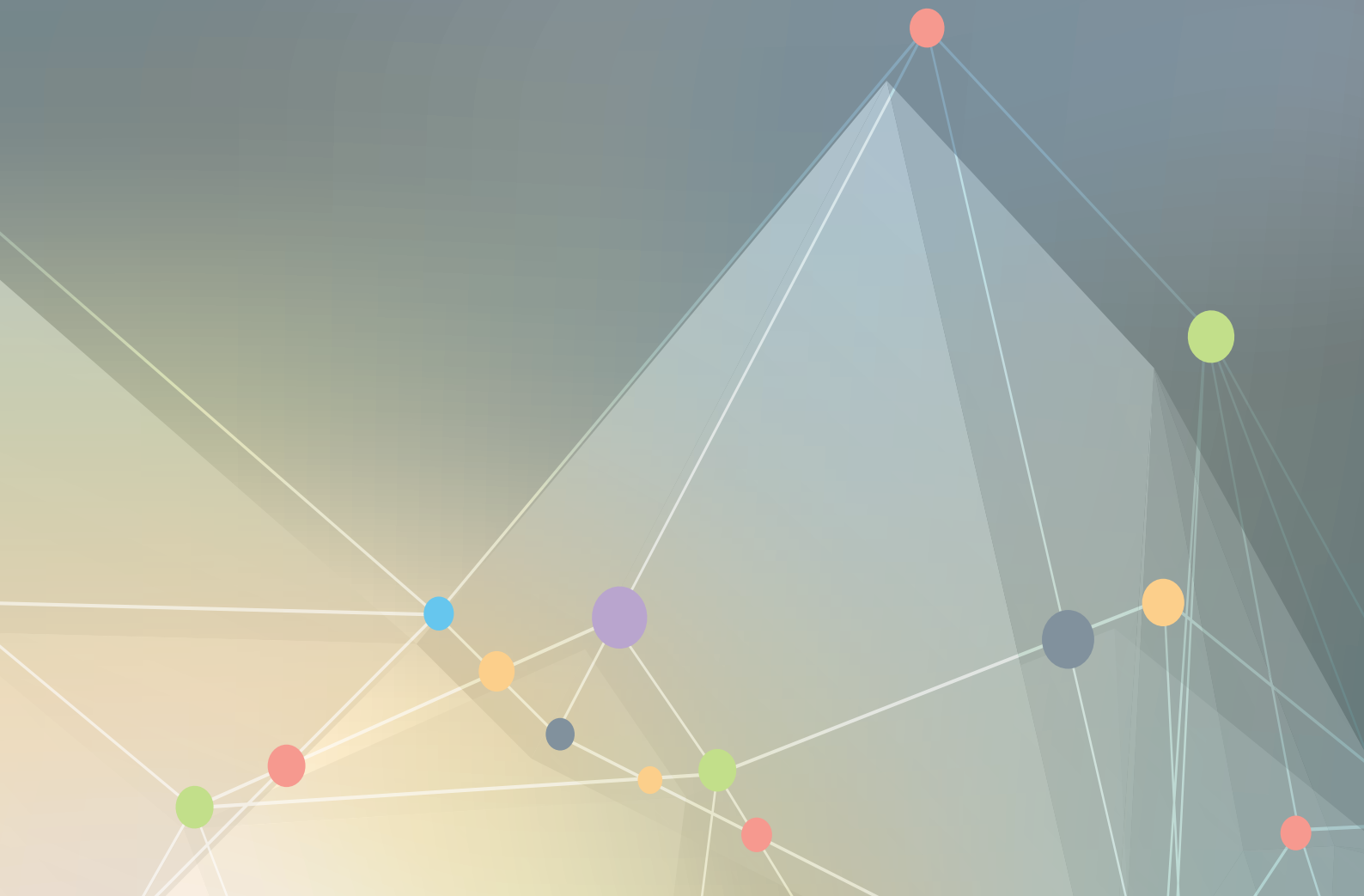


BOOK OF ABSTRACTS

Oral Presentations



2023



2D Materials

(Last update: August 23th, 2022)

Description

Since the discovery of graphene and the subsequent Nobel Prize for its fascinating two-dimensional (2D) properties, a wide variety of atomically thin materials has been discovered. Among them, we can quote metal dichalcogenides, hexagonal boron nitride, Xenes, layered double hydroxides, clays, layered oxides, MXenes, van der Waals heterostructures, 2D-MOFs...

The properties of this family of nanomaterials in the domains of magnetism, catalysis, superconductivity, optoelectronics, spintronics, topological insulation, biomedicine, etc... are singularly different from their three-dimensional counterpart, opening new perspectives in many applications.

