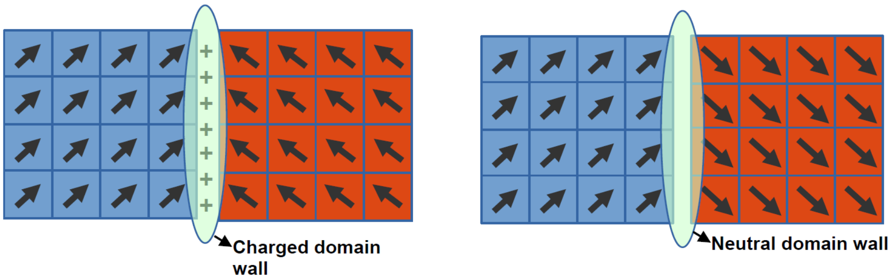
Caractérisation et contrôle de la structure électronique aux parois de domaines ferroélectriques

Information Technologies have acquired a leading role in economic growth and prosperity but several key intertwined issues still need to be solved to fit into the new model of sustainable low-carbon economy: low power consumption, further miniaturization and environmental friendliness. In this context, **an energy saving, ultrahigh density and lead-free domain wall technology** tackles these three challenges and could represent a major breakthrough.

Ferroelectric-based devices are intrinsically low power because the polarization state can be switched simply by applying an electric field instead of heat dissipating electric currents, and the active states are non-volatile. Ferroelectric materials naturally form domains of uniform polarization separated by domain walls (DWs).

Ferroelectric (FE) materials are insulating by nature but the recent discovery of **DW conduction** [Seidel2009] triggers a new era for these materials: DWs exhibit very different electronic properties than the parent materials and can be controlled (written or erased) under application of low power electrical fields. They are naturally nano-sized objects with a thickness of few unit cells, and therefore highly scalable. Their variable conductivity opens the door to numerous applications where the electronic properties can be tuned both through the density and the conductivity of DWs [Béa2009, Guyonnet2011]. The conceptual breach is based here on the **domain wall itself becoming the active element of the device** [Salje2010].

The origin of DW conductivity is under debate and further work is mandatory to untangle the different mechanisms at play (for example, intrinsic or defect related). A comprehensive picture of DW conduction can be achieved by **controlling the DW electrostatic nature** (head to head, head to tail, tail to tail) and the **chemical doping** (for instance with oxygen vacancies trapped at the domain wall). The fundamental understanding and the technological mastering of DWs properties is expected to unleash the potential of **FEs for novel applications in oxide electronics** (sensors, actuators, and memories) with low power reconfigurable DWs.



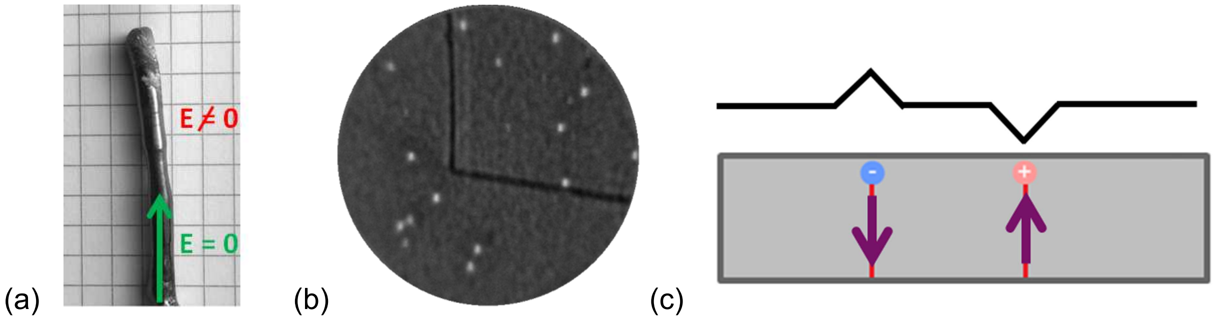
Schematic of two types of domain wall: left head-to-head (positively charged) and right head-to-tail (neutral)

Neutral domain walls (NDW) are by far the most common in ferroelectrics since they easily minimize the electrostatic energy but they show only limited conductivity enhancement. The free charge density required to screen a **Charged Domain Wall** (CDW) is of the order of 10^{20} cm^{-3}, much greater than typical values on FE oxides. For this reason CDWs are rarely observed. Nevertheless, they appear as a true, new paradigm for post-CMOS electronics precisely because they can be understood as **nanometric metallic conductors separated by highly insulating dielectric regions**.

In order to stabilize CDWs, charge compensation is required. For head-to-head (H-H) walls, this results in the formation of a quasi 2D electron gas (2DEG) with metallic conductivity. The conductivity can be modulated by the presence of defects. Positively charged oxygen vacancies, V_O, create, for example, two free electrons per defect. The chemical potential might therefore be used to control the DW conductivity by modulating the free charge carrier density.

It has been shown that CDWs support currents two orders of magnitude greater than NDWs [Crassous2015] and nine orders of magnitude greater than in the intervening insulating domains [Sluka2013]. Metallic conductivity appears when a potential difference is applied to a CDW. The onset of the conductivity is determined by electrode material, defect concentration and sample history. The possibility of **rapidly switching** the conducting state would represent an important step forward towards viable electronic architectures.

