# Satellite Workshop
# High-resolution Spectroscopies for Applied Research
# Hi-SPEAR - 2016

**Synchrotron SOLEIL - L’orme des Merisiers**
**Saint-Aubin, France**

**19th- 20th of January 2016**

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# ABSTRACTS BOOKLET

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## Summary

## Welcome

Spectroscopy is a powerful and widespread technique that can be used to elucidate the chemical make-up and the electronic and magnetic structure of materials. The energy tunability, high photon flux, small photon beams and polarization control that are delivered by synchrotron radiation facilities are extremely advantageous for the various spectroscopic tools that are used by researchers in applied research. For example, the characterization of a materials electronic structure with high-resolution is desired in order to begin to understand the complex mechanisms in play and to disentangle contributions from competing processes. These can then be employed in the development of novel materials with increased efficiencies or in the investigation of real devices under operando conditions. With higher energy resolution, greater detail can be obtained which can lead to a greater understanding of the system under study and provide the necessary knowledge to refine and develop new models.

Hi-SPEAR (Hi-resolution Spectroscopy for Applied Research) is the satellite workshop of the SOLEIL 2016 Users' meeting that is designed to bring together researchers who use or are interested in applying high resolution spectroscopy in the fields of applied research with a strong emphasis on energy storage (fuel cells, catalysis and solar cells), micro-electronics and semiconductors, spintronic devices and the use of magnetic nanoparticles.

Various spectroscopic techniques such as Infrared spectroscopy, X-ray Photoelectron Spectroscopy, XAFS (NEXAFS / XANES), X-ray Magnetic Circular Dichroism and Inelastic X-ray Scattering will all be presented and discussed during the meeting. Potentials for further developments in these fields will be greatly welcomed. Ample opportunities for discussion will be available during coffee and lunch breaks and also at the poster session.

## Bienvenue

La spectroscopie est une technique puissante et répandue pour l'étude des propriétés chimiques, la structure électronique et la structure magnétique des matériaux.

Les sources de rayonnement synchrotron présentent de nombreux avantages pour l'utilisation des techniques spectroscopiques dans le domaine de la recherche appliquée comme l'énergie de photon accordable, le flux de photon intense, l'accès à des petits faisceaux et le contrôle de la polarisation. Par ailleurs, la haute résolution en énergie s'avère souvent nécessaire, par exemple pour la caractérisation de la structure électronique des matériaux, afin de mieux comprendre les mécanismes complexes mis en jeu et de démêler les différentes contributions des processus en compétition. Les résultats peuvent servir par la suite au développement de nouveaux matériaux avec des efficacités accrues ou à la compréhension des dispositifs en conditions réelles de mesures. Enfin, la haute résolution en énergie permet d'améliorer la sensibilité des méthodes spectroscopiques et conduire à une meilleure compréhension des systèmes étudiés et au développement de nouveaux modèles.

Hi-SPEAR (Hi-resolution Spectroscopy for Applied Research) est une conférence satellite du colloque annuel des utilisateurs de SOLEIL en 2016 (Users' Meeting 2016) dont le but est de rassembler les chercheurs intéressés par la spectroscopie de haute résolution dans les domaines de recherche appliquée avec une fort accent sur le stockage ou la production d'énergie (piles à combustible, catalyse et cellules solaires), la microélectronique, les semi-conducteurs, la spintronique et les nanoparticules magnétiques. Différentes techniques seront abordées pendant la conférence comme les spectroscopies infrarouge, de photoémission X, d'absorption (NEXAFS /XANES), le dichroïsme circulaire magnétique et la diffusion inélastique de rayons X. Les propositions pour améliorer les applications techniques dans ces domaines seront les bienvenues. La conférence laissera une grande place à la discussion pendant les pauses café, les déjeuners ou la session de posters.

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# High-resolution Spectroscopies for Applied Research
# Hi-SPEAR - 2016

## Synchrotron SOLEIL - L'orme des Merisiers
## Saint-Aubin, France

## 19th- 20th of January 2016

## COMMITTEES

### Scientific committee

| | |
|---|---|
| James ABLETT | Synchrotron SOLEIL |
| Victor BALEDENT | Laboratoire de Physique des Solides |
| Fadi CHOUEIKANI | Synchrotron SOLEIL |
| Jean-Pascal RUEFF | Synchrotron SOLEIL |

### Local committee

| | |
|---|---|
| James ABLETT | Synchrotron SOLEIL |
| Camille DUCROT | Synchrotron SOLEIL |
| Frédérique FRAISSARD | Synchrotron SOLEIL |
| Jean-Marc LUCACCHIONI | Synchrotron SOLEIL |
| France POCHARD | Synchrotron SOLEIL |
| Jean-Pascal RUEFF | Synchrotron SOLEIL |

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# Programme

## Tuesday, January 19th

13:00 - 13:45 Registration

13:45 - 14:00 Opening Remarks and Welcome from Jean Daillant, Director, Synchrotron SOLEIL

### SESSION I
MICRO-ELECTRONICS & SEMICONDUCTORS

Chairperson: James ABLETT

14:00 - 14:35 In situ synchrotron photoemission studies of III-V semiconductor-dielectric interface formation
***Christoph Adelmann*** *- IMEC, Kapeldreef , Leuven Belgium*

14:35 - 14:55 Ferroelectric polarization dependance of the $SrRuO_3/BaTiO_3$ interface electronic structure studied by operando hard X-ray photoemission spectroscopy
***Nicholas Barrett*** *- SPEC, CEA, CNRS, Gif-sur-Yvette, France*

14:55 - 15:15 Near-total reflection hard X-ray photo-emission spectroscopy for depth-resolved investigation of functional oxide interfaces
***Julien Rault*** *- Synchrotron SOLEIL, Gif-sur-Yvette, France*

15:15 - 15:35 *Inelastic background analysis of HAXPES spectra for device technology*
***Olivier Renault -*** *CEA, LETI, MINATEC Campus, Grenoble, France*

15:35 - 15:55 Interface passivation of III-V/high-k materials by high energy X-ray photoelectron spectroscopy : A quantitative evaluation
***Thierry Conard*** *- IMEC, MCACSA, Leuven, Belgium*

*15:55 - 16:25* *Coffee break*

# SESSION II

## ENERGY STORAGE I: FUEL CELLS & CATALYSIS

Chairperson: Jean-Pascal RUEFF

| | |
|---|---|
| 16:25 - 17:00 | In-situ XAS, TXM and RIXS experiments<br>***Frank de Groot*** *- Debye Institute of Nanomaterials Science, Utrecht, The Netherlands* |
| 17:00 - 17:20 | In situ detection of electronic structure changes in a bifunctional electrocatalyst using a wavelength-dispersive X-ray emission spectrometer.<br>***Benedikt Lassalle-Kaiser -*** *LBNL, Berkeley, USA and Synchrotron SOLEIL, Gif-sur-Yvette, France* |
| 17:20 - 17:40 | Study of the reduction of $TiO_2$ supported molybdenum oxide catalysts by combining K and $L_{2,3}$ edge XANES and DFT<br>***Sylvain Cristol*** *- Unité de Catalyse et Chimie du Solide, Lille, France* |
| 18:00 – 19:00 | Poster Session, *Cocktails & Snacks* |
| *19:00 - 21:00* | *Dinner at SOLEIL* |

## Wednesday, January 20th

### SESSION III
MAGNETISM I : MAGNETIC NANOPARTICLES / FERROFLUIDS

Chairperson: Fadi CHOUEIKANI

09:00 - 09:35 X-ray magnetic circular dichroism applied to single molecule magnets and ferrofluids
***Philippe Sainctavit*** *– IMPMC, Paris and Synchrotron SOLEIL, Gif-sur-Yvette, France*

09:35 - 09:55 Molecule-based anisotropy enhancement of superparamagnetic nanoparticles
***Laurent Lisnard*** *- IPCM, UPMC/CNRS, Paris, France*

09:55 - 10:15 XMCD investigation of photo-switchable Fe/Co Prussian blue molecular magnets
***Sadaf Fatima*** *- IMPMC, Paris, France*

10:15 - 10:35 Antiferromagnetic long range spin ordering in Fe and NiFe$_2$ doped BaTiO$_3$ multiferroic layers
***Hélène Magnan*** *- DSM/IRAMIS/SPEC, CEA, CNRS, Gif-sur-Yvette, France*

*10:35 - 11:05 Group photo & coffee break*

### SESSION IV
MAGNETISM II: SPINTRONICS

Chairperson: Amina TALEB-IBRAHIMI

11:05 - 11:40 Electronic and magnetic reconstruction at interfaces between iron and manganese perovskites
***Manuel Bibes*** *- Unité Mixte de Physique CNRS / Thales, Palaiseau, France*

11:40 - 12:00 Beam-induced CO dissociation for magnetic patterining in ultrathin Co films
***Tevfikonu O. Mentes*** *- Elettra Sincrotrone, Trieste, Italy*

12:00 - 12:20 1s2p RIXS-MCD measurements on CrO$_2$
***Patric Zimmermann*** *- Debye Institute of Nanomaterials Science, Utrecht, The Netherlands*