The purpose of this session is to present the latest advances in this field in full effervescence concerning their synthesis, characterization and properties.

Keywords

Atomically thin materials, 2D synthesis, 2D characterization, 2D properties

Scientific committee

Stéphane CELERIER * (CNRS – IC2MP, Poitiers)

Catherine JOURNET-GAUTIER (Lyon Univ. – LMI, Lyon)

Laurence MASSON (Aix Marseille Univ. – CINaM, Marseille)

Geoffroy PREVOT (CNRS – INSP, Paris)

Loranne VERNISSE * (Univ.Poitiers – Pprime, Poitiers)

* *Session Coordinator*

In partnership with...

2023

Wednesday March 15th

11.00 am – 12.00 pm

Room 13/14

Program of the session

Chairs: Geoffroy PREVOT & Lorraine VERNISSE

2D MATERIALS

11:00	2D Materials revealed by Angle-Resolved Photoemission Spectroscopy	Yannick FAGOT-REVURAT • Univ. Lorraine – IJL, Nancy – France
11:30	Molecular adsorption on Dumbbell Silicene	Laurita FLOREAN • Ye MOU • Sorbonne Univ. - INSP & LCPMR, France
11:45	Visualizing In-Plane Junctions in Nitrogen-Doped Graphene	Cyril CHACON • Univ Paris Cité - MPQ, France
12:00	Propane/hydrogen CVD growth of graphene on SiC for applications	Adrien MICHON • CNRS - CRHEA, France
12:15	Quantum nanophotonics with 2D crystals	Antoine RESERBAT-PLANTEY • CNRS - CRHEA, France
12:30	Mechanical behavior and stability of 2D-Materials	Michel DROUET • CNRS - Inst. Pprime
12:45	Complete determination of thermoelectric and thermal properties of supported few layers 2D materials	Mehrdad RAHIMI • Univ Paris Cité - MPQ, France

Keynote Speakers

2D MATERIALS



Yannick FAGOT-REVURAT

University of Lorraine | Professor

Jean Lamour Institute

<https://ijl.univ-lorraine.fr/equipes/equipe-surfaces-spectroscopies-et-modelisations-supreme>

BIOGRAPHY

Yannick Fagot-Revurat has a professor position at the Lorraine University in Nancy (France) since 2012 and do his reasearch at the Institut Jean Lamour (IJL) in the Physics of Matter and Materials (P2M) department. He is now the leader of the Surfaces, Spectroscopies and Modelization research group. His main recent research has been carried out combining in situ Angle-Resolved Photoemission Spectroscopy (ARPES) and Scanning Tunneling Microscopy and Spectroscopy (STM/STS) in order to study the electronic structure of ultra-thin films and nanostructures. With his group he got recent results on electronic properties of organic/metal interfaces as well as of 2D oxides. He is in charge of a new spin-ARPES set-up installed on the IJL-TUBE-Daum connecting more than 20 UHV set-ups dedicated to elaboration (MBE, reactive MBE, PLD, PVD, ALD...) and characterization (MOKE, XPS, STM, STM-AFM, Spatially resolved AES...) of thin films and nanomaterials. He is an expert of using synchrotron radiation as a photon source for photoemission experiments.

2D MATERIALS REVEALED BY ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY

On one hand, 2D materials are the subject of increasing research activity owing to their singular electronic/optical/magnetic properties (direct band gap, topological states and QSH effect, room temperature ferromagnetism...) and to the possibility to combine them in fonctionnal heterostructures [1,2]. On the other hand, Angle resolved Photoemission Spectroscopy (ARPES) is a powerfull tool to characterize band structure, spin-polarized band structure, band topology and finally intra/inter-layer coupling in Van der Waals materials. Bottom up synthesis (CVD, MBE...) as well as exfoliation and transfer strategies have been recently used to investigate the band structure of 2D Materials by various ARPES technics [3].

In a first part we will focus on three examples of our recent work :

- k-resolved ARPES was combined to local STS spectroscopy and DFT calculations in order to reveal on-surface synthesis of 1D polymers [4] and beyond, a 2D polymeric architecture presenting a Dirac cone as expected in such graphene-like materials [5];
- More recently, it has been shown that silicon and germanium oxides exist in their ultra-thin forms (monolayer and bilayer) when deposited on a pre-oxidized Ru(0001) substrate. In this case, the combination of ARPES and DFT calculations reveal a transition between a monolayer strongly coupled to the substrate whereas the bilayer is shown to be a transferable VdW material with a large band gap comparable to h-BN [6,7];
- Electronic properties of GeTe, synthetized on Si(111)-Sb and on graphene/SiC(0001) and known as a Ferroelectric Rashba material in its bulk form, has been studied as function of its thickness.

