework, and we have investigated the electrical and electronic properties of different ferroelectric materials, including thin films of $Pb(Zr_{0.2}Ti_{0.8})O_3$, $BiFeO_3$, and $BaTiO_3$. Using atomic force microscopy (AFM) and derived techniques (Piezoresponse Force Microscopy, Conducting-AFM), we have mapped and measured the local ferroelectric response and conductivity at natural and artificial domain and domain walls, and studied the different factors controlling the creation and manipulation of domains. We will discuss these results with the aim to provide a larger understanding of means to exploit the localized conduction in integrated ferroelectric devices.

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# Tuning the Rashba effect at $LaAlO_3$ / $SrTiO_3$ interface

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In 2004, the discovery of a two dimensional electron gas (2DEG) at the interface of $LaAlO_3$/$SrTiO_3$ (LAO/STO) [1] has motivated a large research effort to understand and tune its properties, with possibly the hope of creating new electronic devices. Subsequently, new interfacial properties linked to this 2DEG have been evidenced, such as magnetic ordering, superconductivity and strong Rashba spin-orbit coupling [2]. This last property is in particular now well studied because of its interesting potentiality for designing new spin-orbitronic devices and the LAO/STO interface appears as a good playground in order to test and understand its new physics.

We will present our results concerning the electronic structure at the LAO/STO interface (001), calculated using first-principles calculations. We will focus our discussion on the variation of the Rashba spin-orbit interaction as a function of some experimentally-tunable parameters, such as the applied gate voltage, the in-plane strain, the dimensionality or the interface terminations.

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# Physical chemistry of the TiN/$Hf_{0.5}Zr_{0.5}O_2$ interface

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Ferroelectric hafnia-based thin films are one of the most promising candidates for emerging high-density embedded non-volatile memory technologies thanks to their compatibility with silicon technology and the possibility of 3D integration. The electrode-ferroelectric interface and the annealing temperature may play an important role in such memory cells. The interface between a 2 nm TiN top electrode and a 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO) films in a metal-ferroelectric-metal (MFM) stack annealed at different temperatures was investigated with X-ray photoelectron spectroscopy (XPS). The uniformity of the 2nm TiN top electrode was verified prior to XPS experiments by photoemission electron microscopy and conductive atomic force microscopy. Partial oxidation of the top electrode and presence of reduced Hf near the interface are identified. A 0.8 nm interface layer ($TiO_xN_y$) is formed and the oxygen vacancy concentration near the interface was estimated to be 1.25%. Annealing at higher temperatures did not affect the concentration of oxygen vacancies at the interface while it causes the generation of additional vacancies in the ferroelectric film leading to a decrease of the conduction band offset. These interface redox reaction and film n-doping are believed to be the reason of several problems encountered with these systems including wake-up, imprint and endurance. Our results provide the physical chemistry of the accumulation of defective charges at the top interface causing a local imprint effect reported to be the reason of the wake-up behavior as well as a possible reason of the weaker endurance observed with these systems when increasing the annealing temperature.

# Bandgap tuning in tetragonal tungsten bronze ferroelectrics

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Recently, ferroelectrics have aroused widely for their potential use in optical applications including photovoltaic solar cells, innovative elasto-optic or electro-optic devices [1,2,3]. One of the key parameter for those applications is the bandgap of the materials. The mostly studied photoferroelectrics are materials with perovskite structure (such as $BiFeO_3$ or $BaTiO_3$) with rather high bandgap due to the large difference in electronegativity between the metal and oxygen atoms [1]. However in order to have more choice, there is a need to look for alternative photoferroelectrics with other structures. There are few reports of bandgap values in ferroelectrics with tetragonal tungsten bronze structure which can widen the photoferroelectrics family due to its flexible and tunable crystal structure as well as its polar uniaxial which may favors the so-called bulk photovoltaic effect [1]. Here we report on the bandgap of different tetragonal tungsten bronze compounds with the general formula $(A1)_4(A2)_2C_4Nb_{10}O_{30}$. We varied the nature of the A1/A2 cations and measured the direct and indirect optical gaps. The values of bandgap at room temperature change from 3.4 to 3.1 eV in $(Ba/Sr)BiNb_5O_{15}$ and $Sr_2AgNb_5O_{15}$ which shows the lowest bandgap, as shown in Figure 1. For $(Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb_5O_{15}$ (SBNN), we show the bandgap raises up slowly with the increase of the degree of filling. We also doped some of these compounds with rare-earth (RE) elements. We found that the value of the bandgap is about 3.6-3.8 eV in the system of $Sr_{1.90}Ca_{0.15}Na_{0.9}Nb_5O_{15}$ doped by $RE^{3+}$($Eu^{3+}$, $Sm^{3+}$, $Pr^{3+}$) respectively. We also measured the bandgap as a function of temperature and we linked the changes to the crystal structure.

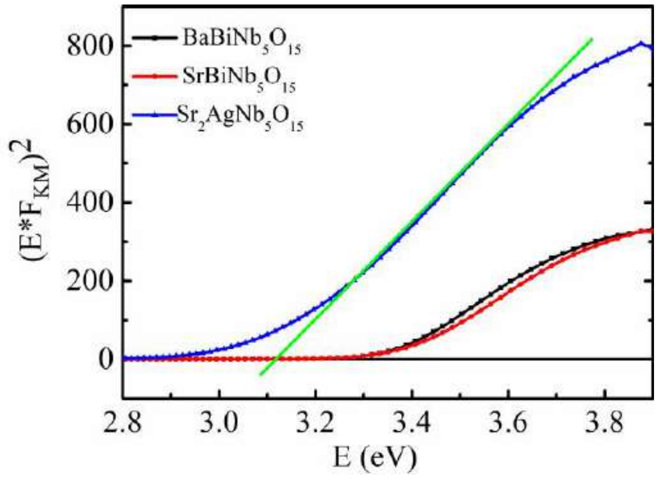

Figure 1. hν - $(h\nu F_{KM})^2$ Curve of $(Ba/Sr)BiNb_5O_{15}$ and $Sr_2AgNb_5O_{15}$

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The authors acknowledge the projects “UP-DOWN” ANR-18-CE09-0026 and “RelaxSolaire” ANR-18-CE92-0025

# Towards Spin-Orbitronics integrating perovskite oxide

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Among the numerous functionalities displayed by perovskite oxides such as superconductivity at the interface [1], multiferroism [2] or colossal magnetoresistance in manganites…, they may also be very useful materials for generating spin currents with weak relaxations.

Moreover, thanks to the Rashba spin-orbit coupling appearing at interfaces, spin currents can generate charge currents and *vice versa* through the Edelstein effects [3]. In order to improve current interconversions, several pathways have been envisaged to improve the conversion rate between spin/charge current: (i) involve heavy elements to enhance spin-orbit coupling strength, (ii) study 2DEGs [4] or (iii) integrate barrier tunnels, etc.

In our study, we focus on heterostructures based on $La_{2/3}Sr_{1/3}MnO_3$ (LSMO), grown by pulsed laser deposition. We investigate the role of strain, thickness and temperature on the magnetization dynamics in order to estimate the ideal parameters to integrate LSMO as spin injector into heterostructures. We observe that the damping depends on the thickness of the layers and the strain imposed by the substrate. But above all, temperature-dependent damping show a peak at 25K indicates a relaxation of magnetic moments. From these measurements, it is possible for us to disentangle damping effects related to the surface and to the bulk.

In addition, we looked at heterostructures including Pt and $BiFeO_3$ -- heavy elements --, combined with thin layers of LSMO. We study the dependence of spin-mixing conductance $g_{\uparrow\downarrow}$ for these materials with temperature and the thickness of the compounds. In any case, this whole preliminary study will allow us to estimate the best conditions for obtaining high spin/charge current conversion.

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# Imaging the magnetic order in antiferromagnetic thin films using scanning NV magnetometry

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Antiferromagnetic materials are emerging as a new platform for spintronic devices. Their robustness to external magnetic fields, the absence of stray fields and the fast magnetization dynamics make them a strong competitor to conventional ferromagnetic storage devices. Due to the cancellation of the magnetic moments in these materials, resulting in no or a very weak magnetic field, it is a challenge to probe their magnetic order.

A non-perturbative technique based on the single NV defect in diamond is used to image the antiferromagnetic order in real space, combining unprecedented nanoscale spatial resolution and a high magnetic sensitivity under ambiant conditions. As a proof of principle, bismuth ferrite or BFO is studied using NV-magnetometry. BFO is an exceptional multiferroic that exhibits both ferroelectric and antiferromagnetic orders at room temperature. The magnetoelectric coupling of the two orders, gives rise to a spin cycloid propagating at a wavelength of 64 nm in bulk. It also allows the control of the cycloid propagation direction via electrical fields, which opens pathways for future low power consuming memory devices.

The nanoscale thickness of BFO is imperative for realizing such devices, and therefore it is necessary to investigate the effect of epitaxial constraint on the behaviour of the magnetic order in strained BFO thin-films. Different substrates were used for the growth in order to tune the strain. Using scanning NV-magnetometry, we proved that tuning strain can stabilize different propagation directions of the cycloid, can change the plane in which the cycloid rotates or can collapse the cycloid into antiferromagnetic domains in highly strained films.

# Probing Band-to-Band Transitions in $BiVO_4$ Single Crystals by Resonant Raman Spectroscopy

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Bismuth vanadate $BiVO_4$ belongs to the class of ferroelastic oxides with a characteristic structural phase transition from monoclinic to tetragonal phase at 528 K. Early investigations on bismuth vanadate single crystals by optical absorption techniques show that the band gap falls in the range of visible light and exhibits a strong temperature dependence [1] revealed by a shift of the optical absorption edge. However, whether the band-to-band transition is indirect [2–4] or direct [5,6] is controversy discussed.

In this study, we tackle this problem using a method proposed by Weber et al. [7], where resonant Raman spectroscopy is exploited to study band-to-band transitions with respect to direct and indirect electronic transitions. One major advantage of the proposed technique is that the study of electronic transitions can be combined with a study of the structural phase transition.

We show how the strong temperature dependence of the band-gap in $BiVO_4$ can be used to make the band-to-band transition visible in Raman Spectra by a selective enhancement of 2nd order scattering processes. This analysis suggests that the Raman resonant processes are linked to indirect electronic transitions.

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# Epitaxial and atomically flat gallium ferrite thin films for low power Spintronics.

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The focus of research in Spintronics currently aims at reducing the energy cost for magnetic memory bit manipulation, with particularly great implications for the magnetic storage industry. A possible route involves the control of magnetization through spin current based torque such as Spin-Orbit Torque (SOT). SOT is realized in a bilayer system where one layer is magnetic and the second layer is a non-magnetic metal with a high spin-orbit coupling (SOC). In the non-magnetic metal, a spin current is generated via the Spin Hall Effect (SHE) and can be injected into the magnetic layer through the interface. A net torque affects the magnetic layer state. We have considered constructing such a device using $Ga_{2-x}Fe_xO_3$ (GFO) as the magnetic layer and platinum as the non-magnetic layer. GFO, apart from being ferrimagnetic at room temperature, also possesses a strong magneto-electric (ME) coupling which makes it possible to have electric field control of magnetization. We will investigate the impact of the ME effect on the SOT in such GFO/PT bilayer. Using a low energy consuming electric field, the magnetization of GFO can be tuned, offering new avenues towards the decrease of the critical current needed to switch magnetization by SOT.

