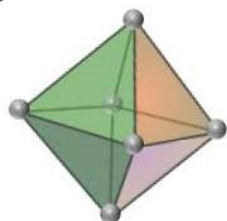


**Oxyde+**  
**Virtual workshop on functional oxides**

**Tuesday March. 14<sup>th</sup> – Wednesday March 15<sup>th</sup> 2023**

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**GDR OXYFUN**

## Program

Tuesday, march 14<sup>th</sup> 09H15-9H30 : Introduction (Guillaume Saint-Girons – INL)

**Tuesday, march 14<sup>th</sup> AM : Nanofabrication, technological developments**

Chair : Nathalie Lemée

9H30—10H15 **Invited 1 : Stéphane Calvez (LAAS - Toulouse)**

***Oxydation des matériaux III-V et applications***

S. Calvez, N. Monvoisin, E. Hemsley, A. Monmayrant, H. Camon et G. Almuneau

LAAS-CNRS, Université de Toulouse, CNRS, 7 avenue du colonel Roche, F-31400 Toulouse, France

10H15 – 10H30 **Flash 1**

Improved magnetoelectric coupling in multiferroic  $\text{CoFe}_2\text{O}_4/(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.89}\text{Sn}_{0.11})\text{O}_3$  core-shell nanofibers elaborated by co-axial electrospinning method

Y. Hadouch (1,2), D. Mezzane (1,2), M'B. Amjoud (1), Y. Gagou (2), Z. Kutnjak (4), H. Uršič (4), V. Laguta (5,6), Y. Kopelevich (7), K. Hoummada (3), M. El Marssi (2)

(1) Laboratory of Innovative Materials, Energy and Sustainable Development (IMED), Cadi- Ayyad University, Faculty of Sciences and Technology, BP 549, Marrakech, Morocco.

(2) Laboratory of Physics of Condensed Matter (LPMC), University of Picardie Jules Verne, Scientific Pole, 33 rue Saint-Leu, 80039 Amiens Cedex 1, France.

(3) Aix-Marseille University - CNRS, IM2NP Faculté des Sciences de Saint-Jérôme case 142, 13397 Marseille, France.

(4) Jozef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia.

(5) Institute of Physics AS CR, Cukrovarnicka 10, 162 53 Prague, Czech Republic.

(6) Institute for Problems of Materials Science, National Ac. of Science, Krjijanovskogo 3, Kyiv 03142, Ukraine.

(7) Universidade Estadual de Campinas-UNICAMP, Instituto de Física "Gleb Wataghin", R. Sergio Buarque de Holanda 777, 13083-859 Campinas, Brazil.

10H30 – 11H00 Break

11H00 – 11H45 **Invited 2 : Adrian Carretero (IES - Montpellier)**

***Épitaxie sur silicium assistée par la chimie douce : une plateforme pour des dispositifs à oxydes fonctionnels intégrés***

A. Carretero-Genevri

Institut d'Electronique et des Systèmes (IES), CNRS, Université de Montpellier, 860 Rue de Saint Priest 34095 Montpellier, France

11H45 – 12H00 **Flash 2**

Thin film of lanthanum cobaltite  $\text{LaCoO}_3$  for solar thermal collectors

A.A. Bande (1,2)

(1) Institut Jean Lamour (IJL) CNRS, Institut Jean Lamour (CNRS – Université de Lorraine)

(2) Université de Poitiers, CNRS, Institut Pprime, Département Physique et Mécanique des Matériaux

Chair : Romain Bachelet

14H—14H45 **Invited 1 : Monica Burriel (LMGP - Grenoble)**

***MOCVD deposition strategies to obtain Solid Oxide Fuel Cell thin films with improved functional properties***

M. Burriel (1), Alexander Stangl (1), Adeel Riaz (1,2), R. Rodriguez-Lamas (1), C. Pirovano (3), L. Rapenne (1), E. Sarigiannidou (1), D. Pla (1), O. Chaix-Pluchery (1), Michel Mermoux (2), R.-N. Vannier (3), and C. Jiménez (1)

(1) Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France

(2). Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

(3). Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

14H45 – 15H **Flash 1**

**Design for large optical transparency window of Correlated Transparent Conductors**

A. Cheikh (1), M. Rath (2), A. David (2)

(1) Centre de recherche sur les ions, les matériaux et la photonique (CIMAP) Centre National de la Recherche Scientifique, Ecole Nationale Supérieure d'Ingénieurs de Caen, Université de Caen Normandie

(2) Laboratoire de Cristallographie et sciences des matériaux CRISMAT-ENSICAEN

15H00 – 15H30 Break

15H30 – 16H15 **Invited 2 : Mariona Coll (ICMAB - Barcelone)**

***Challenges and Opportunities of chemical deposited functional complex oxide membranes***

P. Salles, M. Ramis, M. Coll

Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB 08193 Barcelona, Spain

16H15 – 16H30 **Flash 2**

**Epitaxial lithium niobate thin films grown by Chemical Beam Vapor Deposition for optical integrated applications**

R. Moalla, W. Maudez, T. Bui, R. Bachelet, B. Masenelli, C. Grillet, G. Benvenuti and E. Wagner

(1) INL - Institut des Nanotechnologies de Lyon, Université de Lyon, Ecole Centrale de Lyon, CNRS, UMR5270, 69134 Ecully, France

(2) 3D-Oxides, Technoparc, 01630 Saint-Genis Pouilly, France

(3) IEMN- Site de Valenciennes - CNRS UMR 8520, Université Polytechnique Hauts de France (UPHF), 59300 Famars, France

## Wednesday, march 15<sup>th</sup> AM : Physical properties and applications

Chair : David Munoz-Rojas

9H00—09H45 **Invited 1 : Sylvia Matzen (C2N - Palaiseau)**

*Shining light on ferroelectric thin films: towards multistate memories and photostrictive devices*

S. Matzen, S. Gable, K. Rani, A. Zing, L. Guillemot, T. Maroutian, G. Agnus, P. Lecoeur

Centre for Nanoscience and Nanotechnology (C2N), CNRS, Paris-Saclay University, 10 Boulevard Thomas Gobert, 91120 Palaiseau, France

09H45 – 10H00 **Flash 1**

Couches minces ferroélectriques de  $Ba_{1-x}Sr_xTiO_3$  accordables pour une antenne patch millimétrique reconfigurable en fréquence

C. Borderon (1), S. Ginestar (1), R. Renoud (1), H. Gundel (1), V. Muzzupapa (2), L. Huitema (2), A. Crunteanu (2)

(1). IETR, UMR CNRS 6164, Nantes Université, 2 rue de la Houssinière, 44322 Nantes CEDEX 3, France;

(2). XLIM, UMR CNRS 7252, Université de Limoges, 123 Avenue Albert Thomas, 87060 Limoges, France;

10H00 – 10H15 **Flash 2**

Elaboration of perovskite thin films with metal-insulator transition for infrared optical modulation

A. Tausch (1), F. Capon (2), J. Drévilon (1), S. Hurand (1), K. Joulain (1)

(1) Institut Pprime, (UMR 3346 CNRS), Département FTC, Université de Poitiers, Poitiers, France

(2) Institut Jean Lamour, (UMR 7198 CNRS), Département CP2S, Université de Lorraine, Nancy, France

10H15 – 10H45 Break

10H45 – 11H30 **Invited 2 : Alexandre Tallaire (IRCP - Paris)**

*Epitaxial rare-earth doped oxide thin films deposited by liquid injection CVD for quantum technologies applications*

A. Tallaire, D. Serrano, A. Ferrier, M.A. Arranz-Martinez, I.G. Balasa, P. Goldner

IRCP, Chimie ParisTech, PSL University, CNRS, 75005 Paris, France

11H30 – 11H45 **Flash 3**

Simulation of Zinc Oxide anode based Organic Light Emitting Diode

M. Bouchaour (1), Y. Tahir (1), S. Bensmaine (1), A. Chiali (1,2) L. Merad (1), N. Maloufi (3)

(1) Unité de Recherche de Matériaux et Energies Renouvelables - Faculté des Sciences, Université de Tlemcen, Algérie

(2) Ecole supérieure des sciences appliquées

(3) Université de Lorraine – CNRS – LEM3, 7 rue Félix Savart, 57070 Metz, France

11H45 – 12H00 **Flash 4**

Tungsten-doped  $VO_2$  films for large area modulation of THz waves

E. N. Sirjita (1,2), A. Boule (2), R. Mayet (2), J.C. Orlianges (1), A. Crunteanu (1)

(1) XLIM, UMR 7252 CNRS/Université de Limoges, 123 Av. Albert Thomas, 87060 Limoges, France