Circular dichroism in ARPES has been first used as an indirect evidence of the disappearance of ferroelectricity measuring the sign change of the Berry curvature in k-space. In addition, our spin-ARPES measurements on a 5 nm GeTe/Si(111)-Sb unambiguously demonstrate a shift of spin-polarized bulk bands leading to a 100% spin-polarized Fermi surface [8-9].

In a second part, we will briefly shown recent nano [3] and in operando [10] ARPES measurements evidencing the possibility to get a spatially resolved band structure on 2D materials as well as on electronic devices with the capability to play with the band structure and control the electronic properties by tuning external parameters (doping, bias voltage...)

KEYWORDS:

ARPES on 2D Materials; ARPES on 1D, 2D polymers at surface; ARPES on 2D Oxides; CD-ARPES and spin-ARPES on GeTe ultrathin films; Nano and in operando ARPES

REFERENCES

[1] L. Marty et J. Renard, Les nouvelles frontières des matériaux 2D, l'Usine Nouvelle 24 juin 2022

[2] B. Dubertret et al., Chem. Res. 48, 1, 1–2 (2015)

[3] I. Cucchi et al., Comptes Rendus. Physique, Tome 22, no. S4, pp. 107-131 (2021)

[4] G.Vasseur et al., Nature Communication, vol. 7, 10235 (2016)

[5] G. Galeotti et al., Nature Materials, vol. 19 (8), 874 (2020)

[6] G. Kremer et al., ACS Nano 13, 4720 (2019)

[7] G. Kremer et al., 2D Materials 8 035021 (2021)

[8] B. Croes et al., Phys. Rev. Mat. 7, 014409 (2023)

[9] C. Tagne-Kaegom, B. Croes, A. Llopez et al., to be published (2023)

[10] P. Hofmann, AVS Quantum Sci. 3, 021101 (2021)

Keywords: Dumbbell silicene, adatom, surface, STM

Disciplinary field involved: Physics

Molecular adsorption on Dumbbell Silicene

Laurita FLOREAN^{1,2}, Geoffroy PREVOT¹, Fabrice BOURNEL², Romain BERNARD¹, Yves BORENSZTEIN¹,
Hervé CRUGUEL¹, Jean Jacques GALLET², Rabah BENBALAH²

1. Institut des NanoSciences de Paris, Sorbonne University, Paris, France
2. Laboratoire de Chimie Physique - Matière et Rayonnement, Sorbonne University, Paris, France

Following graphene discovery, 2D materials attracted rising attention due to their remarkable properties. Among them, silicene has been particularly studied as Si is essential in semi-conductor industry. Silicene presents an electronic structure very similar to the one of graphene [1], but is more sensitive to chemical environment. The possibility of tuning the electronic properties of silicene by molecular adsorption associated with the 2D geometry makes it a promising candidate for highly sensitive molecular sensors.

We have recently proven the existence of Dumbbell Silicene (DBSi) obtained by thermal evaporation of Si onto Ag(110) at 200°C. [2] It shows a low density of adatoms, on top of Si atoms of the silicene layer (Fig. 1b), forming DB units. Adsorption of molecules onto these sites is expected to open a small gap in the electronic structure, while preserving the overall silicene band structure. [3]

Using operando STM, we have followed the evolution of DBSi upon exposure to oxygen, ammonia and triethylamine at room temperature. If some molecules adsorb on top of DBs, other molecules are found to adsorb on the DB free regions silicene or on defects of the surface. From a quantitative analysis of the adsorption sites, we conclude that there is not any clear tendency for the molecules to adsorb on top of Si adatoms. Therefore, the DB sites don't seem to be more reactive than the rest of the silicene layer for the molecules cited above.

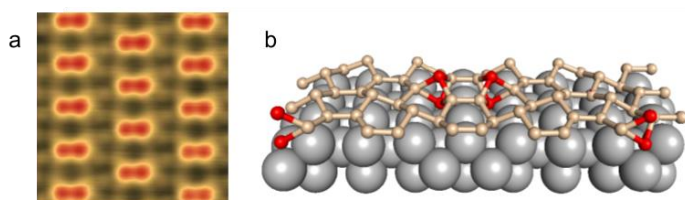


Fig. 1. a) STM image of the periodic DBSi mono-layer (5x5 nm²) on Ag(110). b) schematic of silver substrate (gray) with the silicene layer above and the DBSi (highlighted in red).

