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Optimizing steady-state negative capacitance

Jorge Íñiguez

Materials Research and Technology Department, Luxembourg Institute of Science and Technology, Luxembourg
Department of Physics and Materials Science, University of Luxembourg

My group is interested in the behavior of ferroelectric materials that, in particular circumstances, display a persistent voltage drop that opposes the overall applied electric field; that is, materials that behave as a static negative capacitance [1]. More precisely, we investigate PbTiO3/SrTiO3 ferroelectric/dielectric superlattices as a convenient model system [2,3], using second-principles simulation methods [2,4] to monitor their behavior as a function of the available control knobs: temperature, applied electric field, epitaxial strain and layer thickness. This allows us to better understand the factors affecting the negative-capacitance response of the PbTiO3 layers, and thus identify strategies to optimize it. In this talk I will review our most recent results, focusing on the possible persistence of the negative-capacitance response down to very low temperatures and the evolution of the differential capacitance as a function of applied electric field.

Work done in collaboration with M. Graf and H. Aramberri, postdocs working at the Luxembourg Institute of Science and Technolgoy.

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Scaling of HZO ferroelectric in Ge MFS for low power FTJ

N. Siannas[1,2], P. Tsipas[1], C. Zacharaki[1,2], S. Chaitoglou[1], **A. Dimoulas**[1]

[1] *NCSR DEMOKRITOS, Athens, Greece*

[2] *National Kapodistrian University of Athens, Department of Physics, Athens, Greece*

Scaling of $Hf_{1-x}Zr_xO_2$ (HZO) ferroelectric thickness has scientific and technological interest, especially for low voltage/low power Ferroelectric tunnel Junctions (FTJ) non-volatile memories (NVM). Using Ge as bottom electrode offers larger screening length and clean crystalline interfaces necessary for efficient, low power operation of FTJs. We will present the design space that we have obtained using Brinkman's model [1]. Remanent polarization Pr and HZO thickness window of 20 $\mu C/cm^2$ and 3-4 nm, respectively, are predicted to be optimal parameters combining acceptably high values of TER >70 and J_{ON} ~ 1 A/cm^2. High J_{ON} is required to ensure the readability of small area integrated FTJs in real applications

We have used plasma assisted MBE to grow in-situ Metal Ferroelectric Semiconductor (MFS) device layer structure Ge(100)/HZO/TiN (x~ 0.5), as previously reported [2-4]. 5-nm-thick HZO show pinched anti-ferroelectric-like (AFE) characteristics which typically recover to full P-V ferroelectric hysteresis ("wake-up") after field cycling of ~ 100 cy. The waked-up capacitors show robust ferroelectricity with high remanent polarization ~ 22 $\mu C/cm^2$ as required for FTJ operation and a coercive voltage of 1.4 V, indicating that they can be operated as at low voltage/low power. The measured endurance of 4 $x10^4$ cycles is considered satisfactory given the large cycling field of 4.4 MV/cm. Also, the 5 nm MFS show no retention loss at 85 ^0C for more than 10^4 sec and very small imprint (<0.2 V), indicating good reliability exceeding 10 years.

Despite the good characteristics, 5 nm HZO is rather thick for FTJ. To enter the tunneling regime, HZO less than 4 nm is required. However, scaling HZO beyond 5 nm is very difficult. Although an orthorhombic phase without monoclinic contributions is detected by XRD, the devices show either pinched AFE-like characteristics that cannot be recovered or no polar characteristics at all. Our analysis using the phenomenological Landau-Ginsburg-Devonshire theory of ferroelectric phase transitions shows that the depolarization field due to uncompensated charges at the interfaces, which becomes significant in thin films, makes ferroelectricity metastable below 5 nm leading to the pinched characteristics with small remanent polarization. We will propose ways to reduce the depolarization field and by changing the Zr composition in HZO to mitigate its influence on the switching characteristics in ultrathin HZO.

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NIOBATES FERROELECTRIC THIN FILMS:
i/ GROWTH AND CHARACTERIZATION OF PEROVSKITE AND TTB PHASES IN THE K-Na-Nb-O SYSTEM
ii/ POTENTIAL OF APPLICATION IN HIGH FREQUENCY MINIATURE TUNABLE DEVICES

B. Aspe[1,2], V. Demange[1], X. Castel[2], B. Gautier[3], Q. Simon[4], D. Albertini[3], M. Zaghrioui[4], K. Nadaud[4], S. Députier[1], V. Bouquet[1], R. Sauleau[2], M. Guilloux-Viry[1]

1. Univ Rennes, CNRS, ISCR – UMR 6226, ScanMAT – UMS 2001, F-35000 Rennes, France
2. Univ Rennes, CNRS, IETR – UMR 6164, F-35000 Rennes, France
3. Univ Lyon, CNRS, UMR 5270, Inst Nanotechnol Lyon, Inst Natl Sci Appl Lyon, F-69621 Villeurbanne, France
4. GREMAN – UMR 7347, University of Tours, CNRS, INSA CVL , F-41000 Blois, France

Nowadays lead free materials are of first importance for piezoelectric/ferroelectric devices. Piezoelectrics films are well known for MEMS [1] and energy harvesting [2] applications. In ferroelectrics, the strong electric field dependence of the dielectric permittivity allows a great solution to elaborate tunable devices. Moreover the high value of the dielectric permittivity favors the miniaturization of such devices. During the last decades, intensive studies were focused on BaxSr1-xTiO3, which is a quite low dielectric loss perovskite compound, for which the Curie temperature (TC) can be tuned by selecting a suitable composition. Alternative multifunctional materials were also investigated, such as KTa1-xNbxO3 (KTN) which also allows to tune TC. More generally multifunctional oxide thin films from the lead-free system (K,Na) – (Nb,Ta) – O are of great interest due to their piezoelectric and ferroelectric properties.

The KxNa1-xNbO3 (KNN) perovskite is known to present large piezoelectric effects and shows highly tunable properties at microwaves [3, 4]. Among piezoelectric oxides, tetragonal tungsten bronze phases (TTB) are also of major interest for efficient devices on a reduced scale. The control of thin films is a prerequisite. The composition and structure of the thin films strongly depend on the deposition conditions, especially in the case of materials containing alkaline volatile elements. Whereas the K0.5Na0.5NbO3 perovskite is well documented, no precise description of the K-Na-Nb-O system exists when the alkaline/niobium ratio is lower than 1.

The presentation will be organized in two parts. The first part will be dedicated to the elaboration and characterization of KxNa1-xNbO3 thin films with a specific focus on the control of either the perovskite phase or the TTB phase. Single phase K0.5Na0.5NbO3 ferroelectric thin films and TTB thin films of composition close to (K0.5,Na0.5)0.45NbO3 were deposited by pulsed laser deposition. The TTB phase was identified by X-ray and electron diffraction and the surface microstructure consisting mainly of nanorods supports the formation of hallmark of the TTB phase [5,6]. Dielectric characteristics have been measured at low (1 kHz - 1 MHz) at microwave (1 GHz - 40 GHz) frequencies on films deposited on Pt-coated silicon, and sapphire or MgO, respectively. In the case of the TTB thin films, Piezoelectric Force Microscopy evidenced a piezoelectric signal although no switching could be performed [5]. However, the dielectric measurements, complicated by high leakage currents when a DC voltage was applied, did not evidence a ferroelectric behaviour.

The second part of the talk will illustrate the potential of the KNN perovskite for microwave tunable devices. For this purpose coplanar waveguide (CPW) devices were fabricated consisting of transmission lines to retrieve the KNN dielectric characteristics (□*r, tanδ*) and a CPW stub resonator designed to resonate at *X*-band.

Dynamic dielectric characterization of ferroelectric capacitors- Evidencing negative capacitance

Georgia Andra Boni[1], Cristina Chirila[1], Lucian Dragos Filip[1], Ioana Pintilie[1], Lucian Pintilie[1]

[1]National Institute of Materials Physics, Atomistilor 405A, Magurele, Ilfov, 0771125, Romania

Ferroelectricity was discovered more than 100 years ago and since then ferroelectric materials are a very important class of materials used in many applications. The most important properties of them are the switchability of polarization under an applied field together with the tunability of capacitance. In this context dielectric characterization is very important in this field, valuable information being extracted by capacitance-voltage measurements and by impedance spectroscopy.

The present study represents an implementation of a new dynamic dielectric characterization method to evaluate the components of the equivalent circuit of a ferroelectric capacitor. By applying short trapezoidal voltage pulses of variable amplitude different currents results through the circuit. Considering the ferroelectric capacitor as a parallel Rp-Cp equivalent circuit the values of the components are estimated from the resulting currents. The values of Rp and Cp are obtained for different stages of polarization switching. When the amplitude of the pulse is around coercive voltage an abrupt decrease of the Rp value (about 2 orders of magnitude) is deduced while the equivalent Cp does not present a dramatic variation. The results obtained by using this new method are in agreement with classic capacitance-voltage measurements. A total capacitance, Ctotal, is defined as the contribution from all charges from the structure, as the equivalent of both Rp and Cp. The total capacitance presents negative values around coercive voltage where is determined predominantly by the resistive component. In the classic small-signal CV measurements, similar results are obtained if the a.c. signal is set to the values around coercive values and is evidenced by obtaining dielectric losses greater than 1. The negative capacitance regime associated with the changes from capacitive to the resistive regime could be stabilized for a longer time if the series resistance of the circuit is increased in such a way as to delay the compensation of the new polarization state.

Multifunctional Barium Titanate-Based Systems with Restrictive Geometries: Preparation, Microstructure and Functional Properties

Adelina-Carmen Ianculescu

"Politehnica" University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gh. Polizu, 011061 Bucharest, Romania

Barium titanate-based compositions represent one of the most widely studied classes of oxide materials, due to their unique and multiple useful properties as ferroelectricity, high dielectric permittivity, positive temperature coefficient of resistivity (PTCR effect), high-voltage tunability, piezoelectricity and pyroelectricity. The electrical properties of $BaTiO_3$ can be tailored by two different approaches which involve: (*i*) *A* or *B*-site doping with homovalent or aliovalent species due to the high flexibility of the perovskite lattice and (*ii*) adjusting structure and microstructural features by adopting suitable synthesis procedures and sintering strategies. The change of structuring from micro- toward nano-scale in $BaTiO_3$-based bulk ceramics leads to new functionalities, while elaboration of products with confined geometry, as nanowires, nanotubes and thin films ensures high integrability degree, providing new alternatives for the design and manufacture of nanoscale actuators, ultrasonic devices, and memories. Taking into account these aspects, the preparation and characteristics of some $BaTiO_3$-based systems were considered.

A and *B*-site doped $BaTiO_3$ nanopowders were prepared by wet chemical methods. Electron microscopy investigations emphasized the significant influence of the synthesis conditions in controlling particle size and morphology. An exhaustive study was devoted to $BaTi_{1-x}Zr_xO_3$ (BTZ) ceramics prepared by alternative sintering procedures from nanopowders synthesized by the modified Pechini method [1]. The functional properties in micro and nanostructured BTZ ceramics obtained by conventional and spark plasma sintering (SPS) are comparatively discussed. The alkoxide variant of the sol-gel method was used to prepare $BaTi_{0.85}Zr_{0.15}O_3$ thin films of various thicknesses. The influence of the deposits number on the crystallinity degree, surface topography and optical characteristics of these films was investigated.

As *A*-site homovalent and aliovalent dopants in $BaTiO_3$, strontium (Sr^{2+}) and cerium (Ce^{3+}) were chosen. Powders with various concentrations of solutes synthesized by the acetate route of the sol-gel method, as well as related nanocrystalline ceramics obtained by SPS were investigated. In the case of $Ba_{1-x}Sr_xTiO_3$ ceramics not only chemically-homogeneous materials, but also compositionally-graded samples were prepared by an innovative procedure in order to improve the pyroelectric properties.