(2) Institut de Recherche sur les Céramiques (IRCer), CNRS UMR 7315, Université de Limoges, Centre Européen de la Céramique, 12 rue Atlantis, Limoges, 87068, France



## Wednesday, march 15<sup>th</sup> PM : Characterization and instrumentation

Chair : Thomas Maroutian

14H—14H45 **Invited 1 : Alex Morata (IREC - Barcelone)**

***Operando ellipsometry and Tip-enhanced Raman spectroscopy (TERS) applied to li-ion battery materials***

A. Morata (1), J.C. Rosillo (1), Y. Tang (1), V. Siller (1), F. Chiabrera (1), M. Stchakovsky (2), M. Nuñez (1), N. Alayo (1), M. Chaigneau (2), A. Tarancón (1,3)

(1) Department of Advanced Materials for Energy Applications, Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Sant Adrià del Besòs, Barcelona, Spain

(2) HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

(3) ICREA, Passeig Lluís Companys 23, 08010, Barcelona, Spain

14H45 – 15H **Flash 1**

***In situ isotopic tracer Raman spectroscopy to study oxygen exchange in thin films***

A. Stangl (1), D. Pla (1), C. Pirovano (2), O. Chaix (1), S. Ambrosio (1), F. Baiutti (3), F. Chiabrera (3), M. Mermoux (4), A. Tarancón (3), C. Jimenez (1) and M. Burriel (1)

(1) Univ. Grenoble Alpes, CNRS, Grenoble-INP, LMGP, 38000 Grenoble France

(2) Univ. Lille, CNRS, Centrale Lille, ENSCL, 59000 Lille, France

(3) Catalonia Institute for Energy Research (IREC), Barcelona, Spain

(4) Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000, Grenoble, France

15H00 – 15H30 Break

15H30 – 16H15 **Invited 2 : Alexandre Boule (SPCTS - Limoges)**

***Diffraction des rayons X couplée aux simulations numériques et l'intelligence artificielle pour l'étude de couches minces épitaxiales***

A. Boule

Institut de Recherche sur les Céramiques (IRCER), UMR CNRS 7315, Limoges

16H15 – 16H30 **Flash 2**

***Inserexs: reflection choice software for Resonant Elastic X-ray Scattering***

A. Peña Corredor, N. Viart and C. Lefevre

Institut de Physique et Chimie des Matériaux de Strasbourg. Strasbourg, France

16H30 – 16H45 **Flash 3**

***Towards non-volatile memory applications with  $(V_xCr_{1-x})_2O_3$  Mott insulator thin films***

M. Haydoura, M. Rodriguez-Fano, J. Tranchant, B. Corraze, E. Janod, M.-P. Besland and L. Cario

CNRS, Institut des Matériaux de Nantes Jean Rouxel, (IMN), F-44000 Nantes, France

**16H45 – 17H00 : Closure (Guillaume Saint-Girons – INL)**

# **Invited contributions**

# Oxidation of III-V semiconductors and applications

S. Calvez<sup>1,\*</sup>, N. Monvoisin<sup>1</sup>, E. Hemsley<sup>1</sup>, A. Monmayrant<sup>1</sup>, H. Camon<sup>1</sup> et G. Almuneau<sup>1</sup>

1. LAAS-CNRS, Université de Toulouse, CNRS, 7 avenue du colonel Roche, F-31400 Toulouse, France

The wet oxidation of aluminum-containing III-V semiconductors is an established technological process that induces, at depth into III-V semiconductor heterostructures, a localized reduction in electrical conductivity and in optical refractive index. The associated engineering of the electrical path and/or the optical confinements have been used to facilitate the fabrication of edge-emitting lasers [1], vertical-cavity surface-emitting lasers (VCSELs) [2] and other photonic devices [1,3].

In this paper, we will review recent experimental investigations and model developments that we have carried out to measure, describe and analyse in detail this lateral oxidation process. In particular, we will present the implementation of a hyperspectral in-situ monitoring technique based on a spectrally-shaped illumination to obtain resolution-limited images of the optical apertures [4]. We will exploit this capability to draw out how the intrinsic anisotropy [5] and the geometry of the etched mesa from which the oxidation proceeds [6] affect and control the resulting shape of the produced oxide apertures. Finally, we will also present a method to artificially engineer the oxidation anisotropy to create aperture profiles that would not be fabricated otherwise [7], thereby opening new application opportunities for this technological process.

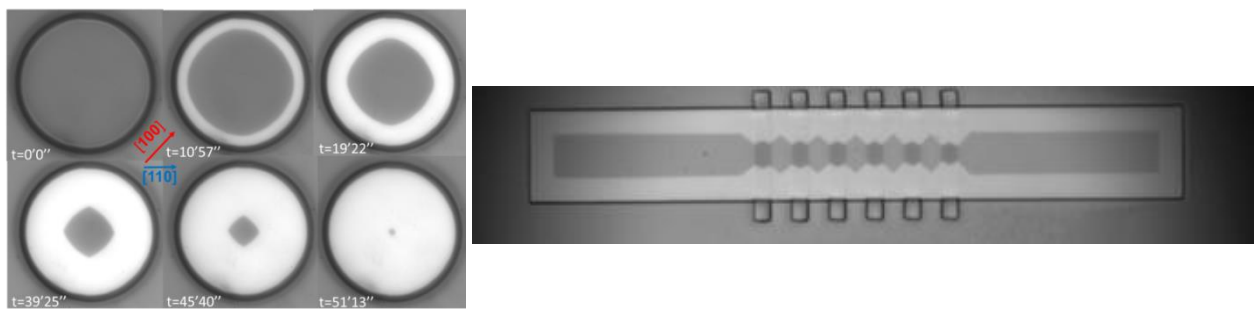


Fig. 1. Examples of oxidation aperture contours (white-to-grey central boundary) (left) resulting from an intrinsic anisotropy deformation [5] and (right) induced by an artificial anisotropy [7].

- 
1. J. M. Dallesasse and N. Holonyak, "Oxidation of Al-bearing III-V materials: A review of key progress," *J. Appl. Phys.* **113**, 051101 (2013).
  2. D. L. Huffaker, D. G. Deppe, K. Kumar, and T. J. Rogers, "Native-oxide defined ring contact for low threshold vertical-cavity lasers," *Appl. Phys. Lett.* **65**, 97–99 (1994).
  3. S. Calvez, G. Lafleur, A. Larrue, P.-F. Calmon, A. Arnoult, G. Almuneau, and O. Gauthier-Lafaye, "Vertically Coupled Microdisk Resonators Using AlGaAs/AlOx Technology," *IEEE Photonics Technol. Lett.* **27**, 982–985 (2015).
  4. N. Monvoisin, E. Hemsley, G. Almuneau, S. Calvez, and A. Monmayrant, "Spectrally-shaped illumination for improved optical monitoring of lateral III-V-semiconductor oxidation," *Submitt. Opt. Express* (2022).
  5. S. Calvez, G. Lafleur, A. Arnoult, A. Monmayrant, H. Camon, and G. Almuneau, "Modelling anisotropic lateral oxidation from circular mesas," *Opt. Mater. Express* **8**, 1762–1773 (2018).
  6. S. Calvez, A. Arnoult, A. Monmayrant, H. Camon, and G. Almuneau, "Anisotropic lateral oxidation of Al-III-V semiconductors: inverse problem and circular aperture fabrication," *Semicond. Sci. Technol.* **34**, 015014 (2019).
  7. S. Calvez, A. Arnoult, and G. Almuneau, "Engineering the anisotropy of AlAs wet oxidation using silicon implantation," *Opt. Mater. Express* **11**, 3600 (2021).