- References:** [1] Cahangirov, S. et al., Phys. Rev. Lett. 102, 236804 (2009) doi:10.1103/PhysRevLett.102.236804
[2] Leoni, T. et al., J. Phys. Chem. C 125, 17906–17917 (2021) doi:10.1021/acs.jpcc.1c02088
[3] V. O. Özçelik et S. Ciraci, J. Phys. Chem. C 2013, 117, 26305

Visualizing In-Plane Junctions in Nitrogen-Doped Graphene

M. Bouatou¹, C. Chacon¹, A. Bach Lorentzen², H. T. Ngo¹, Y. Girard¹,
V. Repain¹, A. Bellec¹, S. Rousset¹, M. Brandbyge², Y. J. Dappe³ and J. Lagoute¹

¹ Laboratoire Matériaux et Phénomènes Quantiques (MPQ), CNRS, Université Paris Cité, Paris, France

² Center for Nanostructured Graphene, Technical University of Denmark, Denmark

³ SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, France

Tuning the physical properties of graphene is an important challenge in the field of 2D materials. Soon after the first isolation of graphene, its chemical doping has been investigated with particular attention in nitrogen doping which is an n-type dopant [1]. A promising perspective opened up by the chemical doping of graphene is the realization of band engineering. However, one challenge to overcome is the control the spatial distribution of dopants. Here, we show that a nanopatterning of nitrogen dopants in graphene can be achieved by using monolayer islands of adsorbed molecules as a resist during the doping procedure. The resulting formation of domains with different nitrogen concentrations allows obtaining nn' and pn junctions in graphene. This method leads to the formation of a large collection of domains on a sample, allowing to address the junctions at the atomic scale by scanning tunneling microscopy (STM). Using STM and scanning tunneling spectroscopy, the electronic properties of the junctions have been measured. In particular, the evolution of the Dirac point along the junction makes it possible to measure the width of the space charge zone (Figure) which appears to be smaller than the Fermi wavelength [2].

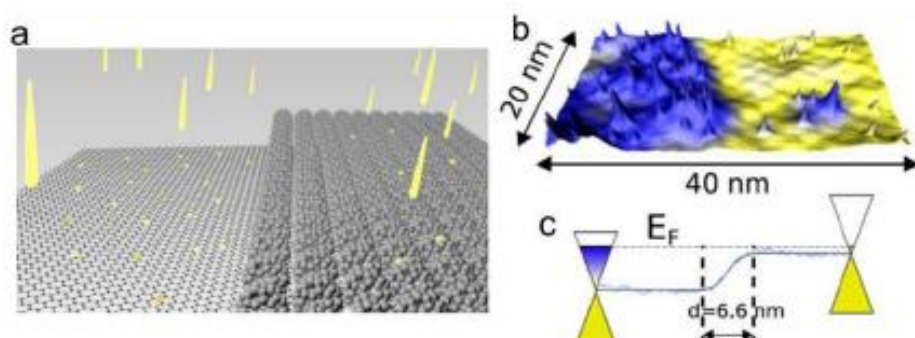


Figure: (a) 3D representation of a monolayer resist used to achieve nanodomains of different concentration of dopants in graphene. (b) STM topography color code with a differential conductance map showing the variation of the Dirac point on a junction between two domains of different nitrogen concentration in graphene. (c) Linescan of the conductance map used in (b) showing the variation of the Dirac point across the junction.

References:

- [1] F. Joucken, L. Henrard and J. Lagoute, Phys. Rev. Materials **3**, 110301 (2019)
- [2] M. Bouatou et al., Adv. Funct. Mater. **32**, 2208048 (2022)

Keywords: Graphene, SiC, epitaxy, metrology

Disciplinary field involved: Physics

Propane/hydrogen CVD growth of graphene on SiC for applications

A. Michon¹, C. Mastropasqua^{1,2}, A. Lamrani Alaoui¹, M. Portail¹, S. Vézian¹, A. Reserbat-Plantey¹, M. Al Khalfioui¹, M.-T. Dau¹, M. Abel², M. Koudia², I. Berbezier², Y. Cordier¹

1. Université Côte d'Azur, CNRS-CRHEA, Sophia Antipolis, France

2. Aix-Marseille Université, CNRS-IM2NP, Marseille, France

Propane/hydrogen CVD growth of graphene on SiC, studied since 2010 [1], consists simply to grow graphene from propane in a hydrogen/argon atmosphere. The presence of hydrogen in the gas phase promotes Si excess on the surface, hence making impossible graphene growth without propane flow [2]. This makes propane/hydrogen CVD very different from silicon sublimation where graphene grows from a carbon excess on SiC. The presence of hydrogen during growth, beyond strongly changing the chemistry during growth, allows to tune graphene properties from p-type multilayer to n-type monolayer. The quality of graphene monolayers prepared by hydrogen CVD is appealing for electronics applications, such as electrical metrology [3]. Graphene is also seen as a surface of choice for van der Waals epitaxy of nitrides [4] or 2D materials [5]. This contribution will present the main achievements and the current research based on graphene growth using Propane/hydrogen CVD.