One-dimensional $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ (BCT) nanostructures were elaborated by template-mediated colloidal chemistry. The as-prepared BCT nanowires and nanoshell tubes revealed piezoelectric and ferroelectric properties. The imprint found in the "butterfly"-loop of the piezoresponse amplitude signal of 5 mol.% Ce^{3+}-doped $BaTiO_3$ nanoshell tubes is almost missing in the case of the nanowires with similar composition, indicating that the restrictive tubular geometry might play a key-role in generating flexoelectric effect.

Ferroelectricity and rhombohedral distortion in the electronic band structure of strained $PbZrTiO_3$

M.A. Husanu[1,2], D. G. Popescu[1], C. I. Bucur[1], C. Chirila[1], L. D. Filip[1], L. Pintilie[1], L. L. Lev[3], T. Schmitt[2], C. M. Teodorescu[1] and V. N. Strocov[2]

[1] *National Institute of Materials Physics, Atomistilor 405A, 077125 Magurele, Romania*

[2] *Swiss Light Source, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland*

[3] *Moscow Institute of Technology, Dolgoprudny, Russia*

* ahusanu@infim.ro

Perovskite oxides extend in application prospects from electronics to energy conversion and catalysis. Such abundant functionalities are a direct consequence of the rich physics which derives from the interplay of their multiple degrees of freedom. Ferroelectrics in particular are promising to catalysis and energy conversion due to their intrinsic property of efficiently separating the electrons and holes as a requirement to stabilize a well-defined ferroelectric state. However, a major drawback is their generally wide band-gap which drastically limits the absorption efficiency in the visible range. Strategies to circumvent this shortcoming include heterostructuring [1], doping [2] or defect engineering [3] in order to either decrease the electronic band gap or to introduce localized electronic states in the band-gap, which may account for absorption at convenient energies in the visible range. Assessing the energy and width of these localized levels or possible hybridization mechanisms between the dopant and the bulk band structure are essential aspects for understanding and tuning the properties of the ferro-functional systems for energy storage and conversion.

Deriving the most fundamental electronic properties of ferroelectrics as encoded in their experimental band structure is challenging due to charging effects and band-bending induced broadening of the region close to the surface. With some notable exceptions [4–6], FEs are significantly underrepresented in ARPES measurements compared with their FM ferroic analogues. GeTe and GeMnTe were studied [5,6], however they are systems where the ferroelectric state is generally oriented in-plane which does not introduce any surface band-bending, while bulk band structure of BaTiO3 has been obtained only in the n-doped, paraelectric case[4].

Here we record the ferroelectric-dependent three-dimensional electronic structure of ferroelectric $PbZr_xTi_{1-x}O_3$ x=0.2 PZT in **k**-resolved soft X-ray photoelectron spectroscopy (Figure 1) experiments. We identify the signature of the rhombohedral distortion which features the low temperature T=12 K phase (Figure 1) and we show that it maintains up to the room temperature. The band structure extracted across the whole Brillouin zone reveals on the one hand the immune character of the PZT to oxygen vacancies formation under the X-ray beam - which is a common mechanism of obscuring the intrinsic band structure in ARPES studies of oxides. On the other hand the recorded intrinsic band structure (Figure 2) reveals that the additional charges needed to screen the depolarizing field of the ferroelectric with well-defined FE polarization $\mathbf{P}^+$ or $\mathbf{P}^-$ are either incoherent electrons in the valence band or the carriers (ionized impurities) above the Fermi level, close to the conduction band minimum.

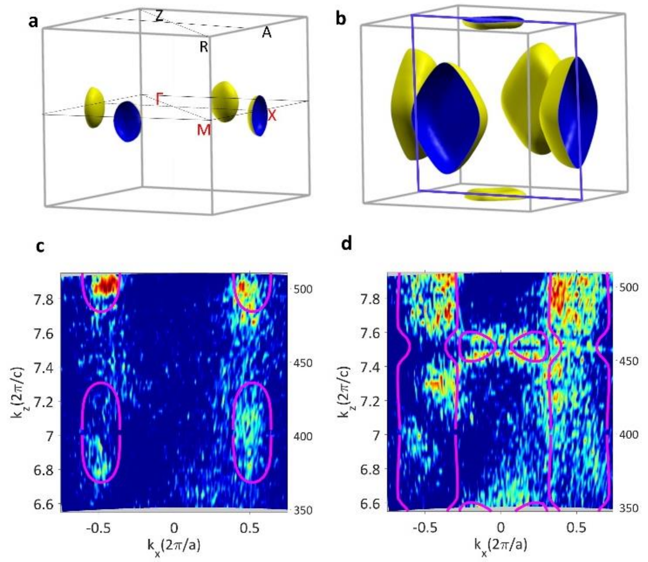

Figure 1. Theoretical electronic structure of ferroelectric PbZrTiO$_3$ in the tetragonal phase across the 3D Brillouin zone at (**a**) the valence band maximum (VBM) and (**b**) 0.75 eV below. Out-of-plane iso-energy (iso-E) maps of PZT recorded by varying the incoming energy between 350 eV and 520 eV in the XΓZ plane of the bulk Brillouin zone. Experimental Iso-E at the valence band maximum - VBM (**c**) and at 0.75 eV below the VBM (**d**) with the calculated iso-E cuts overlaid with magenta contours.

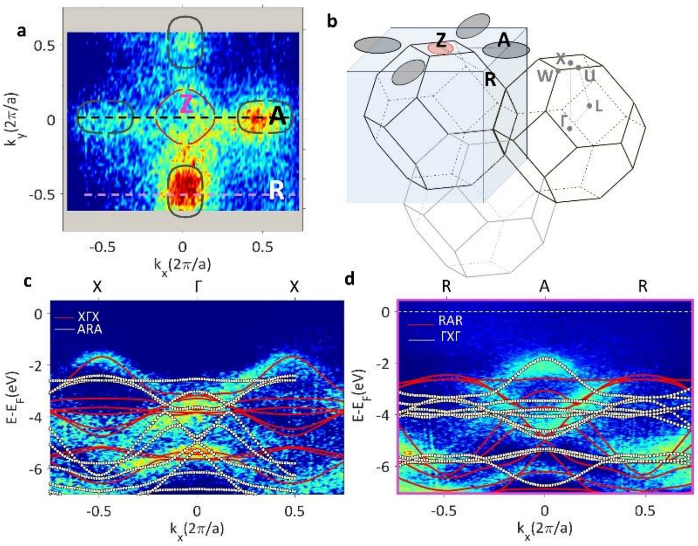

Figure2. In-plane (k_x,k_y) iso-E maps of PZT at 0.75 eV below the VBM in the ZAR plane of the tetragonal cell (**a**). The signature of the rhombohedral distortion is rendered into the tetragonal unit cell in **b.** Experimental band structure of PZT recorded along XΓX (**c**) and RAR (**d**) directions of the tetragonal BZ

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Scale-dependent properties in $BaTiO_3$ ceramics with structural instability

A. Lukacs, L. Padurariu, L. Curecheriu, C. Ciomaga, L. Mitoseriu

Dielectrics, Ferroelectrics & Multiferroics Group, Faculty of Physics, Al. I. Cuza University Iasi, Romania

The scale-dependent phenomena in $BaTiO_3$-based ferroelectrics with broad size range are among the most long-lasting research topics, with a major interest concerning aspects as: (i) preserve high material constants while reducing grain size (GS) at nanoscale (downscaling in electroceramics); (ii) understand the intrinsic/extrinsic interplay to generate the exceptional dielectric and piezoelectric properties around the critical size of 1 µm [1,2]. Landau-based calculations for $BaTiO_3$-based ceramics (Fig. 1) indicated that at any GS, the transitions between crystalline phases take place within temperature ranges of phase coexistence and such polymorph superposition exists around room temperature [3]. The role of phase superposition in relationship with GS-dependent properties were disregarded to-date. In the present work, $BaTiO_3$ ceramics with variable GS in the range (75 – 2250) nm showing phase superposition around room temperature have been investigated in order to check how their structural and functional properties are affected by GS reduction.

Superposition of O-T or even more polymorphs around room temperature, with variable amounts as a function of GS, were detected. Permittivity and d_{33} still show maxima in the range of GS~1µm at any field and temperature, even above Curie range, with enhanced permittivity for fine ceramics (ε_r~2500 for GS=75 nm) and strong nonlinear character, as result of the phase superposition, were detected. Permittivity vs. dc field dependences show a field-induced structural transformation (slope modification) at dc fields ~10 kV/cm (Fig. 2), which were confirmed by XRD analysis on poled ceramics. HRTEM analysis performed to understand the mechanisms promoting the stabilization of O phase and other low-symmetry polymorphs in such $BaTiO_3$ ceramics at room temperature revealed a large number of strained dislocations in the starting powders and sintered ceramics (Fig. 2).

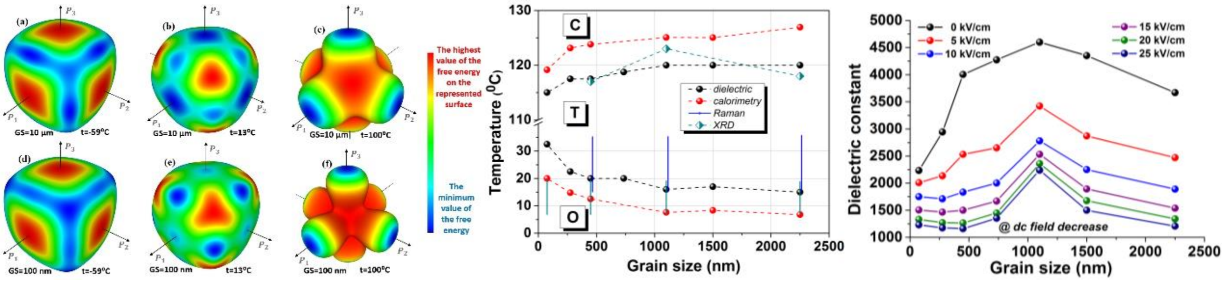

Fig. 1. Landau free energy calculations for GS=100 nm and 1µm; transition temperatures and permittivity as a function of GS and at various dc fields.

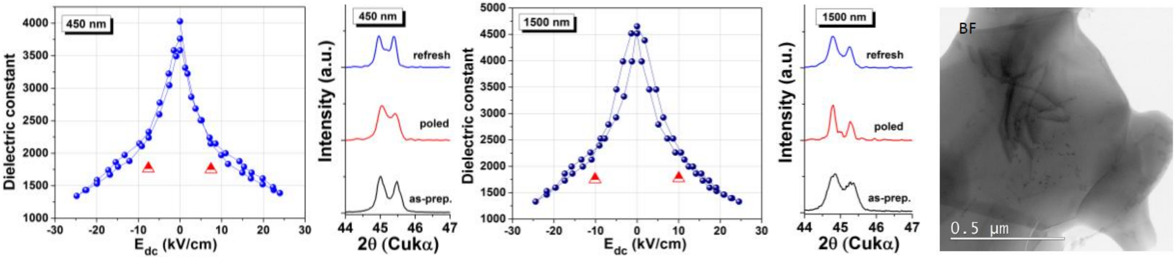

Fig. 2 Permittivity vs. dc field and (002)/(200) XRD peaks (as-prepared, poled: 10kV/cm, refreshed) of $BaTiO_3$ ceramics with GS= 450 mm, 1500nm; strained dislocations inside a ceramic grain.

