EPIDOX
Virtual workshop on oxide epitaxy

Wednesday Nov. 17th – Friday Nov. 19th 2021

Book of abstracts

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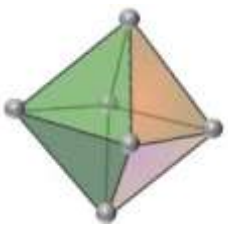

GDR OXYFUN

Program

Wednesday, november 17th 13H40-14H : Introduction (Guillaume Saint-Girons – INL)

Wednesday, november 17th PM : **Growth and structure I**

Chair : Nathalie Lemée (LPMC – Amiens)

14H—14H45 **Invited 1 : Hubert Renevier (LMGP – Grenoble)**

In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs and lamellar dichalchogenides

E.V. Skopin (1), P. Abi Younes (1), (2), L. Rapenne (1), H. Roussel (1), J.-L. Deschanvres (1), E. Blanquet (3), N. Aubert (4), G. Ciatto (4), L. Pithan (5), D. D. Fong (6), M.-I. Richard (7), C. Camp (8), M. Zhukush (8), (9), E. A. Quadrelli (9), N. Gauthiern (2), D. Rouchon (2) and H. Renevier (1)

(1) LMGP – Grenoble, (2) CEA/LETI – Grenoble, (3) SIMAP – Grenoble, (4) Synchrotron SOLEIL – Gif-sur-Yvette, (5) ESRF – Grenoble, (6) Material Science Division, Argonne National Laboratory – Argonne (USA), (7) CEA/IRIG/MEM/NRS & ESRF – Grenoble, (8) LCOMS – Villeurbanne, (9) IRCELYON – Villeurbanne

14H45 – 15H **Flash 1**

Growth-mode and interface structure of epitaxial ultrathin MgO/Ag(001) films

M. De Santis (1), V. Langlais (2), K. Schneider (2) and X. Torrelles (3)

(1) Institut Néel – Grenoble, (2) CEMES – Toulouse, (3) ICMAB – Barcelone

15H – 15H15 **Flash 2**

Unravelling the complex optical properties of heterogeneous transparent and conducting vanadates thin films grown on a 2D nanosheet layer by the means of Spectroscopic Ellipsometry

Hurand Simon (1), Boileau Alexis (2), Baudouin Florent (3), Luders Ulrike (2), Dallochio Marie, Cheikh Aimane (2), David Adrian (2), Paumier Fabien (1), Girardeau Thierry (1), Marie Philippe, Labbé Christophe (4), Cardin Julien (4), Aureau Damien (5), Frégnaux Mathieu (5), Guilloux-Viry Maryline (3), Prellier Wilfrid (2), Dumont Yves, Demange Valérie (3), Fouchet Arnaud (2)

(1) Institut Pprime – Poitiers, (2) CRISMAT – Caen, (3) ISCR – Rennes, (4) CIMAP – Caen, (5) Institut Lavoisier - Versailles

15H15 – 15h45 Break

15H45 – 16H30 **Invited 2 : Christophe Lefevre (IPCMS – Strasbourg)**

Structural characterization of oxide thin films by resonant x-ray diffractions

Christophe Lefevre

IPCMS – Strasbourg

16H30 – 16H45 **Flash 3**

The growth and properties of p-type transparent conducting thin films of the perovskite type

Oualyd El Khaloufi (1), Aimane Cheikh (1), Moussa Mezhoud (1), Adrian David (1), Christophe Labbé (2), Ulrike Lüders (1)

(1) CRISMAT – Caen, (2) CIMAP - Caen

16H45 – 17H00 **Flash 4**

Tuning transport properties by epitaxial strain in p-type Sr-doped LaCrO3 transparent thin films grown by MBE

Dong Han (1), Rahma Moalla (1), Ignasi Fina (2) Valentina M. Giordano (3), Marc d'Esperonnat (1), Claude Botella (1), Geneviève Grenet (1), Régis Debord (3), Stéphane Pailhès (3), Guillaume Saint-Girons (1) and Romain Bachelet (1)

(1) INL – Lyon, (2) ICMAB – Barcelona, (3) ILM – Lyon

Thursday, november 18th AM : **Growth and structure II**

Chair : Olena Popova (IPR – Rennes)

9H—9H45 **Invited 1 : Houssny Bouyanfif (LPMC – Amiens)**

Antiferroelectric like state in BiFeO3/LaFeO3 superlattices

Houssny Bouyanfif

LPMC - Amiens

9H45 – 10H **Flash 1**

Effect of the buffer layer on bias-field effects in Bi2FeCrO6 ferroelectric thin films

L. Wendling, X. Henning, F. Roulland, M. Lenertz, G. Versini, L. Schlur, A. Dinia, S. Colis, M.V. Rastei

IPCMS – Strasbourg

10H – 10H15 **Flash 2**

Epitaxial growth of Pb(Mg1/3Nb2/3)O3-33PbTiO3/SrRuO3 heterostructures on ReScO3 (RE=Dy, Gd, Sm, Nd) atomically flat single terminated substrates using pulsed laser deposition

Jamal Belhadi (1), (2), Urska Gabor (2), Hana Uršič (3), Nina Daneu (2), Gertjan Koster (4) and Matjaz Spreitzer (2)

(1) LPMC – Amiens, (2) Advanced Material Department, Josef Stefan Institute – Ljubjana (Slovenia), (3) Electronic Ceramics Department, Josef Stefan Institute – Ljubjana (Slovenia), (4) MESA+ – Twente (The Netherlands)

10H15 – 10H30 **Flash 3**

Electric field and temperature induced phase transitions in antiferroelectric thin films of PbZrO3

P. Dufour (1), A. Chanthbouala (1), T. Maroutian (2), C. Jacquemont (1), F. Godel (1), L. Yedra (3), M. Otonicar (4), N. Guiblin (3), M. Bibes (1), B. Dkhil (3), S. Fusil (1) and V. Garcia (1)

(1) UMR CNRS/Thales – Palaiseau, (2) C2N – Palaiseau, (3) LSPMS – Saclay, (4) Electronic Ceramics Department, Jožef Stefan Institute, Ljubljana

10H30 – 10h45 Break

10H45 – 11H30 **Invited 2 : Franck Vidal (INSP – Paris)**

Vertically self-assembled nanostructures : growth, structure and properties

Marcel Hennes, Thomas Tran, Dominique Demaille, Yunlin Zheng, Franck Vidal

INSP - Paris

11H30 – 11H45 **Flash 4**

Stabilization of the perovskite phase in Sr-doped NdNiO3 thin films grown by pulsed laser deposition

Guillaume Krieger, Nathalie Viart and Daniele Preziosi

IPCMS - Strasbourg

11H45 – 12H00 **Flash 5**

Pulvérisation cathodique radiofréquence de couches minces de titanates de nickel (NiTiO3) sur substrats de saphir : Croissance épitaxiale et axiotaxiale

Chettab Meriem (1), Simon Quentin (1), Demange Valérie (2), Laffez Patrick (1)

(1) GREMAN – Tours, (2) ISCR - Rennes

Thursday, november 18th PM : **oxides/semiconductors/2D systems**

Chair : Romain Bachelet (INL-Lyon)

14H—14H45 **Invited 1 : V. Demange (ISCR - Rennes)**

Nanofeuillets d'oxydes métalliques : templates pour la croissance orientée d'oxydes complexes

F. Baudouin (1), A. Boileau (2), J.J. Manguele (2), M. Dallocchio (2), S. Ollivier (1), P. Turban (3), J.C. Le Breton (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) ISCR, ScanMat – Rennes, (2) CRISMAT – Caen, (3) IPR – Rennes, (4) Institut PPrime – Poitiers, (5) GEMAC – Versailles

14H45 – 15H **Flash 1**

Transfert des couches minces d'oxyde de manganite (La0.7Sr0.3MnO3) et étude de leurs propriétés magnétiques

Moussa Mezhoud (1), Alexandre De Fonvillars (1), Saidur Rahman Bakaul (2), Wilfrid Prellier (1), Ulrike Lüders (1)

(1) CRISMAT – Caen, (2) Material Science Division, Argonne National Laboratory – Lemont (USA)

15H – 15H15 **Flash 2**

Growth analysis of thermal CVD alumina films deposited on bonding layers

Maoxiang Zhu (1), (2), (3), Sofiane achache (1), (2), Jean-François Pierson (3), Frédéric Sanchette (1), (2)

(1) LASMIS – Nogent, (2) NICCI – Nogent, (2) Institut Jean Lamour - Nancy

15H15 – 15h45 Break

15H45 – 16H30 **Invited 2 : Florencio Sanchez (ICMAB – Barcelona)**

Epitaxial ferroelectric doped HfO_2 thin films on Si(001)

Florencio Sanchez

ICMAB – Barcelona (Spain)

16H30 – 16H45 **Flash 3**

Integration of oxide ferromagnets with high spin polarization onto ZnO-based 2D, 1D nanostructures: growth, structure, properties of Fe3O4 onto ZnO(0001) substrates

Madaci Ismail (1) (2), Popova Elena (3), Philippe Vennéguès (2), Nemoz Maud (2), Berini Bruno (1), Stenger Ingrid (1), Morhain Christian (2), Dumont Yves (1)