# Épitaxie sur silicium assistée par la chimie douce : une plateforme pour des dispositifs à oxydes fonctionnels intégrés

Adrian Carretero-Genevriér

*1. Institut d'Electronique et des Systèmes (IES), CNRS, Université de Montpellier, 860 Rue de Saint Priest 34095 Montpellier, France*

Les oxydes sont des matériaux robustes qui peuvent présenter des propriétés électriques, magnétiques, optiques et thermiques exceptionnelles. Pour ces raisons, une intégration industrielle de couches minces et de nanostructures d'oxyde épitaxiées sur le silicium est souhaitable étant donné cette large gamme de propriétés qui peuvent fournir de nouveaux dispositifs sur puce. Cependant, pour parvenir à une intégration efficace des technologies de couches minces épitaxiées, le substrat de silicium doit être à la fois chimiquement et structurellement compatible avec la couche souhaitée afin d'éviter la formation de défauts interfaciaux indésirables, et doit être économiquement réalisable pour une production à grande échelle. Par conséquent, les défis techniques tels que la compatibilité des étapes de fabrication individuelles pour exploiter ces avancées et les déployer sur le marché imposent des conditions sévères pour l'ensemble du processus d'intégration des matériaux. Par exemple, l'industrie piézoélectrique produit des capteurs presque uniquement à partir de cristaux massifs et il n'existe actuellement aucun processus efficace et rentable pour le dépôt de ces matériaux sous forme de couche mince monocristallin sur du silicium au niveau industriel. Dans ce travail, je présenterai différents exemples d'intégration directe réussie sur silicium de couches minces d'oxydes piézoélectriques en utilisant exclusivement des technologies de dépôt chimique. C'est-à-dire (i) des couches de quartz-alpha épitaxiés et nanostructurés [1,2], de nouvelles couches minces d'oxydes à base d'hollandite ferroélectrique [3], et (iv) une intégration sans précédent par épitaxie et sans catalyseur de ZnO sur du silicium. Toutes ces nanostructures d'oxydes fonctionnels sont des matériaux piézoélectriques, pas chère et non toxiques, qui sont actuellement utilisés dans différents projets pour produire des capteurs rentables, des catalyseurs efficaces ou des micro-sources d'énergie, entre autres applications [4,5]. Certaines des applications de ces dispositifs développés seront détaillées et discutées au cours de cet exposé.

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[1] Qianzhe Zhang et al. *Nanoscale Advances* 2 (2019).

[2] David Sanchez-Fuentes et al. *ACS Appl. Mater. Interfaces*, 12, 4, 4732–4740, (2020).

[3] José Manuel Vila-Fungueiriño et al. *Nanoscale*, 13, 9615-9625, (2021).

[4] C. Jolly et al. *Adv. Mater. Technol.* 6, 2000831, (2021).

[5] Laurent Lermusiaux, et al. *Accounts of Chemical Research, Acc. Chem. Res.* 2022, 55, 2, 171–185, (2022).

## MOCVD deposition strategies to obtain Solid Oxide Fuel Cell thin films with improved functional properties

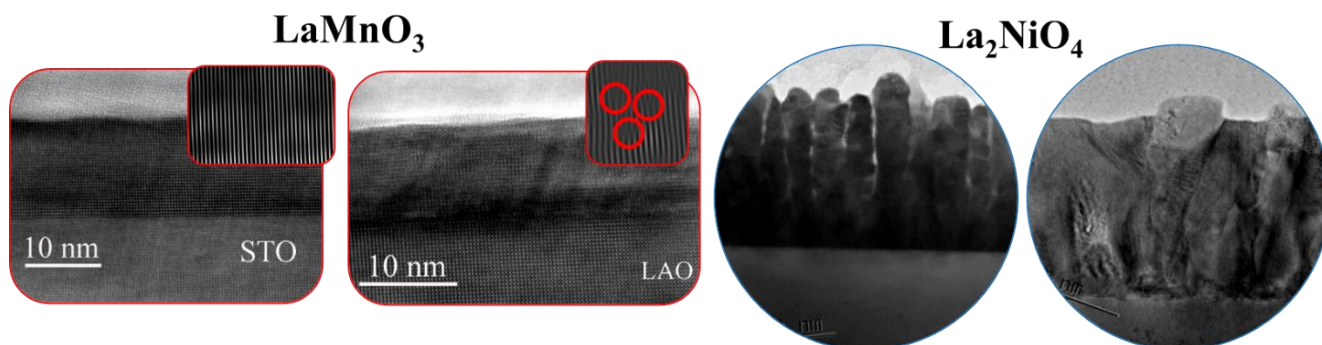
M. Burriel<sup>\*1</sup>, Alexander Stangl<sup>1</sup>, Adeel Riaz<sup>1,2</sup>, R. Rodriguez-Lamas<sup>1</sup>, C. Pirovano<sup>3</sup>, L. Rapenne<sup>1</sup>, E. Sarigiannidou<sup>1</sup>, D. Pla<sup>1</sup>, O. Chaix-Pluchery<sup>1</sup>, Michel Mermoux<sup>2</sup>, R.-N. Vannier<sup>3</sup>, and C. Jiménez<sup>1</sup>

1. Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France

2. Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

3. Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

Ionic transport is of primary importance for the development and miniaturization of numerous devices such as solid oxide fuel cells and electrolyzers, oxygen separation membranes, and memristive devices. When prepared in the form of thin films, the functional properties can largely vary in comparison to the intrinsic bulk ones. There is thus a large interest in understanding and controlling the influence of parameters such as epitaxy, substrate-induced strain, and nano-structure, for the use of ionic conducting oxides in applied functional devices. Using Pulsed-Injection Metalorganic Chemical Vapor Deposition we have developed different strategies to control the growth of perovskite, and perovskite-related thin films, such as  $\text{LaMnO}_{3\pm\delta}$ [1] and  $\text{La}_2\text{NiO}_{4\pm\delta}$ [2]. The oxygen stoichiometry, oxygen diffusion, and both the intrinsic and apparent oxygen exchange activity can be tailored in these thin films by tuning the deposition parameters, leading to differences in the amount of point and extended defects in the films, to different strain states, as well as to diverse controlled nano-architectures (dense, nano-columnar, nano-hierarchical). Ultimately by selecting the appropriate deposition conditions a substantial enhancement of the ionic transport properties in the films is achieved.



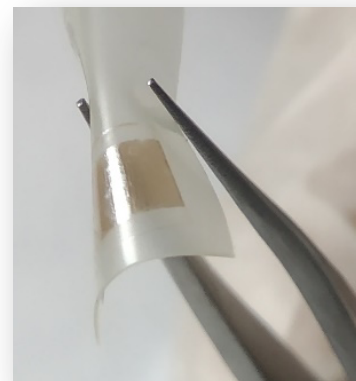
- 
- [1] R. Rodriguez-Lamas, C. Pirovano, A. Stangl, D. Pla, R. Jónsson, L. Rapenne, E. Sarigiannidou, N. Nuns, H. Roussel, O. Chaix-Pluchery, R.-N. Vannier, and M. Burriel, "Epitaxial  $\text{LaMnO}_3$  films with remarkably fast oxygen transport properties at low temperature," *J. Mater. Chem. A*, vol. 9, no. 21, pp. 12721–12733, 2021.
- [2] A. Stangl, A. Riaz, L. Rapenne, J. M. Caicedo, J. de Dios Sirvent, F. Baiutti, C. Jiménez, A. Tarancón, M. Mermoux, and M. Burriel, "Tailored nano-columnar  $\text{La}_2\text{NiO}_4$  cathodes for improved electrode performance," *J. Mater. Chem. A*, no. ii, 2022.

# Challenges and Opportunities of chemical deposited functional complex oxide membranes

Pol Salles<sup>1</sup>, Marti Ramis<sup>1</sup>, Mariona Coll<sup>1</sup>

1. Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC, Campus UAB 08193 Barcelona, Spain

Flexible electronics are gaining more and more importance towards the conception of the Internet of Things (IoT) and integrating all kind of versatile devices in our daily lives. Complex transition-metal oxides are a very promising family of materials that offer a wide range of functionalities, including ferroelectricity, metal-to-insulator transitions, piezoelectricity, colossal magnetoresistance and superconductivity, to name a few. These functionalities are often associated to its crystalline quality and orientation. Therefore, the processing of such materials is constrained on substrates that can stand high temperature treatments and on single crystal substrates when epitaxy is pursued. These constraints are not compatible with flexible electronics, hence approaches to detach these epitaxial oxides from the growth substrate are crucial. The use of a sacrificial layer is an appealing approach for the fabrication and manipulation of freestanding epitaxial complex oxides membranes. This method consists on adding a buffer layer between the substrate and the complex oxide which allows subsequent detachment upon selective etching. Recently,  $\text{Sr}_3\text{Al}_2\text{O}_6$  (SAO) has been proved as an attractive candidate to be used as water-soluble sacrificial layer. The deposition techniques to prepare such structures is also a key factor to be considered not only for film quality but also for process scalability. While high vacuum deposition techniques such as molecular beam epitaxy and pulsed laser deposition are well established techniques to produce high quality films, alternate procedures that can deliver low-cost production such as solution processing and atomic layer deposition are gaining interest. [1]



Here we present a robust chemical and low-cost methodology to prepare water-soluble SAO thin films to be used as sacrificial layer [2] however, when it is exposed to air to perform an ex-situ growth of the functional oxides on it, it forms an amorphous capping layer that jeopardizes the transfer of the epitaxy. Using this ex-situ approach, bendable and polycrystalline  $\text{CoFe}_2\text{O}_4$  membranes with robust magnetization at room temperature are obtained [3]. Vacuum annealing and cation substitution in SAO films is a simple combination to modify the SAO softness while reconstructing their surface crystallinity to ultimately obtain epitaxial complex oxide membranes. As a case example, here we will show that the chemical nanoengineering of the sacrificial layer allows to modulate the strain and physical properties of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  membranes. [4] Therefore, we put forward a procedure to prepare a wide variety of thin film oxide membranes and can allow the fabrication of artificial heterostructures to go beyond the traditional electronic, spintronic and energy storage and conversion devices.