*12:20 - 14:00 Lunch*

### SESSION V
ENERGY STORAGE II: SOLAR CELLS

Chairperson: Victor BALEDENT

14:00 - 14:35 Hybrid perovskites for photovoltaic and optoelectronic applications
***Jacky Even*** *- Institut National des Sciences Appliquées, Rennes, France*

14:35 - 14:55 *Electronic and structural periodicities on MAPI hybrid perovskite*
***Antonio Tejeda -*** *LPS, Orsay and Synchrotron SOLEIL, Gif-sur-Yvette, France*

14:55 - 15:15 Photoemission study of irradiation impact on amoprphous / crystalline (a-Si :H/ c-Si) silicon heterojunction
***Min-I Lee*** *- LPS, Orsay, France*

*15:15 - 15:45 coffee break*

# SESSION VI

## ENERGY STORAGE III: BATTERIES

Chairperson: Stéphanie BELIN

15:45 - 15:55 SOLEIL : Collaboration SOLEIL/RS2E (Réseau sur le stockage électrochimique de l'énergie)
***Stéphanie Belin** - Synchrotron SOLEIL, Gif-sur-Yvette, France*

15:55 - 16:30 Operando characterization of lithium battery materials by XRD and XAS
***Guy Ouvrard** - Institut des Matériaux Jean Rouxel, Nantes, France*

16:30 - 16:50 Nanoscale PEEM spectroscopy combined with XPS to elucidate the surface reaction mechanism of cycled battery electrodes
***Mario El Kazzi** - Paul Scherrer Institute, Villigen, Switzerland*

16:50 - 17:10 Combined HAXPES / soft PES / XPS study of interfaces in lithium-ion batteries
***Remi Dedryvère** – IPREM CNRS, Pau, France*

17:10 *End of workshop*

# ABSTRACTS

## Tuesday, January 19th, 2016

### SESSION I & II

# Satellite Workshop
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## Tuesday, January 19th

### SESSION I
MICRO-ELECTRONICS & SEMICONDUCTORS
Chairperson: James ABLETT

| | |
|---|---|
| IT-01 | In situ synchrotron photoemission studies of III-V semiconductor-dielectric interface formation<br>*C. Adelmann* |
| OC-01 | Ferroelectric polarization dependance of the $SrRuO_3/BaTiO_3$ interface electronic structure studied by operando hard X-ray photoemission spectroscopy<br>*N. Barrett* |
| OC-02 | Near-total reflection hard X-ray photo-emission spectroscopy for depth-resolved investigation of functional oxide interfaces<br>*J. Rault* |
| OC-03 | Inelastic background analysis of HAXPES spectra for device technology<br>*O. Renault* |
| OC-04 | Interface passivation of III-V/high-k materials by high energy X-ray photoelectron spectroscopy : A quantitative evaluation<br>*T. Conard* |

### SESSION II
ENERGY STORAGE I: FUEL CELLS & CATALYSIS
Chairperson: Jean-Pascal RUEFF

| | |
|---|---|
| IT-02 | In-situ XAS, TXM and RIXS experiments<br>*F. de Groot* |
| OC-05 | In situ detection of electronic structure changes in a bifunctional electrocatalyst using a wavelength-dispersive X-ray emission spectrometer.<br>*B. Lassalle-Kaiser* |
| OC-06 | Study of the reduction of $TiO_2$ supported molybdenum oxide catalysts by combining K and $L_{2,3}$ edge XANES and DFT<br>*S. Cristol* |

# In Situ Synchrotron Photoemission Studies of III-V Semiconductor-dielectric Interface Formation

C. Adelmann

*IMEC, Kapeldreef , Leuven Belgium*

## ABSTRACT

III-V semiconductors have recently received renewed interest because Si as the standard semiconductor for CMOS microelectronic devices is reaching its intrinsic limits. A main obstacle that has prevented III-V semiconductors from being used in MISFETs is the absence of a high quality native oxide with a low interface defect density. Therefore, strategies have to be developed to deposit gate dielectrics on III-V semiconductors without the presence of a native interfacial oxide and a low interface defect density. A key breakthrough has been the observation of the in situ removal of native III-As oxides during the atomic layer deposition of dielectrics, such as Al2O3, the so-called self-cleaning effect. In this presentation, we review our results on the interface formation between III-V semiconductors and dielectrics during the initial stages of deposition using in situ synchrotron radiation photoemission spectroscopy. The different behavior of ALD on III-As and III-P semiconductors is discussed in detail and the importance of the choice of gate dielectric is highlighted. We also discuss Sulfur-based strategies to passivate III-V-dielectric interfaces, including the usage of self-assembled monolayers.

# Ferroelectric Polarization Dependence of the $SrRuO_3/BaTiO_3$ Interface Electronic Structure Studied by Operando Hard X-ray Photoemission Spectroscopy

S. Gonzalez[1], C.Mathieu[1], J. E. Rault[2], D. Ceolin[2], J-P. Rueff[2],
T. Maroutian[3], G. Agnus[3], V. Pillard[3], C.M. Schneider[4] and N. Barrett[1]

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*3 Institut d'Electronique fondamentale, Université Paris-Sud, Batiment 220, 91405 Orsay, France*
*4 Peter Grünberg Institute (PGI-6) and JARA-FIT, Research Center Jülich, D-52425 Jülich, Germany*

## ABSTRACT

Ferroelectric (FE) materials exhibit a spontaneous polarization, switchable under applied electric field, making them interesting candidates for integration into low energy consumption electronic devices. Importantly, the interface between FE thin films and metallic electrodes can play a determining role in device performance[1,2] but the physical phenomena at work at the interface are still only partially understood[3]. Here we study the top electrode/FE interface in a $SrRuO_3/BaTiO_3/SrRuO_3$ capacitor by *operando* Hard X-ray PhotoElectron Spectroscopy (HAXPES) using *in-situ* voltage bias to switch the polarization state. Saturation measurements show an interface thickness of 1.0 and 0.3 unit cells for up and down states, respectively. The interface $BaTiO_3$ is heavily n-doped by electron spill-over from the electrode. Thus, the main effect of the polarization is to shift the effective metal-insulator junction of the capacitance from the $SrRuO_3/BaTiO_3$ to the n-doped $BaTiO_3$/bulk $BaTiO_3$ interface. A Schottky barrier height for electrons of 1.2 eV is observed, consistent with the electrical characterization.

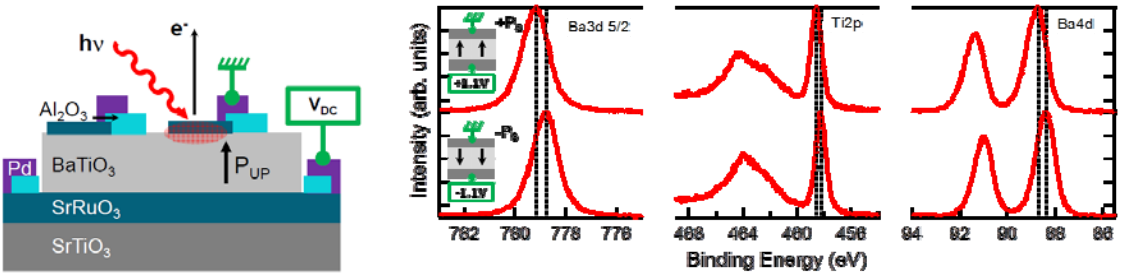

**Figure** Left: schematic of sample architecture for operando HAXPES analysis. Right: Ba 3d, Ti 2p and Ba 4d core level spectra as a function of saturation polarization state.

## REFERENCES

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3. M. Stengel, Phys. Rev. B 83, 235112 (2011)

# Near-total Reflection Hard X-ray Photo-emission Spectroscopy for Depth-resolved Investigation of Functional Oxide Interfaces

J. E. Rault[1], M. Marinova[2], A. Gloter[2], S. Nemsak[3,4], G. K. Palsson[3,5],
J-P. Rueff[1], C. S. Fadley[3], C. Carrétéro[2], H. Yamada[7], K. March[2],
V. Garcia[6], S. Fusil[6], A. Barthélémy[6], O. Stéphan[2],
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## ABSTRACT

The electric field control of functional properties is a crucial goal in oxide-based electronics. Non-volatile switching between different resistivity or magnetic states in an oxide channel can be achieved through charge accumulation or depletion from an adjacent ferroelectric. However, the way in which charge distributes near the interface between the ferroelectric and the oxide remains poorly known, which limits our understanding of such switching effects.

Here, we use a first-of-a-kind combination of near-total-reflection hard X-ray photoemission spectroscopy, scanning transmission electron microscopy with electron energy loss spectroscopy and ab initio theory to address this issue.