In this work, we will demonstrate the optimization of $Ga_{0.6}Fe_{1.4}O_3$ (001) thin film growth by pulsed laser deposition on $SrTiO_3$ (111) substrates in order to achieve atomically flat surface. Interface quality with the top platinum layer is indeed critical for the SOT efficiency. We have observed the influence of the deposition parameters (fluence, repetition rate, deposition atmosphere and substrate temperature) and films thickness on the surface quality and crystallization. We report the crucial parameters required for obtaining smooth surface growth. The samples characterizations include structural characterization of the deposited material using X-ray diffraction, RHEED, and transmission electron microscopy, as well as topography by atomic force microscopy. The magnetic properties are probed by SQUID magnetometry as well as XMCD, and the thickness dependence of the GFO magnetic properties will be presented, as well as a study of the non-centrosymmetric character of GFO thin films by second harmonic generation (SHG).

# Enhanced piezoelectricity of thin film hafnia-zirconia (HZO) by inorganic flexible substrates

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Next-generation wearable electronics for round-the-clock health monitoring require the development of non-toxic and flexible ferro- and piezoelectric materials which can be readily coupled to the human body. Here, $(Hf_{0.5}Zr_{0.5})O_2$ films are deposited by non-rapid thermal annealing on both mechanically cyclable, flexible polyimide and rigid glass substrates and studied using high-resolution Piezoresponse Force Microscopy (PFM).[1] PFM contact mode reveals mechanical clamping effects of film-substrates through electrically written ferroelectric domains and domain walls, polarization electric (P-E) loops, and DC biasing. The polarization electric field (P-E) measurements reveal that the ferroelectric characteristics of these thin films agree with the observed switchable piezoresponse hysteresis loops as well as electrically written, oppositely oriented domains (as seen in Figure 1 left).

Our investigation of HZO ferroelectric domain walls suggests that the piezoelectric response is heightened on HZO flexible substrates and may originate from the mechanical releasing effects of the flexible substrate (Figure 1 right).[2] The hysteresis behavior on both samples suggests that the positive piezoelectric response of HZO is heightened by at least 30% on the flexible substrate when compared to the rigid substrate. The enhanced magnitude of piezoresponse on HZO is likely due to the decreased biaxial stress experienced between the polyimide substrate and HZO film which significantly enhances domain wall motion. Our findings suggest that improving domain wall motion by depositing HZO on mechanically released substrates such as polyimide may provide opportunities to improve functionality of future piezoelectric elements.

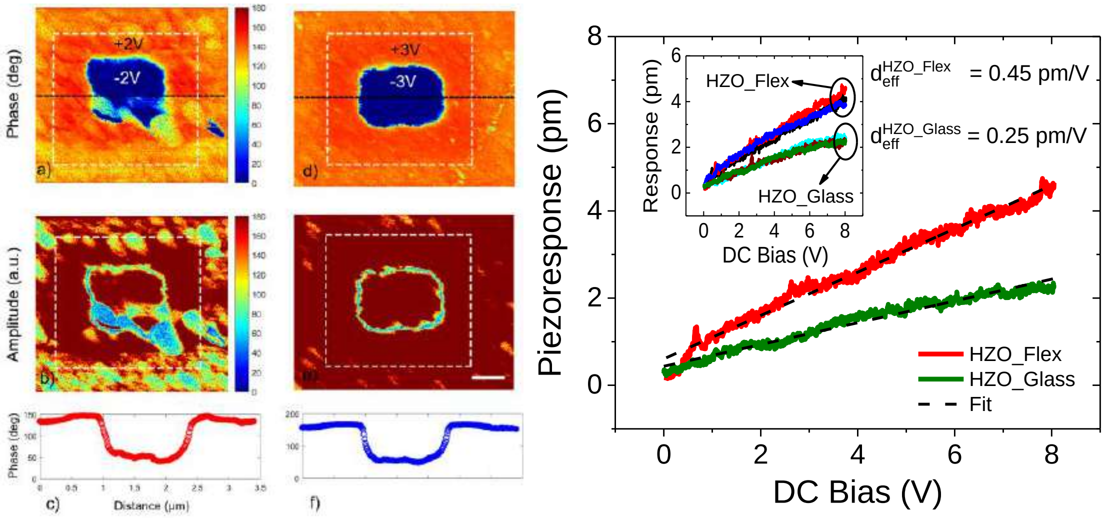

Figure 1. Domains can be written reversibly onto both flexible and rigid substrates (left). The piezoelectric response of hafnia-zirconia is heightened on flexible substrates (right).

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# Structural and ferroelectric characterization of pulsed laser deposition grown Aurivillius $Bi_2WO_6$ thin films

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$Bi_2WO_6$ (BWO) is the end member of the Aurivillius family, with one $WO_6$ octahedron sandwiched between two $Bi_2O_2$ layers. BWO undergoes a paraelectric-ferroelectric transition below $950^oC$, driven by the relative displacement of the W and O atoms in the basal plane of the paraelectric tetragonal phase, and exhibits a large spontaneous polarization about 50 $\mu C/cm^2$ [1,2]. The high Curie temperature combined with the in-plane polarization, thereby makes BWO an attractive candidate for non-volatile memory devices that could overcome the deleterious "size-effect" problem of canonical ferroelectrics like $BaTiO_3$ or $PbTiO_3$. Moreover, BWO has gained considerable attention regarding its high ionic conductivities and photocatalytic activity [3]. Despite these technological appeals, a systematic study focusing on the growth optimization, structural, and ferroelectric characterization of BWO thin films is missing. Using the pulsed laser deposition (PLD) technique, we have grown epitaxial BWO thin films on (001)-oriented $SrTiO_3$ substrates and characterized their structural properties by the X-ray diffraction (XRD) and atomic force microscopy (AFM) techniques. In this poster, we will present the systematic structural characterization of BWO films grown under various PLD conditions. Also, the ferroelectric property of the optimized BWO film probed by various electrical characterization tools including the piezoresponse force microscopy (PFM) technique will be presented.

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# Characterization of Switchable Polarization States in Epitaxial Bismuth Ferrite Thin Films Using the Bulk Photovoltaic Effect

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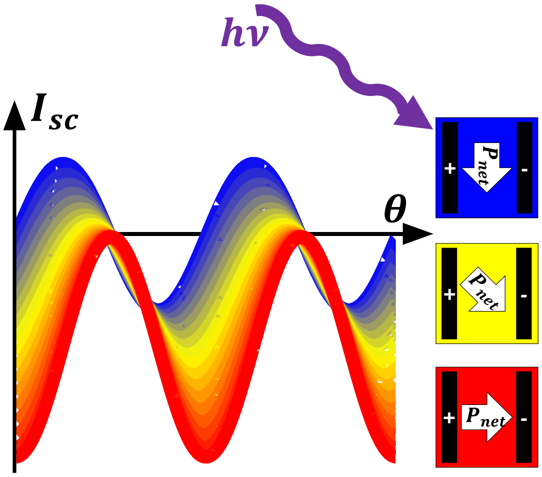
Several studies have demonstrated the role of the electrode interface for the resultant photovoltaic effect in ferroelectric materials.[1] This effect has been utilized to characterize the out of plane polarization.[2] In this work, however, the focus is on the bulk photovoltaic (BPV) effect which is, alike ferroelectricity, a symmetry driven property. The photoresponse of bismuth ferrite thin films with different domain configurations were investigated using an in-plane electrode configuration. The BPV characteristics, viz. short circuit current ($I_{sc}$) as a function of the orientation of the linearly polarized light ($\theta$), are surprisingly sensitive to the change of the domain configuration after applying electric fields (see Figure). This can be attributed to the analogous form of the BPV and piezoelectric tensor. Analysis with previously developed mathematical relations manifested in a model that is capable of estimating the proportion of switched and un-switched regions. The results unravel the potential utility of BPV effect as means to trace the rotation of polarization vectors in areas much larger than can be accommodated in probe-based techniques like piezo-force microscopy.



*Schematic transformation of the bulk photovoltaic response ($I_{sc}(\theta)$) during the rotation of in-plane net polarization $P_{net}$ by applying electric fields*

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# Influence of layer thickness on exchange-spring behavior of $SrRuO_3$-$La_{0.7}Sr_{0.3}MnO_3$ bilayers

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Thin epitaxial bilayers of $SrRuO_3$/$La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$(001) substrates have been suggested to form an exchange spring in $SrRuO_3$ at the interface where strong antiferromagnetic exchange coupling with the adjacent manganite layer is present. We analyze temperature- and field-dependent magnetization data in sample series of systematically varied layer thicknesses of both components grown by pulsed laser deposition on $TiO_2$-terminated substrates. Magnetic switching of such bilayers is strongly different from that of a conventional exchange-bias-coupled bilayer. A model of the interfacial spin structure is suggested as a vertical Bloch wall with gradually increasing out-of-plane spin canting, with in-plane magnetic easy axes at the interface and strained-bulk-like $SrRuO_3$ characteristics in sufficient distance from the interface. Results indicate a maximum extension of the exchange spring of about 10 unit cells (4 nm) into the $SrRuO_3$ layer. We discuss the impact of such interfacial spin textures on magnetic switching as well as on further properties which are important for spintronics applications.

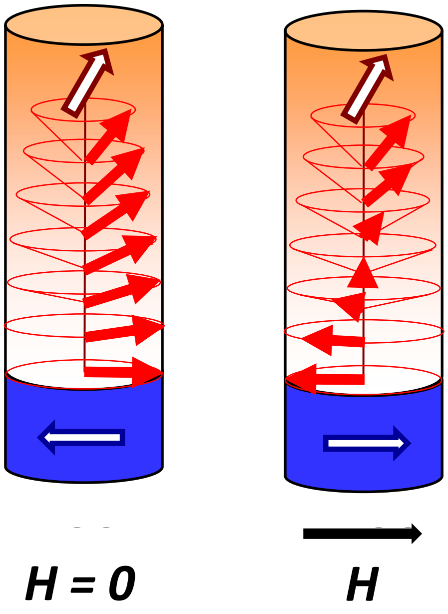

**Fig.1**: Magnetic spring in relaxed ($H$ = 0) and twisted state in an in-plane magnetic field ($H$) at a coherent oxide interface.

The arrows indicate the direction of magnetic moments of Mn (blue layer, $La_{0.7}Sr_{0.3}MnO_3$) and Ru (red layer, $SrRuO_3$).

This spin texture has been suggested for the interface in $SrRuO_3$/$La_{0.7}Sr_{0.3}MnO_3$/$SrTiO_3$(001) bilayers.

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# Phase transition on epitaxially strained $BiFeO_3$ thin films

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The coexistence of ferroic orders with several lattice instabilities makes BiFeO3 (BFO) an interesting material to investigate strain engineering [1]. In particular, a "T-like" phase with giant tetragonality and the highest measured spontaneous polarization among perovskites ($P_S = 150\ \mu C/cm^2$) [2] was revealed for misfit strain of around -4%. Also the coexistence of several polymorphs has been demonstrated in multiferroic BFO thin films grown on highly mismatched substrates [3], leading to a strong temperature dependence of the material structural and ferroic properties.

We report a surface analysis of epitaxial BFO thin films grown on YAlO3 (YAO), LaAlO3 (LAO) and NdAlO3 (NAO) substrates by low energy electron microscopy (LEEM) with a high temperature stability. Each thin film Curie temperature has been determined, increasing with strain above -4.8%.