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Shapes (of) Matter

Michael Springborg

Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrücken, Germany
m.springborg@mx.uni-saarland.de

The properties of crystalline materials continue to be exploited for a very large range of applications. In many cases, it is the bulk properties that are of interest. In the thermodynamic limit, i.e., for sufficiently large systems, these properties are either intensive or extensive depending upon whether they are independent of the system size or proportional to it. In either case, since the boundary regions make up a very small part of the complete system, it may be suggested that the boundary regions are of no importance. On the other hand, the properties of the boundaries themselves can also be of interest for applications. An example is heterogeneous catalysis, in which case the bulk part of the sample is often irrelevant.

These considerations suggest that bulk properties and surface properties are essentially independent of each other and can be treated separately. Theoretical studies of the properties of crystals often utilize this approach. For bulk properties, one typically treats the system as being infinite and periodic, thus completely ignoring the boundary regions. For the study of surface properties, one often constructs a simple model system that contains the surface of interest while ignoring other surfaces as well as the bulk region.

We demonstrate that there is a close connection between surfaces, shapes, and bulk properties of macroscopic, crystalline materials. Thus, the requirement that no atom in the bulk shall experience a force from charges associated with the surface, a requirement we formulate in terms of a generalized Tasker condition, leads to an interplay between the charge densities of different surfaces for a given sample. Thereby, we also demonstrate that so-called polar surfaces that often are considered as unstable essentially always can be stabilized, although the details of this stabilization then depend on all surfaces of the sample, i.e., on the shape of the material. The consequences of this interplay are studied through one property that usually is considered a bulk property, i.e., the polarization / dipole moment per volume, and one property that usually is related to surfaces, i.e., the activity of a surface in heterogenous catalysis. Our theoretical findings are illustrated through results of model calculations that are demonstrated to provide useful information.

Preliminary results have been published in:

M. Molayem, M. Springborg, and B. Kirtman: *Surface effects on converse piezoelectricity of crystals,* Phys. Chem. Chem. Phys. **19** (2017) 24724-24734.

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Switching in HfO_2-based ferroelectrics: an insight from nanoscopic analysis

Igor Stolichnov

Nanoelectronic Devices Lab (Nanolab), EPFL, Lausanne, Switzerland

HfO_2-based ferroelectrics have dramatically changed the application perspectives of hysteretic materials for information processing and storage. Their CMOS compatibility, preservation of the switching properties down to few nanometer thickness and high reversible polarization make them attractive for various device concepts including non-volatile memories and negative-capacitance-enhanced steep-slope FETs. In the context of these applications, the long-standing discussion of intrinsic (thermodynamic) or extrinsic (nuclei-controlled) switching in ferroelectrics has recently re-gained importance. Furthermore, understanding physical mechanisms of domain nucleation is essential for optimization of the polarization response for low-voltage applications.

Piezo-force microscopy (PFM) is a powerful tool for mapping the polarization and studying its dynamics on the nanometer scale. For ultra-thin hafnia-based ferroelectrics, an accurate quantitative analysis of the electro-mechanical response is challenging because the very weak signals down to small fractions of pm need to be measured. The practically relevant cases of thin film capacitors and transistor gates imply sensing a weak responses through a relatively thick electrode. In recent works we have shown that an accurate quantitative PFM analysis is possible by combining the conventional resonance PFM and non-resonant frequency-independent PFM. In-depth analysis of the local switching and high-resolution polarization maps reveal a reach palette of switching modes and domain structures for different hafnia-based ferroelectric systems explored. Among other intriguing phenomena a nontrivial thickness dependence of the coercive filed has been observed on hafnia-based ferroelectrics, were the coercive field strongly decreased with the film thickness. This behavior is shown to be consistent with a change of the domain nucleation mechanism. The practical implication of this effect is a robust ferroelectric switching under the extraordinary low millivolt-range driving signal, which is not expected for the standard coercive voltage scaling law. In addition to nucleation-limited switching we have investigated a different switching mode occurring in ferroelectric/dielectric negative capacitance structures. Our analysis that includes the two limiting cases of quasi-static switching and ultra-fast polarization response suggests the intrinsic character of the polarization reversal. The compatibility of this switching scenario with the commonly observed region-by-region switching with remarkably low domain wall mobility is discussed. Our results confirm the usability of CMOS-compatible polycrystalline hafnia-based ferroelectric films for gates operating in the negative-capacitance regime. Furthermore, they point towards new solutions for optimizing the switching properties for future generations of low-voltage functional electronics.

Nanostructuration effect on the wake-up effect of $Hf_{0.5}Zr_{0.5}O_2$ capacitor

Jordan Bouaziz, Greta Segantini, Benoit Manchon, Rabei Barhoumi, Ingrid Canero Infante, Nicolas Baboux, Pedro Rojo Romeo, Damien Deleruyelle, Bertrand Vilquin

Institut des nanotechnologies de Lyon
Université de Lyon, Ecole centrale de Lyon, INSA Lyon, CNRS
Ecully, France
bertrand.vilquin@ec-lyon.fr

Keywords— ferroelectric, ferroelectricity, FRAM, HfO_2, HZO, wake-up, imprint, fatigue, endurance, retention.

Various applications have been suggested for fluorite-structure ferroelectrics due to their advantages over the conventional perovskite-structure ferroelectrics [1]. In this presentation we will focus on $(Hf,Zr)O_2$ (HZO) thin films deposition for the capacitor of Ferroelectric Random Access Memories (FRAM) in the 1Transitor-1Capacitor (1T-1C) model. $(Hf,Zr)O_2$ thin films are studied to either fully understand the stabilization of the ferroelectric phase (f-phase) or to fit with industrial requirements. In 2015, Park et al. wrote: "[…] it seems critical that the dielectric layer is deposited in the amorphous phase and crystallized in a latter annealing step." [2] However, there was no clear evidence of the phenomenon as films are grown amorphous by atomic layer deposition. Changing the pressure in our sputtering chamber lead to the deposition of crystalline or amorphous films at room temperature. After a Rapid Thermal Annealing (RTA), only the amorphous films crystallize in the f-phase. This result was the starting point for many studies led by the authors. Samples are stacks of $Si/TiN/Hf_{0.5}Zr_{0.5}O/TiN/Pt$. All materials are grown by sputtering at room temperature following by a rapid thermal annealing during 30 seconds under N_2 atmosphere. The samples are called NM, and M. NM and M refers to two different architectures, respectively non-mesa and mesa structures. The description and size of NM and M samples is given in figure 1 for each sample. Fabrication and architecture details can be found in reference [3].

The set-up for electrical measurements have been described in reference [4]. This set-up allows us to wake the samples with bipolar square pulses. Measurements are performed with a positive up negative down (PUND) sequence. It consists in applying a negative setting pulse followed by two positive ones (P and U) and finally two negative ones (N and D). PUND maximum amplitude voltage equals that of the set/reset sequence. PUND pulses are triangular pulses with a rising/falling time of 100µs. We report the fabrication of two samples deposited by magnetron sputtering with excellent performances, quite similar to samples deposited by ALD. P_r values are among the highest for samples deposited by sputtering. Although the N-sample and NM-samples show very close P_r values, the two samples show completely different electrical behaviors. During cycling, the increase of P_r value for the NM-sample is more than an order of magnitude higher than the M-sample. It is accompanied by a decrease of the endurance which is two order of magnitude higher for the NM-sample than for the M-sample.

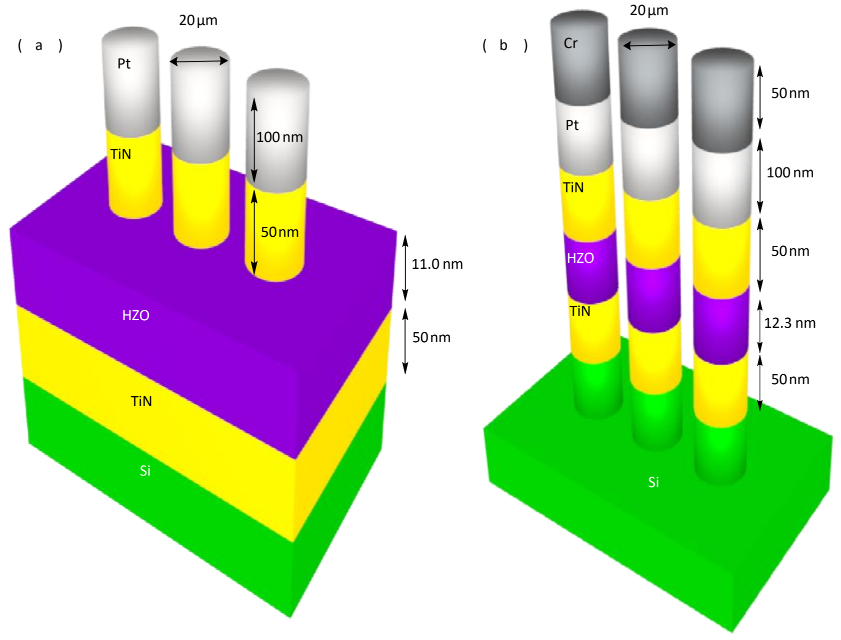

Figure 1: Scheme of (a) NM-sample and (b) M-sample.

As electrical behaviors are not the same, for low stress conditions M-sample has a higher P_r value during cycling whereas for high stress conditions NM-sample has a higher P_r value during cycling. As a matter of fact, it has been proven that maximum P_r values are more sensitive to stress conditions than the structures themselves. The origins of the different electrical behaviors come from the micro-crystalline structures of the two samples, according to GIXRD results. The crystallization takes place during the annealing step. During annealing, M-sample is built with a TiN TE fully covering the HZO layer whereas the TiN covers only partially the HZO layer in case of the NM-sample. It induces different stress states which lead to two different micro-crystalline patterning. The M-sample shows no monoclinic peak, whereas the NM-sample shows many monoclinic orientations. It can explain the huge reduction of the wake-up effect.

ACKNOWLEDGEMENT

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Playing with domains in ferroelectric polymers and hidden states in relaxors for neuromorphic computing

Brahim Dkhil*

*on behalf of many co-authors

Université Paris-Saclay, CentraleSupélec, Laboratoire Structures, Propriétés et Modélisation des Solides, CNRS-UMR8580, 91190 Gif-sur-Yvette, France

An artificial neural network is basically an ensemble of neurons connected by weighted synaptic connections allowing superior computing performances over classical von Neumann-based systems in processing cognitive and data intensive tasks, such as such as real-time image recognition, data classification or natural language processing, to cite a few. Typically, the information represented by a weight for each synapse is transmitted from the pre-synaptic neuron to the post-synaptic neuron. The network is then trained by updating its synaptic weights to perform a specific task. In the race for efficient materials to emulate neuronal and synaptic functions, ferroelectrics can provide key ingredients. Here, we take advantage of the dynamic of the ferroelectric domains (nucleation, domain wall creep motion) in PVDF-based polymer ferroelectrics and the ultrafast field induced hidden states in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) relaxors. In both aforementioned ferroelectric-like materials, we exploit these characteristics to mimic neuromorphic elements.

Using a P(VDF-TrFE) ferroelectric layer as a gate dielectric and a 2D MoS_2 as the channel, we fabricate a ferroelectric field-effect transistor (FeFET) that mimics a biological synapse. The competition between the external field stimulus and the internal depolarization field governs the ferroelectric creep of domain walls and enables fundamental learning aspects and rules including short-term memory (STM) to long-term memory (LTM) transition, spike-timing- and spike-rate-dependent-plasticity (STDP and SRDP). As an illustration we use these features to design a ferroelectric-based associative spiking neural network able to realize Pavlov'dog conditioning experiment.

Using atomistic simulations, ultrafast THz electric field excitation is employed to explore in PMN the many out-of-equilibrium states in the quasiflat energy landscape characteristic of relaxors. Interestingly, the THz pulses can generate both neuronic and synaptic behavior, via the creation of hidden phases of polarization order, resulting from the ultrafast response of polar nanoregions. Such phases further possess different dielectric constants, which is also promising for memcapacitor devices. Since polar nanoregions and nonlinear response exist in other relaxors these results may open a new field of research dedicated to employ this special class of materials for the design of ultrafast neuromorphic architecture and computing.