The element-specific chemical and electronic profile at a single (Ca,Ce)$MnO_3$/$BiFeO_3$ interface in a bilayer sample has been investigated by standing-wave (SW) hard X-ray photoemission spectroscopy (HAXPES), in which depth profiling of buried layers and interfaces is achieved in grazing incidence or in near total reflection (NTR) conditions. In previous studies, the SW-HAXPES technique has been successfully shown to provide depth-resolved chemical state and electronic structure for samples grown either as or on top of a superlattice multilayer mirror. In this study we show that the multilayer mirror is not necessary, by using X-ray wave interference effects, including SW effects, in NTR conditions for a bilayer system. We achieve a direct, quantitative, atomic-scale characterization of the polarization-induced charge density changes at the interface between the ferroelectric and the doped Mott insulator. An excess of electron occurs over 1 nm, in agreement with the expected screening length of the CCMO electrode for downward BFO polarization. Our results furthermore agree with measurements of peak shifts in Mn L-edge TEM-EELS data. These observations explain well the macroscopic, polarization-dependent transport behavior of this heterostructure. By using DFT calculations, we also provide insight on how interface-engineering can be used to tune such screening effects.

NTR HAXPES measurements are thus a promising new probe of buried interfaces chemical and electronic structure for materials with great potential applications in electronics and catalysis.

# Inelastic Background Analysis of HAXPES Spectra for Device Technology

P. Risterucci[1-3-4], O. Renault[1], C. Zborowski[1-3-4], J-P. Rueff[2],
G. Grenet[4], and S. Tougaard[3]

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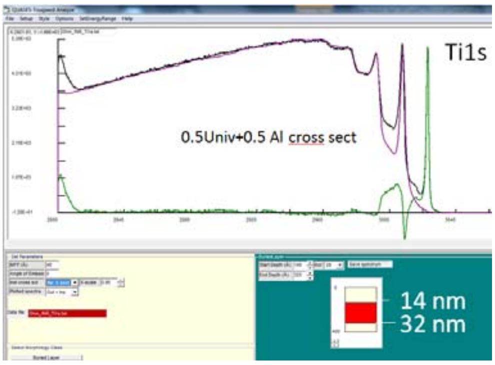
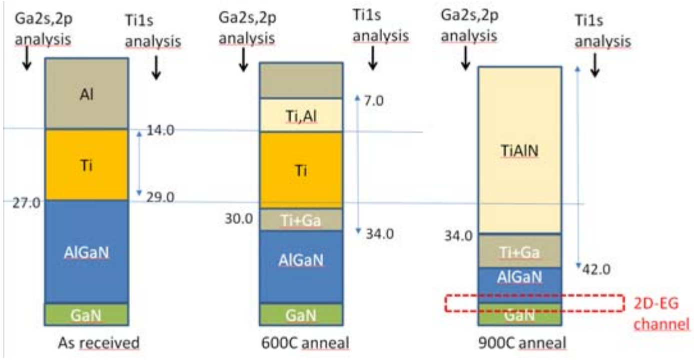
## ABSTRACT

There is a pressing need to develop photoemission methods able to address the challenge of non-destructive analysis of deeply buried interfaces (>25 nm) as required for instance in device technology. We have recently shown [1] how inelastic background analysis [2] could be successfully applied to Hard X-Ray Photoelectron Spectroscopy (HAXPES) in order to overcome the current limitation in probing depth of core-level analysis. In the case of a well-known multilayer structure, background analysis in HAXPES is able to quantify a nm-thick layer buried up to 55 nm below the surface [1, 3]. However, when the stack consists of materials with widely different scattering properties, the choice of inelastic scattering cross-section is crucial. To this end, we have developed an approach where optimized combinations of inelastic cross sections are used for background analysis. We applied this approach to the case of TiAl alloys used in High Electron Mobility power Transistors (see Figure) studied at GALAXIES [4]. The 900°C annealing is mandatory to form an ohmic contact with the AlGaN layer in the final device, without Ti diffusing down to the GaN interface. For the as-deposited stack, the retrieved Al and Ti distributions from the Ti1s and Ga2s, 2p background analysis using a blend of pure Al and Universal-cross sections are in agreement with the thicknesses measured by TEM (Al: 15 nm; Ti: 10 nm). After annealing, the background analysis shows formation of a TiAlN top layer and slight diffusion of Ti into the bulk without reaching the GaN interface. The structures found from analysis of the background of Ga2s,2p and Ti 1s are consistent (see Figure).





## REFERENCES

1. P. Risterucci, O. Renault, et al., *Appl. Phys . Lett*. **104**, 051608 2014
2. S. Tougaard, Quases software Ver 5.3 www.quases.com
3. P. Risterucci et al., *Surf. Interface Anal*. 2014, **46**, 906
4. P. Risterucci et al., in preparation.

# Interface Passivation of III-V/high-k Materials by High Energy X-ray Photoelectron Spectroscopy: A Quantitative Evaluation

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## ABSTRACT

The use of InGaAs as a high carrier mobility CMOS-channel material requires a proper electrical passivation of its interface with the gate dielectric. One of the passivation schemes investigated involves the use of Sulphur. In this work, high-k stacks on Sulphur passivated InGaAs substrates involving both Al2O3 and HfO2 are investigated. A major question related to the use of Sulphur relates to the chemical states at the interfaces. XPS is traditionally an important technique for interface analysis but faces several challenges in its application to the above mentioned stacks. First, due to the large number of elements involved, numerous peak interferences are present limiting the choice of useful photoemission peaks. Second, relevant stacks have total thicknesses of the order of 4 nm, which lead to very low intensities , certainly for minority elements like Sulfur. In this work, we discuss the impact of the $H_2S$ passivation temperature as well as the use of TMA pre-pulses in the growth of $Al_2O_3$. We show that the Sulphur bind to In but that no As-S or Ga-S bonds could be detected. The use of a TMA pre-pulse after surface passivation leads to a reduction of the amount of Sulphur present at the interface and likely increases the amount of In-O bonds. Higher temperature $H_2S$ passivation leads to a reduction of the amount of Sulphur at the surface.

We also observe that the presence/absence of S at the interface, as well as the presence of the $Al_2O_3$ buffer, which has a major impact on the relative peak position in the spectra between the substrate and the overlayer. This will be compared with the electrical characteristics of the stacks.

Finally, we show that using the Sessa software, full quantification of the stack can be obtained under the condition that all instrumental parameters are correctly taken into account.

# In-situ XAS, TXM and RIXS Experiments

F. de Groot

*Debye Institute of Nanomaterials Science Utrecht University, Netherlands*
http://www.anorg.chem.uu.nl/people/staff/FrankdeGroot/

## ABSTRACT

New developments in in-situ x-ray absorption (XAS), transmission x-ray microscopy (TXM) and resonant inelastic x-ray scattering (RIXS) will be discussed [1,2]. Nanoscale chemical imaging of catalysts under working conditions is possible with transmission x-ray microscopy. We have shown that TXM can image a catalytic system under relevant reaction conditions and provides detailed information on the morphology and composition of the catalyst material in situ [3]. The 20 nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under reaction conditions opens up new opportunities to study many chemical processes. I will discuss the present status of in-situ TXM, with an emphasis on the abilities of the 10+ nm resolution TXM technique in comparison with 0.1 nm STEM-EELS [4,5]. Hard X-ray TXM allows the measurement of chemical images and tomographs under more realistic conditions, using a capillary reactor at 10 bar Fischer-Tropsch conditions [6].

The second part of the talk deals with resonant inelastic x-ray scattering (RIXS), In 2p3d RIXS one scans through the 2p XAS edge and measures the optical excitation range. As an example, the RIXS spectra of CoO and $Fe_3O_4$ will be discussed [7]. The experimental resolution of (sub) 100 meV allows the detailed observation of the electronic structure. The implications for in-situ measurements of coordination compounds and nanoparticles is discussed, in particular the comparison with optical spectroscopy [8].

## REFERENCES

[1] Core Level Spectroscopy of Solids Frank de Groot and Akio Kotani (Taylor & Francis CRC press, 2008)
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[8] M. van Schooneveld et al. Angew. Chem. 52, 1170 (2012)

# *In Situ* Detection of Electronic Structure Changes in a Bifunctional Electrocatalyst Using a Wavelength-dispersive X-ray Emission Spectrometer.

S. Gul,[a] R. Alonso-Mori,[b] J. Kern,[a] Y. Gorlin,[c] D. Sokaras,[b]
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V.K. Yachandra,[a] T.F. Jaramillo[c] and J.Yano.[a]

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## ABSTRACT

The Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR) are key processes to electrolyzers and fuel cell technologies. The advent of these devices on large scales requires the use of abundant and cheap materials. Research efforts have been directed in the last years towards the preparation and study of transition metal-based inorganic catalysts for both the OER and ORR. Some of us have reported on a manganese oxide bifunctional electrocatalyst capable of performing both reactions.[1] This catalyst has been studied by *in situ* X-ray absorption spectroscopy, and the ORR- and OER-active phases where identified as $Mn_2O_3$ and $MnO_2$ (birnessite-type) phases, respectively.[2] The system has been improved recently by the adjunction of nickel in the manganese matrix. We report here on the *in situ* study of this $NiMnO_x$ electrocatalyst by *in situ* X-ray absorption and emission spectroscopy using a wavelength dispersive X-ray emission spectrometer.[3]

In order to study the $NiMnO_x$ catalyst *in situ*, we used a custom-made electrochemical cell, with a Ti/Au coated $Si_3N_4$ membrane as the working electrode, which is transparent to incoming and outgoing X-rays. A wavelength-dispersive X-ray emission spectrometer described elsewhere[4] was used with two sets of crystals and a position-sensitive detector in order to probe both the nickel and manganese elements at the same time. XES $K\beta_{1,3}$ spectra were recorded at the K-edges of these two elements while the electrochemical potential applied to the system was changed. The XES spectra obtained were analyzed using Integrated Absolute Differences (IAD), which proved to be appropriate given the small differences in 1st moment observed. The data show that the oxidation state changes in the manganese and nickel elements follow the same trend as a function of potential, but with a significant potential lag. These observations suggest a cooperative effect between the two metals, the oxidation of manganese being required to promote the oxidation of nickel.