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- [1] Mariona Coll and Mari Napari Atomic Layer Deposition of functional multicomponent oxides APL Materials (2019)  
[2] Pol Salles, Ivan Caño, Roger Guzman, Camilla Dore, Agustín Mihi, Wu Zhou, and Mariona Coll\*, Facile Chemical Route to Prepare Water Soluble Epitaxial  $\text{Sr}_3\text{Al}_2\text{O}_6$  Sacrificial Layers for Free-Standing Oxides, Adv. Mater. Interfaces 8, 2001643 (2021)  
[3] Pol Salles, Roger Guzmán, David Zanders, Alberto Quintana, Ignasi Fina, Florencio Sánchez, Wu Zhou, Anjana Devi, and Mariona Coll\* Bendable Polycrystalline and Magnetic  $\text{CoFe}_2\text{O}_4$  Membranes by Chemical Methods ACS Appl. Mater. Interfaces, 14, 12845–12854 (2022)  
[4] Pol Salles, Mariona Coll et al. On the role of the  $\text{Sr}_{1-x}\text{M}_x\text{Al}_2\text{O}_6$  sacrificial layer composition for improved epitaxial  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  membranes. To be submitted (2022)



# Shining light on ferroelectric thin films: towards multistate memories and photostrictive devices

Sylvia Matzen<sup>1</sup>, Stéphane Gable<sup>1</sup>, Komalika Rani<sup>1</sup>, Alexandre Zing<sup>1</sup>, Loïc Guillemot<sup>1</sup>,  
Thomas Maroutian<sup>1</sup>, Guillaume Agnus<sup>1</sup>, Philippe Lecoœur<sup>1</sup>,

1. Centre for Nanoscience and Nanotechnology (C2N), CNRS, Paris-Saclay University,  
10 Boulevard Thomas Gobert, 91120 Palaiseau, France

Ferroelectric materials are known to exhibit a reversible spontaneous electric polarization whose magnitude and sign can be precisely tuned, in particular by electric field. What makes ferroelectrics very interesting, by offering rich physics and a high potential for applications, is the coupling between their electric polarization and other properties. The coupling between electric polarization and mechanical deformation leads, for instance, to remarkable piezoelectric response with numerous applications in microelectromechanical systems (MEMS) - actuators and sensors. Their interaction with light has shown above bandgap photovoltages, induced by a particular polarization-related charge-separation mechanism in ferroelectrics, the so-called bulk photovoltaic effect. In addition, the complex interplay between light, ferroelectric polarization, and deformation induces photostriction – a mechanism of non-thermal deformation under illumination – which is usually described in a ferroelectric as a combination of photovoltaic and piezoelectric effects. Photoinduced effects in ferroelectrics offer thus a wide field of possible investigations into interesting physics and exciting new applications, with the potential for remote (optical) control.

In this talk, I will present studies on the control of photovoltaic effect and photostrictive response by tuning the ferroelectric polarization in the prototypical  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) ferroelectric material, epitaxially grown in thin films and integrated into microdevices. In the first part, I will show how the photocurrent and the photovoltage can be used as a non-destructive read-out signal of the polarization states [1, 2], which offers great promise for next-generation ferroelectric memory devices with increased memory storage density and lower power consumption. In the second part, I will demonstrate that we can control both magnitude and sign of the photo-induced strain in ferroelectric devices by tuning the ferroelectric polarization, at ultrafast timescales in capacitors [3] and in PZT integrated in MEMS [4]. These results have important implications for the development of optically driven microdevices, and more generally for the light-mediated engineering of materials and devices functionalities.

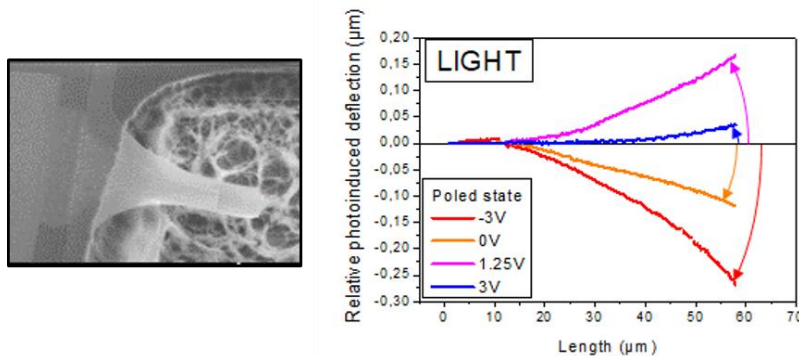


Figure: SEM picture of a PZT cantilever and relative photoinduced deflection for four different electrical states showing the control of optically driven bending by the applied voltage.

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# Epitaxial rare-earth doped oxide thin films deposited by liquid injection CVD for quantum technologies applications

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Rare-earth (RE) ions are promising solid state qubits for quantum information technologies. They indeed offer ultra-narrow optical transitions (including in the useful telecom-band wavelength for erbium) and exceptionally long spin and optical coherence time for europium at cryogenic temperatures [1]. Their 4f shells are only partially filled and are screened from their environment by outer 5p shells leading to weakly allowed yet sharp optical transitions. They thus behave as a kind of isolated ions embedded in a crystalline matrix in which a large variety of optical and spin levels can be optically addressed and manipulated to perform quantum storage or quantum processing operations. Macroscopic bulk oxide crystals (such as RE:Y<sub>2</sub>SiO<sub>5</sub>) have been largely studied to this aim as they can be produced with high crystallinity and purity. The development of those oxides as thin high-quality films would however offer greater prospects of scalability and ease post-processing and integration into photonic chips and optical resonators [2].

In this work, we focus on the synthesis of nanoscale Eu-doped Y<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>SiO<sub>5</sub> thin films on different substrates including silicon, sapphire and yttria-stabilized zirconia wafers. We used a specially developed direct liquid injection chemical vapour deposition (DLI-CVD) reactor in which liquid precursors are sprayed and flash-evaporated before being carried to the reaction area (Fig. 1a) [3]. By optimising the growth conditions, including evaporation and deposition temperatures, composition and film architecture, we produced textured polycrystalline and epitaxial thin films doped with varying amounts of europium or erbium. The optical properties of the films were then assessed by advanced spectroscopy techniques and benchmarked to optimized RE-doped bulk oxides. At low temperature, inhomogeneous linewidths of about 18 GHz were reached for the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>0</sub> optical transition of Eu (Fig. 1b), while, by spectral hole burning spectroscopy, holes as narrow as 10 MHz (Fig. 1c) could be measured. These properties are still behind those observed for single crystals but are already a first step towards more integrated rare-earth doped oxide platforms for this field of application.

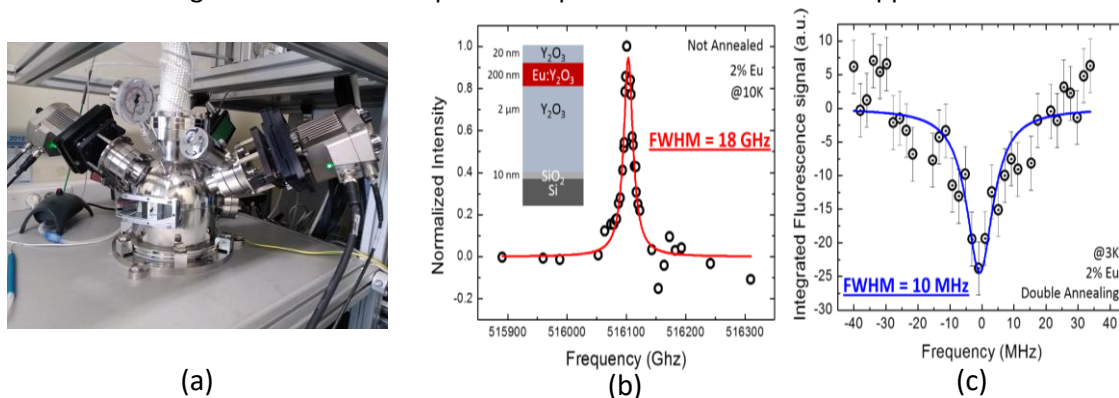


Fig. 1. (a) DLI-CVD reactor developed at IRCP, (b) inhomogeneous linewidth measured at 10K for a thin Eu-doped Y<sub>2</sub>O<sub>3</sub> film on Si, (c) spectral hole burnt in the same film at 3K.