References:

- [1] A. Michon et al., Appl. Phys. Lett. 97, 171909 (2010)
- [2] R. Dagher et al., Cryst. Eng. Comm. 20, 3702 (2018).
- [3] R. Ribeiro-Palau et al., Nature Nanotechnology 10, 965 (2015).
- [4] C Paillet et al., Nanotechnology 31, 405601 (2020).
- [5] Z. Ben Jabra et al., ACS Nano, 2022

Acknowledgment:

This work has been partly funded by the Region Sud project PlaGGe, FlagERA-JTC 2019 project ETMOS and by the Joint Research Project GIQS (18SIB07).

Keywords: quantum photonics, 2D crystals, quantum emitters

Disciplinary field involved : Physics

Sustainable Development Goals* eventually involved in your research: Quality education (Goal 4), Industry, Innovation & Infrastructure (Goal 9), Reduced Inequality (Goal 10), Sustainable Cities and communities (Goal 11), Partnerships for the goals (Goal 17)

Quantum Nano-Photonics with 2D crystals

Antoine RESERBAT-PLANTEY¹

1. *Université Côte d'Azur, CNRS, CRHEA, 06905 Sophia-Antipolis. France*

The field of two-dimensional (2D) materials-based nanophotonics has been growing at a rapid pace, triggered by the ability to design nanophotonic systems with in situ control, unprecedented number of degrees of freedom, and to build material heterostructures from the bottom up with atomic precision [1]. A wide palette of polaritonic classes have been identified, comprising ultraconfined optical fields, even approaching characteristic length-scales of a single atom. These advances have been a real boost for the emerging field of quantum nanophotonics, enabling quantum technologies harnessing single-photon generation, manipulation, and detection using 2D materials. Here, I will show several hybrid systems consisting in lifetime-limited single emitters [2, 3] (linewidth ~ 40 MHz) and 2D materials at sub-wavelength separation without degradation of the emission properties [4]. We have demonstrated that their nanoscale dimensions enable ultra-broadband tuning (tuning range > 400 GHz) and fast modulation (frequency ~ 100 MHz) of the emission energy [5], which renders it an integrated, ultra-compact tuneable SPS. I will also present recent results on unusual Stark tuning of ultra-narrow quantum emitter located at the edge of a graphene transistor and electrostatic engineering of excitons in 2D semiconductors.

References:

- [1] A. Reserbat-Planthey, I. Epstein, I. Torre, A. T. Costa, P. A. D. Gonçalves, N. A. Mortensen, M. Polini, J. C. W. Song, N. M. R. Peres, F. H. L. Koppens, Quantum Nanophotonics in Two-Dimensional Materials. *ACS Photonics*. 8, 85–101 (2021)
- [2] K. G. Schädler, C. Ciancico, S. Pazzagli, P. Lombardi, A. Bachtold, C. Toninelli, A. Reserbat-Planthey, F. H. L. Koppens, Electrical Control of Lifetime-Limited Quantum Emitters Using 2D Materials. *Nano Letters*. 19, 3789–3795 (2019).
- [3] C. Toninelli, I. Gerhardt, A. S. Clark, A. Reserbat-Planthey, et al. Single organic molecules for photonic quantum technologies. *Nature Materials*. 20, 1615. (2021).
- [4] C. Ciancico, K. G. Schädler, S. Pazzagli, M. Colautti, P. Lombardi, J. Osmond, C. Dore, A. Mihi, A. P. Ovvyan, W. H. P. Pernice, E. Berretti, A. Lavacchi, C. Toninelli, F. H. L. Koppens, A. Reserbat-Planthey, Narrow Line Width Quantum Emitters in an Electron-Beam-Shaped Polymer. *ACS Photonics*. 6, 3120–3125 (2019).
- [5] D. Cano, A. Ferrier, K. Soundarapandian, A. Reserbat-Planthey, M. Scarafagio, A. Tallaire, A. Seyeux, P. Marcus, H. de Riedmatten, P. Goldner, F. H. L. Koppens, K.-J. Tielrooij, Fast electrical modulation of strong near-field interactions between erbium emitters and graphene. *Nature Communications*. 11, 4094 (2020).