This study shows the exciting potential of multicolor dispersive X-ray emission spectroscopy and its application to catalysis, electrochemistry or other time-resolved processes involving multiple elements.

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# Study of the Reduction of $TiO_2$ Supported Molybdenum Oxide Catalysts by Combining K and $L_{2,3}$ edge XANES and DFT

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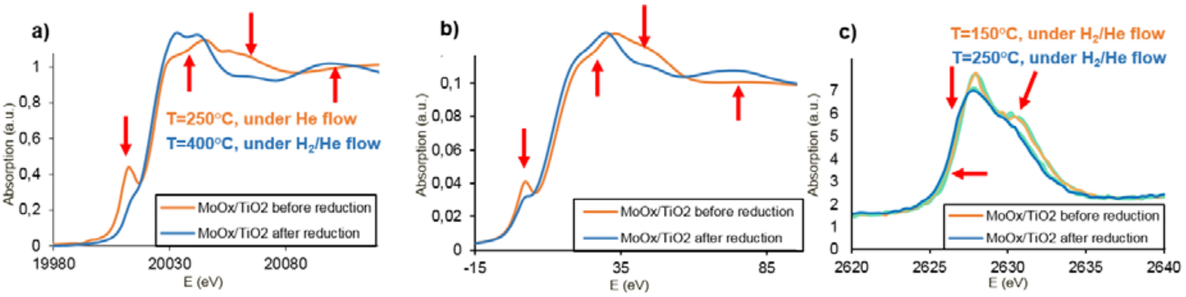
## ABSTRACT

Supported Molybdenum catalysts are extensively investigated as they are actives for numerous reactions like olefin metathesis and selective oxidation reactions. Furthermore this system (after sulfidation) is also widely used in the hydrotreating industrial processes, which represent 10% of the total world market for catalysts. Hence the improvement of the performance of this class of catalysts is of paramount economic and environmental importance. In recent works, with the combination of XANES spectra (Mo K edge), DFT calculation and modeling XANES spectra using multiple scattering (MS) theory, we were able to draw a clear picture of the structure of the activated catalyst[i]. However, electronic and geometric structure adopted by this catalyst during the catalytic reaction is still unknown. Indeed, drastic changes were observed upon reduction of the catalyst with methanol and it was rather complex to distinguish the changes in electronic structure and the changes in the geometry. In order to get more insights on the electronic structure of the system under operando conditions, the reducibility of this catalyst is studied by *in-situ* XANES at Mo $L_{2,3}$ edge (spectra are recorded at LUCIA beamline), Mo K edge (spectra are recorded at SAMBA beamline) and DFT modeling (using VASP code). The reducibility of supported oxomolybdates species depends on its number of oxo bonds (oxo vs dioxo). With spectra simulation of structures with an adsorption of 7 or 11 H atoms, experimental spectra obtained under $CH_3OH$ or $H_2$ flow can be reproduced. It is shown that the main difference between these two reduction processes is the spin density localized on each reduced Mo atom



a) Experimental XANES Mo K edge spectra of MoOx/$TiO_2$ before and after reduction (by $H_2$)
b) Modelling XANES Mo K edge spectra of MoOx/$TiO_2$ structure before and after reduction c) Experimental XANES Mo $L_3$ edge spectra of MoOx/$TiO_2$ before and after reduction (by $H_2$)

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# ABSTRACTS

## Wednesday, January 20th, 2016

### SESSIONS III, IV & V

# Satellite Workshop
# High-resolution Spectroscopies for Applied Research
# Hi-SPEAR – 2016

## Wednesday, January 20th

### SESSION III
MAGNETISM I : MAGNETIC NANOPARTICLES / FERROFLUIDS
Chairperson: Fadi CHOUEIKANI

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| IT-03 | X-ray magnetic circular dichroism applied to single molecule magnets and ferrofluids<br>*P. Sainctavit* |
| OC-07 | Molecule-based anisotropy enhancement of superparamagnetic nanoparticles<br>*L. Lisnard* |
| OC-08 | XMCD investigation of photo-switchable Fe/Co Prussian blue molecular magnets<br>*S. Fatima* |
| OC-09 | Antiferromagnetic long range spin ordering in Fe and $NiFe_2$ doped $BaTiO_3$ multiferroic layers<br>*H. Magnan* |

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| OC-10 | Beam-induced CO dissociation for magnetic patterining in ultrathin Co films<br>*T.O. Mentes* |
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### SESSION V
ENERGY STORAGE II: SOLAR CELLS
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| OC-12 | Electronic and structural periodicities on MAPI hybrid perovskite<br>*A. Tejeda* |
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## SESSION VI

### ENERGY STORAGE III: BATTERIES

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| OC-14 | Nanoscale PEEM spectroscopy combined with XPS to elucidate the surface reaction mechanism of cycled battery electrodes<br>*M. El Kazzi* |
| OC-15 | Combined HAXPES / soft PES / XPS study of interfaces in lithium-ion batteries<br>*R. Dedryvère* |

# X-ray Magnetic Circular Dichroism Applied to Single Molecule Magnets and Ferrofluids

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## ABSTRACT

In this presentation, we shall review some recent results dealing with the magnetic properties of nano-objects such as Single Molecule Magnets (SMMs) and nanospinels in ferrofluids.

SMMs are molecules that behave like magnets at low temperature. We shall show that the magnetic properties of the SMMs are completely dependent on the substrate on which they are deposited. XMCD that is an element selective probe of magnetism helps determine the interplay between the intrinsic magnetic properties of the SMMs and the interaction with the substrate:

-for the case of $Fe_4$ SMM, the magnetization of Iron ions depends strongly on the orientation of the symmetry axis of the molecule with the magnetic field;

-for the case of $TbPc_2$, one observes that the crystallographic organization of the molecules on the substrate depends on the nature of the substrate whether it is an oxide layer, a metallic layer or a semiconducting layer.

Ferrofluids are colloidal suspensions of ferrimagnetic nanospinels embedded in a liquid carrier and the generally nanoparticles ($\gamma$-$Fe_2O_3$, $MnFe_2O_4$, $CoFe_2O_4$). Their magnetic and optical properties make them good candidates in various applications ranging from medicine to optics or mechanical engineering. We shall show that the magnetic properties of the nanospinels cannot simply be determined by averaged properties such as their chemical composition or their diameter. Beyond these averaged properties, XMCD can determine the local organization of the magnetic ions in the nanospinels and help understand the magnetic properties.

# Molecule-based Anisotropy Enhancement of Superparamagnetic Nanoparticles

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M-A. Arrio[b], C. Cartier-dit-Moulin[g,h], P. Sainctavit[b,c], B. Fleury[g,h],
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## ABSTRACT

Owing to their magnetic properties, iron oxide nanoparticles are of considerable interest for applications in high-density data storage or in medicine.[1,2] In the case of small particles though, the superparamagnetic limit is reached and the relevant magnetic properties lost.[3] Retaining appealing magnetic properties while maintaining a small nanoparticle size has thus proved a highly challenging task. However, in these small nanoparticles, the magnetic properties are predominantly governed by the magnetic anisotropy. Modifying it represents thus one of the best approaches to improve the properties.

To enhance the anisotropy of sub-10 nm nanoparticles we have been investigating a novel synthetic strategy. It consists in the elaboration of composite materials where anisotropic molecular complexes are coordinated to the surface of the nanoparticles. Reacting 5 nm $\gamma$-$Fe_2O_3$ nanoparticles with the $[Co^{II}(TPMA)Cl_2]$ complex (TPMA: tris(2-pyridylmethyl)amine) has led to the desired composite materials.[4] The characterisation of the functionalised nanoparticles has evidenced the successful coordination –without nanoparticle aggregation and without complex dissociation– of the molecular complexes to the nanoparticles surface. XMCD-detected element-specific magnetisation curves have also confirmed the existence of a magnetic interaction between the cobalt(II) complexes and the iron(III) ions of the nanoparticles. SQUID and Mössbauer measurements indicate the significant enhancement of the anisotropy in the final objects. Indeed, the functionalised nanoparticles show a three-fold increase of the blocking temperature and a coercive field increased by one order of magnitude (Figure 1).