(1) GEMAC – Versailles, (2) CRHEA – Valbonne, (3) IPR - Rennes

16H45 – 17H00 **Flash 4**

Effect of chromium substitution on structural and chemical properties of Fe3-xCrxO4(111) epitaxial thin films

Pâmella V. B. Pinho (1), (2), Alain Chartier (1), Frédéric Miserque (1), Cécile Marcelot (3), Bénédicte Warot-Fonrose (3), Antoine Barbier (2), Philippe Ohresser (4), Denis Menut (4), Jean-Baptiste Moussy (2)

(1) Den/SCCME/CEA/Université Paris-Saclay - Gif-sur-Yvette, (2) CEA/DRF/IRAMIS/SPEC – Saclay, (3) CEMES – Toulouse, (4) Synchrotron SOLEIL – Gif-sur-Yvette

Friday november 19th AM : **Oxide epitaxy techniques**

Chair : Thomas Maroutian (C2N – Palaiseau)

9H—9H45 **Invited 1 : Karine Dumesnil (IJL – Nancy)**

Ozone assisted MBE for the epitaxial growth of complex oxides

Karine Dumesnil

(1) IJL - Nancy

9H45 – 10H **Flash 1**

Sensitive RHEED signature of Ti-excess enabling enhanced cationic composition control during the molecular beam epitaxy of SrTiO3 based solid solutions

Masoumeh Razaghi, Marc d'Esperonnat, Claude Botella, Sébastien Cueff, Romain Bachelet and Guillaume Saint-Girons

INL - Lyon

10H – 10H15 **Flash 2**

Rare-earth oxide thin films deposited by direct liquid injection chemical vapour deposi-tion (DLICVD) for quantum technologies applications

Nao Harada, Alexandre Tallaire, Alban Ferrier, Diana Serrano, Philippe Goldner

IRCP – Paris

10H15 – 10h45 Break

10H45 – 11H30 **Invited 2 : Jerôme Wolfman (GREMAN – Tours)**

Exploration de diagrammes de phases et de propriétés interfaciales par synthèse combinatoire de films oxydes

Jerôme Wolfman

GREMAN - Tours

11H30 – 11H45 **Flash 3**

High quality, large area deposition of vanadium dioxide (VO2) using magnetron sputtering

Sirjita Eduard-Nicolae (1) (2), Boulle Alexandre (2), Mayet Richard (2), Orlianges Jean-Cristophe (1), Crunteanu Aurelian (1)

(1) XLIM – Limoges, (2) IRCer – Limoges

11H45 – 12H00 **Flash 4**

Chemical Beam Epitaxy and Sybilla Equipment

G. Benvenuti (1), E. Wagner (2), W. Maudez (2), R. Rani (2), S. Bagdzevicius (2)

(1) ABCD Technology – Nyon (Switerland), (2). 3D-Oxides – St Genis Pouilly

12H – 12H15 : Closure (Guillaume Saint-Girons – INL)

Invited contributions

In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs and lamellar dichalchogenides

E.V. Skopin[1], P. Abi Younes[1,2], L. Rapenne[1], H. Roussel[1], J.-L. Deschanvres[1], E. Blanquet[3], N. Aubert[4], G. Ciatto[4], L. Pithan[5], D. D. Fong[6], M.-I. Richard[7], C. Camp[8], M. Zhukush[8,9], E. A. Quadrelli[9], N. Gauthier[2], D. Rouchon[2] and H. Renevier[1]

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[2]Univ. Grenoble Alpes, CEA, LETI, F-38054 Grenoble, France;
[3]Univ. Grenoble Alpes, CNRS, Grenoble INP*, SIMAP, 38000 Grenoble, France
[4]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, F-91192, Gif sur Yvette, France
[5]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
[6]Materials Science Division, ANL, 9700 S. Cass Ave., Argonne, Illinois 60439, United States
[7]Univ. Grenoble Alpes, CEA Grenoble, IRIG, MEM, NRS, F-38000 Grenoble, France & European Synchrotron Radiation Facility, F-38043 Grenoble, France
[8]Université de Lyon, CP2M, Laboratoire de Chimie Organométallique de Surface UMR5265 CNRS-CPE-UCBL1 43, Boulevard du 11 Novembre 1918, BP 2077 F-69616, Villeurbanne Cedex, France
[9]Université de Lyon, IRCELYON, Institut de Recherche sur la catalyse et l'environnement (UMR 5256 CNRS Université Lyon1), 2 av. Albert EINSTEIN, 69100 Villeurbanne, France.
*Institute of Engineering Univ. Grenoble Alpes
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In the microelectronics industry, Atomic Layer Deposition (ALD) is widely employed for the growth of conformal thin films with sub-nanometer thickness control, as it can be performed at the low temperatures compatible with industry specifications. An outstanding problem in the ALD community is understanding how to reproducibly synthesize an ultrathin layer on a given substrate with the desired structural and electronic properties. Achieving this requires precise understanding of the surface chemistry, growth and crystallization mechanisms that take place.

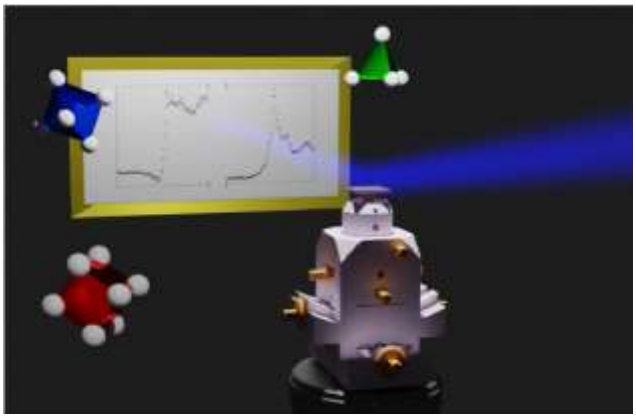
We will report on the fabrication of nanometer thick ZnO films used as tunneling insulators at the metal-$In_{0.53}Ga_{0.47}As$ (InGaAs) heterojunction [1,2] and Titanium disulfide (1T-TiS_2) which belongs to the layered transition metal dichalcogenide family (TMDC), with electrical properties ranging from semiconductor to semi-metallic [3]. Exploiting an unique ALD chamber built to mount onto an heavy duty X-ray diffractometer [4], we have conducted a suite of *in situ* synchrotron X-ray experiments to reveal the atomistic and microstructural processes taking place during the growth of ALD ZnO on InGaAs from 0 to ~10 nm in film thickness, and to study a 2-steps synthesis of TiS_2 ultra-thin films on 100 nm thick SiO_2, by molecular layer deposition (MLD) and thermal treatment [5].

The approach and techniques we employ are broadly applicable to a wide range of other oxides/semiconductor systems, ultrathin films and lamellar 2D materials.

[1] E. Skopin et *al*. (2018) Nanoscale 10, 11585.
[2] E. Skopin et *al*. (2020) Phys. Rev. Mat. 2, 043403
[3] Stoliaroff et *al*. (2019) Inorg. Chem. 58, 1949. Stoliaroff et *al*. (2019) Physical Review B 99, 165122. Wang et *al*. (2019) J. Phys. Chem. Lett. 10, 699.
[4] R. Boichot et *al*. (2016) Chem. Mater. 28, 592. M.-H. Chu et *al*. (2016). Crystal Growth & Design 16, 5339.
[5] P. Abi Younes et *al*. (2021). *To be published*.

Structural characterization of oxide thin films using Resonant Elastic X-ray Scattering (REXS)

Christophe LEFEVRE
Institut de Physique et Chimie des Matériaux de Strasbourg (CNRS – Univ. Strasbourg UMR 7504)



Oxide thin films have been enthusiastically considered for introducing new features in electronic devices over this last decade. Crystal structure of those samples is a key point for the studies since it's linked to some properties such as magnetic properties or electric ones (polarization). If both cationic distribution and crystallographic position can be easily determined in bulk materials using classical methods such as X-rays or neutron diffraction, they are extremely tricky to determine in thin films owing to the relatively small amount of material to probe.

Anomalous scattering experiments have shown over the past ten years their capabilities for locating metal atoms on different sites, even in cases of small occupancies, and even in mixed metal situations (e.g. [1-4]). X-ray anomalous diffraction, benefiting from the tunable energy of the synchrotron, consists of recording the intensity of a Bragg reflection as a function of the energy of the scattered photons crossing an atomic absorption edge. It results to a variation of the atomic form factors leading to REXS spectra [5]. REXS is sensitive both to the local environment of the absorbing atom through the anomalous process and to the long-range order involved in the diffraction process.

Here, we will show that this non-destructive technique is perfectly adapted to probe the crystal structure. Moreover, the orientation of the polar cell on the substrates can be easily determinate (even visually on recorded spectra) [6]. Cationic distribution in spinel type (2 cationic sites) samples or in the GaFeO3 (4 cationic sites) compounds will be introduced [6-7]. Finally, recent work on cationic position and oxygen position in thin films will be shown.