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# Metal-insulator transition of perovskite neodymium nickelate nanobridges

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Competition between two co-existing electronic phases in first-order phase transitions can lead to a sharp change in the resistivity as the material is subjected to small changes in the driving parameter, *e.g.*, the temperature. One example of such a phase transition is the metal-insulator transition (MIT) in perovskite rare-earth nickelates. When the measurement area of resistance becomes comparable to the domain size of electronic phases around MIT, the nucleation and evolution of domains can strongly affect the shape of a resistance-temperature (*R*-*T*) curve. By measuring the local resistance and the domain distribution of $NdNiO_3$ at nanoscale as a function of temperature, we demonstrate that resistance jumps appearing below the MIT temperature directly correlate with the emergence and coalescence of individual domains. Our observation provides a useful insight into the *R*-*T* characteristic of MIT materials.

# Tailoring $LaTiO_3$ for Mottronics

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3d transition metal oxides exhibit fascinating phenomena - absent in conventional semiconductors - like Mott insulating behaviour due to pronounced electron-electron interactions. The field of Mottronics dreams of harnessing the phase transition between the correlated metal and the Mott insulating phase of such strongly correlated materials for novel electronic devices.

We have recently demonstrated that the prototypical Mott insulator $LaTiO_3$ can undergo the band filling controlled Mott transition if it is chemically p-doped by excess oxygen during thin film growth by pulsed laser deposition[1]. Here we report on the influence of dimensionality in the ultrathin film limit for varying doping levels by photoelectron spectroscopy, tuning the material in the generic phase diagram (correlation strength versus band filling) close to the boundary of the phase transition. Doing so the metal-insulator transition can possibly be triggered by electric field gating.

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# Effect of lanthanum doping on the photoelectronic processes in epitaxial $BaTiO_3$ thin films

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$BaTiO_3$ (BTO) was the first ferroelectric material wherein abnormal photovoltaic effect was observed[1]. Subsequent investigations studied the relation between photoresponse, symmetry and ferroelectric character, which led to the term bulk photovoltaic effect. Doping with La in BTO has been known to affect the ferroelectricity and symmetry[2][3]. However, its impact on the photoreponse and conductivity is still under deliberation.

In this work, BTO thin films with different percent of lanthanum were fabricated by pulsed Laser Deposition (PLD) and characterized by piezo force microscopy (PFM) and X-Ray Diffraction (XRD). Electrical measurements were conducted in vertical and planar geometries. Properties such as photo conductivity and short circuit current were measured and analyzed in respect to La-doping. In conjunction, the states within the band gap were investigated by temperature dependent measurements. The intricate co-relations highlight the impact of doping on the photo electronic processes.

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# Free-standing ferroelectric $PbTiO_3/SrTiO_3$ superlattices

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Ferroelectric oxide thin films and their heterostructures have attracted broad interest on account of their novel physical properties as well as technological applications. In ferroelectric thin films and superlattices, the strong coupling between strain and polarization can be utilized to tune the film properties and induce novel polar phases and functionalities.[1] Within the realm of ferroelectric superlattices, $PbTiO_3/SrTiO_3$ superlattices have been extensively studied as a model system, both theoretically and experimentally. The epitaxial strain imposed by substrates and the complex interplay between the mechanical and electrostatic boundary conditions experienced by ferroelectric $PbTiO_3$ layers give rise to the formation of distinctive domain patterns such as vortex arrays[2] and flux closure domain structures[3], and surprising properties like negative capacitance[4]. However, the mechanical clamping of the films on substrates also restricts many of the film properties and the true potential of strain engineering.

To go beyond conventional strain engineering, $PbTiO_3/SrTiO_3$ superlattices were released from the underlying substrates by selectively dissolving away an epitaxial sacrificial layer[5]. The morphology and the domain structure of the free-standing superlattices were probed by X-ray diffraction, atomic force microscopy, and piezoresponse force microscopy. Upon releasing the substrate-imposed strain, a new complex polarization state with in-plane ferroelastic superdomains formed due to the modified balance between the mechanical and electrostatic boundary conditions. An unexpected local anisotropy in the superdomain morphology was observed and seems be associated with the film curvature arising from the built-in strain gradient across the film thickness.

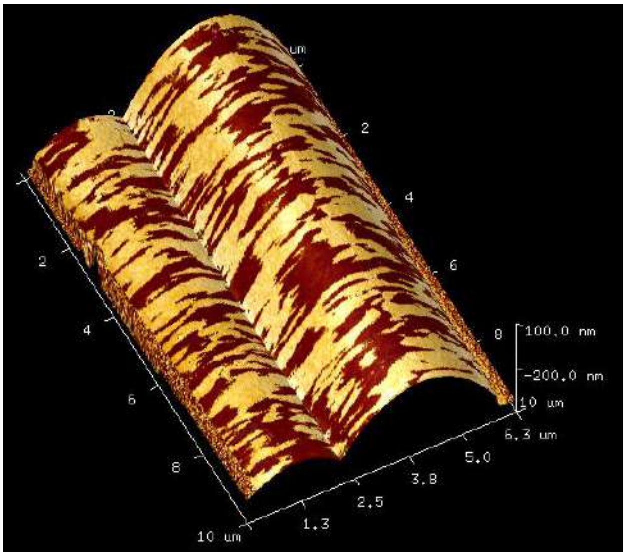

*Figure 1 Piezoresponse Force Microscopy image of a free-standing PbTiO3/SrTiO3 superlattice flake sitting on a Si substrate. Here the lateral PFM phase image is superimposed on the 3D image of the sample topography.*

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# Metal-doped $BaTiO_3$ : synthesis and properties

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BaTiO3 is an insulator with a band gap of 3.2 eV. It can become semiconductor or even metallic when doped with metals or reduced. Aliovalent doping with 3+ ions creates *d*-states in the transition-metal sites, inducing an Anderson-type insulator-to-metal phase transition[1] and oxygen-deficient $BaTiO_{3-\delta}$ can retain ferroelectricity even above the insulator-to-metal transition[2,3].

We have synthesized $BaTiO_3$ ceramics doped with aliovalent $Fe^{3+}$ ions ($Fe_2O_3$) and isovalent (CuO) by ball-milling.

We report on the evolution as a function of temperature of their structure measured by X-ray diffraction, of their dielectric, ferroelectric and electro-mechanical properties as well as of their band gap. Comparison between aliovalent and isovalent doping underline the mechanism at play in metal-doped ferroelectrics.

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# Ferromagnetic Resonance and Inverse Spin Hall Effect in Permalloy/Pt bilayers

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The temperature dependence of magnetodynamical physical effects such as Spin Pumping and Inverse Spin Hall effect (ISHE) has been measured in a set of Py/Pt bilayers as a function of the Pt thickness. Additionally, important physical parameters such as Gilbert damping, saturation magnetization and anisotropy field have been determined as well. We found that the Gilbert damping follows a non-monotonic behaviour with temperature (**Fig. 1**), as reported in other systems [1]. Previous measurements on the temperature dependence of Spin Pumping and ISHE [2] in this system have the serious drawback of requiring the use of complex fabrication process to prepare the samples. In this work we present an easy-to-implement ferromagnetic resonance (FMR) setup for measuring all those effects and parameters straightforwardly. We found that the amplitude of the FMR absorption curves is constant from room temperature to approximately 100K and then it starts to decrease. Because of this reduction, it is of major relevance to normalise the measured ISHE voltage with the FMR absorption amplitude in order to obtain physically coherent results. The resulting normalised ISHE voltage, depicted in **Fig. 2**, follows an inverse linear relation with temperature.

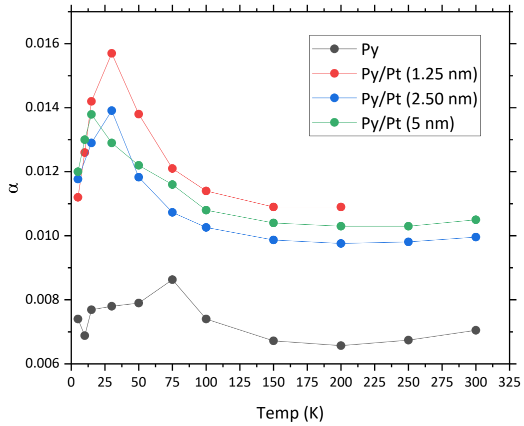

**Fig. 1** Temperature dependence of the Gilbert damping of the Py/Pt system as a function of the Pt layer thickness.

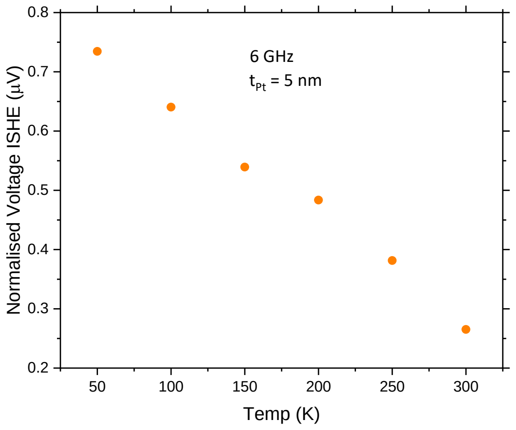

**Fig. 2:** Temperature dependence of the normalized ISHE in a Py (20nm)/Pt (5nm) bilayer at 6 GHz.

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# Epitaxial growth of $RVO_3$ by ozone assisted MBE : Towards multiferroism in $(LaVO_3)_n/(PrVO_3)_m$ superlattices

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Oxides, in particular transition metal oxides with perovskite structure $ABO_3$, attract widespread interest driven by their possible degrees of freedom and their interactions. These lead to a wide range of physical properties (insulator, metallic, superconductor, piezoelectric, ferromagnetic ...) that can be tailored by tuning for example chemical pressure and/or lattice strains. This great versatility offers the opportunity to functionalize these materials in nanometric heterostructures for new electronic devices.

In this class of materials, we are particularly interested in $RVO_3$ rare-earth vanadates (R=La-Lu, Y) the spin ordering temperature ($T_{Néel}$) of which lies in the [100K-150K] temperature range. At higher temperatures, a V $3d$-$t_{2g}$ orbitals ordering is accompanied by a structural transition with a decrease in symmetry, from *Pnma* orthorhombic to $P2_1/m$ monoclinic [1]. In addition to $VO_6$ octahedra rotations, it was predicted by *ab initio* calculations that a rare earth shift could be exploited to introduce hybrid improper ferroelectricity by taking advantage of super-exchange interactions and Jahn-Teller distortions [2]. Our objective is to obtain a multiferroic material by strains modulation and interfaces engineering in $R_AVO_3/R_BVO_3$ superlattices. The systems are grown by co-deposition in a Molecular Beam Epitaxy chamber with controlled ozone pressure. Single films of $LaVO_3$ and $PrVO_3$ have been first synthesized on $SrTiO_3$ (001) substrates. RHEED and X-ray diffraction analysis permit the optimization of the growth window (deposition temperature and ozone pressure) in order to obtain perfectly controlled 2D growth and controlled stoichiometry.

Electronic microscopy (TEM and STEM) experiments performed for the films and $(LaVO_3)_n/(PrVO_3)_m$ superlattices highlight the orthorhombic structure and the 3 growth domains on the square symmetry surface of $SrTiO_3$. We have also been able to observe the $X_5^-$ displacements of rare-earth atoms, thanks to the atomic positions accurate determination and the vertical and horizontal displacements analysis [3] (see Fig.1).