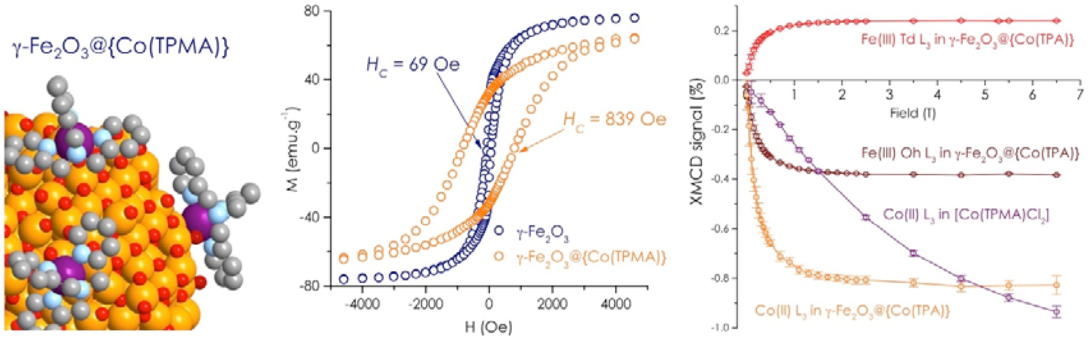

*Figure 1. Anisotropy enhancement in functionalised maghemite nanoparticles: surface coordination of molecular complexes.*

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# XMCD Investigation of Photo-switchable Fe/Co Prussian Blue Molecular Magnets

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## ABSTRACT

Nanoscale magnetic materials are potential candidates for energy efficient, photoswitchable molecule-based information storage. Molecular complexes exhibiting externally-controlled bistable physical properties are well-suited for these applications. The family of Prussian Blue and its analogues, referred as Prussian Blue analogues (PBA), exhibit thermal and photomagnetic bistability [1]. Recently, Koumousi *et al*. achieved "Ultimate Miniaturization" by synthesizing first FeCo PBA dinuclear complex that display the photoinduced and thermally induced magnetization [2]. It represents the simplest elementary motif of 3-dimensional Fe/Co PBA network. The current challenge of designing systems for information storage requires the deep understanding of the thermally and light-induced electron transfer phenomenon and its driving mechanism. Therefore, advanced characterization techniques like X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are the excellent tools to probe the change in the macroscopic magnetic properties of PBAs and can give local information about the metal centers existing in the structure. In this talk, we present XAS/XMCD results obtained on this molecule. Element specific XAS and XMCD measurements at Fe and Co $L_{2,3}$ edges were performed on the DEIMOS beamline (SOLEIL, France). XMCD at Fe and Co $L_{2,3}$ edges was measured as a function of temperature ranging from 300K to 4K to follow the thermally induced charge transfer between Fe(III)-Co(II) paramagnetic pair and Fe(II)-Co(III) diamagnetic pair. At 4K, the sample is irradiated by a 660 nm laser that switched the diamagnetic Fe(II)-Co(III) pair to the Fe(III)-Co(II) paramagnetic one. We also followed the relaxation of the photoinduced metastable state as a function of temperature and determined the fraction of paramagnetic Fe(II) low spin and Co(III) high spin species. Another important aspect is to check for the reversibility of the charge-transfer that has been measured by warming the sample to 300 K. In order to achieve detailed interpretation of data and to extract quantitative information XAS and XMCD spectra were modeled using the Ligand Field Multiplet theory (LFM).

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# Antiferromagnetic Long Range Spin Ordering in Fe and $NiFe_2$ Doped $BaTiO_3$ Multiferroic Layers

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## ABSTRACT

Doping ferroelectric compounds to produce novel multiferroic materials is a seductive approach. We report on the Fe doping and on the comparative $NiFe_2$ co-doping of fully oxidized $BaTiO_3$ layers (~ 20 nm) elaborated by atomic oxygen plasma assisted molecular beam epitaxy. The films were thoroughly characterized by synchrotron radiation X-Ray diffraction and X-Ray absorption spectroscopy. For purely Fe doped layers, the native tetragonal perovskite structure evolves rapidly towards cubic-like up to 5% doping level above which the crystalline order disappears. On the contrary, low co-doping levels (~5%) fairly improve the thin film crystalline structure and surface smoothness; high levels (~27%) lead to more crystallographically disordered films, although the tetragonal structure is preserved. Magnetic dichroic measurements reveal that metal clustering does not occur and allowed determining the ion valences. Ferromagnetic long range ordering can be excluded with great sensitivity in all samples as deduced from X-Ray magnetic absorption circular dichroic measurements. On the contrary, our linear dichroic X-Ray absorption results support antiferromagnetic long range ordering while piezo-force microscopy give evidence of a robust ferroelectric long range ordering showing that the films are excellent candidates for magnetic exchange coupled multiferroic applications.

# Electronic and Magnetic Reconstruction at Interfaces between Iron and Manganese Perovskites

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## ABSTRACT

At interfaces between complex oxides electronic, orbital and magnetic reconstructions may produce states of matter absent from the materials involved, thereby offering novel possibilities for electronic and spintronic devices. In this presentation, we will highlight two such interfacial systems combining iron perovskites and (mixed-valence) manganese perovskites.

In the first part, we will discuss heterostructures combining the high temperature antiferromagnetic insulator $LaFeO_3$ (LFO) and the half-metallic ferromagnet $La_{0.7}Sr_{0.3}MnO_3$ (LSMO). We will see how a net magnetic moment is induced in the first few unit planes of LFO near the interface with $La_{0.7}Sr_{0.3}MnO_3$ (LSMO). Using X-ray photoemission electron microscopy, we will show that the ferromagnetic domain structure of the manganite electrodes is imprinted into the antiferromagnetic LFO, which, when using the LFO as a tunnel barrier, endows it with spin selectivity. We find that the spin arrangement resulting from coexisting ferromagnetic and antiferromagnetic interactions strongly influences the tunnel magnetoresistance of LSMO/LFO/LSMO junctions through competing spin-polarization and spin-filtering effects [1].

In the second part, we will describe heterostructures combining $(Ca, Ce)MnO_3$ (CCMO) with multiferroic $BiFeO_3$. Compared to the widely investigated hole-doped manganites, in CCMO the chemical substitution of $Ca^{2+}$ by $Ce^{4+}$ in $CaMnO_3$ leads to electron doping and induces a transition to metallic behavior at very low doping levels. In bulk CCMO, this transition happens at 5% Ce doping and is accompanied by the development of a weak ferromagnetic state with a magnetic moment of $\sim 0.4 \mu B/Mn$. After a description of the physical properties of epitaxial CCMO films, we will present charge redistribution effects in CCMO at interfaces with $BiFeO_3$ [2] and describe how they can be used to control electronic and magnetic responses by ferroelectric field effect [3].

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# Beam-induced CO Dissociation for Magnetic Patterning in Ultrathin Co Films

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## ABSTRACT

Spin reorientation transitions (SRT) are often encountered in ultrathin films due to the interplay between the surface, interface, and volume contributions to the magnetic anisotropy. In general, the reorientation transition can be modified by varying the temperature, the thickness, or by introducing foreign species on the surface [1]. Here, we focus on the latter effect, and we show that the magnetization direction in ultrathin Co films on Re(0001) can be switched from in-plane to out-of-plane by CO adsorption and dissociation [2]. The evolution of the magnetic domains in the Co film across the spin reorientation transition is visualized using X-ray Magnetic Circular Dichroism PhotoEmission Electron Microscopy (XMCD-PEEM) [3]. Together with Low Energy Electron Microscopy (LEEM) [4], the measurements relate the crystal structure to the magnetic properties, and reveal that magnetoelasticity plays a principal role in the SRT. Furthermore, a focused low-energy electron beam is used to locally induce CO dissociation on Co, making it possible to pattern the magnetization axis. To conclude the presentation, we demonstrate that the patterned magnetization can be preserved under ambient conditions by depositing noble metal capping layers on the ultrathin magnetic film.

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# 1s2p RIXS-MCD Measurements on $CrO_2$

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## ABSTRACT

We report on the first experimental RIXS-MCD measurements of a CrO2 powder performed at the GALAXIES beamline at SOLEIL. The magnetic circular dichroism (MCD) of the half-metal CrO2 was measured as two-dimensional 1s2p RIXS-MCD map. It displays the Ka1 and Ka2 decay channels after quadrupole excitation (1s->3d) with circular polarised light in the Cr K pre-edge. The final average yields a clearly visible dichroism in the Ka1-region while the Ka2 dichroism is only weakly pronounced.

The chromium K edge of CrO2 shows a large pre-edge before the main edge. The MCD shows that the quadrupole pre-edge is shifted to lower energy by approximately 2.5 eV. This is not visible as a separate RIXS feature in the pre-edge structure, but becomes visible in the MCD spectrum due to the position if the dichroic signal.

Using a simple empirical Gaussian fitting approach to exploit the intrinsic connection between the sum (lcp+rcp) and the MCD (lcp-rcp) spectra, RIXS-MCD reveals that the visible Cr Ka1 pre-edge structure is dominated by dipolar contributions. Due to symmetry considerations we relate this to non-local transitions caused by inter-site hybridisation in which the local 4p character mixes with the 3d character of next neighbour metal ion.