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1 J.-L. Hodeau, V. Favre-Nicolin, S. Bos, H. Renevier, E. Lorenzo, and J.-F. Berar, Chem. Rev. **101**, 1843 (2001).
2 O. Oeckler, M.N. Schneider, F. Fahrnbauer, and G. Vaughan, Solid State Sci. **13**, 1157 (2011).
3 S. Welzmiller, P. Urban, F. Fahrnbauer, L. Erra, and O. Oeckler, J. Appl. Crystallogr. **46**, 769 (2013).
4 V. Favre-Nicolin, M.G. Proietti, C. Leclere, N.A. Katcho, M.-I. Richard, and H. Renevier, Eur. Phys. J. Spec. Top. **208**,
189 (2012).
5 S. Grenier, Y. Joly, Journal of Physics: Conference Series 519 (2014) 012001
6 C. Lefevre *et al.*, Small Methods. 1 (2017) 1700234
7 E. Martin *et al.*, Journal of Alloys and Compounds. 836 (2020) 155425.

Antiferroelectric like state in $BiFeO_3/LaFeO_3$ superlattices

H. Bouyanfif

LPMC, Université de Picardie Jules Verne, Amiens, France

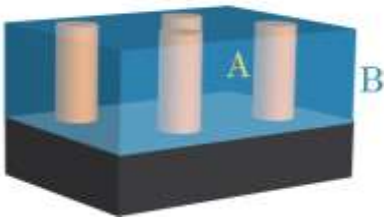
Bismuth ferrite ($BiFeO_3$ or BFO) is the most studied multiferroic due to its robust ferroelectric state (TC = 1100K) coexisting at room temperature with an antiferromagnetic order (TN=640K). Such coexistence and the possible cross coupling between both ferroic orders pave the way to so-called MagnetoElectric RAM combining advantages of the ferroelectric and the antiferromagnetic state. BFO also shows an anomalous photovoltaic response and an important piezoelectric response when doped with rare earth ($(Bi,RE)FeO_3$ solid solution). Similarly to the relaxor-ferroelectric systems ($PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$) a morphotropic phase boundary has been observed in La doped BFO $(Bi,La)FeO_3$ solid solution with peculiar nanoscale mixture (incommensurate and antiferroelectric ordering). Emergence of such MPB is believed to arise from the competition between antiferrodistortive and ferroelectric instabilities. Our approach to investigate the structural interaction between BFO and LFO is based on superlattices. These epitaxial multilayers were grown by pulsed laser deposition and characterized by Raman spectroscopy, electronic and X-Ray diffraction. Structural characterizations and Raman spectroscopy indicate an anti-polar structure in the BFO layers of the SLs that is strongly dependent on the BFO thickness and temperature[1]. This antiferroelectric like structure, very similar to the $PbZrO_3$ system, cannot be explained solely by the nature of the induced strain (compressive vs tensile) but by the symmetry mismatch at the interfaces of the SLs. Compatibility of the octahedral tilt system seems to be the main driving force for this induced anti-polar state.

[1]. B. Carcan, H. Bouyanfif, M. El Marssi, F. Le Marrec, L. Dupont, C.Davoisne, J. Wolfman, D. C. Arnold, Phase diagram of $BiFeO_3/LaFeO_3$ superlattices: antiferroelectric-like state stability arising from strain effects and symmetry mismatch at heterointerfaces, Advanced Materials Interfaces 4 (11), 1601036 (2017)

Vertically self-assembled epitaxial nanostructures: growth, structure and properties

Marcel Hennes[1], Thomas Tran[1], Dominique Demaille[1], Yunlin Zheng[1], Franck Vidal[1]

1. Institut des NanoSciences de Paris, Sorbonne Université, CNRS UMR7588



Self-assembled vertically aligned nanocomposites (VANs) have recently emerged as a novel playground for strain engineering of physical properties in nanostructures. In contrast to thin films obtained by classical planar heteroepitaxy, VANs consist of two (or more) intertwined phases, coupled along vertical interfaces (as illustrated in the Figure, in the case of a two-phases A-B composite). Their unique nanoarchitecture, which can be tuned by choosing appropriate growth conditions, results in deformations that cannot be easily attained in traditional flat geometries [1].

In this contribution, we will show how nanometer-sized acicular inclusions of magnetic 3d metals in various oxide host matrices can be obtained via sequential pulsed laser deposition [2]. We will then present experimental results on the strain state of the VANs, obtained by x-ray diffraction and transmission electron microscopy, and discuss the mechanisms involved in the relaxation of strain in VANs [3-4]. We will demonstrate how the magnetic properties of the thin films can be controlled accurately by relying on the strain applied along the backbone of the nanowires [5].

We will finally present possible extensions of the sequential growth approach to more than one embedded phase and sketch some of the remaining challenges that must be overcome to create novel functional nanoarchitectures.

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[1] M. Hennes, D. Demaille, G. Patriarche, T. Tran, Y. Zheng, F. Vidal, Strain, magnetic anisotropy, and composition modulation in hybrid metal–oxide vertically assembled nanocomposites, MRS Bulletin 46, 136 (2021)

[2] M. Hennes, V. Schuler, X. Weng, J. Buchwald, D. Demaille, Y. Zheng, F. Vidal, Growth of vertically aligned nanowires in metal-oxide nanocomposites: kinetic Monte-Carlo modeling versus experiments, Nanoscale 10, 7666 (2018)

[3] X. Weng, M. Hennes, A. Coati, A. Vlad, Y. Garreau, M. Sauvage-Simkin, E. Fonda, G. Patriarche, D. Demaille, F. Vidal, Y. Zheng, Ultrathin Ni nanowires embedded in $SrTiO_3$: Vertical epitaxy, strain relaxation mechanisms, and solid-state amorphization, Physical Review Materials 2, 106003 (2018)

[4] X. Weng, M. Hennes, T. Tran, N. Casaretto, D. Demaille, F. Vidal, Y. Zheng, Orientation and lattice matching of CoNi
nanowires embedded in SrTiO3: unveiling novel strain relaxation mechanisms in vertically aligned nanocomposites, CrystEngComm, 22, 4730 (2020)

[5] G. Radtke, M. Hennes, M. Bugnet, Q. Ramasse, X. Weng, D. Demaille, B. Gobaut, P. Ohresser, E. Otero, F. Choueikani, A. Juhin, Ph. Sainctavit, Y. Zheng, F. Vidal, Atomic-Scale Study of Metal-Oxide Interfaces and Magnetoelastic Coupling in Self-Assembled Epitaxial Vertically Aligned Magnetic Nanocomposites, Advanced Materials Interfaces 1900549 (2019)

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], J.C. Le Breton[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]

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[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

Functional properties such as ferroelectric, multiferroic or transparent conducting oxide in 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 $SrTiO_3$) 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 $KCa_2Nb_3O_{10}$, $K_{0.8}Ti_2O_4$, $K_4Nb_6O_{17}$ and $Cs_6W_{11}O_{36}$ 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 $La_{0.67}Sr_{0.33}MnO_3$ [4], $KNbO_3$ [5] and $BiFeO_3$ [6] on glass, silicon and mica. Significant results have also been recently obtained on the integration of $SrVO_3$ and $CaVO_3$ 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]. As a perspective, we will present first results of attempts to obtain self-supported films by the means of nanosheets.

[1] M. A. Timmerman, R. Xia, P.T.P. Le, Y. Wang, J.E. Elshof. Chem. Eur. J. **26**, 1 (2020)
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Epitaxial ferroelectric doped HfO_2 thin films on Si(001)

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Ferroelectric HfO_2 is a promising material for new memory devices, but the microstructure of HfO_2 films needs to be better controlled, and some properties such as endurance have to be improved. Research of ferroelectric HfO_2 is mainly focused on polycrystalline films. In contrast, epitaxial films have been much less investigated [1]. The recent stabilization of the orthorhombic ferroelectric phase in epitaxial doped-HfO_2 films on perovskite $La_{0.7}Sr_{0.3}MnO_3$ electrodes has allowed an important progress, including the control of the formed crystalline polymorphs through substrate selection [2,3]. It has also allowed the epitaxial integration of doped-HfO_2 on Si(001) [4-7]. Here I will show that different buffer layers permit epitaxial growth on Si(001) of $Hf_{0.5}Zr_{0.5}O_2$ and other doped-HfO_2 films exhibiting excellent ferroelectric properties. Epitaxial doped-HfO_2 films on Si(001) have high polarization, endurance and retention. These properties can occur simultaneously, without the dilemmas often seen in polycrystalline samples between these three properties. The robust ferroelectric properties are observed in films even thinner than 5 nm. The epitaxial doped-HfO_2 films on Si(001) are thus of great interest for understanding ferroelectric properties and for prototyping devices.

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Ozone-assisted Molecular Beam Epitaxy for the growth of complex oxides systems

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Transition metal oxides attract an increasing interest driven by their wide range of physical properties and the opportunity to functionalize them in nanometric heterostructures for new electronic devices. Among these, the rare earth (RE) vanadates-based nanosystems have been highlighted as potential new multiferroic materials [1]. Ab initio calculations namely predict (i) the emergence of hybrid improper ferroelectricity in layered structures combining different cations, and (ii) the coupling of the polarization to Jahn-Teller distortions leading to a direct and strong coupling between polarization and magnetism [1]. Our objective is therefore to synthetize a multiferroic material in combining strains and interfaces engineering in AVO_3/$A'VO_3$ superlattices. In order to achieve an ultimate control of the interfaces where the ferroelectricity should emerge, the systems are grown in a Molecular Beam Epitaxy chamber with controlled ozone pressure.