Keywords: Buckling, stress, FvK theory

Disciplinary field involved: Physics S

Mechanical behavior and stability of 2D-Materials

M. Drouet, L. Vernisse, E. Fodeke, C. Coupeau

1. Institut Pprime, UPR 3346, CNRS-Université de Poitiers-ENSMA ; SP2MI 11 Bd M&P Curie, Chasseneuil du Poitou, TSA 41123, 86073 POITIERS CEDEX 9

Buckling phenomena of thin plates have been studied and well described based on the thin plate model developed at the beginning of the 19th century by A. Föppl and T. von Kármán (referred to as FvK). The theory makes it possible to understand the mechanical properties of the plate under stress based on the buckling phenomenon and has been used to determine the elastic properties of metallic thin films which generally differ from those of the same materials at the bulk state (1). But as thin films are well described, the theory is yet in the dark to describe 2D materials.

Indeed, understanding the properties of 2D materials gradually unlocks a wide range of opportunities in the technological revolution, particularly in applications like flexible electronics and nanodevices (2). This requires a controlled mechanical stability of the material under severe conditions. It is therefore essential to study how 2D films respond to stress/strain. However, the study of mechanical properties of these materials is often set aside compared to their electronic properties.

The objective of this research is double :

- To experimentally explore by SPM the behaviour under deformation by uniaxial compression of two well-known materials: graphene and MoS₂.
- To take advantage of the buckling phenomenon induced on the 2D material by its substrate to extend the FvK theory to 2D scale.

This presentation will give a first insight of our studies towards those two objectives.

References:

- 1- C. Coupeau, "From thin film and coating buckling structures to mechanical properties," *Materials Science and Engineering: A*, **483**, 617–619 (2008).
- 2- B. Zhao, "2D Metallic Transition-Metal Dichalcogenides: Structures, Synthesis, Properties, and Applications." *Adv. Funct. Mater.* **31**, 2105132 (2021).

Keywords: energy conversion, thermoelectricity, two dimensional materials

Disciplinary field involved: Physics

Sustainable Development Goals eventually involved in your research: Affordable and clean energy (goal 7)

Complete determination of thermoelectric and thermal properties of supported few layers 2D materials

Mehrdad Rahimi¹, Karen Sobnath¹, Philippe Lafarge¹, François Mallet¹, Clément Barraud¹, Danièle Fournier², Willy Daney de Marcillac² and Maria Luisa Della Rocca¹

1. *Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Cité, CNRS-UMR7162, 75013 Paris, France*
2. *INSP, Sorbonne Université, UFR925, 75005 Paris, France*

Modern micro and nanodevices produce heat dissipation during their operations, which is lost in the environment. Thermoelectric energy conversion, that is the ability of generating an electrical field in the presence of a temperature gradient in certain materials, could represent a reliable solution recover the energy dissipated at low dimensions [1].

Layered bidimensional (2D) materials, such graphene (GN) and transition metal dichalcogenides (TMDs), as well as their heterostructures, have demonstrated a variety of fascinating physical properties making them attractive for electronic, spintronic, and optoelectronic applications. In addition, due to their thermoelectric and thermal properties, 2D materials are promising also for energy conversion, anticipating high efficiencies. Due to the complexity of controlling thermal transport at the nanoscale, actual applicability as thermoelectric materials depends on the ability to fully study their physical characteristics once implemented in actual devices [2-4].

We have demonstrated the possibility to provide a complete thermoelectric characterization of devices based on thin flakes (5 – 6 nm) of tungsten diselenide (WSe₂) and multilayer graphene (MLGN) deposited on hexagonal boron nitride (hBN) by coupling electric and thermoelectric measurements with a non-destructive all-optical approach for thermal conductivity analysis, the modulated thermorefectance (MTR) [5]. We have extracted the anisotropic thermal conductivities of each layer composing the device using flake-by-flake MTR scans, extracting values in agreement with literature. Our work unveils the possibility to perform selective non-destructive complete thermoelectric characterization of thin flakes of 2D materials embedded in a device configuration.

References:

- [1] GD Mahan and JO Sofo. "The best thermoelectric." In: Proceedings of the National Academy of Sciences 93.15 (1996), pp. 7436–7439.
- [2] Jeffrey J Urban et al. "New horizons in thermoelectric materials: Correlated electrons, organic transport, machine learning, and more". In: Journal of Applied Physics 125.18 (2019), p. 180902.
- [3] Jinbing Cheng et al. "Recent advances in optoelectronic devices based on 2D materials and their heterostructures". In: Advanced Optical Materials 7.1 (2019), p. 1800441.
- [4] Qing Hua Wang et al. "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides". In: Nature nanotechnology 7.11 (2012), pp. 699–712.
- [5] Daniele Fournier, Massimiliano Marangolo, and C Frétigny. "Measurement of thermal properties of bulk materials and thin films by modulated thermorefectance (MTR)". In: Journal of Applied Physics 128.24 (2020), p. 241101.