CDWs are formed via frustrated poling: will explore how the **applied electrical field during growth** can be used to form **high density arrays of CDWs in single crystal samples.** Single $BaTiO_3$ will be grown under frustrated poling. ICMMO, partner in this consortium and responsible for the sample growth, has already demonstrated the dramatic effect of growth under a strong electric field.



(a) Single crystal rod grown first under zero then under strong electric field by floating zone method at ICMMO (b) Ferroelastic domain wall in $CaTiO_3$ *with positive charge at the surface imaged using LEEM (c) Schematic of the surface potential in presence of charged domain walls.*

The initial V_O concentration can be controlled during growth and also as a function of redox atmosphere (oxygen partial pressure). The electrode material will be varied to tune the conductivity onset via the work function difference with respect to $BaTiO_3$. These choices correspond perfectly to the consortium expertise.

Another class of materials improper ferroelectrics (manganites) which exhibit CDWs are not considered since the FE polarization is not the primary order parameter and as a result compensation of the polarization charge with free charge carrier sheets may not be necessary.

The aim of the project is to **lay the basis for the usability of CDWs for electronic devices** and to **demonstrate the control by electric field of CDWs**.

- **Controlled synthesis** of single-crystals by frustrated poling with high density arrays of domain walls with varying V_O concentration
- Full description of the **electronic properties** of **the DWs** using state-of-the-art local and full field microscopy techniques: C-AFM, PFM, LEEM, PEEM.
- **Switching of DW resistance state** by applied electric field using different electrodes
- **Conductivity control by the chemical potential**

On a fundamental level the project aims to provide a better understanding of the **conductivity mechanism**: hopping related or via delocalized, metallic states.

- Structure/chemistry related **band gap modification**
- Defects interaction DWs, for example **oxygen vacancies V_O,**
- **Free charge sheet** formation to screen the polarization charge
- **Conduction and valence band offsets** at the electrode/$BaTiO_3$ interface
- **In-situ characterization of the quasi 2DEG** as a function of the oxygen partial pressure

Workplan

Sample preparation

Single crystal samples with desired CDW arrays will be grown by ICMMO (Université Paris Sud) using proven frustrated poling set-up. Vertical floating zone growth will be carried out in a dedicated set-up allowing the simultaneous application of an intense electric field during growth [Hicher2015].

R. Haumont (ICMMO) has ANR funded young researcher grant (RECIPE) to develop an innovative crystalline growth device under electric field. During the crystalline growth, the goal is to apply an electric field to create new chemical structures and original multimaterials. Close collaboration between the partner laboratories and several iterations will be necessary to optimize the CDW arrays.

The thesis student will hence benefit from double expertise in crystal growth and nanoscale surface characterization available in the consortium.

Characterization of Charged Domain Walls

Electron Spectromicroscopy

Low Energy Electron Microscopy (LEEM) will be used to measure the variation in the electrostatic surface potential across the DW [Rault2012]. Accumulation of electrons or oxygen vacancies near the DW screening the wall surface charge can also be identified [Barrett2013]. **Photoelectron Emission Microscopy** (PEEM) will map the local work function and chemistry across CDWs.

Near field microscopy

The mapping of ferroelectric films and domains will be obtained by **Piezoresponse Force Microscopy** (PFM) in controlled atmosphere. **Conducting tip-AFM** will be used for the measurement of the electrical properties of domain walls. Local I-V characteristics will be recorded.

Control of Charged Domain Walls

Device fabrication

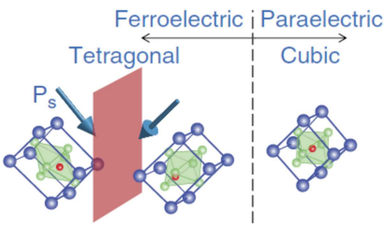
Thanks to the nanofabrication facilities of SPEC, specific samples with conduction and control electrodes will be fabricated to allow in-situ characterization in LEEM and PEEM.

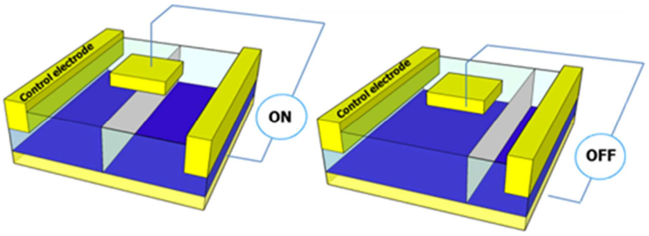
Chemical control of 2DEG at CDWs

Using a custom-designed oxidation chamber with in-situ annealing facilities, the V_O concentration may be varied over several orders of magnitude allowing a systematic study of the influence of V_O on the formation/annihilation of the quasi 2DEG at H-H CDWs

Strain control of CDWs

In $BaTiO_3$, the 90° H-H CDWs only exist in the tetragonal phase. We will exploit the in-situ heating facilities of the LEEM and PEEM experiments to demonstrate the structural control of the CDWs





Electrical control of CDW conductivity

Imaging of the CDWs by C-AFM, LEEM and PEEM will be carried out. The conductivity onset will be controlled by the applied voltage and by the electrode material. Additional control electrodes may be used to induce DW migration and hence provide a basis for device switching speed.

Références

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