The scope of this presentation is first to give an extensive presentation of this ozone-assisted MBE equipment (Fig. 1 (a)). This technique is namely rather unusual in the field of oxides growth, widely dominated by Pulsed Laser Ablation. We will emphasize the specificities of ozone MBE for the growth of oxides, compared to conventional MBE for metals and detail our specific MBE (DCA) connected to the UHV Daμm instrument at IJL.

In a second step, we will present our recent results obtained on $LaVO_3$ and $PrVO_3$ thin films [3], and $LaVO_3$/$PrVO_3$ superlattices. The growth window (deposition temperature and ozone pressure) has been optimized to obtain highly controlled 2D growth and stoichiometry. Electronic microscopy experiments allowed the accurate determination of the atomic positions [2,3] (Fig.1 (b)) and enabled the observation of the RE atoms displacements required for the appearance of ferroelectricity. $(LaVO_3)_n$/$(PrVO_3)_m$ superlattices of high quality have been grown, ultimately as a stacking of one unit cell individual layers, for which first electric characterization suggests a ferroelectric behavior.

The last part of the presentation will be devoted to other examples of systems synthetized by ozone-MBE. In these later, the authors take full benefit of the Atomic-Layer-by-Layer growth by MBE to design materials at the atomic level and explore new magnetic, supraconductive, multiferroic or thermoelectric properties [4-7].

Fig. 1: (a) Picture of the IJL ozone-MBE connected to the Daμm equipment at IJL (b) Local displacement of RE atoms extracted from HRTEM observation of a $LaVO_3$ epitaxial film.

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Flash presentations

Growth-mode and interface structure of epitaxial ultrathin MgO/Ag(001) films

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MgO ultrathin films are of great technological importance as electron tunneling barriers in electronics and spintronics. They are also well suited for on-surface-synthesis of molecular networks for 2D electronics, the wide-band gap of MgO allowing for a decoupling from the substrate. Their crystallographic quality, interface structure, and surface morphology play a crucial role in applications. On Ag(100), MgO films form islands whose morphology is function of the growing temperature [1] and of aftergrowth treatments [2]. Using surface x-ray diffraction, we studied the growth-mode and the structure of MgO/Ag(001) ultrathin films elaborated by reactive molecular beam epitaxy as function of the substrate temperature [3]. At 620 K, MgO is (001) oriented and forms, in a first stage, sharp bilayer islands in coherent epitaxy with the substrate. Oxygen at the interface is on top of silver atoms, as predicted by DFT calculations [4], at an interlayer distance of about 270 pm. The experiment was performed using the INS2 set-up on the French CRG-IF beamline at ESRF.

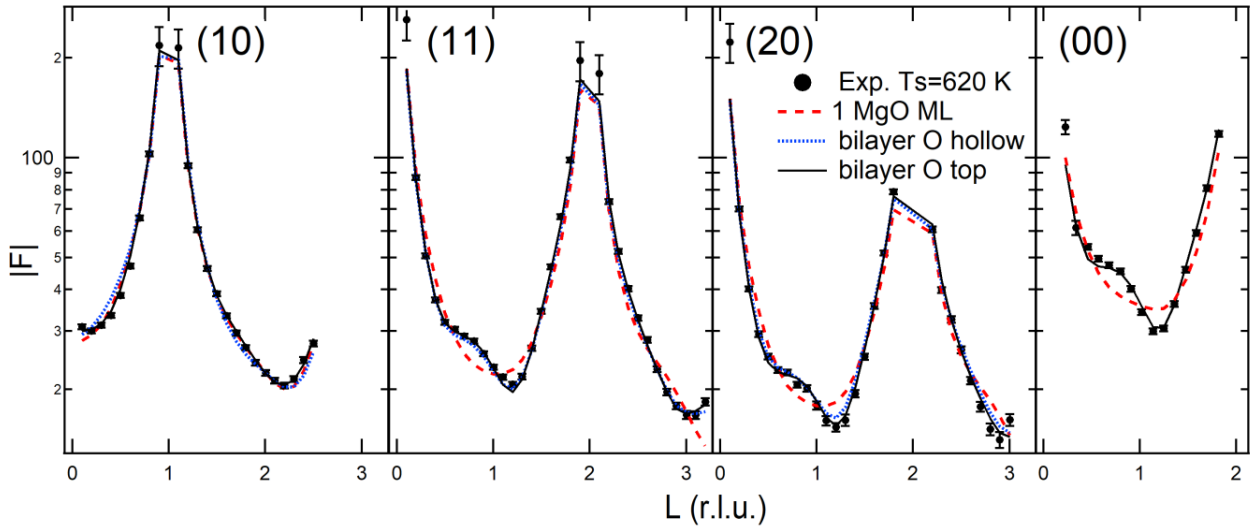

Fig. 1: Experimental crystal truncations rods (CTRs) of a MgO/Ag(001) film grown by deposition of 0.8 Mg ML in 10^{-6} mbar of O_2 at Ts=620 K (black circles); best fit bilayer model with O on top of Ag (continuous black line, χ^2=2.3), monolayer model (red dashed line, χ^2=22), and O in hollow sites model (blue dotted line, χ^2=7.2).

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EPIDOX Workshop sur l'épitaxie des oxydes ☒ **Oral** ☐ **Poster**

The growth and properties of p-type transparent conducting thin films of the perovskite type

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The aim of our project is to grow solid solution thin films of (La,Sr)VO_3 (LSVO) and (La,Sr)CrO_3 (LSCO) by pulsed laser deposition (PLD). These materials have been recently identified as new p-type transparent conducting oxides (TCO) [1], with a high potential for the development of transparent p-type electrodes for a more efficient holes collection in photovoltaic cells or transparent electronics. We will explore different compositions to understand the impact of doping on the electrical and optical properties, and to evaluate the p-type conduction in this type of materials in order to constitute a p-n junction with the n-type TCO $SrVO_3$ (SVO).

All samples were grown on a $SrTiO_3$ (001) monocrystalline substrates. In order to gain a high flexibility concerning the composition of the solid solution, the deposition of the thin films is made from two targets of the respective parent compounds. By choosing a number of pulses on each target allowing the growth of less than one unit cell, the solid solution can be formed in the thin film by successive depositions from each target. Several optimizations were performed in order to evaluate the impact of the different deposition parameters (temperature, energy, distance…) on the quality of the thin films, and to gain an overview on the phase diagram of the solid solutions in the thin film form.

Concerning the LSVO films, we show that doping SVO with La improves the electrical n-type properties, with a resistivity of pure SVO of 270 μΩcm at 300K to 159 μΩcm for the composition $La_{1/2}Sr_{1/2}VO_3$. The samples were confirmed to be transparent, making LSVO a TCO with improved electrical behaviors compared to SVO. The metal-insulator transition for about 80% of La doping [2] is observed, but nevertheless, no p-type behavior was found within the realized vanadate thin film solid solutions.

Similar studies were carried out for the LSCO solid solution. In this system, we show that a certain amount of oxygen background pressure during the deposition is necessary to generate p-type conduction in this solid solution, ranging in the area of 30 mΩcm, which is an excellent value for p-type TCO [2]. The relations between the deposition parameters, the structural and chemical changes of the thin films and the resulting properties will be discussed on the basis of these two, closely related solid solutions, showing however a quite different evolution of the properties with the growth parameters.

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Unravelling the complex optical properties of heterogeneous transparent and conducting vanadates thin films grown on a 2D nanosheet layer by the means of Spectroscopic Ellipsometry

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Indium-tin-oxide (ITO) is a widely employed transparent conducting oxide (TCO), but indium scarcity and price encourage developing some alternatives. The correlated metals $CaVO_3$ and $SrVO_3$ have been recently identified as new TCOs with functional properties being comparable to ITO [1]. However, their technological potential is limited by the critical requirement of a perovskite structure of the film, impossible to achieve by a direct growth on substrates commonly used for applications. In a recent work [2], we tackle this limitation by demonstrating the crystalline growth of vanadate TCOs on glass at temperatures below 600 °C, with the help of 2D nanosheets as transparent seed layers. The functional properties do not suffer from the textured structure of the films, as confirmed by an in-depth spectroscopic ellipsometry study, thus providing an industrially viable approach to integrate vanadate TCOs on virtually any surface and to exploit their promising performances as a new generation TCO.

To investigate the optical properties of such complex heterogeneous thin films, there is a need to develop the adequate tools. Indeed, the thin films result in a percolating network of crystalline $CaVO_3$ and $SrVO_3$, on the regions of the film covered by the nanosheet, with the inclusion of amorphous $CaVO_3$ and $SrVO_3$ on the regions not covered by them. We use advanced optical models taking into account the anisotropic and heterogeneous nature of the film in order to decorrelate and quantify the contributions of these two phases (crystallized and amorphous) by the means of spectroscopic ellipsometry. We are thus able to extract the optical indexes of the crystallized phase, and its coverage rate in the film. As $CaVO_3$ and $SrVO_3$ exhibit strong electronic correlations, we also investigate the infrared optical properties of these films in order to determine their effective mass and plasma frequency through a generalized Drude model analysis. This innovative optical modelling provides a framework to investigate the optical properties of such heterogeneous thin films grown on a nanosheet template.