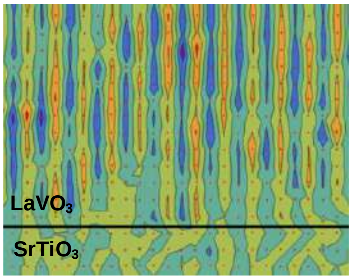

Fig. 1. Mapping of La and Sr cations vertical displacement at the $LaVO_3/SrTiO_3$ interface.

Magnetic measurements (FC-ZFC as well as magnetic field loops) confirm ordering temperatures ($T_{Néel}$) in agreement with stoichiometric bulk compounds. The coming electrical transport measurements should make it possible to determine the multiferroic character of $(LaVO_3)_n/(PrVO_3)_m$ superlattices. These results will constitute a significant advance in the understanding of the electronic properties of oxide-based heterostructures, in particular for the emergence of their ferroelectric and multiferroic characters.

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# Antiferroelectricity and ferroelectricity of $PbZrO_3$ and $BiFeO_3$-based sol-gel films

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The interest for antiferroelectric materials has been increasing over the last years, largely because of their potential for high-energy storage **[1]** and electrocaloric **[2]** applications but also because they still are insufficiently known compared with ferroelectrics. The model antiferroelectric in inorganic perovskites is $PbZrO_3$. However, research is shifting away from lead-based materials, hence the interest in $BiFeO_3$-based antiferroelectrics. As is, $BiFeO_3$ at room temperature is a ferroelectric but substituting bismuth by a rare-earth such as lanthanum, samarium or neodymium could change the structure to a non-polar *Pbam* phase allowing antiferroelectricity **[3]**.

In this study, we synthesize and characterize polycrystalline films of $PbZrO_3$ and $Bi_{1-x}La_xFe_{0.95}Mn_{0.05}O_3$. These samples have been processed via chemical solution deposition on $Pt/TiO_x/SiO_2/Si$ substrates, with a process derived from our previous work on deposition of $Pb(Zr,Ti)O_3$ films **[4]**. Nitrates-based route was adapted to prepare $(Bi,La)(Fe,Mn)O_3$ films **[5]**. The film quality has been assessed by XRD, SEM and electric measurements. Composition and oxidation states were checked by XPS. Manganese substitution was found a successful way to reduce leakage currents in the Lanthanum-doped $BiFeO_3$ system. The ferroelectric (resp. antiferroelectric) properties of the films are demonstrated.

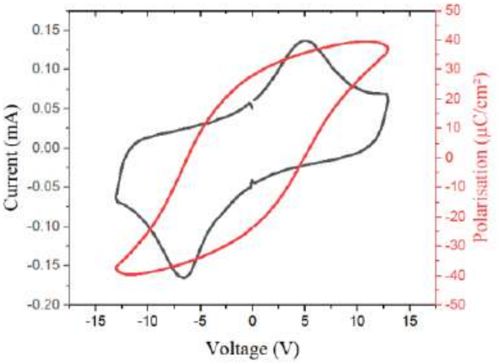

Figure 1. Characteristic I-V curve and ferroelectric polarisation hysteresis of a 250 nm-thick film of $Bi_{0.8}La_{0.2}Fe_{0.95}Mn_{0.05}O_3$

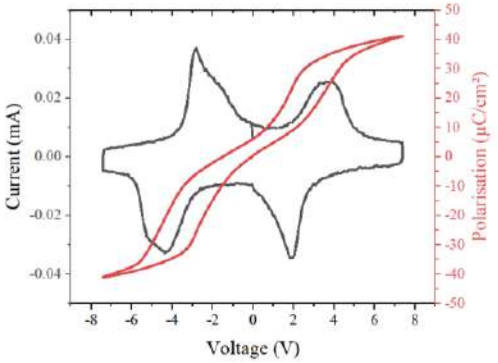

Figure 2. Characteristic I-V curve and antiferroelectric polarisation hysteresis of a 200 nm-thick film of $PbZrO_3$

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# Quasi-2DEG at Al/STO and Al/KTO heterointerfaces

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Since the discovery of the formation of a high-mobility quasi two-dimensional electron gas (q2DEG) at the interface between $LaAlO_3$ and $SrTiO_3$ *[1]*, this system has been shown to exhibit a wide array of properties. In particular, its Rashba spin-orbit coupling (SOC) can be harnessed to achieve very efficient spin-charge conversion *[2]*. This makes this q2DEG interesting for future technological applications such as the MESO logic device proposed by Intel in which a SOC element is needed to convert spin currents into charge currents *[3]*.

In parallel, some other oxide material systems have also been found to host a q2DEG. Examples include q2DEGs based on $SrTiO_3$ *[4]* as well as on $KTaO_3$. In contrast to the case of depositing (≥ 4 u.c.) $LaAlO_3$ on $SrTiO_3$ ($TiO_2$-term), the essential ingredient for the formation of q2DEG in most of these other systems is the formation of oxygen vacancies near the interface *[5]*. This is a process that takes place spontaneously when depositing on this type of substrates elements such as Al, with a great affinity for oxygen. Here, we have deposited Al by sputtering onto $SrTiO_3$ and $KTaO_3$ and studied the formation of the q2DEG. Compared to the well-known $LaAlO_3$ / $SrTiO_3$ system, this approach is more scalable since it does not require a termination of the substrate in specific atomic planes and it is possible to perform the deposition of Al by sputtering, which is applicable to large area wafers.

In this work we have studied the evolution of the valence states with the thickness of Al deposited and their distribution in depth by in situ XPS, as well as the influence of the Al thickness on the transport properties. We will discuss these results with a view towards determining the optimal Al thickness in terms of (i) being sufficient to protect the Q2DEG from re-oxidation (min. thickness), (ii) allowing the passage of (spin) current through the formed $Al_2O_3$ barrier (max. thickness) and (iii) achieving good q2DEG transport properties.

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# Strain-induced magnetization control in a LSMO/BTO heterostructure

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The possibility of controlling magnetic properties through external parameters such as electric field or structural variations is a fascinating field of research both for the interplay of several physical properties between different materials [1] and for possible technological implementations [2]. Indeed, multiferroic heterostructures, integrating individual ferroelectric and ferromagnetic materials, are gaining interest in the scientific community as possible spintronic devices [3].

Here we provide experimental evidence, and supporting density functional theory analysis, of a transition in $La_{0.65}Sr_{0.35}MnO_3$ (LSMO) thin film to a stable ferromagnetic phase, that is induced by the structural and strain properties of the ferroelectric $BaTiO_3$ (BTO) substrate, which can be modified by temperature or applying external electric fields [4]. X-ray magnetic circular dichroism measurements on Mn L edges show, in fact, two magnetic transitions as a function of temperature that correspond to structural changes of the BTO substrate. We also show that ferromagnetism, absent in the pristine condition at room temperature, can be established by electrically switching the BTO ferroelectric domains in the out-of-plane direction.

These observations can be explained as the effects of a strong interplay between the structural properties of the BTO substrate, resulting in variations of the LSMO thin layer strain, and the magnetic properties of the latter.

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# Photoexcitation processes in self-assembled layered $PbTiO_3$ thin films

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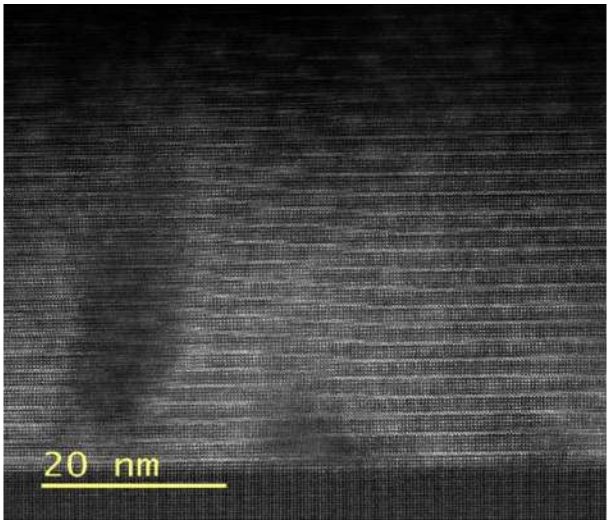
The bulk photovoltaic effect arising from shift-current mechanism in ferroelectric oxides has attracted immense attention ever since strategies to overcome the biggest hurdle-– inherent high bandgap – have been employed in $[KNbO_3]_{1-x}$ $[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ [1]. *Ab intio* studies conducted with $PbTiO_3$ system suggest coupling between cation and oxygen vacancy essential for this purpose. One route to achieve and stabilize such coupling involves nanolayering mediated by cation ordering which poses a severe challenge for experimentalists. [2]

Inspired by this challenge and the preceding work, we deposited single crystalline thin films of $PbTiO_3$ doped with Bi, Ni, Nb epitaxially on single crystal $SrTiO_3$, $LaAlO_3$ and scandate substrates by pulsed laser deposition using a single ceramic target. The structural properties of the resulting films were investigated by high-resolution X-ray diffraction and transmission electron microscopy. Besides high degrees of phase purity and crystallinity, a long range structural ordering along the [001]-direction was observed, corresponding to a self-assembled layered superstructure with a period length of a few nanometers. The photoexcitation processes in these novel structures were investigated by conducting transport measurements over a broad range of temperature and in different charge collection geometries.



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# Energy Efficiency of Electro-Caloric Materials

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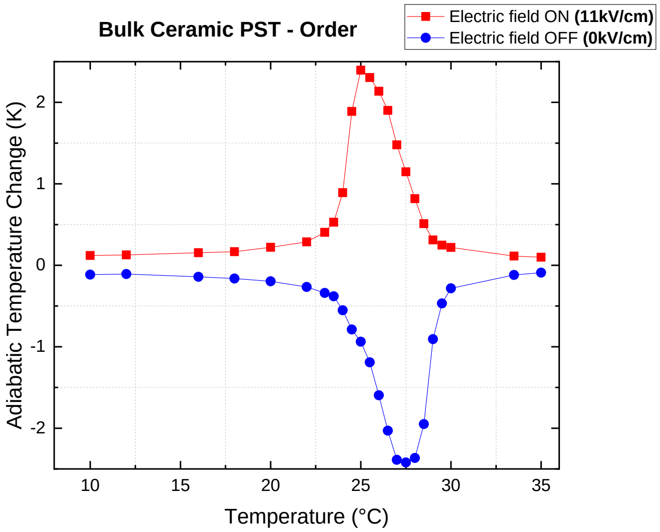
How energy efficient are electro-caloric (EC) materials for future cooling devices? This question has barely been studied particularly directly. An EC material is a dielectric material, which exhibit adiabatic temperature change or isothermal entropy when triggered with an electric field. The application or removal of the electric field results respectively, in the heating or cooling of the EC material under adiabatic conditions. This adiabatic temperature change $\Delta T_{\mathrm{ad}}$ is higher near the phase transition in most electro-caloric materials [1-4]. So far, research on EC materials have been focused on the performance of the EC materials i.e increasing the adiabatic temperature change [5-8] and, developing EC prototypes [6-7]. However, the energy efficiency of EC materials has been overlooked especially using direct methods [9]. In comparison to the Carnot efficiency of different cooling technologies [10], EC systems stand out as one of those able to overtake the most used vapour compression systems [9]. In addition, their ecofriendly features: noiseless (compressor-free) and greenhouse gases free make them promising for future cooling devices. The dimensionless materials efficiency, called *EC efficiency*, is the ratio between the heat generated and the electrical work needed to trigger the EC effect [11]. This is defined as a tool to compare how energy efficient are different caloric materials [9] [11]. By direct measurements of heat using infra-red (IR) camera, DSC, and electrical work, we will determine the EC efficiency of three excellent EC materials: PST, PZO, BZTO. These measurements will be done on different type of samples: bulk ceramic, multi-layer capacitors (MLCs) and thin films. We observe a $\Delta T_{\mathrm{ad}}$ of 2.4 K in both bulk ceramic and MLCs PST. A comparative study on efficiency of different caloric materials worked out indirectly and directly will be discussed. Our study gives an insight into the efficiency of EC materials and helps to rank excellent candidate for future efficient EC cooling devices.