Electron transport and plasmonic response of metallic oxides

Josep Fontcuberta

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)
Bellaterra 08194. Catalonia. Spain

Metallic oxides are commonly viewed as examples of electron-correlated systems, where the electron-electron interactions within narrow 3d bands govern electrical and optical properties. However, analysis of some electrical properties suggests some fundamental difficulties with this approximation, may be pointing to different scenarios. Here we shall review properties of SrVO3 and SrNbO3 thin films, probably the simplest seemingly correlated systems, and argue that electron-phonon interaction plays a major role. Phonon dressed carriers are heavier and account, among other properties, for the transparency of these oxides in the visible range.

ANTIFERROELECTRIC SWITCHING AND GIANT ELECTROCOOLING

Gustau Catalan*, Pablo Vales-Castro, Romain Faye, Miquel Vellvehi, Youri Nouchokgwe, Xavier Perpiñà, J. M. Caicedo, Xavier Jordà, Krystian Roleder, Dariusz Kajewski, Amador Perez-Tomas, Emmanuel Defay.

*Presenting author. Affiliation: ICREA and ICN2, Campus Universitat Autonoma de Barcelona, Catalonia.

Ferroelectrics increase their temperature upon application of voltage, and this is known as the electrocaloric effect. In ferroelectric materials, the transition from the paraelectric to the ferroelectric phase can be induced by application of an external electric field near Tc. When that happens, the electrocaloric response is larger, reaching a few K; this is known as the “giant electrocaloric effect”. Antiferroelectrics are, in some ways, the opposite of ferroelectrics. Instead of having a spontaneous arrangement of parallel dipoles, they have a spontaneous arrangement of antiparallel dipoles. And, when a voltage is applied to them, instead of getting hotter, they get colder. This is known as the “negative electrocaloric effect”, henceforth “electrocooling”.

Though it can seem surprising that a material gets cold despite energy (voltage) being pumped into it, there are at least two physical mechanisms capable of explaining such behavior: increase in the entropy of the dipole sublattice within the AFE state, or endothermal nature of the field-induced transition from the antipolar to the polar state (double-hysteresis characteristic of antiferrerroelectrics). These two models are both physically valid, but as I will show in my talk only the second can account for the giant electrocooling (-4K) observed in the archetypal antiferroelectric, $PbZrO_3$.

In turn, the link between giant electrocooling and antiferroelectric switching has also allowed us to use an infrared camera to monitor in real time the dynamics of antiferroelectric switching in an antiferroelectric capacitor. In my talk I will show these results and discuss their implications.

Stabilization of the Ferroelectric Phase in Doped Hafnium Oxide Films: Influence of Dopants and Oxygen Vacancies

Uwe Schroeder, NaMLab gGmbH, Noethnitzer Strasse 64a, 01187 Dresden, Germany

Fluorite-structured ferroelectrics have outstanding potential for commercial applications due to their scalability, CMOS compatibility, and ease of fabrication. These advantages make ferroelectric HfO_2 very attractive for nonvolatile memory solutions such as ferroelectric random-access memory (FRAM), ferroelectric field effect transistors (FeFET), and ferroelectric tunnel junctions (FTJ). Significant efforts have been made for the physical understanding and technological exploitation of ferroelectric HfO_2. Due to the wide range of conditions under which ferroelectricity can arise in HfO_2 thin films, the scientific community has improved and optimized ferroelectric properties using a variety of approaches. As a result, progress in thin film technology for ferroelectric capacitors and memory arrays is advancing rapidly, but researchers are still busy unraveling the various causes of ferroelectricity in doped HfO_2 and also ZrO_2 thin films. Among them, dopants and oxygen content in a layer seem to play a major role, affecting both the formation of the crystalline phase and the performance of HfO_2-based devices. This talk will review recent results and provide a comprehensive picture on this topic, starting with an overview of dopants and existing oxygen-related defects, evaluating the calculations and experimental reports on phase stabilization in both undoped and doped HfO_2, and concluding with a discussion on the reliability of devices with oxygen vacancies in the three main groups of ferroelectric nonvolatile memory devices mentioned above.

Conducting Ferroelectric Domain Walls: Fundamentals of Transport and Device Opportunities

J. M. Gregg

School of Mathematics and Physics, Queen’s University Belfast, Belfast, N. Ireland BT7 1NN. U. K.

The fact that ferroic domain walls can show dramatically enhanced electrical conduction, compared to that of domains, is not new: it was theoretically predicted almost half a century ago [1] and experimental observations of enhanced transport (superconductivity in WO3-d twin walls) are now over 20 years old [2]; the first landmark scanning probe microscopy images of conducting walls in BiFeO3 have now been published for over a decade [3]. Despite ample available time, our research community has been surprisingly slow to unequivocally establish the physics responsible for domain wall transport phenomena. This rate of progress contrasts dramatically with that made in the exploration of conduction phenomena at LaAlO3-SrTiO3 (LAO/STO) interfaces, or in conventional 2D materials such as graphene. The difference is both stark and baffling. After all, the physics involved may be every bit as interesting and exotic. More than that, the fact that domain walls can be created, moved and annihilated brings with it the unique possibility of applications in which the presence and positioning of conducting sheet elements can be controlled dynamically.
In this talk, some recent progress in establishing fundamental aspects of domain wall carrier mobility and density, using combinations of nanoscale Hall voltage [4] and geometric magnetoresistance measurements will be discussed. In addition, specific domain wall memristive devices [5] and their potential applications in neuromorphic applications will be considered.

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Incommensurate spin crystal phases in ferromagnetic and ferroelectrics

Marin Alexe

University of Warwick, Department of Physics, Coventry CV4 7AL, W Midlands, UK

Email: m.alexe@warwick.ac.uk

Ferroics can form complex topological spin structures such as vortices and skyrmions, when subjected to particular boundary conditions. Especially in ferromagnets these whirling magnetic structures are chiral, generating abnormal behaviour such as topological Hall effect (THE) in ferromagnets. They are caused by local symmetry breaking induced for example by interface Dzyaloshinskii–Moriya interaction (DMi). We reveal that a PbTiO3 ferroelectric layer can break the surface inversion symmetry in a contiguous SrRuO3 layer generating a periodic chiral domain. Instead of skyrmions, the domains that emerge are an incommensurate (I-C) spin crystal which is seen to coincide with a significant topological-like Hall effect. [1]

One the other side in ferroelectrics vortex-like electric dipole-based topological structures have been observed in dedicated ferroelectric systems, especially ferroelectric/insulator superlattices, such as PbTiO3/SrTiO3 that have proven ideal environment due to high depolarising field. Thus, the large electrostatic energy is minimised by local rotations of surface dipoles, similar to ferromagnetic Kittel domains, in the which local dipoles rotate in such a way so as to reduce both the depolarization and stray fields avoids the suppression of the ferroelectricity in the thin films.

We observe in single PbTiO3 epitaxial layer sandwiched between SrRuO3 electrodes a domain structure analogue of the double-$\vec{\mathrm{Q}}$ magnetic spin crystal phase. We observe periodic clockwise and anti-clockwise ferroelectric vortices which are modulated by a second cycloidal ordering along their toroidal core. [2] The presence of such a double-$\vec{Q}$ structure, mediated by incommensurate interactions, would require an electric counterpart of the magnetic DMi to be permitted through symmetry.

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Anomalous photovoltaic effect in low-leakage solution-deposited BiFeO$_3$ films: Influence of doping and substrate stress

A. Blázquez Martínez, N. Godard, N. Aruchamy, C. Milesi-Brault, S. Glinsek, T. Granzow

Luxembourg Institute of Science and Technology, Materials Research and Technology Department, 4422 Belvaux – Luxembourg

Perovskite-structured bismuth ferrite (BiFeO$_3$, BFO) is nearly unique among oxide materials, as it displays both ferroelectric and antiferromagnetic ordering at room temperature. Its Curie temperature is very high at more than 1000 K; therefore, solid solutions of BFO are often considered for high-temperature piezoelectric applications. Values of the remanent polarization P_r as high as 100 μC/cm^2 along the pseudocubic [111] polar direction have been reported in high-quality epitaxial BiFeO$_3$ films [1]. Its electrically conducting domain walls make BFO a candidate for domain wall engineering [2, 3]. In addition, photovoltaic energy conversion with efficiencies up to 10% for above-bandgap photons was reported in domain-engineered BFO films [4]. In the visible and near-IR spectral range, BFO has a refractive index around 3 and a massive birefringence of 0.15 – 0.31, at least three times as high as other typical perovskites such as BaTiO$_3$ [5]. One problem that plagues BFO is its high conductivity, strongly connected to oxygen vacancies. This makes it difficult to achieve fully polarized samples and saturated hysteresis loops except in very high quality thin film or single crystal samples [6, 7]. To reduce conduction losses in polycrystalline BFO films created by cost-effective methods such as solution deposition, several approaches have been developed: an accurate control of the Bi/Fe stoichiometry to reduce the oxygen vacancy concentration [8], isovalent B-site doping with Mn^{3+} to trap oxygen vacancies at dopant ions [9, 10], or use of a seed layer such as PbO [11] or PbTiO$_3$ to increase the degree of texturing.

This presentation shows how highly (001)-textured polycrystalline BFO films with a thickness between 50 nm and 200 nm can be created on different substrates by spin-coating, using an interlayer of PbTiO$_3$ nanocrystals. The remanent polarization of the films reaches values in excess of 50 □C/cm^2, rivalling the properties of epitaxial films with the same orientation. Leakage current can be modulated with doping. While the undoped samples show relatively low leakage at low fields, conductivity increases strongly with increasing field. In contrast, doping with Mn or co-doping Mn and Ti increases leakage at low electric fields, but leakage current densities remain moderate, in the order of 100 mA/cm^2, at an electric field of 1.5 MV/cm. Temperature-dependent impedance spectroscopy in a large frequency range down to 0.1 mHz show that the charge transport mechanism does not change notably from that of the undoped sample with Ti-doping, but Mn-doping notably reduces the charge transport. Similarly, light-induced photovoltaic charge transport at sub-bandgap photon energies is low in the undoped sample, but increases with Mn-doping. Evidence for the anomalous (bulk) photovoltaic character of the light-induced charge transport is presented. Using different substrate materials, the residual stress in the BFO films is modulated, while leaving other relevant parameters such as microstructure largely unchanged. The photovoltaic behavior changes with changing stress level. Correlating these changes with the absorption spectra in the visible spectral range and the ferroelectric domain structure strongly suggests that they are based on an intrinsic piezo-photovoltaic effect rather than extrinsic or indirect stress effects. The results are discussed with respect to potential applications in energy harvesting as well as other fields involving light-induced charge transport.