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Tuning transport properties by epitaxial strain in *p*- type Sr-doped $LaCrO_3$ transparent thin films grown by MBE

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Transparent conducting and thermoelectric perovskite oxides of general formula ABO_3 are appealing because of their chemical flexibility with abundant and low toxicity elements, property tunability by doping and correlation effects, thermal stability, structural compatibility for epitaxy and direct integration on semiconductors (Si, Ge, GaAs) by molecular beam epitaxy (MBE) [1-3]. Whereas various *n*-type ABO_3 are available, as $SrTiO_3$-based solid solutions exhibiting large transmittance (>60%) in the visible range, low resistivity (10^{-3} Ω.cm) and large thermoelectric power factors (PF ~40 μW cm^{-1} K^{-2}) [4-6], the counterpart *p*-type ABO_3 are much less known. Sr-doped $LaCrO_3$ is one of the few *p*-type transparent thermoelectric ABO_3 exhibiting optimal PF around 25 at.% Sr ($La_{0.75}Sr_{0.25}CrO_3$) [7].

In this communication, we will first show that high-quality Sr-doped $LaCrO_3$ epitaxial films can be elaborated by solid-source MBE [8], and secondly that the transport (electronic and thermoelectric) properties of $La_{0.75}Sr_{0.25}CrO_3$ can be largely tuned by epitaxial strain within ± 2% range (see Figure) [9]. In particular, the electric conductivity can be controlled over two orders of magnitude, ranging from ~0.5 S cm^{-1} (tensile strain) to ~35 S cm^{-1} (compressive strain). Consistently, the Seebeck coefficient can be finely tuned by a factor of almost two from ~127 μV K^{-1} (compressive strain) to 208 μV K^{-1} (tensile strain). The thermoelectric power factor can consequently be tuned by almost two orders of magnitude. The compressive strain yields a remarkable enhancement by a factor of three for 2% compressive strain with respect to almost relaxed films.

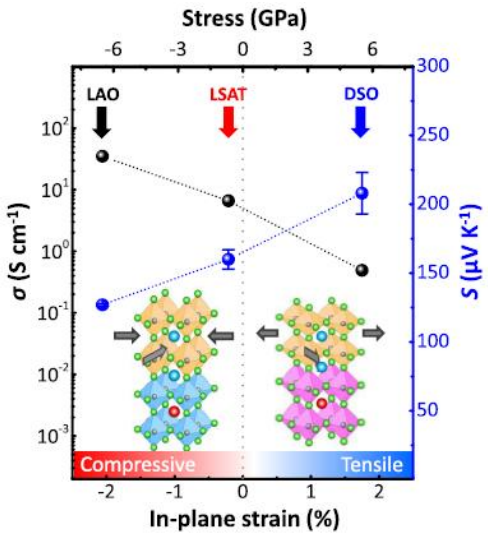

Figure: *In-plane electrical conductivity and Seebeck coefficient of $La_{0.75}Sr_{0.25}CrO_3$ epitaxial thin films as a function of in-plane strain and corresponding stress.*

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Epitaxial growth of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$33PbTiO_3$/$SrRuO_3$ heterostructures on $ReScO_3$ (Re=Dy, Tb, Gd, Sm, Nd) atomically flat single terminated substrates using pulsed laser deposition

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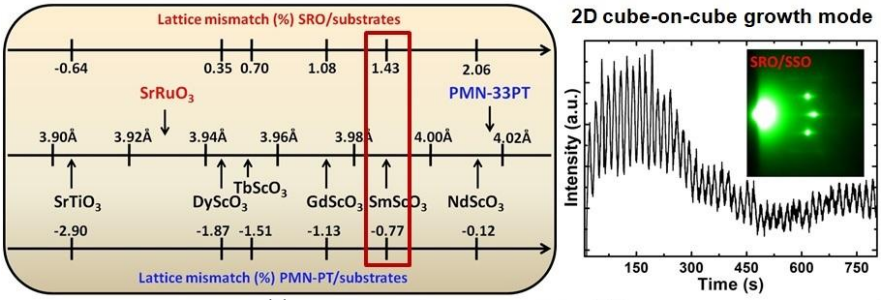
Relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-xPT) system is widely studied because their outstanding dielectric and electromechanical properties in single crystal and ceramic materials which are related to the presence of a complex polar domain structure near the morphotropic phase boundary (MPB). However, thin film materials have received little effort compared to their bulk counterparts, particularly the correlations between the local nano-domain structures and the functional properties which are mainly due to the experimental challenge of growing epitaxial high quality samples free from pyrochlore phases. In this work, by optimizing the pulsed laser deposition parameters and by designing the composition of PMN-xPT targets, high quality thin films near the MPB are grown on high crystalline quality and single terminated $ReScO_3$ (Re=Dy, Tb, Gd, Sm, Nd) substrates with different unit-cell sizes. In-situ Reflection High-Energy Electron Diffraction is used to monitor the growth mode and surface quality of the layers during the growth. The phase, crystalline quality and the domain structure of the as grown films are controlled using high resolution X-ray diffraction and scanning transmission electron microscopy. The functional properties of PMN-xPT are determined locally using piezoresponse force microscopy and by macroscopic electrical measurements and are correlated to the growth conditions, domain structures and strain state.



Stabilization of the perovskite phase in Sr-doped $NdNiO_3$ thin films grown by pulsed laser deposition

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Perovskite rare-earth nickelates[1] $R NiO_3$ (*R* being a rare-earth) have been the leitmotiv of intense theoretical and experimental research efforts assuming that they could mimic the high-T_c superconductivity[2] of cuprates for which a Cu 3d-e_g orbital selective Cooper pairing is supposed to be responsible of the zero-resistance state[3]. Recently, such a zero-resistance state was obtained in Sr-doped $NdNiO_2$ thin films (isostructural to cuprates), where the pristine (Nd,Sr)NiO_3 thin film was reduced by a CaH_2 powder via a so-called topotactic process[4]. So far, this superconductive state has been really hard to obtain and only 4 groups (Stanford[4], Singapour[5], two in China[6,7]) manage to exhibit this property. Here, we will introduce our efforts to reproduce this result on Sr-doped $NdNiO_3$ grown by Pulsed Laser Deposition technique with different Sr-doping content. The stabilization of the perovskite phase upon Sr doping is a mandatory step to have a superconducting state after the reduction. We will show our results mainly regarding the improvement of the growth conditions (laser fluence, oxygen atmosphere, ablation area) to overcome the problems related to obtain the infinite-layer without any undesired phase. The optimization of the growth conditions has been done without $SrTiO_3$ capping layer on the (Nd,Sr)NiO_3 thin films, but further samples have been grown with a capping layer to study its influence on the quality and stability of the infinite-layer phase. Differences and similarities of synthesis conditions and physical properties between capped and uncapped samples will be discussed.

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Pulvérisation cathodique radiofréquence de couches minces de titanates de nickel ($NiTiO_3$) sur substrats de saphir : Croissance épitaxiale et axiotaxiale

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La stabilisation de structures métastables d'une même composition peut engendrer l'exaltation de propriétés présentes dans certaines classes de matériaux et parfois même faire émerger de nouvelles propriétés physico-chimiques. La famille des titanates $ATiO_3$ (avec A = Mn, Fe, Ni, …) peut être citée pour illustrer ce propos. En effet, les titanates cristallisent sous forme ilménite (IL) sous conditions standards de température et de pression. Si l'ilménite est soumise à de hautes températures et hautes pressions (contraintes) lors de la croissance, elle se stabilise en structure type-$LiNbO_3$ (LN) non-centrosymétrique et par conséquent ferroélectrique (voire multiferroïque) à l'opposé de son homologue centrosymétrique IL. La ferroélectricité des titanates de structure LN a été prouvée par des études théoriques [1] et expérimentales[2].

Une des stratégies pour stabiliser ladite structure est sa structuration sous forme de couches minces afin de mettre à profit les différents types de contraintes résultant de la réduction d'échelle, de la technique de croissance et du substrat utilisé. En outre, la croissance en couches minces permet de manipuler l'orientation des structures et par conséquent les axes de facile aimantation et polarisation afin de tirer le maximum de ces propriétés suivant l'application visée.

Ce travail présente une étude structurale sur la croissance de couches minces de titanates de nickel ($NiTiO_3$) par pulvérisation cathodique magnétron radiofréquence sur substrats de saphir (Al_2O_3). Ces couches sont déposées sur différentes orientations du saphir (R(012), C(006), M(300) et A(110)) afin d'orienter les axes de polarisation perpendiculairement ou dans le plan du substrat en vue de mesures électriques. Les effets de la pression de dépôt, de l'épaisseur de la couche ainsi que de la température du substrat ou de recuit *ex situ* sur la croissance de $NiTiO_3$ y sont discutés. La diffraction des rayons X cinq cercles a permis d'extraire les paramètres de mailles des couches hors et dans le plan du substrat et d'établir des relations épitaxiales entre $NiTiO_3$ et Al_2O_3. En particulier, sur saphir C(006), l'augmentation de l'épaisseur du film conduit à une réorientation des cristallites qui est discutée selon un modèle de croissance par Domain Matching Epitaxy (DME) et par axiotaxie.