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# Operando ellipsometry and Tip-enhanced Raman spectroscopy (TERS) applied to li-ion battery materials

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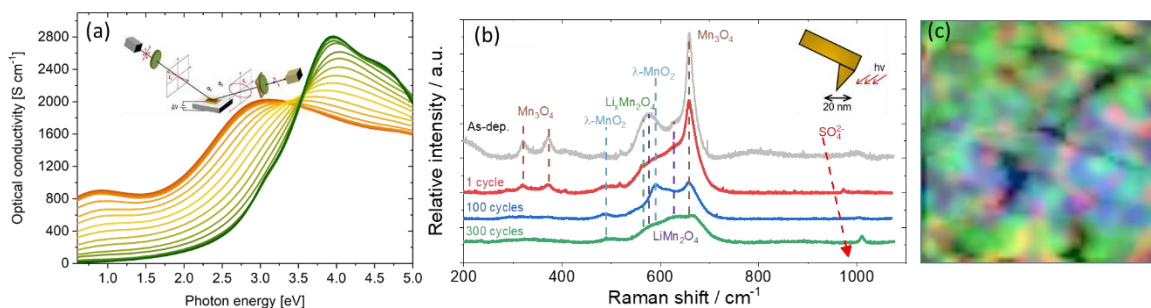
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Ion-based devices such as batteries, fuel cells and electrolyzers will play a major role in the future carbon-free energy systems. Many efforts are being dedicated to find techniques that allow understanding interfacial and ion diffusion phenomena occurring during operation, as these are often limiting overall performance. The sophistication of some of the most powerful techniques, such as isotopic ion exchange methods, in situ TEM and synchrotron radiation based techniques, limits the routine access to essential information for developing next-generation cells. In addition, commonly available techniques have also been explored including X-ray diffraction, atomic force microscopy, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) showing different compromises between spatial and time resolutions.

In this talk, we will discuss the development of procedures based on two optical techniques: spectroscopic ellipsometry (SE), and tip-enhanced Raman spectroscopy (TERS). Despite the well-known capabilities of Spectroscopic Ellipsometry (SE) to infer the properties of thin film and multilayers, such as thickness, crystallinity, materials ratio in mixtures, roughness, structure of the interfaces, electronic band structure etc., the use of this affordable, non-destructive technique for the study of ion-transport under operation is very so-far limited. We will illustrate the potential of SE with several examples on the field of lithium-ion batteries and solid oxide cells. In a first example, we will show the use of SE to monitor  $\text{Li}^+$  transport properties and degradation phenomena through real-time tracking of the oxidation-state and volume changes associated with lithium insertion and extraction along  $\text{LiMn}_2\text{O}_4$ <sup>1</sup> and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ <sup>2</sup> thin-film electrodes in different liquid electrolytes ( $\text{LiSO}_4$  and  $\text{LiPF}_6$ , respectively). In a second example, we use SE for studying the concentration of point defects in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  (LSF) thin films as a function of equivalent oxygen partial pressure, temperature and Sr concentration<sup>3</sup>. Finally, we present our recent advances in the utilization of Tip-Enhanced Raman Spectroscopy (TERS) for the study of the distribution of species in the surface of Li-ion battery cathodes. We show the high potential of TERS for studying phase evolution at grain boundaries thanks to the combination of the chemical sensitivity of Raman spectroscopy with high spatial resolution of scanning probe microscopy (SPM).



Evolution of optical conductivity as a function of the photon energy obtained by spectroscopic ellipsometry in  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  layers (a). Overall spectra from TERS on  $\text{LiMn}_2\text{O}_4$  layers with increasing number of cycles (b). Topographic map of the sample operated for 100 charge-discharge cycles (c). Colors indicate the presence of  $\text{LiMn}_2\text{O}_4$  (green),  $\text{Mn}_3\text{O}_4$  (blue) and  $\text{SO}_4^{2-}$  (red).

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# Diffraction des rayons X couplée aux simulations numériques et l'intelligence artificielle pour l'étude de couches minces épitaxiales.

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L'obtention d'informations sur la structure cristalline des matériaux (espace réel) à partir des données de diffraction des rayons X (espace réciproque) se heurte au « problème de la phase ». En effet, les coordonnées atomiques, incluant les déviations à la structure moyenne, affectent l'amplitude diffusée, alors que la quantité mesurée par DRX est l'intensité, c'est-à-dire le module au carré de l'amplitude. Ainsi, alors que le module de l'amplitude peut être déterminé directement, la phase de celle-ci est perdue. Par conséquent, une inversion directe de l'intensité diffractée ne fournit que des différences de position, à partir desquelles il n'existe aucun moyen direct de retrouver des positions atomiques absolues.

Pendant des décennies, les scientifiques se sont appuyés sur des algorithmes de modélisation et d'ajustement pour contourner ce problème : un modèle structural est utilisé pour calculer l'intensité diffractée et les paramètres du modèle sont affinés de manière itérative jusqu'à obtenir un bon accord avec les données expérimentales. C'est ce qui explique l'importance primordiale des simulations numériques dans l'étude de la nanostructure des matériaux, et notamment des couches minces épitaxiales, dont la bonne qualité cristalline permet en général une détermination très poussée des paramètres nanostructuraux.

Si le succès de ce type d'approche n'est plus à démontrer, de nouveaux défis se présentent à nous, notamment du fait de l'explosion de la quantité de données consécutive aux progrès technologiques, en particulier aux installations de rayonnement synchrotron, mais également sur les diffractomètres de laboratoire. Afin de faire face à ces grandes quantités de données (qui peuvent atteindre plusieurs GO à TO selon les cas), une des solutions possibles consiste à s'appuyer sur des algorithmes d'intelligence artificielle.

Ces problématiques seront abordées au travers de quelques exemples, notamment :

- le rôle des contraintes thermiques et épitaxiales sur la transition métal-isolant de couches minces de  $\text{VO}_2$
- la quantification des dislocations à l'interfaces de couches minces de  $\text{CeO}_2$  déposées sur  $\text{ZrO}_2$
- le développement de gradient de déformations dans des matériaux soumis à irradiation ionique,
- etc.

# **Flash presentations**

# Improved magnetoelectric coupling in multiferroic $\text{CoFe}_2\text{O}_4/(\text{Ba}_{0.95}\text{Ca}_{0.05})$ $(\text{Ti}_{0.89}\text{Sn}_{0.11})\text{O}_3$ core–shell nanofibers elaborated by co-axial electrospinning method

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Multiferroic  $\text{CoFe}_2\text{O}_4\text{-Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.89}\text{Sn}_{0.11}\text{O}_3$  core–shell nanofibers (CFO@BCTSn NFs) were synthesized by a sol-gel co-axial electrospinning technique. The scanning electron microscope and transmission electron microscope were used to check the core-shell structure/configuration of nanofibers, and X-ray diffraction and a high-resolution transmission electron microscope were used to confirm the spinel structure of CFO and the perovskite structure of BCTSn. The magnetic property of the resultant CFO@BCTSn NFs was demonstrated by magnetic hysteresis loop. The piezoelectricity was verified using piezoresponse force microscopy, which revealed an entirely covered ferroelectric shell outline, which is accurate with SEM and TEM observations. The magnetoelectric coefficient ME was measured as a function of the applied external DC magnetic field. The maximum ME coefficient obtained for the CFO@BCTSn NFs was  $346.4 \text{ mV.cm}^{-1}.\text{Oe}^{-1}$ . The high magnetoelectric coupling obtained suggests that CFO@BCTSn NFs could be a promising candidate for magnetic field sensor and magnetoelectric device applications.