Acknowledgment:

I would like to express my very great appreciation to Stephan Suffit and Pascal Filloux, the cleanroom engineers of MPQ laboratory, for their valuable and constructive suggestions during the development of this research work.

Thursday March 16th

10.30 am – 12.30 pm

Room 13/14

Program of the session

Chairs: Yannick FAGOT-REVURAT & Laurence MASSON

2D MATERIALS

10:30	Order-disorder in water confined in natural swelling clays	Eric FERRAGE • CNRS – IC2MP, Poitiers – France
11:00	Controlled friction at the solid-liquid interface in graphene-based nanochannels	Sandra VASILJEVIĆ • CNRS - LPENS, France
11:15	From Biomass Wastes toward Gram-Scale Luminescent Graphene Quantum Dots	Jean-Jacques GAUMET • Univ. Lorraine - LCP/A2MC, France
11:30	On-surface assemblies of DNA-decorated functional nano-objects by supramolecular recognition	Zohreh SAFARZADEH • Sorbonne Univ. - MONARIS, France
11:45	Synthesis, characterization and surface chemistry of 2D Mo/Ti solid solution based MXene. Application to hydrogen evolution reaction in alkaline media	Lola LOUPIAS • Univ. Poitiers - IC2MP, France
12:00	Probing in situ the reactivity in molten salts of carbides and borides: synthesis of layered compounds, etching, and tuning of their composition	David PORTEHAULT • CNRS - LCMCP, France
12:15	Tuning the optical and electrical properties of 2D Ti3C2Tx MXenes: an ion implantation approach	Ayoub BENMOUMEN • Univ.Poitiers - Inst. Pprime, France

Keynote Speakers

2D MATERIALS



Eric FERRAGE

CNRS I Researcher

Light matter institute

<https://ilm-perso.univ-lyon1.fr/~opl/>

BIOGRAPHY

Eric Ferrage obtained his PhD in 2004 from the University of Grenoble (France). He then benefited from a Marie Curie Intra-European fellowship to at the Natural History Museum of London for two years before being hired at CNRS in 2007 at the Institute of Chemistry and Material resources (Poitiers, France). Since then his work revolves around the analysis of structural and dynamical fluids in contact with natural phyllosilicates by means of experiments (mainly X-ray diffraction) and molecular simulations for the understanding of the fate of water and solutes in the environment. His contribution to the field was awarded in 2015 by the bronze medal of the CNRS.

ORDER-DISORDER IN WATER CONFINED IN NATURAL SWELLING CLAYS

Swelling clay minerals are ubiquitous in surface environments, both terrestrial and marine, where they often represent one of the main mineral components. Their bidimensional crystal structure involves colloidal size ($< 2\mu\text{m}$) negatively charged layers constituted with two tetrahedral layers sandwiching an octahedral one. The charge deficit resulting from cationic substitutions in either the tetrahedral or octahedral layer is compensated for by exchangeable cations located in the interlayer space. The moderate charge of the layers (between -0.1 and -0.2 C/m²) allows water molecules to penetrate the interlayer space and hydrate the interlayer cations, which results in a swelling of the crystal structure [1-2].

As a function of relative humidity (RH) and under non-saturated conditions, smectite typically shows a stepwise hydration behaviour corresponding to the intercalation of 0, 1 or 2 discrete sheets of water molecules in its interlayer [1-2]. However, heterogeneities of charge location (between octahedral and tetrahedral sheets) and/or of charge amount (from one interlayer to the other or within a given interlayer) most often lead to the coexistence of different hydration states within smectite crystals [3]. These heterogeneities are best revealed by comparing X-ray diffraction (XRD) patterns recorded on the same smectite sample under contrasting RH conditions. Calculated XRD patterns can then be fitted to experimental profiles using a trial-and-error procedure. The obtained structural models allow describing the hydration behaviour of the swelling smectite layers, and more especially their hydration heterogeneity and the evolution of layer hydration as a function of RH [4-5].

By accounting for smectite hydration heterogeneity it is possible to further refine the interlayer structure of hydrated smectite layers. In that perspective, molecular simulations can be used to unravel the details in the organizational properties of the confined fluid. Combination with experimental diffraction/scattering techniques can provide, however, key quantitative information about the validity of the semi-empirical atomic interaction parameters used in theoretical simulations [6-7]. Application of such a procedure combining experimental diffraction data and molecular simulations will be presented for the specific case of deciphering the molecular organization of interlayer water and cations in the different swelling clay hydrates (mono-, bi-, and tri-hydrated layers) [8-9].