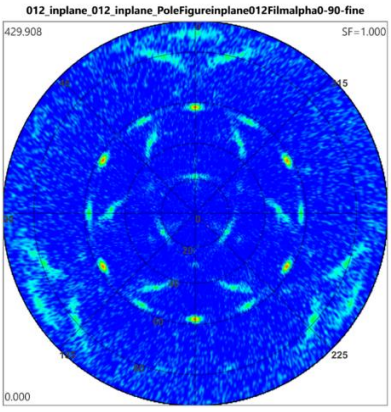

Figure 1 : Figure de poles {012} d'une couche mince de $NiTiO_3$ déposée par pulvérisation cathodique sur un substrat de saphir (0001). Sur cette figure, les spots intenses indiquent une croissance par épitaxie et les arcs de cercles indiquent une croissance par axiotaxie.

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Effect of the buffer layer on bias-field effects in Bi_2FeCrO_6 ferroelectric thin films

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Ferroelectric thin films attract a particular interest due to their potential applications in photovoltaics, spintronics, high-density data storage, ultrafast recording, microactuators, or broadband microwave phase shifters. For most of these applications, highly crystalline thin films are needed. Ferroelectric Bi_2FeCrO_6 (BFCO) double perovskite thin films were grown by pulsed laser deposition on Nb-doped $SrTiO_3$ (001) (Nb:STO) and $SrTiO_3$ (001) covered with a 30 nm thick $La_{2/3}Sr_{1/3}MnO_3$ buffer layer. Because of the mismatch between BFCO and the substrates, the films are therefore strained which is expected to impact the BFCO local properties [1]. In this sense, the ferroelectric properties are explored using piezoresponse force microscopy (PFM). The samples exhibit asymmetric polarization hysteresis loops with respect to the external bias voltage which indicates the presence of a bias field at the interface. This effect corroborates with a preferential ferroelectric polarization direction as the loops become wider with a significant displacement of one of the switching fields when the samples are poled in the opposite direction with respect to the preferential polarization direction. A partial recovery of the asymmetry of the hysteresis loops is obtained when the samples are poled back in their preferential polarization direction. This demonstrates a mutual influence between the polarization and the interface bias field. Surprisingly, the results are close whether BFCO is grown directly on Nb:STO or on LSMO, which shows that even if the mismatch between BFCO and LSMO is slightly larger the bias-field effects aren't impacted. This can be explained by the fully strained character of LSMO on the STO substrate and by the conduction properties of LSMO and Nb:STO. The findings can be of relevance for all strained ferroelectric thin-film materials obtained by epitaxial growth on atomically flat substrates.

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Electric field and temperature induced phase transitions in antiferroelectric thin films of $PbZrO_3$

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Antiferroelectric materials have been mainly investigated for their potential application in high energy storage capacitors. We aim at exploring epitaxial antiferroelectric thin films to integrate them in antiferroelectric tunnel junctions [1]. The ferroelectric phase transition in antiferroelectric tunnel junctions may be accompanied by a change of the tunnel transmission, and exploited as relaxation oscillators that mimic spiking neurons for neuromorphic computing. In addition, antiferroelectric thin films might harbor fundamental peculiarities in the phase transitions or the interplay between strain and tilt patterns.

In this study, we elaborated thin films of $PbZrO_3$ by pulsed laser deposition on $GdScO_3$(110) substrates. The films grow in the (001)-oriented orthorhombic phase under a slight compressive strain. $Pt/PbZrO_3/Ba_{0.5},Sr_{0.5}RuO_3$ capacitors show clear double hysteresis, signature of the antiferroelectric state. The ferroelectric transition can also be probed through the Pt top electrode by the in-field signal of piezoresponse force microscopy (PFM) within a quasi-static regime [2], showing four amplitude peaks assigned to the AFE-FE and FE-AFE transitions. In order to bring together PFM(E) and P(E) measurement dynamics, a new protocol is elaborated to perform fast measurements of the d_{33} piezoelectric response. This new way to probe the AFE-FE switching by PFM also appears to be a powerful tool to investigate ultrathin films. We observed ferroelectric-like state in a 4-nm $PbZrO_3$ thin film, in agreement with theoretical predictions [3]. In addition, phase transitions are observed in the 45-nm-thick films when increasing temperature. Electric measurements suggest a transition to an intermediate ferroelectric phase below the bulk critical temperature. While the characteristic sequences of lead displacements and oxygen octahedra tilts of the antiferroelectric phase are observed at room temperature, scanning transmission electron microscopy images reveal a structural rearrangement to a ferroelectric-like configuration at higher temperature. Finally, we started to optimized two buffer layers $LaScO_3$ and $LaLuO_3$ with large lattice parameters in order to study the effect of epitaxial strain on antiferroelectric properties.

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Growth analysis of thermal CVD alumina films deposited on bonding layers

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Thermal CVD α-Al_2O_3 and κ-Al_2O_3 coatings deposited on Ti(C,N)-based layers are widely used for machining applications. The nucleation of κ-Al_2O_3 is favorably occurring on non-oxidized surfaces of Ti(C,N), if the stable α-Al_2O_3 phase shows excellent thermal stability compared to the metastable κ-Al_2O_3 phase, it is found to be more difficult to be deposited [1]. Furthermore, It is also revealed in the literature that the deposition of intermediate bonding layers consisting of titanium oxides, *e.g.* Ti_2O_3 and Ti_4O_7 could promote the nucleation of α-Al_2O_3 [2,3].

In this work, the α-Al_2O_3 single-phased top layer was obtained on a TiO_2 rutile bonding layer was underneath. The epitaxial growth of α-Al_2O_3 on rutile was observed and the orientation relationships is found as: $(\bar{1}20)_{\alpha-Al_2O_3}//(10\bar{1})_{\mathrm{rutile}}$, $(003)_{\alpha-Al_2O_3}//(010)_{\mathrm{rutile}}$ and $[210]_{\alpha-Al_2O_3}//[101]_{\mathrm{rutile}}$. Additionally, Pure κ-$Al_2O_3$ is obtained while the bonding layer composed of Ti(C,N) needle-shaped grains. The epitaxial growth across the κ-Al_2O_3/Ti(C,N) interface is observed, the orientation relationships can be described as: $(0\bar{1}3)_{\kappa-Al_2O_3}//(\bar{2}20)_{\mathrm{Ti(C,N)}}$, $(100)_{\kappa-Al_2O_3}//(\bar{1}\bar{1}1)_{\mathrm{Ti(C,N)}}$ and $[031]_{\kappa-Al_2O_3}//[112]_{\mathrm{Ti(C,N)}}$. Since processing parameters of alumina deposition were always the same, it is clearly demonstrated that it is possible to control accurately the nucleation of certain polymorphs with the deposition of intermediate bonding layers.

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Transfert des couches minces d'oxyde de manganite ($La_{0.7}Sr_{0.3}MnO_3$) et étude de leurs propriétés magnétiques

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Les oxydes complexes à base de structure pérovskite offrent une gamme de propriétés physiques d'une grande diversité et d'un grand intérêt applicatif, comme la ferroélectricité, le ferromagnétisme, la supraconductivité… [1]. Afin d'exploiter les propriétés remarquables, dans la microélectronique du futur, il est nécessaire d'intégrer ces oxydes complexes dans des dispositifs à base du silicium. Une façon de les déposer sur de tels substrats est de les transférer.

Dans cette étude, nous montrons dans un premier temps qu'en utilisant des couches sacrificielles [2], telles que le $Sr_3Al_2O_6$ (SAO) [3], il est possible d'intégrer des couches minces d'oxydes épitaxiés sur des substrats à bas coût comme le silicium, le verre ou encore les polymères. Dans un deuxième temps, nous comparons les propriétés magnétiques des films minces du $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) déposés sur un substrat du $SrTiO_3$ (STO) et ensuite transférés sur un nouveau substrat en polymère en utilisant le SAO comme couche sacrificielle soluble à l'eau.

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Effect of chromium substitution on structural and chemical properties of $Fe_{3-x}Cr_xO_4$(111) epitaxial thin films

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In the search for novel materials, oxides with spinel structure (AB_2O_4) are very attractive due to their unique physicochemical and magnetic properties. The flexibility of the spinel structure offers the possibility to tailor their functional properties by incorporating different cations into the host lattice. In this regard, the $Fe_{3-x}Cr_xO_4$ spinels are of considerable interest. This series forms a complete solid solution intrinsically defect free for the $0 \leq x \leq 2$ range, in which the two limiting compositions have highly distinct physicochemical and magnetic properties. Whereas Fe_3O_4 is a typical ferrimagnetic half-metal material, $FeCr_2O_4$ is an insulator with low Curie temperature and conical spin structure. As potential materials of high magnetoeletric effect and adjustable band gap, the $Fe_{3-x}Cr_xO_4$ solid solution has attracted attention for applications in many fields [1,2].