**Keywords:** Core-shell; nanofiber; electrospinning; piezoelectric; multiferroic; magnetoelectric.

## Thin film of lanthanum cobaltite $\text{LaCoO}_3$ for solar thermal collectors

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In the past, we demonstrated the feasibility of optimized  $\text{VO}_2$  thermochromic solar collectors whose stagnation temperature can be reduced by more than  $35^\circ\text{C}$ , while keeping the high performance of the system [1][2]. The aim of the present work is to elaborate and optimize a new generation of more effective solar collectors based on thermochromic perovskite-type nano-films of  $\text{LaCoO}_3$ . Thermochromism is the aptitude of materials to reversibly change their properties versus temperature due to structural modifications. Such change occurs at a specific temperature called metal-insulator transition temperature ( $T_{MI}$ ) and thus, thermochromic materials are IR transparent (insulator) below  $T_{MI}$  and IR reflective (metal) above.  $\text{LaCoO}_3$  exhibit complex and temperature dependent behavior leading to a thermochromic effect and an unsharpened transition accompanied by a drastic change in emissivity  $\epsilon$ . The increase in the emissivity increase the thermal radiation and makes this material as excellent candidate for passive thermal regulation. However, due to the structural and chemical complexity of such systems, their design is challenging. For this work, we present the synthesis of  $\text{LaCoO}_3$  thin films deposited on silicon substrates obtained from a magnetron sputtering machine (PVD). The structural, electrical and optical behaviors of two films with different thicknesses has been performed by X-ray diffraction (XRD), four probe method and Fourier transform infrared spectroscopy (FTIR). Finally, ellipsometric spectroscopy measurements have been used to simulated the optimal thickness with the best variation of the emissivity in the wavelength comprise between 7 and  $10\ \mu\text{m}$ .

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Reference: Calibri 10 - Names, title of paper, volume number, pages (year)

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# Design for large optical transparency window of Correlated Transparent Conductors

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Correlated transparent conductors oxides **TCs** have gained great attention because they can overcome the limitation of conventional **TCs** due to their high transparency and high electrical conductivity. The oxide SrVO<sub>3</sub> (SVO) was identified as high-performance transparent conductor oxide TCO in the visible range [1]. However, the functional properties of SVO have never been subject to extensive optimization in order to explore the limits of this technology.

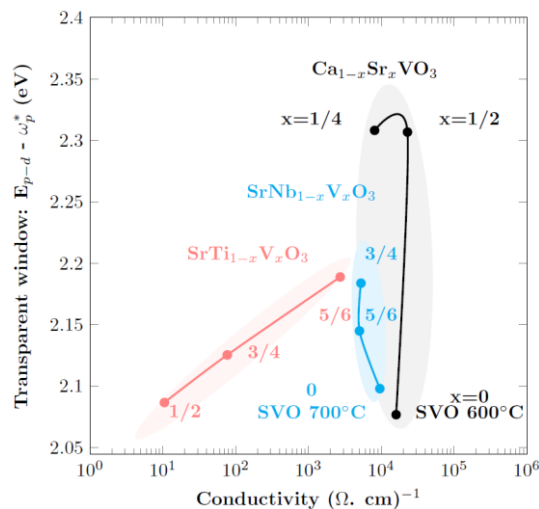
The aim of this study is to expand the optical transparency window of SVO through chemical doping to cover the ultraviolet-visible-infrared range while maintaining high electrical conductivity. In strong correlated metals, the transparent window is bounded by the screened plasma frequency  $\omega_p$  and the inter-band transition  $E_{p-d}$  [1]. In order to adjust these latter, we used three different strategies including the control of band filling, p-d transition energy design and bandwidth tuning.

Regarding the control of band filling strategy, one of the possible ways for this strategy is the use of **SrTi<sub>1-x</sub>V<sub>x</sub>O<sub>3</sub>** (STVO) solid solution grown by pulsed laser deposition PLD on SrTiO<sub>3</sub> substrate. As **STVO** becomes Ti-rich, the transparency window expands but such composition no longer retain the high conductivity required for TCO applications.

For p-d transition energy design, we studied the **SrNb<sub>1-x</sub>V<sub>x</sub>O<sub>3</sub>** (SNbVO) solid solution. For high doping with Niobium,  $\omega_p$  was sufficiently blue shifted into the visible range to open a transparency window that ranged from the visible deep into the UV region due to extensive blue shift of  $E_{p-d}$ .

Concerning the bandwidth strategy, we used the **Ca<sub>1-x</sub>Sr<sub>x</sub>VO<sub>3</sub>** (CSVO) solid solution. Gradual substitution of Sr by Ca shows that  $\omega_p$  remains localized in the IR range to expand the transparency window region by pushing  $E_{p-d}$  into the UV region leading to a wide transparency window covering UV-VIS-IR range.

As a result, by an appropriate choice of chemical doping, we managed to expand the size of transparency window by around **11%** surpassing that one of SVO while retaining high conductivity of around **2,3 × 10<sup>4</sup> (Ω.cm)<sup>-1</sup>** and high charge carriers density **2.93 × 10<sup>22</sup> cm<sup>-3</sup>**.



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# Epitaxial lithium niobate thin films grown by Chemical Beam Vapor Deposition for optical integrated applications

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Lithium niobate [1] thin film on insulator (LNO) has emerged as a very attractive and versatile platform for integrated non-linear photonics [2, 3], surface acoustic wave devices [4] and electronics. These applications require high-quality thin films to reduce the optical/acoustical losses of devices and optimize their efficiency. The standard technique for producing high quality LNO thin films is based on the “smart Cut” approach. However, an approach based on direct epitaxial growth of LNO thin films would offer many benefits such as the direct photonic or acoustic integration in complex devices and heterojunctions and the tuning of properties by doping and strain engineering.

In this work, lithium niobate films, about 300 nm thick, are grown on *c*-cut sapphire substrate by Chemical Beam Vapor Deposition method, and growth conditions are optimized to achieve high-quality epitaxial films. The films are characterized by X-ray diffraction (XRD) and Raman spectrometry. The growth of films with only pure LiNbO<sub>3</sub> phase is achieved. The LiNbO<sub>3</sub> films are (00l)-oriented with low mosaicity of 0.04°, and are twin-free single-domain. These films have a high potential for application in non-linear photonic platforms.

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# Couches minces ferroélectriques de $Ba_{1-x}Sr_xTiO_3$ accordables pour une antenne patch millimétrique reconfigurable en fréquence

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Le  $Ba_{1-x}Sr_xTiO_3$  (BST) est un matériau ferroélectrique très utilisé pour les dispositifs accordables. L'avantage du BST réside dans la possibilité d'ajuster la température de Curie  $T_C$  en faisant varier la composition  $x$  en Strontium du matériau (Fig. 1). Ceci permet d'avoir à température ambiante un matériau soit en phase paraélectrique (composition riche en strontium), soit en phase ferroélectrique (composition riche en baryum). Si on se place au niveau de la transition de phase ferroélectrique/paraélectrique, le matériau présente une grande permittivité et l'accordabilité est élevée. Pour autant, le matériau ne présente pas de comportement hystérétique et les pertes diélectriques sont plus faibles que pour une composition à l'état ferroélectrique [1].

Dans cette étude, le BST et son élaboration par voie sol-gel sont présentés pour différentes compositions en strontium. Le choix de la composition du BST est discuté afin d'obtenir un matériau dont les caractéristiques sont stables en température et en fréquence dans le but de pouvoir l'insérer dans un dispositif antennaire agile.

Le matériau est intégré dans des condensateurs inter-digités (IDC) afin de mesurer l'accordabilité et les pertes diélectriques à des fréquences allant de 200 MHz à 65 GHz [2]. Les couches minces ferroélectriques de BST présentent des accordabilités allant jusqu'à 40 % sous des champs électriques relativement faibles (167 kV/cm pour des tensions de polarisation de 0 à 100 V). Les IDC accordables, insérés dans une antenne patch, conduisent à un fonctionnement de l'antenne autour de 30 GHz avec une agilité fréquentielle de 15,3 % et de bonnes efficacités de rayonnement [3].

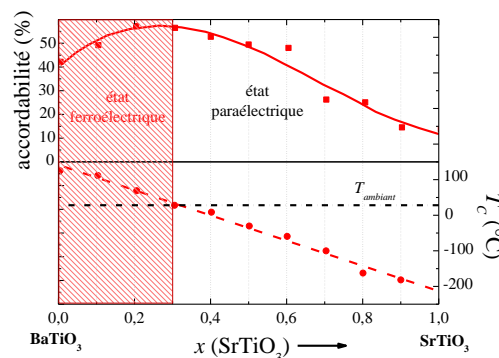


Figure 1 : Evolution de l'accordabilité et de la température de Curie  $T_C$  du BST en fonction du taux de strontium  $x$ .