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Unconventional Dynamics of Domain Walls in Uniaxial Ferroelectric Lead Germanate

*A. Gruverman,[1] O. Bak,[1] T. S. Holstad,[2] Y. Tan,[3] H. Lu,[1] D. M. Evans,[2] K. A. Hunnestad,[2] B. Wang,[3] J. P. V. McConville,[4] P. Becker,[5] L. Bohatý,[5] I. Lukyanchuk,[6] V. M. Vinokur,[7] A. T. J. van Helvoort,[8] J. M. Gregg,[4] L.-Q. Chen,[3] and D. Meier[2]

[1]Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588, USA,
[2]Department of
Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway,
[3]Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA16802, USA,
[4]Centre for Nanostructured Media, School of Mathematics and Physics, Queen's University, Belfast BT7 1NN, UK,
[5]Institute of Geology and Mineralogy, Section Crystallography, University of Cologne, Zulpicher Str. 49b, 50674 Cologne, Germany,
[6]Laboratory of Condensed Matter Physics, University of Picardie, Amiens, 80039, France,
[7]Materials Science Division, Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439, USA,
[8]Department of Physics, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway
*agruverman2@unl.edu

Keywords: lead germanate, domain walls, phase transition, polarization reversal

Application of the scanning probe microscopy techniques, such as Piezoresponse Force Microscopy (PFM), opens a possibility to re-visit the ferroelectrics previously studied by the macroscopic electrical testing methods and establish a link between their local nanoscale characteristics and integral response. Here, we report the nanoscale PFM studies and phase field modeling of the static and dynamic behavior of the domain structure in the well-known ferroelectric material - lead germanate, Pb5Ge3O11 (PGO). Several unusual phenomena were revealed: (1) domain formation during the paraelectric-to-ferroelectric phase transition, which exhibits an atypical cooling rate dependence; (2) unexpected electrically-induced formation of the oblate domains due to the preferential domain walls motion in the directions perpendicular to the polar axis, contrary to the typical domain growth behavior observed so far; (3) absence of the bound charges at the 180° head-to-head (H-H) and tail-to-tail (T-T) domain walls, which typically exhibit a significant charge density in other ferroelectrics due to the polarization discontinuity. This strikingly different behavior is rationalized by the phase field modeling of the dynamics of uncharged H-H and T-T domain walls. Our results provide a new insight into the emergent physics of the ferroelectric domain boundaries, revealing unusual properties not exhibited by conventional Ising-type walls.

High Throughput Studies of Metal Oxide Water Splitting Catalysts for the Development of Structure-Property Relations

Mingyi Zhang, Wenjia Song, Paul A. Salvador, and Gregory S. Rohrer

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh,
Pennsylvania 15213, United States.

The performance of a water splitting catalyst depends on many parameters related to the composition, processing, and structure of the material, as well as the conditions in the reactor. This research uses a newly developed parallel and automated photochemical reactor (PAPCR) that makes it possible to measure the rate of hydrogen yield from up to 108 catalysts in a single experiment, systematically determining the influence of particle shape, particle size, dopants, charged surface domains, protective coatings, co-catalysts, and many other catalyst characteristics on the hydrogen production rate. This talk will focus on the results of studies of SrTiO3, BaTiO3, and heterostructured catalysts consisting of TiO2 coated SrTiO3 and BaTiO3.

We have found that the rate of hydrogen yield from aluminum doped SrTiO3 is a sensitive function of the processing method, the particle size, the particle shape, and the reactor pH. These findings can be understood in terms of the properties of the individual low index surfaces that bound the particles and how they separately promote the reduction and oxidation half-reactions.

The prospects for using the PAPCR to develop additional structure-performance relationships for improved water splitting catalysts will be discussed.

Interface chemistry, oxygen vacancies, charge injection and polarization stability in ferroelectric hafnia-based films for non-volatile memories

N. Barrett

SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France

*e-mail: nick.barrett@cea.fr

The Internet of Things needs intelligent, fast and energy efficient handling of sensory, inhomogeneous data that goes beyond current storage and data processing capabilities. Ferroelectric memory and logic offer these opportunities. The polarization can be used to set logical states in ferroelectric field effect transistors (FeFETs) and binary states in non-volatile memory (NVM) cells. The discovery of the ferroelectricity in silicon-doped hafnium oxide offered the solution for the integration and scalability of ferroelectric-based devices allowing a CMOS compatible 3D deposition [1] and has initiated strong research efforts on different doped hafnium oxide materials [2-5].

An HfO_2-based ferroelectric, random access memory (FRAM) is intrinsically ultra-low power, CMOS compatible and has potential for scalability, meeting the requirements of high-density storage, rapidity, retention and energy consumption will be a revolution from an application prospective. So far, the performance of HfO_2-based ferroelectric capacitors as NVM cells has been limited by long wake-up effect in the initial operation of the device, reduction of the switching polarization during field cycling (fatigue limiting the endurance) and loss of polarization with time (limiting the data retention). Fundamentally, these effects stem from a variety of physical phenomena related to dopants and defects involved into the materials optimization. As the same defects can also be used in the materials optimization, improving our understanding of fundamental physical mechanisms at the origin of these phenomena is crucial.

Two key aspects in determining device performance are the electrode/ferroelectric interface and the defect concentration/profile in the hafnia based film.

Photoelectron spectroscopy is a powerful tool for studying chemistry and electronic structure. By employing both laboratory and synchrotron radiation induced photoemission, the chemical and electronic structure of the interface layer as well as the oxygen vacancy (V_O) concentration profile can be determined and thence correlated with the electrical characteristics of the capacitor.

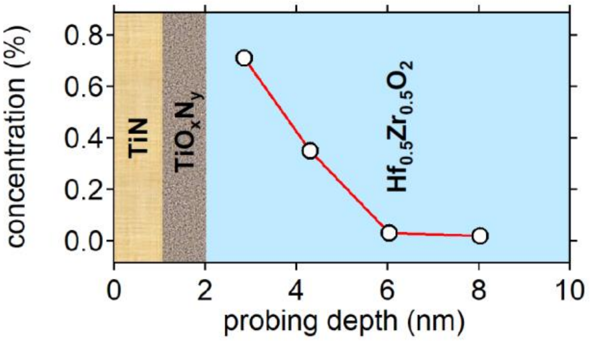

Figure 1 *Oxygen vacancy concentration profile near the top TiN/HfZrO*$_2$ *interface as determined by X-ray photoelectron spectroscopy [7]*

We have studied the interface chemistry in pristine TiN/La-doped $Hf_{0.5}Zr_{0.5}O_2$/TiN capacitors. An oxynitride phase (1.3 nm) is formed at the top interface, while a $TiO_{2-\square}$ phase was detected near the bottom interface. The V_O concentration is higher at the top interface than in the film due to oxygen scavenging by the top electrode. The V_O concentration was also found to increase from 1.5 to 1.9 x 10^{20} cm^{-3} when increasing La doping from 1.7 to 2.7 mol. % [6] . The V_O profile showed a maximum at the top interface (0.71%) and a sharp decrease into the film, giving rise to an internal field. Annealing at higher temperatures did not affect the V_O concentration at the top interface but caused the generation of additional V_O in the film, leading to a decrease of the Schottky barrier height for electrons [7].

The defect concentration and the possibility of charge injection under bias from the electrode can also be decisive in determining the level of leakage current and ultimately the endurance of the capacitor.

Low energy electron microscopy (LEEM) is a powerful technique for the study of the surface potential and charge in ferroelectric films and dipoles. Combining LEEM with ferroelectric domain writing using piezo-response force microscopy (PFM) provides a way of studying polarization stability and charge injection in microscopic ferroelectric domains.

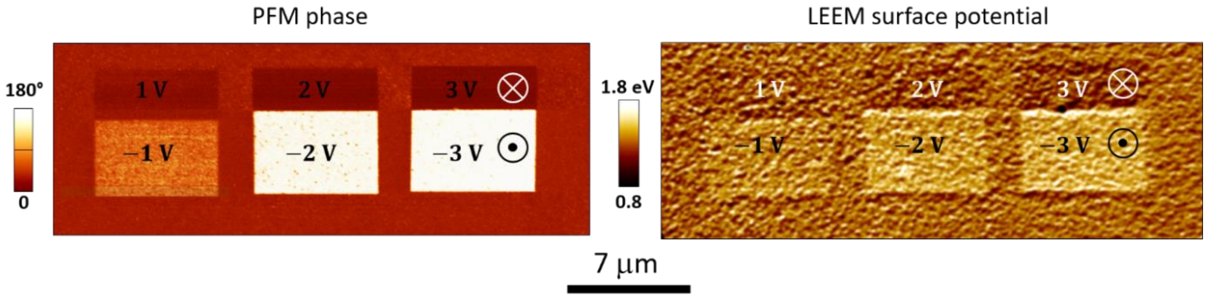

Figure 2 *Microscopic domains written by ±1, ± 2 and ± 3 V bias showing (left) PFM phase response and (right) electrostatic surface potential as measured by LEEM*

We have written locally microscopic domains in a 10 nm $Hf_{0.5}Zr_{0.5}O_2$ film doped by 2.3 % mol La. The optimal bias voltage for writing is ±2 V producing polarized structures stable for several weeks at room temperature. Local surface potential analysis by LEEM shows that positive writing bias leads to charge injection and trapping, contributing to the domain-like contrast in both LEEM and PFM imaging, as well as polarization switching. The domain structures disappear at 200°C due to a combination of thermal untrapping and destabilization of the ferroelectric polarization by mobile V_O. X-ray diffraction shows that the non-centrosymmetric, orthorhombic structure is unaltered and PFM demonstrates that identical microscopic domains can be written again at room temperature. Higher temperature annealing, up to 700 °C, introduces extra V_O as measured by X-ray photoelectron spectroscopy. The ferroelectric domain contrast is much weaker and the film becomes a leaky dielectric.

More generally, electron spectroscopy provides important information on the surface and interface chemistry as well as the electronic structure in $Hf_{0.5}Zr_{0.5}O_2$ films and is a valuable complement to electrical and structural characterizations.

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Interface limited stability of ferroelectricity in thin film heterostructures: Electrostatic interactions, elasticity effects and phase coexistence

Burç Mısırlıoğlu

Faculty of Engineering and Natural Sciences, Sabancı University, Istanbul, Turkey

Interfaces are the regions through which control is exerted on a specific function in a device such as carrier density, dielectric or pyroelectric response and piezo-driven charge exchange. The intrinsic differences between the materials comprising the interface can be a design parameter alone in contrast to traditional approaches focusing on a specific composition and its bulk response. Materials that undergo phase transitions associated with a sudden change in electrical, magnetic, electronic and elastic properties render a very rich variety of phenomena indispensable to investigate when they are fabricated in thin film form on substrates. That a variety of the new semiconductor-based device designs aim to tailor such properties is another driving force behind the seemingly scientific effort to unveil interface driven phenomena in thin films.

In this talk, I will focus on our work centered around the electrostatic and elastic effects mediated between a ferroelectric and a substrate wherein the substrate could be a metal, a semiconductor or an insulator, representing the cases often encountered in experiments. A number of findings that have not been addressed or discussed in depth in earlier studies concerned with effects of a phase transition will be presented for some model systems. In the same context, the effect of electrical boundary conditions at an interface on the elastic domain formation in a ferroelectric will be discussed in the light of numerical simulations based on the phenomenological theory. Some of our findings are especially important in the discussion of the change of order in the phase transitions accompanied by a structural component when occurring in clamped films on substrates. We have shown that the order of a structural transition does not necessarily change from first order to second order when in clamped state as widely accepted by the ferroic community.

Part of the content of this talk is derived from common works and discussions with Prof. Arkady Levanyuk of Univ. of Washington, Dr. Baris Okatan of İzmir Institute of Technology and Prof. Sergei Minykov of Russian Academy of Sciences.