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# Charge-Transfer Characteristic Lengths in Correlated Oxide Heterostructures

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Using interlayer interactions to control functional heterostructures with artificial atomic-scale designs has become one of the most effective interface-engineering strategies nowadays. Here, we demonstrate the effect of the crystalline $LaFeO_3$ (LFO) buffer layer on two sets of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructures with different characteristic lengths of interlayer charge transfers. The LFO buffer layer acts as an energy-favoured electron acceptor in both LAO/STO systems, resulting in modulations on interfacial carrier densities and thus metal-to-insulator transitions (MITs). The 3-and 6-unit cells, LFO-thickness-induced MITs are found in the amorphous and crystalline LAO/STO heterostructures respectively. The different critical LFO thicknesses are explained in terms of distinct characteristic lengths of the redox-reaction-mediated and polar-catastrophe-dominated charge transfers, which are controlled by interfacial atomic contact and Thomas-Fermi screening effect, respectively. Our results shed some light on not only understanding but also modifying interlayer charge transfers across oxide heterostructures based on buffer-layer engineering.

# Ferroelectric control of a 2DEG: Towards artificial graphene heterostructures

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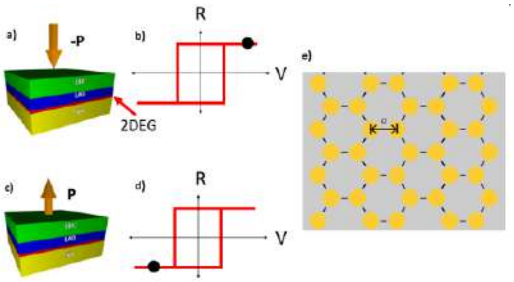
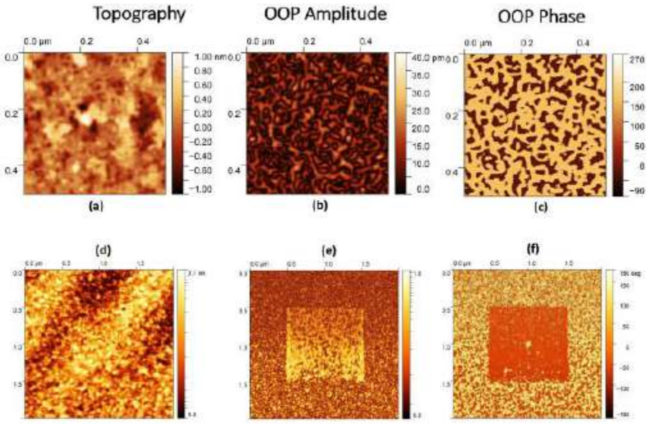
This project aims to bring together two of the most impactful oxide material systems together such that we can design artificial graphene. Artificial graphene can be defined as a designed lattice with hexagonal symmetry for electrons, atoms, or photons such that a Dirac cone emerges in the band structure. This is a useful tool to tune the parameters (such as tunnelling of quasiparticles) in a way that is not possible using real graphene [1]. By depositing the well-known room-temperature multiferroic $BiFeO_3$ (BFO) on top of the $LaAlO_3/SrTiO_3$ (LAO/STO) 2D electron gas (2DEG) system [2,3], we aim to use the 2DEG as a bottom electrode to ferroelectrically write a honeycomb lattice. Under the assumption that the 2DEG sheet resistance is dependent upon the projection of the BFO polarisation along the z-axis directly above it (Figure 1a, b, c, d), the 2DEG resistance would be modulated in space with periodicity equal to a honeycomb lattice (Figure 1e), thereby creating an artificial graphene.





Using *in-situ* Reflection High Energy Electron Diffraction (RHEED) to control the number of LAO layers, a series of BFO/LAO//STO heterostructures have been fabricated. The as-grown ferroelectric domain structure has been found to be fundamentally different from stripe domains typically observed for BFO when grown on STO (Figure 2a, 2b, 2c), and we have successfully been able to ferroelectrically pole the BFO using the LAO/STO 2DEG as a bottom electrode (Figure 2d, 2e, 2f).

The next steps are to measure transport characteristics of the 2DEG and to quantify the sheet resistance change between up and down polarisation states. Once this has been established, a honeycomb lattice can be constructed to implement artificial graphene.

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# Metal-insulator transition in $SrIrO_3$ controlled by doping

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Perovskite $SrIrO_3$ (SIO) is a narrow-band semimetal, which combines strong spin-orbit coupling and electron correlations, properties that open the possibility to explore new emergent phenomena. This system has also attracted much attention because it is at the verge of a Mott transition [1] and a ferromagnetic instability [2]. Epitaxial SIO ultra-thin-layers show a metal-insulator transition (MIT) that is thickness dependent [3]. This transition can be controlled by strain. We have explored the MIT in SIO ultrathin-layers using Electric Double Layer (EDL) techniques, that employ ionic liquid as gate dielectric. This technique allows us to modify the carrier concentrations to extremely high levels, up to one electron per formula unit. In this way, we can stabilize novel phases in strongly-correlated systems. We have simultaneously measured longitudinal (magneto) resistance and Hall effect for different doping levels. Thus, increasing the carrier concentrations, we are able not only to modify the transition temperature, but also to reach an insulating state with a strong temperature dependence on the resistance. This insulating state also exhibits hysteretic-magnetoresistance and anomalous Hall effect at low temperature, characteristics that indicate ferromagnetic order.

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# Doping of ferroelectric K0.5Na0.5NbO3 epitaxial films using PLD

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KxNa1-xNbO3 is a lead-free ferro- and piezoelectric compound, which offers a high potential for memory applications and sensors in thin film form. However, growth of KxNa1-xNbO3 thin films is very challenging due to the high volatility of alkaline components at high temperatures. In this respect, pulsed laser deposition (PLD) appears as a suitable method for the epitaxial growth of K0.5Na0.5NbO3 films. An important requirement for this technique is the use of suitable targets. Therefore, an optimized K0.5Na0.5NbO3 target preparation routine for the growth of stoichiometric thin films is developed. For that purpose, powders with an alkaline excess of 5% are pressed into targets and subsequently a two-step sinter routine based on solid state sintering ensures the formation of a pure perovskite phase. Here, a calcination step at 850 °C and a subsequent sinter step at 1050 °C are executed.

Aliovalent doping in KxNa1-xNbO3 ceramics has been reported to have a significant impact on electrical properties of the material, however, studies on thin films are rarely published. Therefore, doped and undoped K0.5Na0.5NbO3 targets were prepared and applied for thin film growth by PLD. For that purpose, also the impact of Cu- and Mn-doping on the sinter procedure of K0.5Na0.5NbO3 has been studied by means of differential thermal analysis. Finally, under optimized growth conditions, deposition of K0.5Na0.5NbO3 thin films resulted in well-ordered epitaxial films. The impact of Cu- and Mn-doping on thin films has been studied with respect to structural and electrical properties of the films.

# Magnetic and magnetoelectric properties of selected $BiFeO_3$-based multiferroic ceramics

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Recently, multiferroic materials have been the subject of intensive research because of their interesting physical properties as well as variety of potential applications. They exhibit magnetoelectric coupling, which allows controlling of magnetisation by an external electric field, or induction of electric polarisation by applying an external magnetic field [1-2]. One of the most promising and most intensively studied multiferroic material is $BiFeO_3$. This is a rare example of a single-phase material in which ferroelectricity and antiferromagnetic ordering coexist at room temperature. However, the existence of spin cycloid in this compound inhibits a linear magnetoelectric effect [3]. Many current investigations tend to destroy the spin cycloid and to release the inherent magnetization and magnetoelectric coupling in order to improve multiferroic properties of $BiFeO_3$. Thus, many current scientific efforts tend to destroy the spin cycloid and to release the inherent magnetization in order to improve multiferroic properties of $BiFeO_3$.

This work presents investigations of $Bi_5Ti_3FeO_{15}$ compound and the family of $Bi_{1-x}Nd_xFeO_3$ solid solutions prepared by solid-state sintering method. Phase composition and structure of the materials were investigated using X-ray diffraction technique. Vibrating sample magnetometry and Mössbauer spectroscopy were used to study magnetic ordering in the samples. Special attention was paid to magnetoelectric effect measurements. In particular, the experimental set-up which allows us to measure the value of magnetoelectric coupling coefficient was introduced [4]. Moreover, the influence of Nd ions substitution on multiferroic properties of $BiFeO_3$ was discussed.

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# Influence of nanostructurization processes on ferrite oxides

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Ferrite oxide magnetic nanostructures show a high potential for numerous present and future applications, especially in spintronics and biotechnology. Properties of materials are determined by size, dimensionality, symmetry and interface effects. By regulating those parameters, the influence on magnetic reversal processes and/or spin and electron transport phenomena can be exerted. In order to achieve high-performance devices, the understanding and control of nanostructurization processes are required. Despite enormous scientific and industrial engagement in the study and development of spintronic structures made using magnetic oxides, the effects of nanostructurization have not yet been fully addressed experimentally.

Magnetic properties are strongly dependent upon the direction and size of the easy magnetic axis, which is determined by the magnetocrystalline anisotropy (MCA) and shape anisotropy (via stray field). In the case of nanostructures, the smaller the size of features, the stronger is the surface and shape anisotropy. Due to the inherent weak MCA of ferrite oxides, nanostructurization could be a path-way for enhancing the magnetic anisotropy in such materials. However, processes such as electron lithography (e-Beam) and Focused Ion Beam (FIB) used in the nanostructurization proccesess could however hinder this

We have studied a set of ferrite oxide nanostructures in order to assess the impacts of the fabrication on their magnetic properties. Epitaxial layers were obtained by means of Pulsed Laser Deposition (PLD), nanostructured by e-Beam combined with ion etching, and direct lithography using $Ga^+$ Focused Ion Beam. Their magnetic properties, local structure and electronic configuration were studied using VSM, 1s2p HERFD XAS and 1s2p RIXS-MCD at the iron K-edge.

**Acknowledgments**: This work was supported by National Science Center of Poland (grants: 2014/14/E/ST3/00026 and 2015/17/D/ST3/00968).

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# Photo-electronic processes in $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films.

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$Pb(Zr,Ti)O_3$ (PZT) is the most widely used ferroelectric and piezoelectric material and finds application in a variety of sensors and actuators. As a result, several studies have been dedicated to understand and manipulate the associated ferroelectric character. However, most of the pathways that have been explored in this regard, such as post-growth cooling regimes, strain control of a/c domain population and purity starting materials, can also have a direct impact on the photoelectronic processes.