Thus RIXS-MCD enables in the present case to experimentally distinguish the quadrupole and dipolar contributions.

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# Hybrid Perovskites for Photovoltaic and Optoelectronic Applications

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## ABSTRACT

3D hybrid perovskites are currently superstar materials for photovoltaics and attract increasing attention of the scientific community. They also revealed attractive spin-related properties and photoluminescence, as already well known for 2D layered hybrids. After an introduction to the ongoing research developments at the international level, the scientific approach of the joint FOTON/ISCR team in Rennes will be described. This approach starts from the identification of a multifaceted change of paradigm related to the recent advances in this field and is based on concepts of solid-state physics and group symmetry approaches originally developed for conventional semiconductors. It shows that the broad light-harvesting abilities and attractive transport properties of 3D metal-halide hybrid perovskites can be related to the multi-bandgap and multi-valley nature of their band structure, to band folding effects and a non-conventional huge spin-orbit coupling in the conduction band.

# Electronic and Structural Periodicities on MAPI Hybrid Perovskite

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## ABSTRACT

Organic-inorganic hybrid perovskites are promising absorber materials for low-cost photovoltaic solar cells or optoelectronic devices [1-4]. Among these perovskites, methylammonium triiodideplumbate ($CH_3NH_3PbI_3$, $MAPbI_3$ or MAPI) exhibits currently the highest efficiency. Here we have analyzed the structural transition in MAPI between the β and the γ phases, and we have correlated it to the electronic properties. In the first Angle-Resolved Photoemission Spectroscopy measurements in this family of systems, we observe that the electronic and structural periodicities as determined by photoemission and X-ray diffraction do not agree at low temperature, as the periodicity observed by electrons at low temperature corresponds to a single $PbI_2$ octahedron.

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# Photoemission Study of Irradiation Impact on Amorphous / Crystalline (a-Si:H/ c-Si) Silicon Heterojunction

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## ABSTRACT

Ion irradiation of silicon heterojunction solar cells based on a-Si:H/ c-Si stacks has been demonstrated to modify their efficiency [1]. In order to relate these observations to the electronic and structural changes at the buried interface, we have performed Hard X-ray Photoelectron Spectroscopy (HAXPES) [2] at the GALAXIES beamline of SOLEIL synchrotron. We have studied a-Si:H/ c-Si silicon heterojunctions irradiated with pulsed plasma irradiation of 100 eV Ar ions under fluences upto $10^{15}$ ions/cm$^2$ (at this energy, the irradiation is limited to few nm). The HAXPES measurements reveal the impact of irradiation as a function of depth (using different photon energies: 3keV, 5keV and 8keV) via core-level and valence band detection. The density of states (DOS) of the valence band has been determined as a function of the depth (fig. 1b), which also provides information on the the crystalline Si bands in thin heterojunctions. The DOS reveals a state of 0.3 Ev of binding energy in the irradiated samples, compatible with the photoluminescence from these samples (fig. 1c) [1]. The photoemission data as a function of the photon energy allow to identify the depth were this state is localized, necessary to understand the atomistic nature of the electronic state and how it is induced.

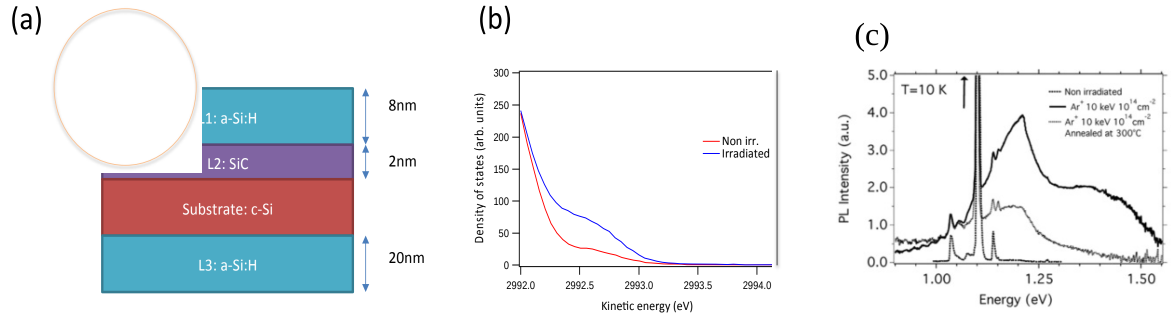

Figure 1. (a) Schematics of the studied a-Si:H/c-Si heterojunctions. Circles represent the inelastic mean free path of the emitted electrons. (b) Density of states near the Fermi level of irradiated and non-irradiated samples (hv = 3 keV) (c) Photoluminescence (PL) spectra at 10 K from crystalline silicon passivated with hydrogenated amorphous silicon layers in the as-deposited, after Ar+ implantation and annealed after irradiation [1].

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# *Operando* Characterization of Lithium Battery Materials by XRD and XAS

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## ABSTRACT

In previous studies, we have used the high flux of synchrotron source to investigate, in *operando* mode, the behavior of lithium battery electrodes [1]. At this time we mainly focused on prototypical compounds to validate the experimental approach. More recently we have studied the complex Li-rich layered oxides $Li_{1+x}M_{1-x}O_2$ (M = Mn, Co, Ni) which are presently considered as good candidates for use as positive electrode in lithium ion batteries regarding on their high specific capacity (250mAh/g), only achieved by loading at high potential (> 4.3 V). Under these charging conditions, a voltage plateau appears at the end of the charge and an extra capacity is obtained. During the first charge, there are clear evidences that the material has been irreversibly modified. Redox phenomena at the origin of voltage plateau have been extensively studied in literature [2]. However, some questions still remain: What is the exact nature of the observed irreversible structural transformation? Are all chemical elements involved in the same way into the irreversible structural changes? How does this transformation impact redox mechanisms?

In a first part, *operando* X-ray diffraction (XRD) and high resolution electron microscopy (HREM) were combined to *operando* X-ray absorption spectroscopy (XAS) to study the structural modifications undertaken during the first charge-discharge cycle. DFT calculations have used to validate proposed structural models. Our results confirm that these compounds must be considered as nano-composites $Li_2MnO_3$-$LiMO_2$ from both structural and electrochemical viewpoints. As shown by *operando* XRD, irreversible structural modifications occur mainly during the plateau. They concern particularly $Li_2MnO_3$ since its characteristics diffraction peaks are no longer observed in XRD patterns at the end of the charge**.** Furthermore, only manganese spectra are notably modified during the plateau as observed in *operando* XAS. In combination with HREM, a structural model has been developed, in considering a migration of Mn atoms into the structure. A coupling of XANES data with DFT calculations performed on $Li_2MnO_3$ delithiation process shows that 3D migration of manganese atoms is coupled with a 2D one inside transition metal layers [3].

In a second part, we have studied the evolution of the XANES spectra for Mn, Co and Ni during the cycling of the battery. We have continuously followed the positions of the white lines for the three edges. The electrochemical “plateau” was identified as the activation of the $Li_2MnO_3$. It is clear that, despite its initial high oxidation state IV, manganese is involved in the redox process during this step and also during the discharge. As expected nickel and cobalt are involved in the redox process, but in a different way after the first charge.

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# Nanoscale PEEM Spectroscopy Combined With XPS to Elucidate the Surface Reaction Mechanism of Cycled Battery Electrodes

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## ABSTRACT

For the first time we explore the potential and feasibility of X-ray PhotoEmission Electron Microscopy (PEEM) to investigate commercial-like battery electrodes and to study separately, at the nanoscale level, the surface layer chemistry evolution on the active materials and on the conductive carbon. Two types of electrodes are investigated, LiM (M=Mn, Ni, Co)$O_2$-$Li_2MnO_3$ (NCM) and $Li_4Ti_5O_{12}$ (LTO), as promising positive and negative electrodes, respectively, for Li-ion batteries. Thanks to the PEEM technique, we are able to overcome the limited spatial resolution and poor sensitivity to transition metals of conventional X-ray photoemission spectroscopy (XPS). Furthermore, both techniques probe the same range of depth (< 8nm). The elemental contrast images in Figure 1.I attest the high lateral resolution of PEEM and its ability to distinguish single particles of the active materials, NCM or LTO, from the conductive carbon in typical commercial-like electrodes, without the need of using model systems. The local XAS spectra (Figure 1.II) at the Ni-, Co-, Mn-L edges and C-K edge acquired on NCM particles allow us to monitor their oxidation states as well as the chemical species present on the surface without interference from the signal arising from the conductive carbon. By combining PEEM with XPS (Figure 1.III) during the early stage of cycling together with long cycling, we can obtain a better insight on the mechanism behind the surface layer formation on the positive and negative electrodes. Moreover, the origin of the surface layer present on LTO was elucidated, alongside the impact of the high potential on the NCM structure stability.