Oxide nanosheets as seed layers for epitaxial growth of complex oxides

F. Baudouin[1], A. Boileau[2], J.J. Manguele[2], M. Dallocchio[2], S. Ollivier[1], P. Turban[3], B. Lépine[3], C. Cibert[2], S. Hurand[4], A. David[2], U. Lüders[2], G. Poullain[2], B. Bérini[5], Y. Dumont[5], V. Bouquet[1], S. Députier[1], W. Prellier[2], M. Guilloux-Viry[1], A. Fouchet[2], V. Demange[1]

1 Univ Rennes, CNRS, ISCR – UMR 6226, ScanMAT – UMS 2001, F-35000 Rennes, France
2 Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 CAEN, France
3 Univ Rennes, CNRS, IPR – UMR 6251, F-35000 Rennes, France
4 Institut Pprime, UPR 3346 CNRS-Université de Poitiers-ENSMA, SP2MI, 86962 Futuroscope-Chasseneuil Cedex, France
5 GEMaC, Université Paris-Saclay, UMR 8635 CNRS- Université de Versailles Saint-Quentin en Yvelines, Versailles, France

Ferroelectric and multiferroic complex oxide thin films are key components in modern devices. Their properties are related to their orientation and to their structural and microstructural qualities in relation with the crystal growth. Epitaxial films are obtained on single-crystalline oxide substrates (such as SrTiO3) that present chemical compatibility and small in-plane lattice parameters mismatch with the film. However these substrates are expensive and size-limited. On the other hand, direct growth of functional oxides on low-cost substrates with large area as silicon or glass leads to amorphous or polycrystalline films with poor properties. Therefore, introduction of a buffer layer is necessary on such substrates in order to achieve the epitaxial growth of complex oxides. Among other candidates, oxide nanosheets have been identified for several years as seed layers to induce the preferential growth of complex oxides with a high crystalline quality, on several low-cost substrates as silicon, glass, mica, polymers and metallic foils [1,2]. These nanosheets are obtained by exfoliation of layered oxides, as KCa2Nb3O10, K0.8Ti2O4, K4Nb6O17 and Cs6W11O36 phases. They possess either 2D square, rectangular or hexagonal lattices, allowing regrowth of [001], [011] and [111] preferentially oriented perovskite oxides. The nanosheets are transferred on low-cost substrates by Langmuir-Blodgett and drop casting methods [3], which allow a high surface coverage of the substrate. As example of epitaxial growth, we will show the possibility to integrate complex oxide perovskites thin films, such as La0.67Sr0.33MnO3 [4], KNbO3 [5] and BiFeO3 [6] on glass, silicon and mica. Significant results have also been recently obtained on the integration of SrVO3 and CaVO3 perovskite as transparent conducting films on glass substrates [7]. In addition, nanosheets can also be used to grow (111)Pt electrode on silicon at very low temperature [8].

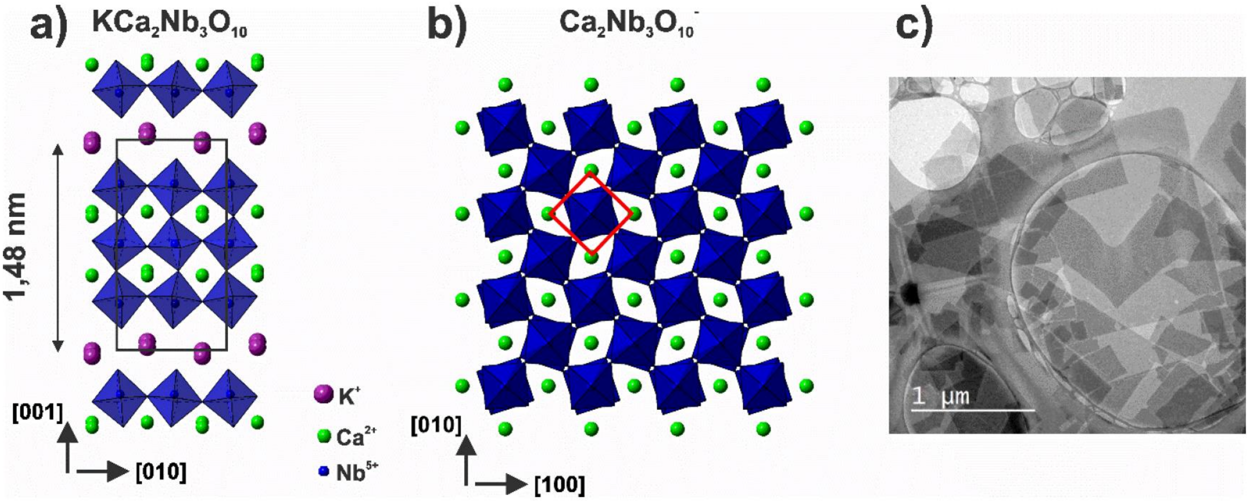

Figure 1. a) Crystalline structure of the layered KCa2Nb3O10 Dion-Jacobson phase along the [100] direction. b) Structure of a [Ca2Nb3O10]- nanosheet along the [001] direction. The 2D square lattice of parameter *a* = 3.854 Å is drawn in red. c) Bright field transmission electron microscopy image of [Ca2Nb3O10]- nanosheets.

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Electro- and magneto- resistance in perovskite-based multiferroic junctions

Nathalie Jedrecy, Anton Khanas, Christian Hebert, Loic Becerra, David Hrabovsky, Xavier Portier

Institut des Nano Sciences de Paris (INSP), Sorbonne Université, CNRS UMR 7588, 4 Place Jussieu, 75252 Paris Cedex 05, France
Email: jedrecy@insp.jussieu.fr

Multiferroic materials carry with them the promise of more efficient memory or logic devices in terms of size, execution speed and energy consumption. Stacks of ferroelectric and ferromagnetic perovskite thin layers concentrate a large number of studies, starting from the first demonstrations of tunnel electroresistance effects in ferroelectric tunnel junctions.

We will focus on the $BaTiO_3/La_{0.7}Sr_{0.3}MnO_3$ (BTO/LSMO) system and on LSMO/BTO/LSMO junctions to investigate in details different sources of modulation of the system resistance when applying a voltage to electrodes and/or when manipulating the ferromagnetic states of these electrodes.

In particular, the emphasis will be given on the importance of cationic intermixing and of oxygen vacancies accumulation at interfaces, which both affect the ferroelectric character of the barrier and the ferromagnetic order of the electrodes.[1] The reversible or irreversible nature of the resistive switching occurring under application of a voltage will be highlighted and assigned to the polarization reversal or to the oxygen vacancies drift, respectively.

The electroresistance and magnetoresistance changes as a function of geometry (from an in-plane to out-of-plane magnetization), temperature, voltage sign/value will be discussed under light of electronic and ionic processes.

1. N. Jedrecy, V. Jagtap, C. Hebert, L. Becerra, D. Hrabovsky, A. Barbier, X. Portier
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Dynamic Finite Element Method for describing complex dielectric properties in ferroelectric-based composites

Leontin Padurariu[1*], Cristina-Elena Ciomaga[2], Lavinia-Petronela Curecheriu[1], Liliana Mitoseriu[1]

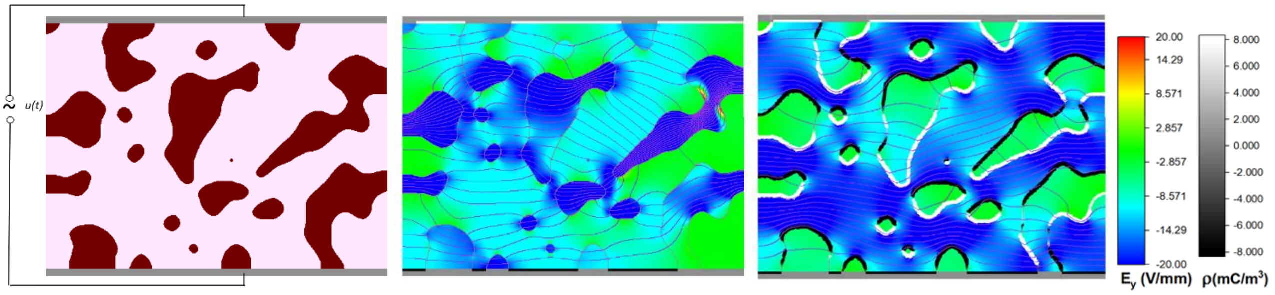
[1]Faculty of Physics, Al. I. Cuza University of Iasi, Blv. Carol I, 700506, Iasi, Romania,
[2]Science Research Department, Institute for Interdisciplinary Research, Al. I. Cuza University of Iasi, Lascar Catargi Str. 54, 700107, Iasi, Romania

[*]email: leontin.padurariu@uaic.ro

Single phase ferroelectrics rarely can accomplish all the technological requirements for broad range of applications, and due to this, a valuable alternative is to develop ferroelectric-based composites with improved or even new properties. For example, even if ferroelectrics are characterised by high permittivity values (thousands) it is very difficult to use them in energy storage applications because they have relatively small breakdown field (few tens of kV/cm) [1]. A more practical way to use ferroelectrics in such applications is to introduce them as a filling phase in composites based on polymers (like PVDF), which is characterized by very high breakdown fields but moderate permittivity of maximum 10 in single-phase form [2]. For other types of applications like wireless communications, the high permittivity of single-phase ferroelectrics is a disadvantage, even if they present promising nonlinear dielectric properties. The difficulty of using single phase ferroelectrics ($BaTiO_3$, $Pb(Zr,Ti)O_3$ and their solid solutions) in these type of applications is also related to their relatively high dielectric loss (at low frequencies and at the phase transitions), and the hysteretic character. Therefore, it has been proposed to develop composite materials by combining ferroelectrics with low permittivity linear dielectrics with low dielectric loss such as MgO, Al_2O_3, $MgTiO_3$, etc. [3]. However, it was demonstrated that the ordinary random mixing of ferroelectrics with linear dielectrics usually leads to a strong suppression of tunability properties and the challenge in this type of applications is to design the optimum microstructural configurations for preserving high tunability values while reducing the dielectric constant and losses [4]. Driven by the current trend of miniaturization in microelectronics and the necessity to incorporate multifunctional properties in small volumes, ferroelectrics were also proposed to be combined with other magnetic materials (for example, ferrites as: $NiFe_2O_4$, $CoFe_2O_4$, etc.) [5,6]. However, magnetic materials present semiconductor or even conductor properties, and therefore, a challenge for this type of magnetoelectric composites is to find the optimum microstructures and the volume ratios of the phases to maintain the insulating behaviour of the entire system together with magnetoelectric coupling.

In parallel with the technological development of dielectric/ferroelectric composite structures, a special interest was dedicated to develop theoretical models able to describe/predict the effective dielectric properties of such composites for different characteristics of the constituent phases and their microstructures. An important role on the effective electrical properties of composites is played by the interfaces between the constituent phases with contrasting permittivity, which produce field lines fringes. The best numerical tool to describe such local field inhomogeneity in composites is Finite Element Method (FEM). Using this approach, we successfully explained the effective dielectric and tunability properties in various composite-like systems: nanostructured $BaTiO_3$ ceramics [7], ferroelectric-ferrite mixtures [5,6], polymer-ferroelectric composites [8] and polymer-metallic nanoparticles structures [9]. Based on the experience in the preparation and electrical characterization of ferroelectric-based composite materials with desired microstructures, as well as in numerical modeling of the effective dielectric properties by FEM, we proposed the original concept of *local field engineering* [9,10] in designing microstructures for specific needs in microelectronics applications. This concept demonstrated that is possible to design composites with controlled microstructural characteristics and with an optimum configuration of the local electric field, aimed to improve the effective dielectric response. This original idea is a much efficient alternative to the classical trial-anderror approach typically employed by experimentalists before. For example, based on *local field engineering* concept we proposed specific porous ferroelectrics as good materials for tunability applications, because they present moderate dielectric constant (few hundreds), low loss and similar tunability values as single-phase ferroelectrics [4,10].