Although the growth of thin films is key for modern applications in electronic and spintronic devices, previous works on the electronic, magnetic and photoconductive properties of the $Fe_{3-x}Cr_xO_4$ solid solution are based on bulk-like samples. Herein, we have performed a comprehensive study of the effect of substitutional Cr on the physical properties of high quality $Fe_{3-x}Cr_xO_4$ epitaxial thin films. The aim is to understand the effects of increasing Cr content on the physicochemical properties of these thin films, which may strongly deviate from the bulk depending on film thickness, surface and/or interface effects.

To do so, epitaxial $Fe_{3-x}Cr_xO_4$ layers (Figure 1a) were grown in a dedicated atomic Oxygen assisted Molecular Beam Epitaxy (O-MBE) setup [3]. Each sample were thoroughly characterized by core level spectroscopies (XPS, XAS, XMCD), X-ray diffraction, transport, magnetometry and electron microscopy. The main aim was to study the physicochemical properties of $Fe_{3-x}Cr_xO_4$ thin films from the fine structure perspective. Evolution of functional properties depends mainly on the Fe and Cr local structure, *i.e.* valence, distribution among the cation sublattices, and relative strength of competing effects. By means of XMCD analysis and Crystal Field Multiplet simulations (Figure 1b), we show that Cr^{3+} ions replace Fe^{3+} ions at octahedral sites (B) of magnetite, whereas Fe^{2+} ions are displaced from octahedral to tetrahedral sites. Primary effects are then: *(i)* the decrease of the average magnetic moment at the B sites, and *(ii)* the blocking of the B-site electron hopping path typical of Fe_3O_4, favoring a new conduction mechanism. The observed tendencies are promising and congruent with the literature [4].

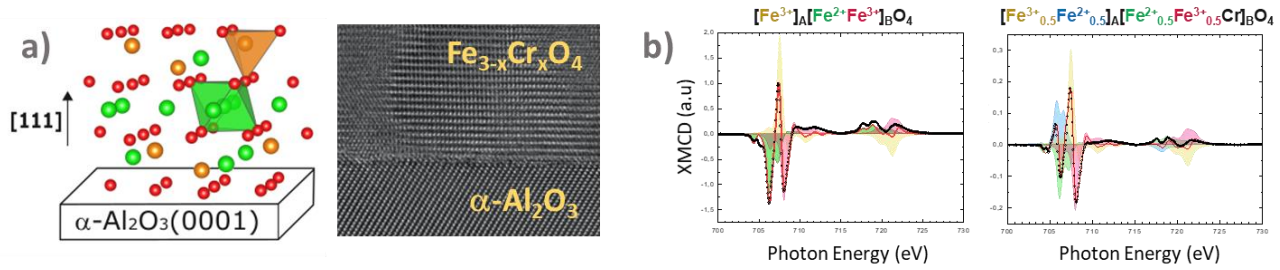

Figure 1: (a) Schematic representation of $Fe_{3-x}Cr_xO_4$ epitaxial thin films grown on sapphire (left) and their corresponding HRTEM image (right). (b) XMCD experimental and calculated spectra at the Fe $L_{2,3}$ absorption edge for Fe_3O_4 (left) in comparison of Fe_2CrO_4 (right) layer.

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Integration of oxide ferromagnets with high spin polarization onto ZnO based 2D, 1D nanostructures: growth, structure, properties of Fe_3O_4/ZnO(0001)

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Abstract:

Spintronics is the field of physics where we exploit the spin of electron instead of, or coupled with its electrical charge which give another degree of freedom. It offers a new range of applications with lower heating generation, smaller packaging, less energy consumption and higher processing speed [1]. The main idea of my PhD project is to pair a magnetic material which controls (manipulates) the spin of electrons with a semiconductor where we exploit these spin polarized charges. Several systems of metallic ferromagnet (FM)/semiconductor (SC) have been investigated by researchers, but always defects and interdiffusion at the interface FM/SC are the major obstacle to an efficient spin injection and detection.

In order to reduce the spin depolarization at the interface FM/SC, we have focused our study on all-oxide structures. The Fe_3O_4 as a ferrimagnetic oxide with a high Curie temperature (Tc ~ 850K) and an expected ~ 100% spin polarization (80% already measured [2]), and the ZnO as a wide bandgap semiconductor with a long spin lifetime [3] and conduction band that can be aligned with the Fermi level of the Fe_3O_4 [4], present a promising combination for opto-spintronics applications.

In this work we present the Pulsed Laser Deposition (PLD) growth of thin Fe_3O_4 films onto (0001)-oriented ZnO substrates. The Fe_3O_4 has an inverse-spinel structure, while the ZnO has a wurtzite structure with lattice parameters of a_{Fe3O4}=8.396Å, a_{ZnO}=3.249Å respectively. This difference of lattice parameters gives rise to a large lattice mismatch (8.6%), from which results the complexity of this growth, besides the possibility of formation of other iron oxide phases (FeO, α-Fe_2O_3, γ-Fe_2O_3). We targeted lower growth temperatures to limit the interdiffusion at the interface FM/SC. Samples have been studied by structural, morphological, and magnetic characterizations (time resolved RHEED, X-ray diffraction, Raman spectroscopy, Atomic Force Microscopy, Transmission Electron Microscopy, Vibrating Sample Magnetometry).

We show that we have achieved an efficient stoichiometry control by adjusting the PLD growth parameters at relatively low growth temperatures (the temperature of the substrate surface ~ 260°C). Thus, the phase diagram of iron oxides formation was established and the appropriate growth conditions for Fe_3O_4 were optimized. The magnetic measurements show a sharp Verwey transition at the expected temperature but magnetization of the grown Fe_3O_4 films is slightly lower than the bulk value, most probably due to the antiphase boundaries.

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Chemical Beam Epitaxy and Sybilla Equipment

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ABCD Technology in partnership with 3D-Oxides has developed a unique equipment on the market for the growth of epitaxial (or not) oxides thin films. Several top level results have been achieved so far[1] that we will present. Among others we will show high uniform (+/-1%) thin films up to 450 mm substrates size and discuss our combinatorial and additive growth facilities for improved R&D enabling fast development of new functional materials both in chemical composition and architectures. We will finally also show some epitaxial materials such as $LiNbO_3$, $BaTiO_3$ and TiO_2 and non-epitaxial materials such as HfO_2 or TiO_2-SiO_2 for a wide range of applications.

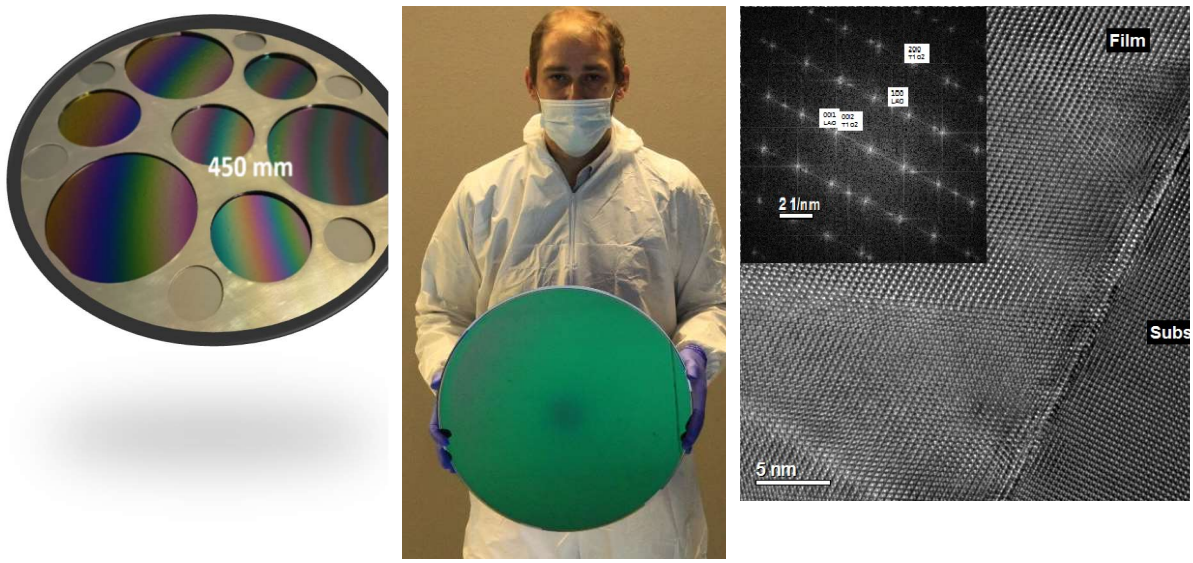

Figure 1: a) Combinatorial facility on 450 mm area; b) Uniform thin film on 450 mm substrate; c) LiNbO3 epitaxial thin film on sapphire.