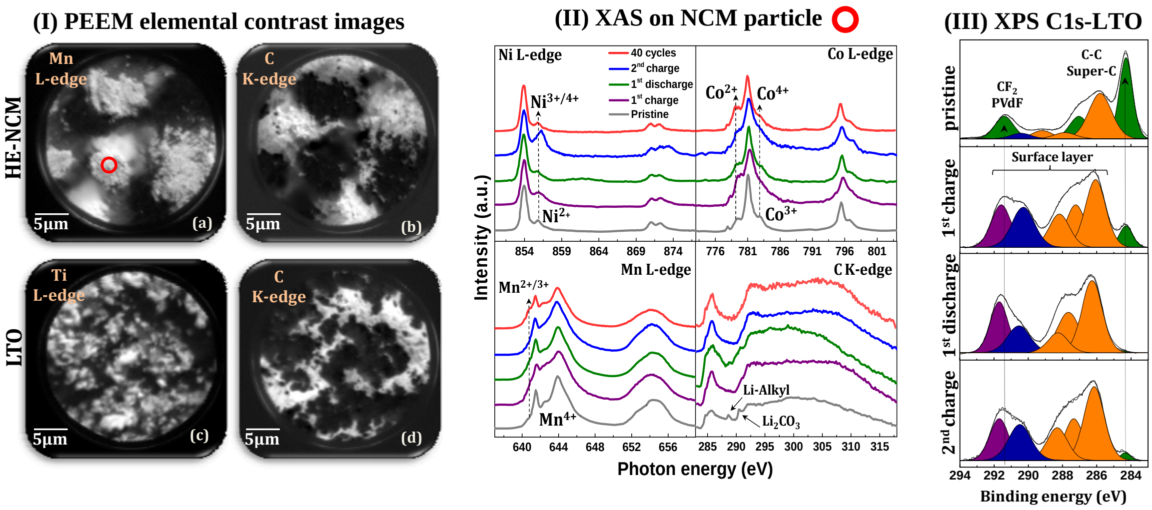

**Fig 1 : (I)** Element-specific PEEM contrast images performed on NCM (a, b) and LTO (c, d) pristine electrodes. **(II)** XAS evolution of the transition metals oxidation states as well as the surface layer formation acquired on one single NCM particle. **(III)** LTO surface layer formation probed by XPS C1s core level.

# Combined HAXPES / Soft PES / XPS Study of Interfaces in Lithium-ion Batteries

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## ABSTRACT

The tunability of X-ray photon energy from several hundreds to several thousands of eV offers great opportunities for Photoemission Spectroscopy (PES) studies of interfaces in electrochemical storage of energy devices, especially in lithium-ion batteries. In these systems, the study of interfaces is of primary importance since most of the failure and aging mechanisms take place at passivation layers and solid electrolyte interphases. Classical in-house X-ray Photoelectron Spectroscopy (XPS) investigation of interfaces allows a fixed probe depth of several nanometers. Depth-profiling analysis requires then the use of ion sputtering, which is a problem for these systems due to the fragility of interfaces that consist of sensitive organic and inorganic species. Comparison of Soft X-ray Photoemission Spectroscopy (Soft PES), Hard X-ray Photoemission Spectroscopy (HAXPES) and classical XPS experiments on the same samples allows a characterisation at different probe depths without any destructive depth-profiling.

The results presented in this talk were obtained on silicon electrodes for Li-ion batteries. Silicon is one of the most interesting negative electrode materials as an alternative to graphite, due its much greater capacity. This material, however, suffers from aging processes at the interface between the active material and the electrolyte. Experiments were carried out at BessyII (Berlin, Germany) for HAXPES (2300-6900 eV), at MaxIV Lab. (Lund, Sweden) for Soft PES (200-800 eV) and at IPREM (Pau, France) for XPS (1487 eV). I will show how this approach allows to understand mechanisms at solid/liquid and solid/solid interfaces.

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# POSTERS SESSION

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| **PO-03** | HAXPES Study of an Enhanced Solid Electrolyte Interphase on Silicon Based Anodes for Lithium-ion Batteries<br>*B. Moeremans* |
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| **PO-05** | Inelastic Background Analysis of HAXPES Spectra for Device Technology<br>*S. Tougaard* |
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# Hard X-ray Photoelectron Spectromicrocopy at PETRA III

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## ABSTRACT

Photoelectron spectroscopy (HAXPES) and microscopy (HAXPEEM) using excitation by hard X-rays in the range of 3–10 keV are rapidly developing at synchrotron light sources worldwide. Their comparatively large probing depth (typ. 10-30 nm) makes them powerful tools for studies of complex materials, magnetic (buried) nanostructures, and multilayered structures relevant for spintronic devices.

The HAXPES instrument at PETRA III beamline P09 has been open for users since Sept. 2010. First HAXPEEM experiments were done in 2011. The HAXPES and HAXPEEM instruments (Fig. 1) will move from beamline P09, where only $^1/_3$ of the beamtime has been available, to the new beamline P22, which is part of the PETRA III extension project. The P22 beamline optics will employ a stability-improved high heat load primary Si(111) and Si(311) monochromator, a 4-bounce zero-offset double Si channel-cut post monochromator, and a diamond phase-retarder for generating linear or circular X-ray polarization. It is planned to have first beam for commissioning at the new beamline in the beginning of 2017.

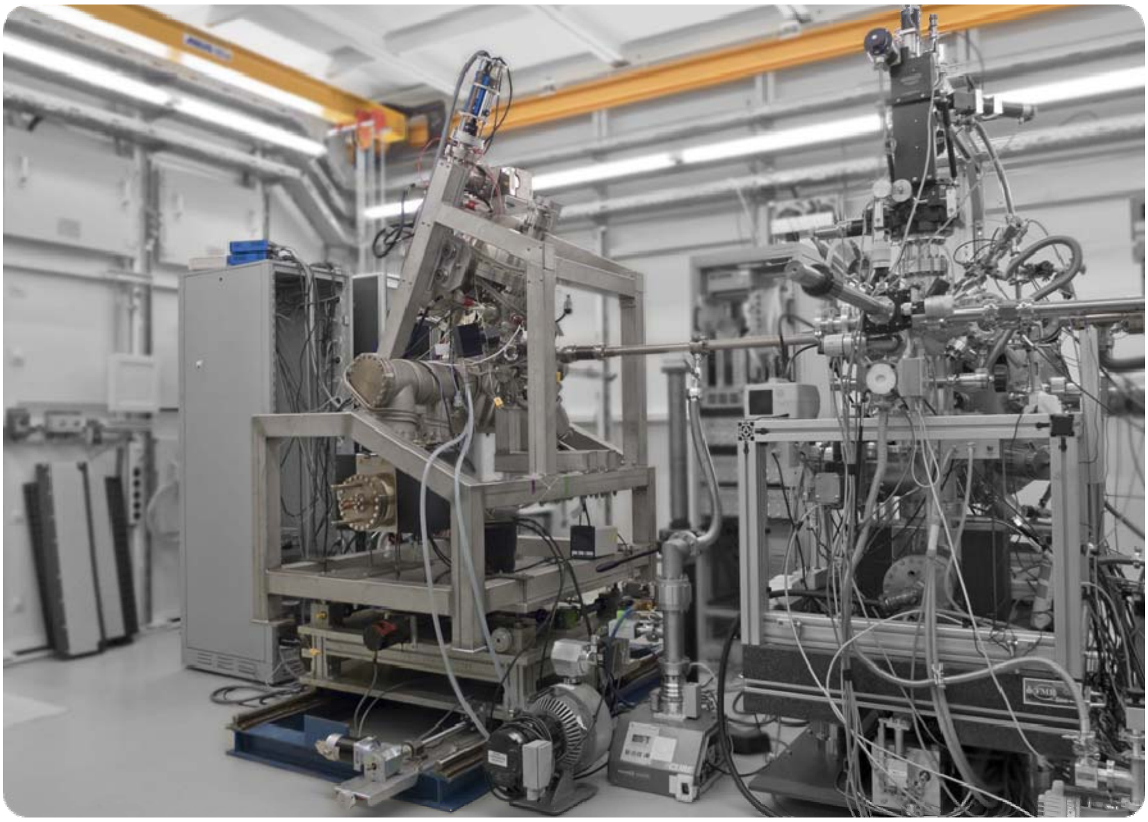

Fig. 1 HAXPES and HAXPEEM instruments at PETRA III beamline P09.

# Probing Metal-metal Charge Transfer with RIXS

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## ABSTRACT

The spectroscopic properties of metal-metal charge transfer (MMCT) transitions are of large importance with regard to photoredox processes but also color of many inorganic compounds and solids.

Metal-metal (or intervalence) charge transfer (MMCT) between Fe and Ti impurities is famously known for coloring sapphire ($Al_2O_3$, corindon) in blue [1]. In ilmenite ($FeTiO_3$), the MMCT have been used to enhance the photocatalytic properties of $TiO_2$ nanoparticles [2,3]. MMCT is predicted to occur between two neighboring metal ions, in the corindon structure, two octahedral metallic sites along the c axis share one face resulting in very small metal-metal distance. However, the determination of the exact nature of this charge transfer is still challenging and depending on both localized and delocalized effects. In particular the role of the “bridging oxygen atoms” is unclear and so far it was considered as a different contribution. MMCT has been suggested to occur in Ilmenite ($FeTiO_3$) by Agui et al[4] using 2p3d RIXS at Ti edge with 0.4 eV-resolution. Recent instrumental developments have strongly increased the energy resolution for 2p3d-RIXS measurements and provide an unprecedented opportunity to investigate the MMCT in $FeTiO_3$ from Fe and Ti respective RIXS.