Here we show on how a below bandgap light can help us in understanding the properties of sub-band levels and its activation within the forbidden bandgap of as-grown $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films. X-ray diffraction (XRD) results helps us in understanding the difference in the crystal structure, obtained by controlling growth related aspects. Piezo-response force microscopy (PFM) helps in characterizing the domain structure of $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films. Temperature resolved transport measurements help in understanding the existence of sub-bandgap levels and associated activation energies. The role of embedded domain walls (90 and $180^o$ domain walls) on the resulting photo-electronic properties will be discussed. Eventually, efforts will be made to investigate the prerequisite conditions for the manifestation of photovoltaic and Ferroelectric effect in these films.

# Photoinduced Current in ferroelectric devices

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Ferroelectrics are typically materials with high dielectric constants, leading to applications as capacitors. They carry a spontaneous electric polarization that can be switched between up and down states using an electric field.[1] This switchability is exploited in ferroelectric-based non-volatile memories and logic devices. Most of the time, the electrical polarization couples strongly with elastic strain, making ferroelectrics good piezoelectrics suitable as sensors, transducers, micro-electro-mechanical systems (MEMS) or very precise actuators.[2]

Recently, ferroelectric thin films have also been investigated for photovoltaic applications.[3] Their remanent polarization and depolarizing field can efficiently separate photogenerated electron–hole pairs, unlike conventional systems based on a potential barrier at p–n materials junctions, thus leading to a large and switchable open circuit voltage whose sign can be controlled by the direction of polarization.[4,5]

In my work ferroelectric polarization and short circuit photocurrent are studied for a (Pt/PbZrTiO3(52/48)/SrRuO3//SrTiO3) capacitor geometry, where Pt and SRO are top and bottom electrode respectively. The photocurrent was measured as a function of time, voltage and wavelength in PZT (130nm) epitaxial thin film. The magnitude and sign of the photocurrent is strongly dependent on the polarization state/prepolarisation voltage. This study shows the possible relation between short circuit photocurrent, polarization, depolarizing field and internal field.

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# Engineering erbium-doped oxide thin layers for integrated optics

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Yttria-Stabilized Zirconia (YSZ) is known to be a thermal and chemically stable functional oxide with a refractive index of about 2.12, which allows good light confinement of the optical mode. Moreover, it has a large optical energy bandgap avoiding two photon absorption (TPA) in near and mid IR and its transparency covers the wavelength range from visible to mid-IR. Additionally, Kerr effect has been recently demonstrated. While these optical properties are crucial for various applications including on-chip optical communications and sensing, YSZ has remained almost unexplored in photonics. In this regard, we recently demonstrated YSZ waveguides with propagation losses as low as 2 dB/cm at a wavelength of 1380 nm [1].

In this work, yttrium-to-erbium substitution is performed in the Yttria-Stabilized Zirconia (YSZ) crystal, so the Er-doped YSZ system allows a nearly perfect allocation of Er ions in the host matrix caused by a similar atomic radius between Y and Er.

We report on the optical and structural properties of Er-doped YSZ thin films showing strong emission at 1.53 and 1.536 µm under a continuous-wave pump laser excitation at about 980 nm. The observed outstanding luminescence will be analyzed and discussed. These results pave the way towards the implementation of new rare-earth-doped functional oxides into hybrid photonic platforms in a customized and versatile manner, adding new functionalities including light amplifiers that may be instrumental for nanophotonics applications.

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# Vortex-like polarization in ferroelectric ultrathin films

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Recent discovery of polarization vortices in PbTiO3/SrTiO3 superlattices attracts enormous interests in the field of condensed matter physics[1,2].

The complex effect that epitaxial strain and electrical boundary conditions can have on a ferroelectric thin film causes it to display new and exotic polarization topologies which are otherwise too energetically costly to form in the bulk ferroelectrics.

Density functional theory calculations within the generalized-gradient-approximation were used to study the polarization pattern in free standing $\mathrm{PbTiO_3}$ ferroelectric films of different thickness, where the screening effects of electrode are absent. Starting from an initial configuration of 180 degrees domains, flux-closure domains or vortex-antivortex patterns are formed depending on the size of the system. The figure below shows the curling of polarization which is an effective way to stabilize the ferroelectric state for a system with uncompensated surface charges.

We also studied the effective band structure of the ferroelectric system with different domain structures, i.e. flux-closure, vortex-antivortex and 180 degrees domains. Results show that there are states within the band-gap which are related to the closure aspect of domain formation while a vortex-antivortex pair induces states furthest away from the valence maximum.

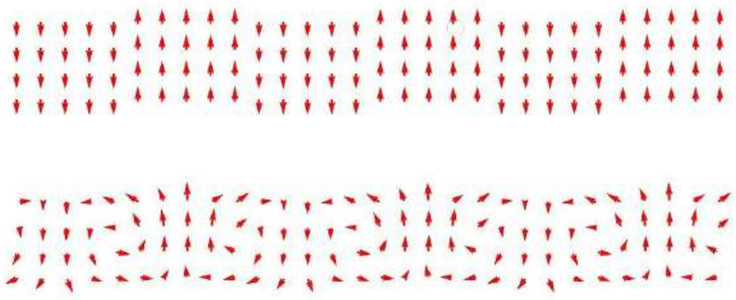

Figure 1. Initial polarization distribution(top); polarization after structural relaxation(bottom)

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# One to two-band superconductivity transition driven by gate voltage at an oxide interface

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The two dimension electron gases (2DEG) at the two band-insulator oxide interface LaAlO3/SrTiO3 interface, first discovered in 2004 [1] have raise interest because it can host multiple electronic state such as metallic, insulating or superconducting, and its properties are tuneable with a gate voltage [2][3]. It is believed that 2D confinement, in addition to the peculiar dielectric properties of SrTiO3, is responsible for the existence of such exotic 2DEG.

In this context, we've probed the superfluid stiffness of the condensate in the (110)-oriented LaAlO3/SrTiO3 interface using resonant micro-wave experiment at dilution temperature. Our work provides evidence of a transition between a single condensate to two-condensate superconductivity, driven by continuous and reversible electrostatic doping. This transition corresponds to the fillings of a higher energy 3d-t2g band of a different symmetries with respect to the confinement direction, according to the numerical simulation of the quantum well. We find that the superconductivity gap is suppressed as the second band is populated. Such behaviour is not expected in the Bardeen-Cooper-Schrieffer theory and can be explained using repulsive coupling between the condensate, characterized by an opposite sign in the order parameter [4]

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# First and second principles study of non-collinear magnetism in rare-earth orthoferrites

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The rare-earth orthoferrites ($RFeO_3$, with R = rare-earth) were discovered in the 1940's and quickly attracted great interests due to their unique magnetic properties. Recently, there has been a renewed interest in these materials because of observed multiferroicity. Due to the presence of two magnetic sub-lattices and their non-trivial interactions, interesting magnetic structures and magnetic phase transitions are observed *i.e.* spin reorientation, magnetization reversal, weak ferro-magnetism and magneto-electricity. Studying and understanding the microscopic origin of these different properties is of great importance in designing and optimizing their useful responses and to get more fundamental understanding of the underneath physics.

In this work we have used density functional theory (DFT) to study these materials. We have mapped the DFT calculations to Heisenberg model Hamiltonian to find different magnetic interactions including exchange, Dzyaloshinskii-Moria (DM) and single ion anisotropy. To study the magnetic behaviour as a function of temperature, the parameters calculated from DFT, used to do atomistic spin dynamics to calculate Neel temperature and study resulting non-collinear magnetic ordering.

We have also studied the DM interactions in these structures to find the relation between different structural distortions and the resulting non-collinear magnetism for each of the sub lattices.

# Topotactic transition mechanisms in $SrCoO_{2.5+x}$ films

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Transition metal oxides are a big research topic, because they offer a wide range of possible applications, particularly in information and energy technology. One such system is strontium cobaltite ($SrCoO_{2.5+x}$), which exists in two distinct topotactic phases, depending on the oxygen content. SrCoO3 is a ferromagnetically ordered metal with a Curie temperature of 305 K, but the system becomes an antiferromagnetic insulator with a Néel temperature of 570 K, when the oxygen content is decreased to $SrCoO_{2.5}$. Along with this magnetic transition, the structure changes from perovskite to the orthorhombic brownmillerite, with the missing oxygen atoms forming vacancy channels [1]. Because of the multivalent Co states and high oxygen mobility it is a promising material for device applications [2]. To control the oxygen content, several possibilities exist. We focus on annealing in oxidising conditions and applying variable strain with a piezoelectric substrate to the film.

We grow thin films of $SrCoO_{2.5}$ by molecular beam epitaxy on $SrTiO_3$ and LSAT substrates for investigations of oxygen annealing induced transitions and $0.7(Pb(Mg_{1/3}Nb_{2/3})O_3)$-$0.3(PbTiO_3)$ (PMN-PT), a piezoelectric substrate, to study the possibility of a strain dependent oxidation state.

To be able to successfully control the oxidation state and transfer strain from the substrate to the film, a high sample quality and epitaxy is mandatory. Thus, we present the results of the film growth and quality, as well as first results of the magnetic characterisation by SQUID and neutron reflectometry for annealed and strained samples.

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# The polarization switching mechanism in polycrystalline ferroelectric/ferroelastic materials

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Ferroelectrics find application in numerous devices and are considered as vital parts of emerging new areas, such as robotics, nanoelectronics and energy harvesting. The fundamental properties of these materials are intimately related to the unique ability to switch the polarization direction with electric fields. However, theoretical and experimental reports are inconsistent regarding the individual events that take place during switching. For example, theoretical models consider that switching in polycrystalline ferroelectric materials takes place by one event occurring at a characteristic switching time [1] or over a distribution thereof, while experimental evidence indicates the presence of multiple steps [2].

To address this issue, we simultaneously measured macroscopic polarization and strain dynamics over a broad time range using high voltage pulses on a model polycrystalline ferroelectric $Pb(Zr,Ti)O_3$ system. Complemented by in situ time resolved diffraction and Landau free energy calculations the sequence of individual switching events could be revealed [3]: initial non-180° domain wall movement from the poled state triggers the main switching phase due to an interplay between local electric and mechanical fields. In the main switching phase >60% of the polarization reversal occurs by 180° or synchronized strain-free non-180° switching events. This is followed by creep-like non-180° domain wall movement, whereby the polarization vector is parallel to the applied electric field. Field-dependent measurements of characteristic switching times allow the determination of the activation barriers of individual events, which are important for micromechanical simulations. Moreover, a strong time correlation of non-180° switching events in different grains was observed, which contradicts the general assumptions made in statistical models. Based on these new insights into polarization reversal novel theoretical approaches, which allow to quantify the contribution of non-180° domain switching events as 34% were developed [4]. Moreover, an improvement of ferroelectric properties may be obtained by a targeted manipulation of individual switching events.

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# Magnetism of $AgFeO_2$ delafossite seen by Mössbauer spectroscopy

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Delafossites with $ABO_2$ structure are a relatively well-recognized group of ternary oxides. They have a unique pseudo-two-dimensional crystal structure, initially observed for the mineral $CuFeO_2$, formed by two alternating layers. One consists of the close-packed monovalent $Cu^+$ or $Ag^+$ ions, and the latter comprises edge-shared $FeO_6$ octahedra. The delafossite structure can form two polytypes depending on the orientation of layers in stacking, i.e., the rhombohedral 3*R* type (space group *R*-3*m*) and the hexagonal 2*H* type (space group $P6_3/mmc$) [1]. $AgFeO_2$ possess two magnetic transitions which are dependent on polytype. The first transition from paramagnetic to collinear magnetic ordering is registered at $T_{N1}$=18K for 2*H* and $T_{N2}$=9K for 3*R* polytype. Whereas, the second change to cycloidal magnetic ordering is seen at $T_{N2}$=11K and $T_{N1}$=15K, respectively. The appearance of the cycloidal magnetic orderings for both polytypes below $T_{N2}$ causes the emergence of the electric polarization, which classifies$AgFeO_2$ as II-type multiferroic [3].