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High–quality, large area deposition of vanadium dioxide (VO_2) using magnetron sputtering

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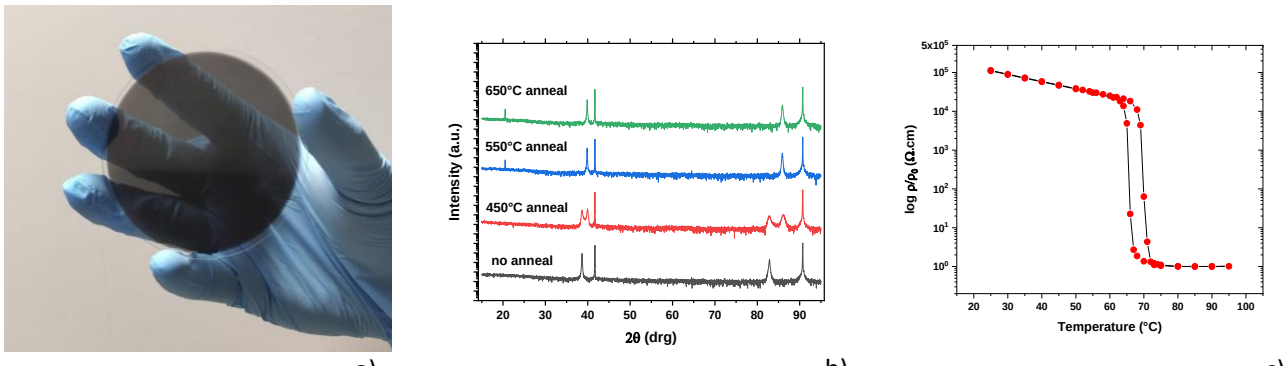
Vanadium dioxide (VO_2) has attracted an increased attention due to its ability to undergo a reversible metal to insulator transition (MIT) which can be thermally induced at a temperature of 340K [1] or, more interesting, via optical or electrical excitations [2]. The MIT is inducing drastic changes in the material's optical and electrical properties which have made VO_2 an interesting material for integration in different electrical and optical devices (high-speed optical and electrical switches, field-effect transistors, oscillators…) [2]. The electrical and optical performances of the obtained films are strongly correlated with the quality, grain size, degree of strain and oxidation of the material [3]. Thus, in order to better control the electrical resistivity or optical transmission changes during MIT (hysteresis and transition width, transition temperature), a good understanding of the film's growth mechanism is needed.

We have investigated the structural, morphological and electrical characteristics of VO_2 thin films obtained by DC magnetron sputtering of a vanadium target in Ar/O_2 atmosphere, on large area substrates, up to 3" (Fig. 1a). We examined the impact of the deposition and post-deposition annealing parameters on the structural and electrical properties of VO_2 coatings. The films were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) (Fig. 1b), Raman spectroscopy and electrical resistivity measurements (Fig. 1c). Preliminary results indicate that the deposition and annealing temperatures along with the oxygen partial pressure are the most important parameters in order to achieve mono oriented VO_2 films with state-of-the-art resistivity changes between the two states (superior to 10^5 orders of magnitude).



a) b) c)

Fig. 1. a) Large area deposition on a 3" SiO_2 wafer by DC magnetron sputtering. b) θ-2θ scans of VO_2 films annealed at different temperatures (0-650°C). c) Normalized electrical resistivity hysteresis loop of a 200 nm thick VO_2 thin film

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Rare-earth oxide thin films deposited by direct liquid injection chemical vapour deposition (DLICVD) for quantum technologies applications

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Harnessing rare-earth (RE) ions outstanding optical coherent properties for quantum information technologies has attracted a lot of attention recently, in the race for exploiting emerging solid-state quantum-grade systems. Indeed, REs offer a wide tunability of their ultra-narrow optical transitions, including the useful telecom-band wavelength of erbium[1] and exceptionally long spin coherence time for europium[2]. While macroscopic bulk oxide crystals (such as Y_2SiO_5) are usually the preferred host material for RE ions, the development of a silicon-compatible thin film platform would greatly facilitate post-processing, up-scalability as well as interfacing with other systems in a hybrid design or coupling to optical cavities[3].

In this work, we focus on the synthesis of nanoscale Eu-doped Y_2O_3 thin films on (111)-oriented silicon wafers using a modified version of Chemical Vapour Deposition based on direct liquid injection (DLI-CVD) of the precursors[4]. We evaluate the films morphology and composition and demonstrate polycrystalline layers with a preferential [111]-texture in a wide range of doping concentrations (Fig. 1a). The optical properties of the films are assessed by advanced spectroscopy techniques and benchmarked to optimized RE-doped bulk oxides. We find that inhomogeneous linewidths (t_{inh}) of about 40 GHz can be reached for the $^7F_0 \rightarrow {}^5D_0$ optical transition of Eu. By spectral hole burning, we also evaluate a homogeneous linewidth (t_h) of 11 MHz (Fig. 1b) at cryogenic temperatures which is the lowest recorded so far for material in this form. While coherent optical properties still lag behind those of single crystals ($t_h < 100$ kHz) there exists room for improvement in particular by modifying the interface with the silicon substrate, by using specific architecture or annealing post-treatments. On this basis, we discuss the relevance of such RE-doped oxide films as a new scalable platform for quantum information processing and propose ways to further optimize their properties.

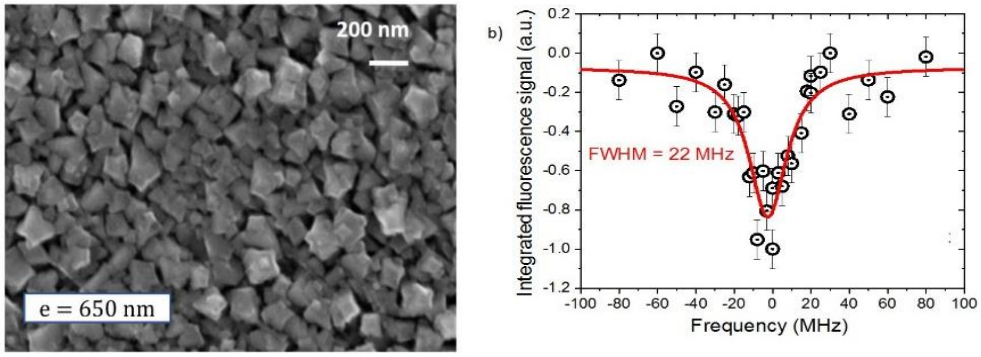

Fig. 1. *a) SEM image of a Eu:Y_2O_3 650 nm-thin film grown by DLI-CVD; (b) Spectral hole burning measured at 4 K for a 200 nm thin, 2% Eu doped Y_2O_3 film indicating a FWHM of 22 MHz.*

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Sensitive RHEED signature of Ti-excess enabling enhanced cationic composition control during the molecular beam epitaxy of SrTiO3 based solid solutions

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Functional oxides with perovskite structure (general formula ABO_3) present a wide range of physical properties attractive in various domains.[1] These properties depend on composition, and in particular on the ratio [A]/[B] between the cation concentrations,[2] which must be accurately controlled. Molecular beam epitaxy (MBE) is particularly well suited to control perovskite oxide composition and physical properties thanks to elemental sources. However, such control remains to date a challenge due to source drift. The latter causes poor growth reproducibility, which makes inoperable calibration strategies using post-growth (*ex-situ*) composition measurements. Monitoring Reflection High Energy Electron Diffraction (RHEED) oscillations enables *in-situ* $SrTiO_3$ (STO) composition control with an accuracy in the 1% range.[3] However, this procedure is not strictly speaking real-time as it requires employing SrO/TiO_2 monolayers (ML) alternated growth and observing oscillations during a large number of alternations, which is not compatible with the growth of any structure. Solving the source drift issue requires a truly real-time procedure, which is the case of STO(001) surface reconstructions monitoring using *in-situ* RHEED.[4,5] This method, the record accuracy of which has been recently reported,[6] relies on the dependence of these reconstructions on the Sr/Ti surface coverage.[7,8] It is operated by monitoring the appearance of half-order streaks along the [100] (respectively [110]) RHEED azimuth, signature Ti-rich (respectively Sr-rich) surfaces, and by tuning the elemental growth rates to prevent their formation.[6]

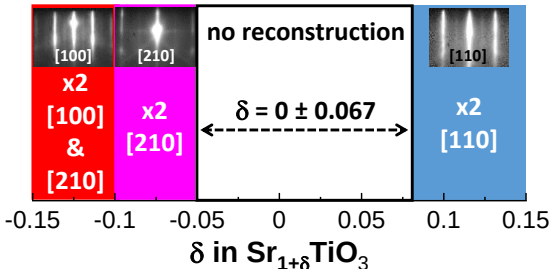

Fig.1 : Monitoring the appearance of half-order streaks along the [210] RHEED azimuths instead of along the [100] azimuths during the MBE growth of SrTiO3 thin layers provides an improved accuracy of +/- 6.7% on the control of the cationic composition.

In this context, we will show here that the observation of half-order streaks along both [100] and [210] azimuths associated with the Ti-rich STO surface reconstruction is preceded by that of half-order streaks along the [210] azimuth only, and that using this signature enables significant accuracy improvement for *in-situ real-time* STO composition control. We quantify this accuracy, and compare it to that provided by high resolution X-ray diffraction measurements (XRD). We propose a strategy to control the cationic composition of quaternary $(La,Sr)TiO_3$ (LSTO) solid solutions using RHEED reconstructions and we show how such strategy allows controlling LSTO thermoelectric properties[9] and engineering the permittivity of short period STO/LSTO superlattices.[10]

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