I will propose an insight into experimental evidences with high resolution X-ray spectroscopies of inter-metallic charge transfers and a discussion of theoretical modelling of these effects in RIXS. Firstly, I will present approaches based on density functional theory to assist the interpretation of the experimental results in terms of electronic structure. Because multi-electronic effects may be involved, a complementary configuration interaction approach should be necessary to model di-metal clusters. Such theoretical approach will not only serve the case of $FeTiO_3$ but would also enable applications to other cases of inorganic chemistry and photo-catalytic systems.

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# HAXPES Study of an Enhanced Solid Electrolyte Interphase on Silicon Based Anodes for Lithium-ion Batteries

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## ABSTRACT

Increasing the capacity of Li-ion batteries and at the same time making the involved interfaces much more stable is one of the crucial problems on the way to a sustainable energy use.[1] Silicon anodes promise almost a 10-fold increase with respect to the capacity of conventional graphite anodes[2], but existing problems are not yet overcome. The continuous degradation of the Solid Electrolyte Interphase (SEI) at the surface of silicon-based active materials in lithium-ion battery anodes has been recognized as the key problem of these electrodes, currently preventing their commercial introduction.[3]

Here we present a methodology to specifically introduce polymer species into the SEI with the aim of providing a flexible backbone to this layer. Polyphenylene vinylene (PPV) was introduced in the SEI via reduction polymerization and analyzed using Hard X-ray Photoelectron Spectroscopy (HAXPES), Raman spectroscopy and electrochemical testing. HAXPES enabled us to address the full depth-dependent layer chemistry and allowed us to probe the interface of the solid-electrolyte interphase and the silicon based electrode. The performance of the additive was investigated by coin-cell lithium ion battery testing and provides an interesting view into the influence of electrolyte additives and of incorporating polymers in the SEI.

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# Study of Exchange Bias in $Fe_{3-\delta}O_4$@CoO Core-shell Nanoparticles

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## ABSTRACT

Single magnetic domain nanoparticles are very promising for many advanced applications such as hyperthermia or magnetic storage media. Nevertheless, the miniaturization of devices which is correlated to the size reduction of nanoparticles usually results in the decrease of the magnetocrystalline anisotropy and in unblocked domains at room temperature, e.g. superparamagnetism. An alternative and very promising approach is heterostructures such as core-shell nanoparticles featured by exchange bias coupling between F(i)M and AFM phases. Although exchange bias has been well investigated during last years, the large panel of parameters which affect it still need to be investigated.

We report on a systematic study which consists in the modulation of the shell structure and of the AFM/FiM interface in order to study their influence on the exchange bias coupling. $Fe_{3-\delta}O_4$@CoO core-shell nanoparticles have been synthesized by a one-pot seed-mediated growth method based on the thermal decomposition of metal complexes at high temperature.[1]The shell structure and AFM/FiM interface are demonstrated to be strongly modulated by the synthetic conditions.[2] While exchange bias coupling is strongly influenced by the shell thickness, the AFM/FiM interface were intermixing of Co and Fe atoms takes place also enhances the magnetic properties.

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# Inelastic Background Analysis of HAXPES Spectra for Device Technology

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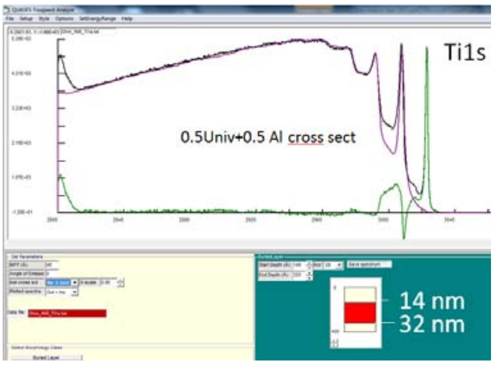
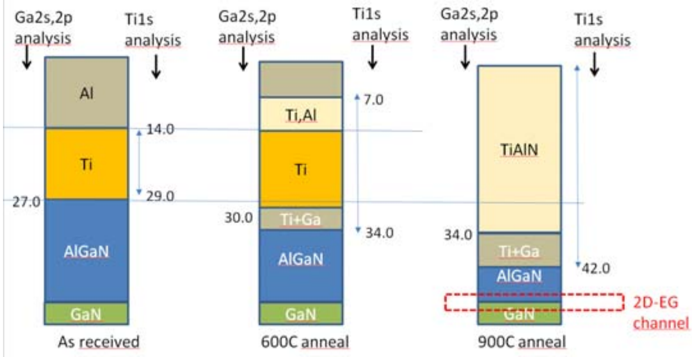
## ABSTRACT

There is a pressing need to develop photoemission methods able to address the challenge of non-destructive analysis of deeply buried interfaces (>25 nm) as required for instance in device technology. We have recently shown [1] how inelastic background analysis [2] could be successfully applied to Hard X-Ray Photoelectron Spectroscopy (HAXPES) in order to overcome the current limitation in probing depth of core-level analysis. In the case of a well-known multilayer structure, background analysis in HAXPES is able to quantify a nm-thick layer buried up to 55 nm below the surface [1, 3]. However, when the stack consists of materials with widely different scattering properties, the choice of inelastic scattering cross-section is crucial. To this end, we have developed an approach where optimized combinations of inelastic cross sections are used for background analysis. We applied this approach to the case of TiAl alloys used in High Electron Mobility power Transistors (see Figure) studied at GALAXIES [4]. The 900°C annealing is mandatory to form an ohmic contact with the AlGaN layer in the final device, without Ti diffusing down to the GaN interface. For the as-deposited stack, the retrieved Al and Ti distributions from the Ti1s and Ga2s, 2p background analysis using a blend of pure Al and Universal-cross sections are in agreement with the thicknesses measured by TEM (Al: 15 nm; Ti: 10 nm). After annealing, the background analysis shows formation of a TiAlN top layer and slight diffusion of Ti into the bulk without reaching the GaN interface. The structures found from analysis of the background of Ga2s,2p and Ti 1s are consistent (see Figure).





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# Inelastic Background Analysis Combined With HAXPES On TaAl-gated HEMT

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## ABSTRACT

Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1]. It was shown that by combining HAXPES with inelastic background analysis [2], structures at a depth >50 nm can be studied. Here, we present a study on technologically relevant High Electron Mobility power Transistors TaAl.

The study is performed on stacks of GaN-based HEMTs. These samples present two metal layers of aluminum and tantalum with different thicknesses deposited on $Al_{0.25}Ga_{0.75}N$/AlN/GaN heterostructure. We have used the technique to non-destructively study the activation annealing. HAXPES was performed at the Spring-8 synchrotron (Japan) using 8 keV photons.

The figure shows spectra measured around Al, Ga and Ta peaks for an as deposited sample. The calculation of inelastic background was performed using two input parameters; the IMFP, calculated using the TPP-2M formula [3] and as the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic cross-sections, which can be determined from reflection electron energy-loss spectra. The figure shows how the modelling of the inelastic background is used to determine the in-depth distributions which are found in good agreement with the TEM results.

We have also successfully used this technique to study the effect of annealing on the interfaces and on the element diffusion.

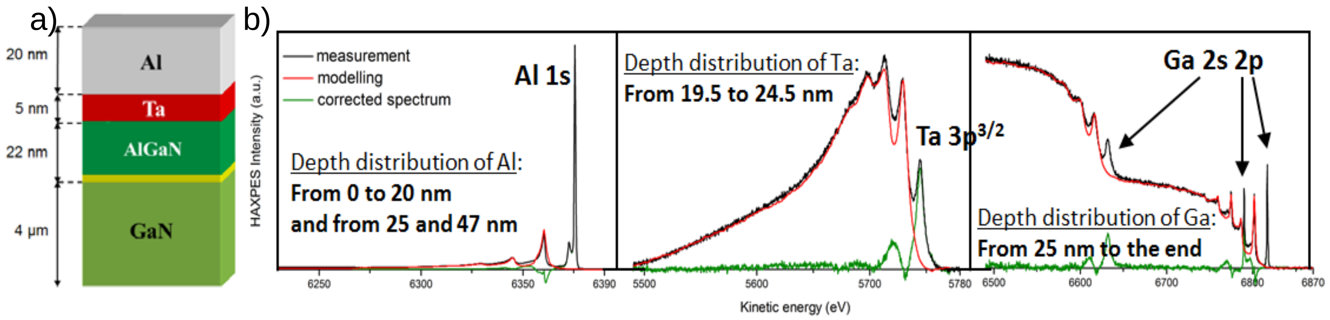

Fig. 1*: a) Sketch of the studied sample with the distribution measured by TEM, b) Spectra of Al 1s, Ta 3p and Ga 2s, 2p with the result find by the inelastic background analysis.*

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*Part of this work was performed at the Nanocharacterization Platform (PFNC) of CEA-MINATEC*