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# Elaboration of perovskite thin films with metal-insulator transition for infrared optical modulation

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Mixed valence manganites ( $Re_{1-x}A_xMnO_3$ , with Re a rare earth element and A an alkaline earth element) present a metal-insulator transition that is not only described by a strong variation in the material's resistivity but also by an optical contrast between the conductor and the insulator state [1]. In the case of Samarium and Calcium mixed valence manganite, room temperature optical transitions were previously observed in Fourier Transform InfraRed spectrometry (FTIR) [2].

In this work, we demonstrate that ex-situ annealed  $Sm_{0.5}Ca_{0.5}MnO_3$  thin films, deposited by magnetron co-sputtering, exhibit a thermochromic effect in the infrared region. This effect is due to variations of the complex refractive index around room temperature. These indexes were characterized with infrared variable angle spectroscopic ellipsometry as a function of temperature (Figure 1a and 1b).

Using scattering matrix method for semi-infinite thin films and an Improved Grey Wolf Optimization meta-heuristic algorithm [3], it is possible to optimize the emissivity decrease with temperature of a multi-layer material in the transparency bands of earth atmosphere knowing the variations in complex optical indexes with temperature [4]. Such tendency allows the control of the material's spectral radiance and therefore its detectability with thermography (Figure 1c).

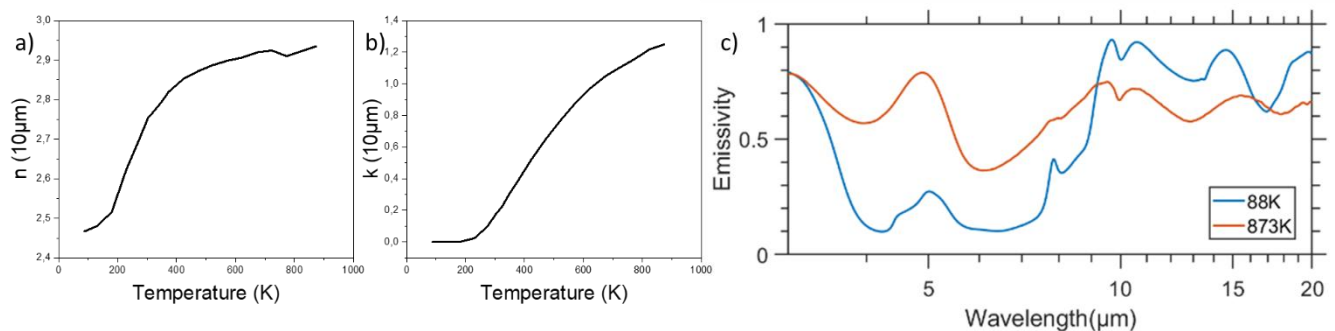


Figure 1: Evolution of a  $Sm_{0.5}Ca_{0.5}MnO_3$  thin film's refractive index  $n$  (a) and extinction coefficient  $k$  (b) at  $10\mu\text{m}$  as function of temperature. c) Evolution of the spectral emissivity of an optimized multi-layer material with temperature exhibiting thermal stealth properties

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# Simulation of Zinc Oxide anode based Organic Light Emitting Diode

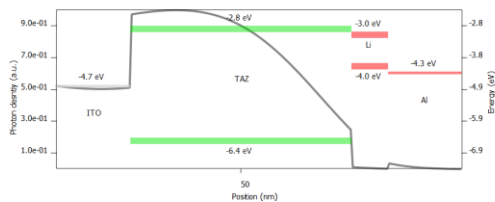
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This work reports the simulation of Zinc Oxide (ZnO) anode based organic light emitting diode (OLED) using GPVDM software. The Indium Tin Oxide (ITO) layer in classical multilayer OLED is replaced by ZnO thin film based material. The influence of thickness on electrical and optical parameters of ZnO anode layer is analyzed. ZnO anodes are expected to increase the reliability of the device. The work function of ZnO compatible with the hole transfer layer (HTL) material, facilitates inefficient charge transfer at the metal-organic interface.



Charge density vs position of ZnO anode based OLED

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# Tungsten-doped VO<sub>2</sub> films for large area modulation of THz waves

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Vanadium dioxide (VO<sub>2</sub>) has continuously attracted a high interest due to its ability to undergo a metal-to-insulator transition (MIT)[1] which abruptly changes the electrical, optical, and structural properties of the material. The MIT in VO<sub>2</sub> is triggered by either thermal, optical, electrical, or mechanical stimuli[2], drastically changing its electrical and optical properties, making the material an interesting active element for a plethora of applications (electrical and optical switching and modulation, reconfigurable antennas, oscillators, neural devices, etc)[2]. The thermal-induced MIT in VO<sub>2</sub> takes place at a relatively low temperature, of 340 K, which can be further lowered down to room temperature, by metal elements doping. This control over the decrease in the transition temperature reduces the energy requirement of activating VO<sub>2</sub> and thus improves the energy-cost efficiency of VO<sub>2</sub> devices as well as opening more options for the customization of the functioning parameters. VO<sub>2</sub> – based devices have proven to be effective modulation elements of terahertz (THz) waves: in the insulating phase, VO<sub>2</sub> has high THz transmission, whereas in the metallic phase VO<sub>2</sub> can effectively block the THz radiation, leading to effective devices as THz modulators, switches, absorbers, polarizers, or agile metasurfaces.

In this work, we investigate the structural, optical, and electrical characteristics of tungsten (W)-doped VO<sub>2</sub> obtained by reactive DC magnetron sputtering in an Ar/O<sub>2</sub> atmosphere and integrated in two-electrode large-area devices (10x 3 mm) allowing to electrically modulate the transmission of an incident THz wave in a convenient way, by altering the size of a metallic channel that evolves with current (Figure 1). The specific mechanisms of doped films activation are studied using in-operando X-ray diffraction and Raman spectroscopy while their modulation performances of THz waves is evaluated as a function of the doping level. We demonstrate that different W% in our THz modulators can effectively decrease the transition temperature and still keep a high contrast between the high and low THz transmission states.

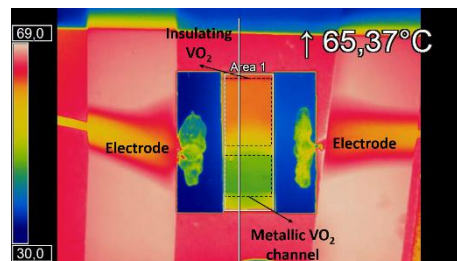


Figure 1 Metallic channel formed by electrical activation of W:VO<sub>2</sub> films

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# ***In situ* isotopic tracer Raman spectroscopy to study oxygen exchange in thin films**

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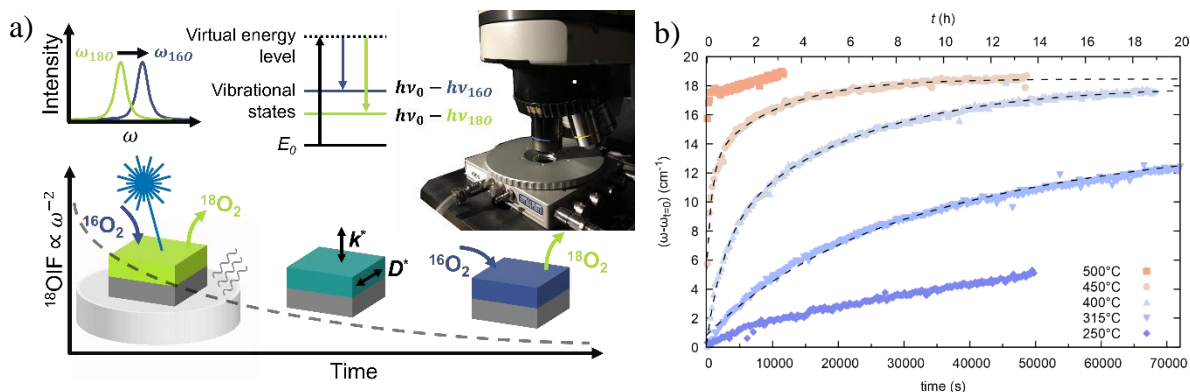


Figure 1: a) Schematic of novel isotopic exchange Raman spectroscopy and corresponding physical processes. b) *In situ* transients of Raman modes due to isotopic exchange.