However, in our previous FEM-based approach, there are some simplifications which we revised in the present work. The component phases of a composite system were approximated as perfect dielectrics and the local field inhomogeneity was calculated only as a consequence of the contrasting local permittivity values. The FEM-based simulation results were usually compared with the experimental dielectric measurements at high frequencies (over 1 MHz) where the dielectric loss of ferroelectric-based composites is in fact, very low. The real dielectrics present a certain level of losses which can be described generally by Debye or Maxwell-Wagner relaxation mechanisms [11]. In this work, a new and a more powerful FEM-based approach is proposed to describe effective dielectric properties of ferroelectric-based composites at any frequency value. The approach is based not only on solving the Poisson equation (like in common FEM approaches proposed in literature before), but also on solving the continuity equation necessary to describe the transport of free charges and their accumulations at interfaces. For example, the simulated images of local field images and charge densities at different frequencies (of an *ac* voltage with amplitude of 10 V) in a $BaTiO_3$-based composite with 30% inclusions of $CoFe_2O_4$ (Fig. 1(a)) are presented in Figs. 1(b-c). The simulations were performed considering a permittivity of ~2000 for $BaTiO_3$ and ~13 for $CoFe_2O_4$. Additionally, a conductivity of 10^{-6} S/m for $CoFe_2O_4$ was taken, while $BaTiO_3$ was considered perfect dielectric. From Fig. 1, it can be noticed the ability of the approach to describe the change of the magnetic/semiconductor phase behaviour at different frequencies. For example, at high frequency (1MHz) the inclusions present a dielectric behaviour: field concentrations on low permittivity component and no accumulation of charges at interfaces, while at low frequency (1 Hz) the inclusions present rather an conductive behaviour: small field inside the inclusions, significant charge accumulations at interfaces and field concentration on ferroelectric matrix.



(a) (b) (c)

Fig. 1 A composite with formula $70\%BaTiO_3$-$30\%CoFe_2O_4$ (a) and the images of local electric field and charge densities simulated at the frequencies of 10^6 Hz (b) and at 1 Hz (c). The intensities of the local electric field are represented in ROGVAIV colour scale and the charge densities are represented in black/white. The images represented in (b) and (c) correspond to the amplitude (10V) of the ac signal-u(t) during the stationary regime. The violet curves are isopotential lines.

The advantage of the new dynamic FEM approach is that can describe the effective dielectric properties of composites and compare with the experimental results. The dynamic FEM approach is able to: (i) simulate the charging/discharging currents during the application of an ac voltage, (ii) identify the stationary regime, (iii) compute the system's impedance and the I-V phase shift. In the end, the numerical approach calculates the complex effective permittivity by modelling the system with RC circuits, like in experimental approaches.

In order to demonstrate its generality, the new dynamic FEM approach was implemented in this work to describe effective dielectric properties in different types of ferroelectric-based composites: with conductive inclusions (Ag-$BaTiO_3$ composites), magnetoelectric composites (matrix of $BaTiO_3$ or $Pb(Zr,Ti)O_3$ and inclusions of $CoFe_2O_4$ or $NiFe_2O_4$ [5,6]) or porous $Ba(Ti,Zr)O_3$ ceramics [13].

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Coupling Elastic, Electrostatic and Magnetic Responses in Transition Metal Silicate Monolayers

N. Doudin[1], K. Saritas[2], S. Ismail-Beigi[2] and E.I. Altman[1]

Department of Chemical and Environmental Engineering[1]
Department of Applied Physics[2]
Yale University
New Haven, CT 06520 USA

Over the past few years it has been shown that single layers of two-dimensional (2D) transition metal silicates can be grown on transition metal surfaces. The materials are constructed from a layer of corner-sharing six-membered rings of SiO4 tetrahedra atop an octahedrally-coordinated transition metal–oxygen (M–O) layer; thereby breaking inversion symmetry perpendicular to the layer and meeting the criterion for piezoelectricity. Further, transition metal cations ranging from Ti to Ni can be incorporated, thereby offering a broad degree of tunability to achieve targeted properties including magnetism. Therefore, we have been investigating the growth, structure, stability, and ferroic properties of these materials theoretically and experimentally. Theory indicates that first row transition metal silicates from Cr through Ni can be stable, and further that the transition metal oxidation state may be tuned through the metal:Si ratio and by altering the hydroxylation of the layer; e.g., by varying the hydrogen partial pressure. Calculations indicate piezoelectric coefficients on par with other 2D piezoelectric materials. Meanwhile, silicates with a single transition metal silicate mostly favor anti-ferromagnetic coupling. However, we find that mixed M–O layers may be engineered to favor ferromagnetic order, particularly those containing Cr in a honeycomb sublattice. Experimentally, we have grown 2D transition metal silicates on Pd and Au(111) substrates and characterized the structure down to the atomic level using scanning tunneling microscopy. Complementary spectroscopic characterization reveals the expected phonon modes of the 2D silicate as well as the expected metal to Si ratio. Ambient pressure x-ray photoelectron spectroscopy measurements on 2D Fe silicate show that the Fe oxidation state can be reversibly tuned by exposure to water and or hydrogen and oxygen, as anticipated from theory. Advanced scanning probe measurements are underway to non-destructively characterize the piezoelectric response of single layer silicates.

Ferroelectric state in a α-Ln2WO6 polymorphes stabilized in thin film

Thomas Carlier [a,b], Mégane Lheureux [a], Marie-Hélène Chambrier [a], Anthony Ferri [a], Antonio Da Costa [a], Florent Blanchard [c], Sonia Estradé [d], Gemma Martin [d], Francesca Peiró [d], Thibaud Denneulin [e, f,] Pascal Roussel [c], Rachel Desfeux [a]

a Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-62300 Lens, France
b HORIBA FRANCE S.A.S., Boulevard Thomas Gobert, Passage Jobin Yvon, 91120 Palaiseau, France
c Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
dLENS, MIND-In2UB, Electronics Department, Universitat de Barcelona (UB), Marti i Franquès 1, Barcelona 08028, Spain.
e Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52425 Jülich, Germany
f CEMES, CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France

In recent years, due to the significant progress in the nanomaterial fields crossed with ecology concerns, performances of nano-devices based on non-toxic piezoelectric and ferroelectric materials are in deep progression. Nowadays, lead zirconate-titanate Pb(Zr,Ti)O3 (PZT), [1,2] (Pb,La)(Zr,Ti)O3 (PLZT) [3] or *x*Pb(MgNb)O3-(1–*x*)PbTiO3 (PMN-PT) [4] are the more efficient piezoelectrics and ferroelectrics but they contain lead and have to be replaced by reference to the European Union legislations [5,6]. In this context, the discovery of new lead-free materials with functional properties has become increasingly important. Recently, we have focused studies on new lead-free oxides and, for the first time to our knowledge, we have stabilized the α-high temperature La2WO6 (LWO) phase in thin film form using pulsed laser deposition.

During this study, the ferroelectric behavior has been highlighted by PFM characterizations. First observations of local ferroelectricity were obtained for LWO films grown on (001)-SrTiO3 and (001)-LaAlO3 substrates [7, 8].

To continue, other lanthanides compounds with Ln2WO6 (Ln = lanthanides) formulation have been explored. For this purpose, Ln2WO6 (A=Ln3+ or Ln) thin films still have been synthesized, for the first time, by pulsed laser deposition and new polymorphes, isostructural to the orthorhombic α-high temperature La2WO6 (LWO) has been evidenced while the bibliography discussed only of the tetragonal polymorph at high temperature for Ln2WO6 with Ln = Ln except La, Ce.

The structural properties of these thin films have been thoroughly investigated by High Resolution X-ray Diffraction and Transmission Electron Microscopy. Remarkable results were obtained in relation with the stabilization of high temperature allotropic varieties.

Furthermore, nanoscale electrical measurements carried out by Piezoelectric Force microscopy demonstrated the piezo / ferroelectric character of some Ln2WO6 thin films. A focus will be done on the Nd2WO6 composition. [9]

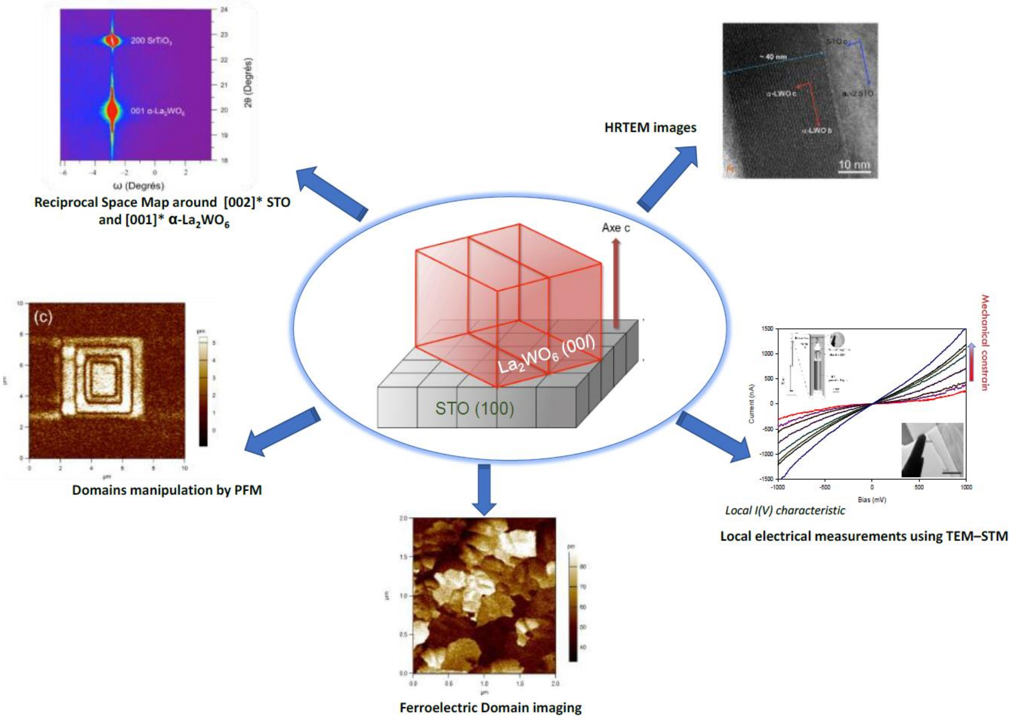

Figure 1 : Scheme of α-La$_2$WO$_6$ thin film structural and ferroelectric main results

In summary, this work allowed the production of new eco-responsible ferroelectric oxide thin films, which opens the way to new multifunctional materials for nanoelectronics and energy applications.

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AFM tip-induced strain effects in $BiFeO_3$ films: from structural phase changes to polarization switching and nanofabrication

Brian J. Rodriguez
School of Physics, University College Dublin, Belfield, Dublin 4, Ireland
E-mail: brian.rodriguez@ucd.ie

Recent studies have emphasized the critical role of local mechanical stress on the functionality of ferroelectric materials. For instance, stress applied from an atomic force microscope (AFM) tip has been shown to induce polarization reversal through the flexoelectric effect in ultrathin films, where the strain gradients can permeate through the film thickness [1]. In addition, local stress can alter electric field-induced switching behavior, changing the coercive field and the remnant polarization [2]. The mixed phase form of epitaxially-strained $BiFeO_3$ thin films, having a coexistence of a rhombohedral-like phase, comprising needle-like structures, within a tetragonal-like phase matrix, meanwhile show a pronounced susceptibility to locally-applied stress. The effects include transitions between phases, with the resulting boundaries demonstrating enhanced conductivity [3], and stress-induced alterations to electric field-induced hysteresis [4]. In this work, an AFM tip loading-force dependent evolution of strain effects is reported, from structural phase changes and mechanically-enhanced switching currents at low forces (< 1 µN) to nanomechanical machining at higher forces (> 10 µN). Switching behavior and switching currents are found to be affected by force, with coercive fields decreasing with increasing loading force. Notably, mechanically-induced currents increase with applied force and may enable polarization state determination in ferroelectric memory applications. Through a systematic investigation of a range of AFM parameters, including force, we demonstrate that AFM-based machining is an effective tool for rapid and precise modification of local regions of the film, as well as for the fabrication of several different nanostructures, including nanocapacitor arrays with individually addressable ferroelectric elements [5]. AFM-based machining of ferroelectric nanostructures offers advantages in select cases over established techniques, such as bottom-up approaches and focused ion beam milling, where low damage and low-cost modification of already-fabricated thin films are required.