In this work, we present the results of $^{57}$Fe Mössbauer spectroscopy (MS) and vibrating sample magnetometer (VSM) studies of $AgFeO_2$ prepared by the co-precipitation method. The spectra were measured in a wide range of temperatures, including the points of both magnetic phase transitions (at $T_{N1}$ and $T_{N2}$), as well as at room temperature. Structural investigations carried by X-ray diffraction confirmed obtaining pure delafossite phase of $AgFeO_2$. According to Mössbauer measurements carried out at room temperature material was in the paramagnetic state. Below $T_{N1}$ Zeeman sextets appeared. All patterns below $T_{N1}$ are complicated and cannot be considered as the superposition of several Zeeman components. Hence, the spectra were fitted by hyperfine magnetic field $B_{hf}$ distriubution with the assumption of relatively strong corelation between $B_{hf}$ and and quadrupole shift $2\varepsilon$. Magnetic measurements were performed using vibrating sample magnetometer. Temperature dependence of magnetization shows several peaks in the low-temperature region, which confirms the results of MS investigations

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# Stoichiometric optimization on pyrochlore iridate epitaxial film

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Recently, pyrochlore iridate ($R_2Ir_2O_7$, R=rare earth) have drawn wide interest due to possible existence of Weyl-semimetllic ground state (WSM) and associated physical phenomena. [1] Furthermore, B. J. Yang *et al* theoretically predicted that WSM and related topological phenomena can appear in the $R_2Ir_2O_7$ thin film. [2] Therefore, numerous theoretical and experimental efforts were focused on fabrication of high-quality $R_2Ir_2O_7$ films to verify the WSM and related topological phenomena.

Despite intensive attempts, the deposition of high-quality $R_2Ir_2O_7$ is notorious for its difficulties. [3] The main difficulty of high quality $R_2Ir_2O_7$ deposition is the iridium volatility and dissociation during the growth. Iridium volatility and dissociation can create three phases ($IrO_2$ solid, Ir metal, $IrO_3$ gas) depending on thermodynamic parameters (temperature and oxygen pressure). Furthermore, from prior report on $IrO_2$, the growth window of $R_2Ir_2O_7$ film is very narrow; therefore, the stoichiometry of the film is very sensitive to the thermodynamic parameters. [4]

Nonetheless, we succeed in the *in-situ* epitaxial growth of $Nd_2Ir_2O_7$ thin film on yittria stabilized zirconia (YSZ) [111]. The film was grown by using pulsed laser deposition (PLD), dual target method, and “repeated rapid pulse annealing” to avoid Iridium volatility and dissociation. The film is grown at low temperature, forming amorphous layer of $Nd_2Ir_2O_7$, and the temperature ($T_f$) is rapidly raised to form crystalline. From unique film growth technique, the high quality fully strained $Nd_2Ir_2O_7$ thin film was obtained.

Although the thermodynamic parameters optimization would be very plausible, the pulse ratio between two targets can be consider as one of critical parameters for $Nd_2Ir_2O_7$ film growth. Here, we varied pulse ratio between two targets and studied its impact on film stoichiometry. The following characterization techniques were used to observe stoichiometric transition: X-ray diffraction (XRD) and temperature dependent resistivity. The XRD patterns and the resistivity curves reveal the transition from $Nd_3IrO_7$ to $Nd_2Ir_2O_7$ phase, which implicate the pulse ratio is another critical parameter. Finally, we observed the anomalous hall conductivity in the $Nd_2Ir_2O_7$ thin film, which can arise from cubic symmetry breaking and incomplete cancellation of chern vectors in Brillouin zone.

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# Molecular functionalization of ferroelectric oxide surfaces

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Properties of ferroelectric thin films are intrinsically entangled to their surface chemistry, essentially mediated by screening mechanisms trying to compensate bound polarization charges, which produce an electric field opposing the bulk polarization. In general, the orientation of polarization greatly determines the composition of adsorbates present on a ferroelectric surfaces as well as their sticking coefficients [1,2]. In the case of thin ferroelectric films, interfacial electrochemical effects can become dominant, creating permanent imprints to bulk ferroelectric polarization [3] or fixing polarization direction. Up to now, focus has been placed on the interplay of adsorbates that normally exist in ambient conditions on ferroelectric surfaces, such as water molecules and carbonates, known to play a critical role as external screening agents as dipole molecules and also by providing ionic species after dissociation [1,2]. Still, the composition of adsorbates layers in ambient conditions shows a low level of control and reproducibility since it is strongly dependent on the history and storage conditions of the samples and moreover, it leads to remarkable aging of ferroelectric polarization. An alternative to prevent environmental damage of ferroelectric surfaces is to gain control on the adsorbate layer by the molecular functionalization of surfaces, providing the right chemical stability while keeping enough electrochemical reversibility to allow ferroelectric polarization switching.

In this contribution we will show our initial results on $BaTiO_3$ thin films functionalized with self-assembled layers (SAMs) of organic and electronically active molecules. The combined use of Piezoelectric Force Microscopy (PFM) and Kelvin Probe Force Microscopy (KPFM) enabled us to study ferroelectric properties of thin films and their surface composition respectively. In this sense, we were able to probe the presence of the molecules on the surfaces on the base of KPFM measurements that revealed the difference in work function between functionalized and bare $BaTiO_3$ thin films. Local hysteresis loops were probed by Switching Spectroscopy PFM (SS-PFM) measurements, whereby an increment of coercive fields of about three times was observed upon molecular deposition. We observed that organic molecules tend to protect the polarization of $BaTiO_3$ thin films in both directions, while keeping ferroelectric switchability. Further efforts will be made toward adsorption control of structurally similar molecules such as differently substituted benzene rings as well as to the elimination of atmospheric adsorbates that are always present in ambient conditions.

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# Improved Switching Stability and Resistance Ratio in $SrTiO_3$-based Resistive Switches by Ni Nanoparticle Exsolution

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Resistive switching emerges as a promising alternative to classical transistor-based computer memory architectures. In order to enable mass adoption of this technology, it is of utmost importance to ensure stable long-term performance of memristive devices.[1] To this end, it has repeatedly been shown that the integration of metal nanoparticles at the interface between the electrode and the switching material can drastically reduce the fluctuations in the switching process.[2,3,4] Here we proposes a novel fabrication approach by exsolving Ni nanoparticles directly from $La_{0.2}Sr_{0.7}Ti_{0.9}Ni_{0.1}O_{3-\delta}$ thin films, hence mitigating any additional particle deposition steps.[5,6] Model devices were fabricated employing exsolved $La_{0.2}Sr_{0.7}Ti_{0.9}Ni_{0.1}O_{3-\delta}$ / amorphous $SrTiO_3$ / Pt heterostructures, Figure 1a. The exsolution process was conducted under 5 % $H_2$ atmosphere at temperatures between 800 and 1000 °C and successful exsolution of Ni nanoparticles was confirmed by SEM, Figure 1b. As proof of concept, stable resistive switching of devices employing exsolved Ni nanoparticles was demonstrated over the course of 1000 cycles.

The influence of particle size on the switching performance was investigated through the fabrication of memristive model devices containing Ni nanoparticles with diameters ranging from 11 to 52 nm. It was shown that tuning the exsolution conditions, namely time and temperature, provides a powerful tool to control particle size. Analyzing the switching performance of model devices identified a trend towards higher resistance ratios for devices containing larger Ni particles, Figure 1c. Furthermore, larger particles were found to decrease the randomness in the set process. This was exemplified by strongly decreased fluctuations in the resistance of the ON state between successive switching cycles.

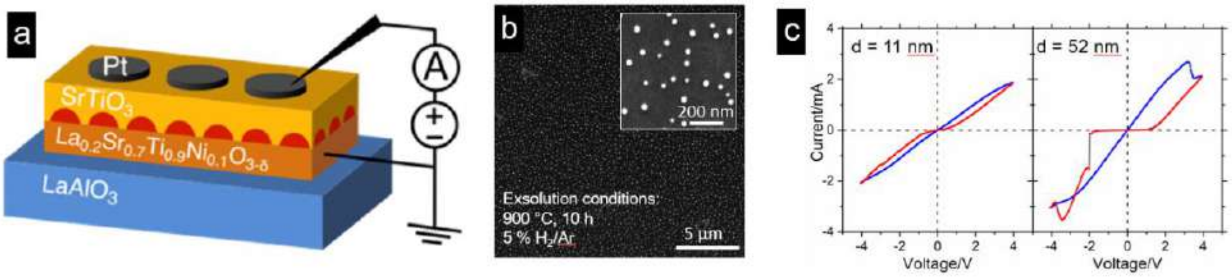

**Figure 1:** (a) Design of model device to investigate the influence of exsolved Ni nanoparticles on memristive performance. (b) Top-view SEM micrograph of a $La_{0.2}Sr_{0.7}Ti_{0.9}Ni_{0.1}O_{3-\delta}$ thin film after reduction for 10 h at 900 °C. The exsolved Ni nanoparticles are clearly visible as bright spots on the dark perovskite backbone. (c) I-V profiles for a device featuring exsolved Ni nanoparticles with 11.3 nm mean diameter and 52.2 nm showing low and high resistance ratio, respectively.

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# Mechanically soft domain walls in hard ferroelectrics

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All ferroic materials are divided into domains that are polarized in different polarization directions. The boundaries between domains, known as domain walls may possess functional properties not existent in the host material, such as conductivity in the walls of insulators, ferromagnetism in the walls of antiferromagnets, or polarization in the walls of ferroelastics. This could potentially be used to make new electronic devices at an unprecedented small scale, where the "active ingredient" are not the domains but the domain walls.

Among the many properties of domain walls, mechanical response appears to have been largely neglected, and there are very few, if any, studies specifically aimed at determining the local mechanical properties of domain walls.

Our work is focused in mechanical properties of 180 degree ferroelectric domain walls. Our first experimental measurements of the stiffness of domain walls in ferroelectric single crystal of $BaTiO_3$ and $LiNbO_3$, and also variable ferroelectric thin films, are achieved using atomic force microscopy. Initially, Piezoresponse Force Microscopy (PFM) was used to image the polarized domains of the materials and consequently to identify different types of domain walls appearing in the materials. PFM is based on the detection of bias-induced surface deformation. The application of an ac voltage to the tip results in alternate expansion or contraction of the sample, depending the polarization direction of the domain, and information on the electromechanical response is extracted by imaging the amplitude and phase difference of the mechanical oscillation of the tip. While the amplitude gives information about the magnitude of the electromechanical response, the phase $\phi$ yields information about the polarization direction. Thereafter, Contact Resonance Frequency (CRF) mode was used to identify the stiffness of the domain walls. In CRF, the stiffness of the material is determined from the measured resonance frequencies of the cantilever when the tip is in contact with the sample, as these contact resonance frequencies depend on the tip sample mechanical coupling and undergo distinct shifts when the tip is scanned over areas with different stiffness.

