# Ph. D thesis funding (duration 3 years)

## Ferroelectric junctions band structure control and performances enhancement through combinatorial modulation of their interfaces

**Keywords**: Combinatorial PLD deposition, Interface engineering, Scanning probe microscopy, Ferroelectricity, Energy efficiency

**Context:** Transition metals oxides of perovskite structure exhibit a large panel of properties due to their strong electronic correlations (ferroelectricity, ferromagnetism…). The common crystalline structure of these materials facilitate their hetero-epitaxy in thin films (« cube on cube growth») with an interface control down to the atomic scale nowadays thanks to in-situ monitoring during the growth. This has enabled the emergence of new physics phenomenon [Oht 04] [Tsu 10] resulting from the symmetry breaking at the interfaces with orbitales, charges and/or spins reconstruction with no equivalent in bulk materials [Hwang 12]. This emerging field is called interface engineering.
Ferroelectric junctions of the type Metal / Ferroelectric (FE) / Metal are used for different applications like non-volatile memories (FeRAM, RRAM), energy efficiency (tunable capacitors), energy harvesting or actuation (direct or inverse piezoelectricity). These junctions suffers from two limitations related to interface problematics. The first limitation is linked to the appearance of a ferroelectric dead layer as the FE films gets very thin. Its polarisation is destabilised in its own imperfectly compensated depolarising field. The second limitation comes from the presence of important leakage currents owing to the relative weakness of the Schottky barrier (SB) at the metal/dielectric interface. In the 90's semi-classical theoretical approaches to these two problems were only taking into account bulk electronic properties of the dielectric and the electrode neglecting interactions at the interface. For depolarising field ones invoked a screening charges spreading on a finite length (Thomas-Fermi's length) characteristic of the metal while the SB height was evaluated using metal's work function and dielectric's electronic affinity [Scott 99]. The emergence of quantum computations (DFT) have since underlined the importance of the metal-dielectric chemical bond, with the possible appearance of an interface dipole, for the evaluation of the SB's height (Bond Polarization Theory [Tung 01]). It has also been reported by DFT calculations that the lower stiffness of Pt-BaO bonds in the Pt / $BaTiO_3$ interface favour the stabilisation of ferroelectricity at the interface [Sten 09]. However, DFT calculations are too time-consuming to carry out an exhaustive exploration of the metal / ferroelectric couples in order to determine the most efficient ones.

**Objectives of the thesis:** We propose a massively parallel and empirical approach by electrode / FE interface engineering via a concept recently developed in our laboratory: the continuous chemical modulation of films deposited by combinatorial pulsed laser ablation [Jab 15] [Daum 16]. The ferroelectric junctions studied will be epitaxial. $Ba_{1-x}Sr_xTiO_3$ was chosen as the lead-free FE material, while the electrodes will consist of conducting oxides or metal. The chemical modulation of the dielectric and the electrodes will be done on a few perovskite unit cells in the vicinity of the interface and will allow to vary the electronic affinity and the gap of the FE, the work function and the carriers' density of the electrode as well as the interface dipoles. These quantities control the band structure of the tri-layer via the alignment of the Fermi levels. The resultant curvatures at interfaces, with accumulation or depletion of carriers, give rise to an internal field (built-in voltage) able to stabilize the polarization [Licht 16]. The use of asymmetric (metal / oxide) electrodes provides an additional mean to stabilize ferroelectricity by acting on the stiffness of the bonds at the interface.

**Environment:** Combinatorial synthesis of interface libraries will be carried out by combinatorial pulsed laser ablation (PLD) and sputtering in vacuum deposition system equipped with a high pressure RHEED for in-situ real-time characterisation. The samples will then be transferred with no vacuum break into UHV characterization chambers in order to study the electronic band structures, chemical composition and topography locally by scanning probe microscopies (direct tunnelling spectroscopy or BEEM mode [Roy 13], AFM, KPM...) or by XPS / UPS (work function, valence band spectroscopy... [Bal 13] [Rault 13]). The combination of AFM / XPS local characterization techniques with combinatorial interface synthesis without vacuum breaking is unique in Europe. These measurements will be supplemented by ex-situ electrical characterisations versus temperature. Devices micro-structuring will be carried out in clean room facilities shared with STMicroelectronics in Tours. The structure and composition of the best interfaces will then be characterized by electronic transmission microscopy. At the end of this thesis, the doctor will have acquired a broad spectrum of skills (synthesis and characterisation of films, fabrication and characterisation of devices) which will promote his professional insertion in academic or industrial research.

**Qualities sought:** we are looking for an enthusiastic and involved student who has
• High motivation
• Strong work capacity, particularly experimental
• A creative mind
• Ability to work as a team and independently
• Strong written, oral and interpersonal skills (English)
• Excellent Master's Degree in Physics, Chemistry or Materials Science
Knowledge of thin films, scanning probe microscopy and vacuum techniques would be a plus.

**Application:** questions and / or applications should be addressed to Jérôme Wolfman (wolfman@univ-tours.fr, tel: +33 (0)247367354) and Antoine Ruyter (ruyter@univ-tours.fr, tel: +33 (0)247366939) with:
• An academic resume
• An official list of courses taken and grades obtained in Master
• Contacts of two referents
• A letter of motivation highlighting your relevance to the proposed topic and your research experience

A first selection of candidates will be done based on the received documents. An interview organized by the doctoral school will then take place on May 18th 2017, possibly via skype.

**Details of the position to be filled:** This is a scholarship from the Ministry of Research for a gross annual amount of 20200 € over 3 years (~ 1300 € net / month). This is an equal opportunity opening, all nationalities are eligible. Funding starts in October 2017.

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