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Charge accumulation, conduction band filling and ferroicity

Cristian M. Teodorescu

National Institute of Materials Physics, Atomiștilor 405A, 077125 Măgurele–Ilfov, Romania

This work will discuss a unified view of ferromagnetism in metals and ferroelectricity in semiconducting heterostructures, including possible interplay between these two types of ordering, by the amount of the conduction band occupied with electrons in the case of ferromagnetism, and by the charge accumulated at surfaces and interfaces for a ferroelectric thin film with uniform polarization oriented out of plane.

The ferromagnetism of metals is still assessed by the elementary Curie-Weiss theory for spins with well-defined positions in the crystal structure interacting *via* the Heisenberg exchange interaction. The mean field theory allows one to predict the equations of state $\boldsymbol{M}(\boldsymbol{H},T)$ ($\boldsymbol{M}$ being the magnetization, $\boldsymbol{H}$ the applied electric field and T the temperature); this yields important parameters such as the Curie temperatures T_C, coercive fields and remnant magnetizations. Starting with the Heisenberg interaction between neighboring spins, one may easily demonstrate the following relation between the coercive field at zero temperature $H_c^{(0)}$ and the Curie temperature [1]:

$$\mu_0 \mu_{\mathrm{B}} H_c^{(0)} = \frac{3 k_{\mathrm{B}} T_{\mathrm{C}}}{g(S+1)}$$

(1)

where k_{B} is the Boltzmann constant, μ_0 is the vacuum permeability, μ_{B} the Bohr magneton, $g(\approx 2)$ the gyromagnetic factor and S the maximum value of the spins involved. The numerator of the right term of eq. (1) is in the fractions of electronvolt range, whereas for pure metals along easy magnetization axes the coercive fields are in the range of 10– 100 A m^{-1}, thus the left term from eq. (1) is in the range of nanoelectronvolt. At non-zero temperatures, the coercive field decreases by some units [2]. This discrepancy cannot be solved unless one accepts a huge value of the spin moment, practically equal to that of a magnetic domain. Then, the inner interaction inside a domain still remains to be explained. Another theory for magnetic hysteresis is that of uniaxial magnetic anisotropy, as formulated by Stoner and Wohlfarth [3] but here, again, to explain the low coercive fields in pure metals one need to accept ultralow values of the magnetic anisotropy energies. Moreover, microscopic *vs*. macroscopic determinations of magnetic anisotropy energies yielded discrepancies of several orders of magnitude [4], still unexplained to date.

Thus, for metals one should rather apply a theory of band ferromagnetism [5], where one stipulates that the asymmetry in the occupancy of states in the continuum with majority and minority spins is favored by the on-site Coulomb repulsion, illustrated by the Hubbard parameter U. This decrease in energy with the spin asymmetry (stabilization of the ferromagnetic state) is in competition with the kinetic energy increase due to the Pauli principle when electrons below the Fermi level from the minority band are promoted above the Fermi level in the majority band. The competition between both effects yields the most stable ferromagnetic state when the Stoner criterion is fulfilled:

$$U g_0(\varepsilon_{\mathrm{F}}) > 1$$

(2)

where $g_0(\varepsilon_\mathrm{F})$ is the one-electron paramagnetic density of states (DOS) (its integral over the whole energy range is unity). This theory of band ferromagnetism has the major drawback of inability to predict correctly the Curie temperatures, which result with $k_\mathrm{B}T_\mathrm{C}$ in the several eV range.

Only recently it was shown that the Stoner theory evaluates incorrectly the electron energies of electrons in the sub-bands with majority and minority spins, by neglecting the different offsets in energies of these sub-bands [1]. A correct evaluation, without taking into account any Hubbard-like parameter, yields a simple criterion for band ferromagnetism in metals such as:

$$\left(\frac{dg_0}{d\varepsilon}\right)(\varepsilon_\mathrm{F})\int_0^{\varepsilon_\mathrm{F}} g_0(\varepsilon)d\varepsilon < {g_0}^2(\varepsilon_\mathrm{F}) \tag{3}$$

By introducing simplified DOSs with two peaks of different widths corresponding to e_g or t_{2g} states in cubic symmetry, one may explain: (i) the different structures encountered along the 3d metals; (ii) the occurrence of ferromagnetism in body centered cubic (bcc) Fe, face centered cubic (fcc), hexagonal close packed (hcp) Co, bcc Co, fcc Ni, fcc V; (iii) the Cr antiferromagnetism; (iv) low coercive fields result from the simple conservation of the electron density; (v) and, also, one obtains reasonable Curie temperatures. ‘Re-entrant’ ferromagnetism is predicted at ultrahigh temperature (above 6000 K), which may offer an alternate explanation for the origin of the geomagnetic field [1,6].

A mean field theory for ferroelectricity was not possible until recently owing to the lack of a microscopic model for this kind of ordering. Instead, the polarization of a crystal was treated in the framework of the ‘Berry phase’ approach, connected to the phase accumulated by electronic wavefunctions when the crystal undergoes a transformation from the centrosymmetric to the non-centrosymmetric state [7]. Also, the polarization is not a single defined value, but rather is represented by a discrete set of vectors separated by ‘polarization quanta’. At the same time, it is well known that thin ferroelectric films present a single domain polarization state oriented perpendicular to their surfaces. Such states would feature huge ‘depolarization fields’, which have to be compensated by charge accumulation at the surfaces or interfaces of these films [8,9]. In Ref. [2], another paradigm of stabilization of single domain ferroelectricity in thin films was proposed in the sense that any elementary dipole moment p_0 present in the film (e. g. that related to a unit cell, including ionic charges and displacement charges due to modifications of electronic wavevectors) is shown to interact with charges accumulated at surfaces or interfaces of the film, whose surface density is close to the value of the polarization P, yielding a stabilization energy which may be expressed as:

$$\varepsilon_s \approx -\frac{Pp_0}{\epsilon_0\kappa} \tag{4}$$

where $\epsilon_0\kappa$ is the vacuum permittivity and κ a ‘pseudo- dielectric constant’, assumed constant. The stabilization energy defined by eq. (4) may be used as input for a Curie-Weiss mean field theory, yielding equations of state $\boldsymbol{P}(\boldsymbol{E},T)$ ($\boldsymbol{E}$ is the applied electric field), coercive fields and Curie temperature in agreement with the experimental values. Effects of the dipolar interaction and possible variations with the polarization and temperature of κ will also be discussed.

It follows that when a ferroelectric thin film is sandwiched between metals close to the criterion for ferromagnetism, the charge accumulation at interface needed to stabilize the ferroelectric state may be used to control the ferromagnetic state of the free metal. This opens the possibility to synthesize multiferroic structures where the coupling mechanism between ferroelectricity and ferromagnetism is of pure electronic nature, being related to the charge accumulated at the interfaces of the ferroelectric and to the way this is reflected in the filling of the conduction band and possible variations across criteria such as Stoner's (eq. (2)) or that defined by eq. (3). Other interplays involving surface chemistry (molecular adsorption accompanied by charge transfer) or more sophisticated interplay mechanisms between ferroelectricity and ferromagnetism, such as indirect exchange [10], will also be discussed.

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Controlling antiferromagnetic textures in $BiFeO_3$ multiferroic thin films

Vincent Garcia

Unité Mixte de Physique CNRS, Thales, Université Paris-Saclay, Palaiseau (France)
e-mail: vincent.garcia@cnrs-thales.fr

Antiferromagnetic materials are currently emerging as a new paradigm for spintronics as they offer key advantages over ferromagnets: insensitivity to external magnetic fields, much faster spin dynamics (THz range), and higher density packing because of the absence of stray fields[1]. As antiferromagnets are insensitive to external magnetic fields, one must find alternative ways to control them. The manipulation of the antiferromagnetic order was recently demonstrated in non-centrosymmetric metallic antiferromagnets[2–4], but the spin-transfer torque requires large current densities, and the efficiency of the writing method is questionable since only a small fraction of antiferromagnetic domains is actually switched[5,6]. An optimal writing mechanism would demand low current densities (or ideally no current) to generate a complete reversal of antiferromagnetic domains or textures. In multiferroic materials possessing both antiferromagnetic and electrical orders, the magnetoelectric coupling is an additional resource expected to channel efficiently electric-field stimuli onto the antiferromagnetic order.

Here, using a highly sensitive scanning magnetometer based on a single nitrogen-vacancy (NV) defect in diamond[7], we visualize in real-space the non-collinear antiferromagnetic order of a multiferroic thin film, at room temperature[8]. We first use epitaxial strain to finely tune the as-grown spin textures, and, then taking advantage of the magnetoelectric coupling in $BiFeO_3$, we deterministically control these textures using an electric field[9]. We find that strain stabilizes different types of non-collinear antiferromagnetic states (bulk-like and exotic spin cycloids) as well as collinear antiferromagnetic textures, in striped-domain ferroelectric structures of $BiFeO_3$. In addition, the modification of the ferroelectric landscape allows us to control the propagation vector of the spin cycloid, to switch from one type of spin cycloid to another, or to convert from a collinear antiferromagnetic texture to a spin cycloid. Using resonant elastic X-ray scattering, we reveal the existence of chiral antiferromagnetic and ferroelectric objects at the domain walls of these periodic arrays[10]. Finally, in a different epitaxy of $BiFeO_3$ thin films, we managed to stabilize a single-domain ferroelectric and cycloidal state, opening further opportunities for investigations of the interplay between non-collinear antiferromagnetic orders and spin transport. These results highlight the unique potential of NV magnetometry for imaging complex antiferromagnetic order at the nanoscale and the potential of multiferroic $BiFeO_3$ for reconfigurable antiferromagnetic spintronics.

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Domains and lattice curvature in ferroelectric superlattices and supercrystals

Pavlo Zubko

Department of Physics and Astronomy, University College London, UK

London Centre for Nanotechnology, UK

Ferroelectric superlattices have proven to be a fruitful playground for exploring the effects of electrostatic and mechanical boundary conditions on ultrathin ferroelectrics. In these heterostructures, the combination of polarization discontinuities at interfaces and epitaxial misfit strain imposed by the underlying substrate can be exploited to engineer complex nanoscale domain patterns with exotic polarization textures, tailored periodicities and enhanced functional properties.

We have found that in $PbTiO_3$-$SrRuO_3$ metal-ferroelectric superlattices deposited on $DyScO_3$ substrates, epitaxial strain and imperfect screening of the polarization at interfaces lead to the appearance of a domain supercrystal—a complex, hierarchical domain structure consisting of a three-dimensionally ordered horizontal and vertical flux-closure elements. To determine the three-dimensional domain pattern, we have employed a combination of laboratory and synchrotron X-ray diffraction, piezoresponse force microscopy, scanning transmission electron microscopy and phase field simulations. Furthermore, we found that the local distortions of the lattice associated with the ferroelectric domain pattern lead to periodic bending of the metallic $SrRuO_3$ layers, with curvatures as large as 10^7 m^{-1}, opening an exciting opportunity for investigating curvature-induced phenomena in correlated-electron oxides.

The large lattice curvatures observed in $PbTiO_3$-$SrRuO_3$ supercrystals, however, are only local, as the rigid clamping imposed by the substrate precludes the development of any macroscopic curvature. To activate this additional degree of freedom, the heterostructure must be removed from the substrate. We will discuss the behaviour of free-standing superlattices of composed of $PbTiO_3$ and $SrTiO_3$, which exhibit dramatic changes in both the local polarization arrangements and the macroscopic shape of the sample upon release of the superlattices from their substrates.

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