This unique mode allowed us to clearly determine the difference between domain´s and domain walls´ stiffness. The key result is that even purely ferroelectric (non-ferroelastic) 180 degree domain walls in uniaxial ferroelectrics are considerably softer than the domains they separate.

# Electroresistance in ferroelectric tunnel $Hf_{0.5}Zr_{0.5}O_2$ barriers

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Hafnium oxide is pivotal in CMOS related applications and is being much investigated for data storage in resistive switching devices [1, 2]. The report of ferroelectricity in polycrystalline metal-doped $HfO_2$ samples [3] opened new perspectives that have been further inflated by recent achievements showing that the ferroelectric phase can also be stabilized in epitaxial thin films [4, 5].

Here we report resistive switching observed in ultrathin ferroelectric films of $Hf_{0.5}Zr_{0.5}O_2$. Films (about 4 nm thick) grown by PLD on STO (001) substrates using $(LaSr)MnO_3$ (LSMO) as bottom electrode. Platinum have been used as top electrodes. We record the electroresistance (ER) by polarizing the junctions with different writing voltages $V_W(t)$. The junction resistance is measured through an $I(t)$-$V_R(t)$ reading loop in small voltage range. Preliminary polarization loops have been recorded. The device displays a remarkable polarization (about 15 $\mu C/cm^2$) when measured at frequency 5 kHz with coercive voltage around 1.5 V. However, when ER is measured in LSMO/ $Hf_{0.5}Zr_{0.5}O_2$/ Pt capacitors using a voltage-writing pulse of similar amplitude (≈2 V) and duration, a small ER is observed. In contrast, larger ER (900 %) is observed for larger writing pulses, around 4-5V. We conclude that ER response has two main regimes; the first, at low writing voltage, the ER value is around 300% and it is mainly due to polarization switching of the ferroelectric layer, meanwhile the second, at higher writing amplitudes and ER around 1000% attributed to the motion of defects into the active layer and, therefore, depending on the thin film microstructure.

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# Experimental improvement of Electrocaloric heat exchangers by guidance of numerical modelling

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In recent years, several Electrocaloric (EC) heat exchangers have been proposed [1-5], covering different kinds of mechanisms and working principles. However, little has been told about the numerical modelling of these devices and the potential impact that these simulations could have on substantially improving their performance. In this work, the authors highlight and prove how finite elements method could exploit and optimize the performance of EC heat exchangers, reporting more than 10 K when the simulation parameters were optimized.

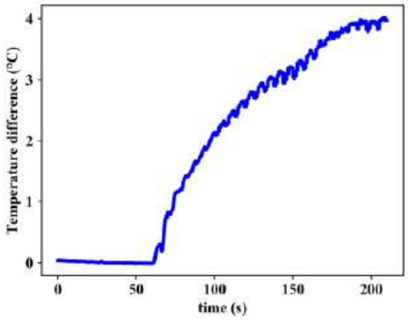

Figure 1. Temperature difference in the device as a function of time.

The simulations presented consist of 2D-representations of the Lead Scandium Tantalate multilayers capacitors (PST MLC) 22mm x 10.4mm x 1mm parallel-plates based active regenerator that is currently being developed in LIST, where a maximum temperature difference of 4K has recently been measured (Fig. 1), as envisioned by the model.

Furthermore, our simulations were used as well to explore new prototype's configurations. The results obtained showed that, for example, by enlarging the length of the regenerator and decreasing the thickness of the parallel-plates, the temperature difference in the device could increase already up to 9 degrees. The performance of other working fluids, which now are not experimentally feasible to implement, was also attempted. In the case of water, which has better thermal properties, the frequency of the cycle could increase up to three times, displaying very encouraging results.

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# Engineering of $HfO_{2-x}$ by MBE for emerging NVMs: RRAM & FeRAM

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**1. Introduction -** Resistive and Ferroelectric Random Access Memory (RRAM and FeRAM) devices based on (doped) hafnium oxides are investigated extensively as emerging nonvolatile memories [1]. Hafnium oxide ($HfO_x$) has gained a lot of attention due to its promising performances: fast switching times, high endurance, low power consumption and its compatibility with complementary metal oxide semiconductor (CMOS) technology. Both, FeRAM and RRAM, can be fabricated with hafnium oxide as the functional layer within a simple metal-insulator-metal (MIM) structure. For FeRAM a stabilization of the orthorhombic phase, e.g. via doping with Zr [2, 3] is necessary to achieve ferroelectric behavior. RRAM devices are based on switching between a stable low resistance state (LRS) and a high resistance state (HRS) by conducting filaments (CF), which are formed and disrupted by applying suitable voltage protocols. FeRAM devices are based on switching between two different remanent polarization states, which require a non-polar, non-centrosymmetric space group. The detailed mechanisms of both memory types in hafnia are still under debate, e.g. the exact origin of the ferroelectric phase or a detailed microscopic picture of the conducting filament are still missing.

**2. Experimental -** For the precisely controlled *in situ* growth of Pt/$HfO_x$/TiN and TiN/$HfZrO_x$/TiN device stacks on *c*-cut sapphire substrates, a molecular beam epitaxy has been used. By using elemental evaporation and RF radical sources with different gases (O and N), highly oriented or epitaxial TiN bottom electrodes and controlled oxygen engineered $HfO_x$ thin films, stabilized beyond the thermodynamic equilibrium, have been achieved.

**3. Results -** Defect engineering is a crucial method for controlling both memory technologies. By doping and oxygen engineering, the orthorhombic phase which is a necessity for FeRAM, can be stabilized. For RRAM, all reported switching modes can be stabilized only by varying the oxygen content of the hafnia layer [1, 4], and by this, influencing the forming process and the shape of the conductive filament. Recently, forming-free RRAM devices were achieved by engineering low energy grain boundaries, interconnecting bottom and top electrode [5]. A predefined path for filament creation could be introduced, reducing the forming voltage variation. Additionally, first operando TEM imaging of the switching process is demonstrated, potentially giving further insights in the resistive switching nature [6].

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# Study of the interface between infinite-layer $CaCuO_2$ and perovskite $SrTiO_3$

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The discovery of high-$T_c$ superconductivity in the cuprates, more than 30 years ago, has led to intensive research focused on the understanding of its origin. A great part of these studies was centered around the parent compound of the cuprates, the infinite-layer (IL) structure, with the chemical formula $ACuO_2$ [1], A being an alkaline earth metal. Even though the undoped IL phase is insulating, it can be made superconducting by electron or hole doping. Consequentially, a major effort has been made to grow the IL phase both in bulk and thin film form, leading to a series of interesting discoveries associated with these materials.

One of these discoveries was the recent observation of interface superconductivity in heterostructures consisting of the insulating perovskite $SrTiO_3$ and the IL $CaCuO_2$ [2,3]. In these systems, the appearance of 2D superconductivity has been attributed to a doping of the interfacial $CuO_2$ plane by apical oxygen atoms introduced into the adjacent Ca plane. The presence of the additional apical oxygens seems to be related to the growth conditions of the layers, since only a highly-oxidizing atmosphere has been shown to give rise to superconductivity.

In the present work, we study $CaCuO_2/SrTiO_3$ bilayers grown by pulsed laser deposition. We investigate the influence of different growth parameters, in particular of the oxidizing environment, on the structure of the bilayers, as well as on their electrical properties. Structural characterization by X-Ray diffraction and AFM measurements were performed on samples grown in a temperature range comprised between 600°C and 800°C and an oxygen pressure comprised between 0.1mbar and 1mbar. In addition to molecular oxygen ($O_2$), we used a mixture of molecular oxygen and ozone ($O_2$ + 5% of $O_3$) or $N_2O$ to increase the oxidizing power of the growth atmosphere. Devices characterized so far show insulating or semi-conducting behavior, with values of resistivity depending on the growth conditions used.

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# "Giant" Electrostrictors: synthesis and properties

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Electrostriction refers to the phenomenon where a quadratic strain is induced by the application of an electric field. This property exists in all insulators regardless of the temperature and does not require poling as on the contrary to piezoelectricity there is no extrinsic contribution due to domains.

"Giant" electrostrictors exhibit electrostrictive coefficients several orders of magnitude higher than expected from the "universal" empirical law put forward[1] for electrostriction: $|Q_h|=2.37/(Y\varepsilon_0\varepsilon_r)^{0.59}$. Among such giant electrostrictors the latest discovered are δ-$Bi_2O_3$[2] and LAMOX[3] that have in common to be oxygen-deficient materials used for their ionic conduction.

These two materials exhibit electrostrictive Q coefficients $10^5$ to $10^6$ times larger than expected from "classical" electrostriction, albeit at frequencies lower than classical electrostrictors.

We have synthesized ceramics of δ-$Bi_2O_3$ and LAMOX and measured their electrostrictive coefficients as a function of temperature and frequency. Our results are compared with those recently published[2,3].

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# Photovoltaic effect in oxide superlattice structures

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One page maximum including references and/or figures

The abnormal photovoltaic effect in ferroelectrics, known as bulk photovoltaic effect (BPVE), has attracted immense attention. The origin of BPVE is related to the non-centrosymmetric structure of ferroelectrics, and exhibits open-circuit voltages that are larger than the band gap with light polarization dependent short-circuit current. Another interesting aspect is the potential to enhance the polarization, indicative of stronger ferroelectric character, by incorporating the ferroelectric within oxide superlattice structures [1]. Superlattices comprising of few unit cell layers of ferroelectric sandwiched between layers of paraelectric materials have been explored for this purpose. However, there are only few reports about the photovoltaic effect in superlattice structure.

In this work, $BaTiO_3$/$CaTiO_3$/$SrTiO_3$ superlattice structures were fabricated on STO (001) substrate with different number of unit cells. High crystallinity and abrupt interfaces were confirmed by X-ray diffraction and transmission electron microcopy. We investigated the ferroelectricity in the superlattice structures, and analyzed the results with single crystalline $BaTiO_3$ thin films. The photovoltaic response was observed as a function of temperature, wavelength and light polarization.

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# Probing the origin of ferromagnetic stability of LSMO/SRO

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Magnetic switching and spin canting in bilayers of oxides heterostructures has a particular significance for spintronic devices [1]. Therefore probing magnetic properties at the oxides interface is required. In this project we used X-ray Absorption Spectroscopy, X-ray Linear Dichroism and X-ray Magnetic Circular Dichroism at the Mn $L_{3,2}$-edges to understand the ferromagnetic stability of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) when interfaced with $SrRuO_3$ (SRO) compared to *LSMO* deposited on $SrTiO_3$ (STO). It has been proposed that charge transfer at the interface between LSMO and SRO allow the $dx^2 - y^2$ orbital to mediate the in-plane double exchange and therefore stabilize the ferromagnetic ordering of LSMO down to 1-2 unit cells [2]. We have probed the orbital anisotropy and magnetism of LSMO on bilayers of LSMO/SRO deposited on $TiO_2$ terminated STO and compared to LSMO//STO, with varying thickness of LSMO (2/4/8/15 u.c.) and SRO (3/20 u.c.). Antiferromagnetic coupling of 2 and 4 u.c. LSMO with SRO was observed even below critical thickness of LSMO. Moreover, 4 u.c. of LSMO shows remanence above SRO $T_c$. On the basis of quantitative analysis and theoretical simulation LSMO/SRO data shows $d3z^2 - r^2$ preferential occupation below 15 u.c. in contrast to thin LSMO//STO, which is in agreement with theoretical prediction for thin LSMO/SRO [2] and LSMO//STO experimental results [3].

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