Thorough understanding of elementary physicochemical processes is the ultimate key in the performance enhancement of electrochemical devices such as solid oxide cells. We have developed a novel *in situ* methodology using Raman spectroscopy for the characterization of kinetic transport properties, such as self-diffusion and surface exchange coefficients of electrode and electrolyte materials based on isotopic exchange using a conventional temperature cell and Raman setup.

Raman Spectroscopy is sensitive to molecular vibrational states. Isotopic substitution leads to changes in these vibrational states, translating into a shift of the corresponding Raman modes. Hence, changes in the isotopic composition due to isotopic exchange can be directly followed *in situ*, with spatial and temporal resolution, not accessible with conventional methods, such as isotope exchange depth profiling. This innovative approach therefore enables complementary insights for the study of ion transport properties of functional materials. Captivating benefits of this elegant *in situ* approach are its cost efficiency, speed, simple setup and sample preparation and its non-destructive nature. The strengths of this new approach will be showcased with our proof of concept study of oxygen isotopic back exchanges in promising electrolyte and electrode materials for micro solid oxide cells, namely  $(\text{CeGd})\text{O}_2$  and  $(\text{La,Sr})(\text{Mn,Co})\text{O}_3$  thin films.

# Inserexs: reflection choice software for Resonant Elastic X-ray Scattering

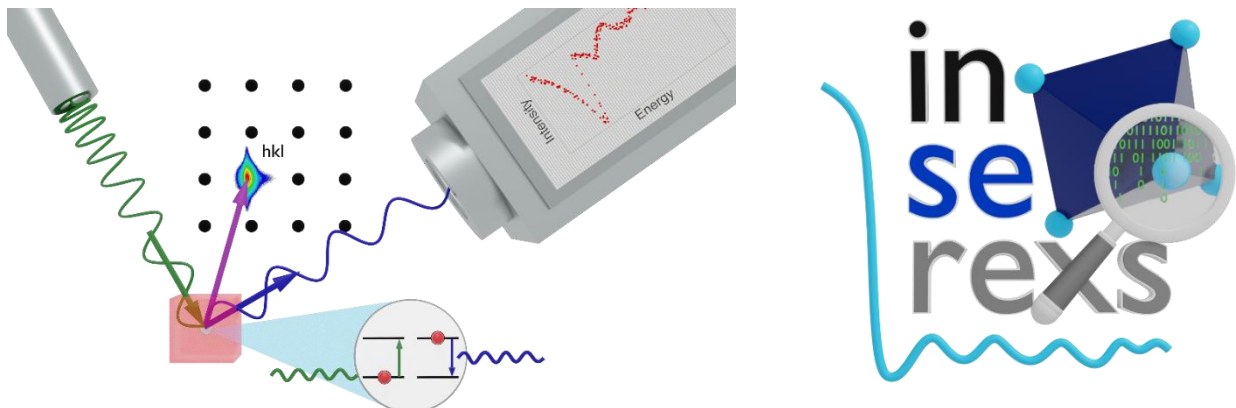
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Resonant Elastic X-ray Scattering (REXS) has been shown successful in locating the atoms in crystalline materials in a non-destructive and straightforward manner. By studying the X-ray Absorption Near Edge Structure (50 eV around the absorption edge), technique also known as Diffraction Anomalous Near Edge Structure (DANES), information about the oxidation state of the absorbing atoms can be retrieved. Beyond this edge, scanning the Extended X-ray Absorption Fine Structure (EXAFS) (50 – 1000 eV above the edge), also known as Extended Diffraction Absorption Fine Structure (EDAFS), information about the chemical environment can be obtained.<sup>1</sup> In thin films, DANES has already been used to study the cations' oxidation state or their occupation factors<sup>2,3</sup>. Besides, we have recently shown that EDAFS can successfully be used to indirectly locate the cation's ligands<sup>4</sup>.

REXS exploits the energy dependence of the dispersive terms ( $f'(E)$  and  $f''(E)$ ) of the atomic scattering factor ( $f = f_0(q) + f'(E) + if''(E)$ ), by measuring the intensity as a function of the energy at a specific Reciprocal Lattice Point (RLP) – see **Figure 1**. These anomalous terms or the crystal's structure factor, however, are not the same for all the crystal's reflections. As a result, in order to determine a certain parameter (an atom's position, a site's occupation), all the RLPs will not be equally useful to provide the desired information. In an ideal case, one could just measure the REXS spectra at all non-null reflections. However, in real experiments, the acquisition of spectra at all RLP is not possible, for measurements time's sake. Access to instruments able to perform such experiments is costly, infrequent and beam-times are time-limited. Prior the measurement itself, an experimentalist should know whether REXS experiments are suitable for their aim and should make a choice of the most adequate reflections.

We have developed a software which fulfills this objective: *inserexs* (Intensity and Sensitivity comparator for REXS). The program has been conceived to help REXS users in knowing which reflections should be explored, in order to determine a certain parameter of their interest. The spectra simulation is performed with the ab initio software FDMNES<sup>5</sup>. *inserexs* aims at helping all potential REXS users in evaluating the experimental conditions (among which the chosen reflection) before carrying out any real measurement.



**Figure 1.** Schematic representation of a REXS experiment and inserexs logo and graphical abstract

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# Towards non-volatile memory applications with $(V_xCr_{1-x})_2O_3$ Mott insulator thin films

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Resistance random-access memory (RRAM) stands among the alternative candidates to replace the flash memory technologies that approach their limits due to miniaturization and short economical payback [1]. In that context, canonical Mott insulator such as  $(V_{0.95}Cr_{0.05})_2O_3$ , or  $AM_4Q_8$  have shown a growing interest as they can reproduce the writing-erasing processes of memory devices thanks to a reversible non-volatile Insulator-to-Metal transition (IMT) triggered by electric pulses [2-3]. Previous studies have demonstrated competitive memory performances with Mott insulator based devices but so far, these studies overlooked the variability of the devices [4].

Here we investigate the resistive switching in Mott insulators thin films of  $(Cr_{1-x}V_x)_2O_3$  ( $x = 0.7$ ) integrated in micro-sized memory cells and report for the first time the cycle to cycle variability and retention time of the high and low resistance states. To this end, thin films were deposited and annealed in order to reach the expected stoichiometry and a good crystalline quality. The electrical behavior was investigated on MIM structures using  $2 \mu m$  via memory cells based on  $50 nm$  thick  $(Cr_{0.3}V_{0.7})_2O_3$  Mott insulator thin films. Preliminary experiments on these devices using short electric pulses for the SET and RESET show an endurance of more than 2000 times (Fig. 1.a). The cumulative distribution function (CDF) curve demonstrates an average  $R_{OFF}/R_{ON}$  ratio close to 20 (Fig 1.b). Moreover, both  $R_{OFF}$  and  $R_{ON}$  resistance states exhibit a very good temporal stability at room temperature and the retention time has been extrapolated up to 10 years (Fig 1.c). This work shows therefore the attractive potential of  $(Cr_{0.3}V_{0.7})_2O_3$  Mott insulator thin films for integration into a next generation of non-volatile memories.

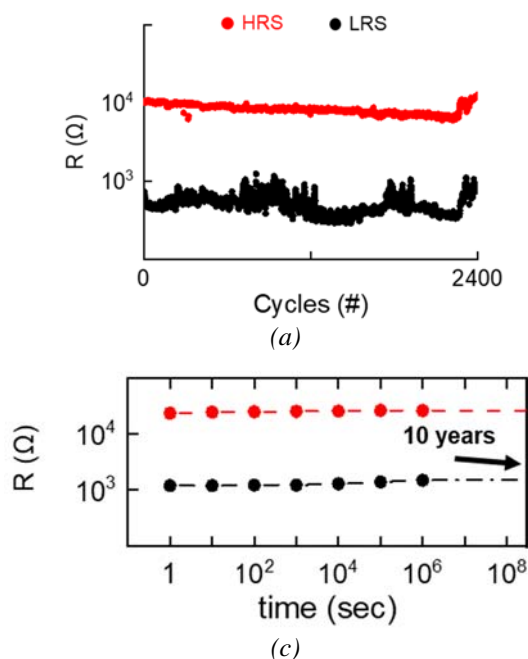


Fig1. (a) Cycling endurance obtained on a device of  $2 \mu m$  via and  $50 nm$  thick  $(Cr_{0.3}V_{0.7})_2O_3$  demonstrator showing 2400 resistive switching cycles. (b) Resistance distribution for the high (HRS) and low (LRS) resistive states. (c) Data retention at room temperature extrapolated to 10 years for HRS and LRS.

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