KEYWORDS:

2D natural lamellar swelling clays; X-ray diffraction; molecular simulations; water confinement

REFERENCES

- [1] Bradley W.F., Grim R.E. & Clark G.F. (1937) A study of the behavior of montmorillonite upon wetting. *Zeitschrift für Kristallographie*, 97, 216-222.
- [2] Hendricks S.B., Nelson R.A. & Alexander L.T. (1940) Hydration mechanism of the clay mineral montmorillonite saturated with various cations. *Journal of the American Chemical Society*, 62, 1457-1464.
- [3] Méring J. (1949) L'interférence des rayons-X dans les systèmes à stratification désordonnée. *Acta Crystallographica*, 2, 371-377.
- [4] Ferrage E., Lanson B., Sakharov B.A. & Drits V.A. (2005) Investigation of smectite hydration properties by modeling of X-ray diffraction profiles. Part 1. Montmorillonite hydration properties. *American Mineralogist*, 90, 1358-1374

Keynote Speakers

2D MATERIALS



Eric FERRAGE

CNRS I Researcher

Light matter institute

<https://ilm-perso.univ-lyon1.fr/~opl/>

(FOLLOWING) REFERENCES

- [5] Ferrage E., Lanson B., Michot L.J. & Robert J.L. (2010) Hydration properties and interlayer organization of water and ions in synthetic Na-smectite with tetrahedral layer charge. Part 1. Results from X-ray diffraction profile modeling. *Journal of Physical Chemistry C*, 114, 4515-4526
- [6] Ferrage E., Sakharov B.A., Michot L.J., Delville A., Bauer A., Grangeon S., Frapper G., Jimenez-Ruiz M. et Cuello G.J., 2011 - Hydration properties and interlayer organization of water and ions in synthetic Na-smectite with tetrahedral layer charge. Part 2. Towards a precise coupling between molecular simulations and diffraction data. *Journal of Physical Chemistry C*, 115, 1867-1881.
- [7] Tesson S., Louisfremea W., Salanne M., Boutin A., Ferrage E., Rotenberg B. & Marry V. (2018) Classical polarizable force field to study hydrated charged clays and zeolites. *Journal of Physical Chemistry C*, 122, 24690–24704.
- [8] Dazas, B., Ferrage, E., Delville, A. & Lanson, B. (2014) Interlayer structure model of tri-hydrated low-charge smectite by X-ray diffraction and Monte Carlo modeling in the grand canonical ensemble. *American Mineralogist*, 99, 1724-1735.
- [9] Ferrage E. (2016) Investigation of the interlayer organization of water and ions in smectite from the combined use of diffraction experiments and molecular simulations: A review of methodology, applications and perspectives. *Clays and Clay Minerals*, 64, 346-371.

Keywords: Graphene nanochannels, ion-transport, nanofluidics

Disciplinary fields involved: Physics, Physical Chemistry

Controlled friction at the solid-liquid interface in graphene-based nanochannels

Sandra Vasilijević¹, Qian Yang^{2,3}, Nikita Kavokine^{4,5}, Alessandro Siria¹, Andre Geim^{2,3}, Lydéric Bocquet¹

1. *Laboratoire de Physique de l'École Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université Paris Cité, Paris, France.*
2. *Department of Physics and Astronomy, University of Manchester, Manchester, UK.*
3. *National Graphene Institute, University of Manchester, Manchester, UK.*
4. *Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany.*
5. *Center for Computational Quantum Physics, Flatiron Institute, New York, USA.*

Fluids confined at the nanoscale show oddities which are strongly related to the nature of the confining material.¹ In particular, water behavior in the vicinity of graphitic surfaces was observed to be very peculiar. Due to their nature, carbon-based nanopores were shown to be superior to alternative materials when it comes to the water permeability.² Carbon-water interfaces are the subject of ongoing theoretical research and one of the possible explanations for this behavior may lie in the quantum friction present at the solid-liquid interface.³ In this sense, various measurements of water permeability have been performed in carbon-based membranes⁴, but the remaining challenge is to control their geometry.

In this talk, the new avenues for the fabrication of graphene-based nanochannels with controlled height will be discussed. Moreover, for the first time, the direct measurement of ion transport in graphene-based nanochannels will be presented using a specific setup, based on fluorescence measurements. Our experimental technique paved the way to better understanding the slippage at the water-carbon-interfaces and is sensitive enough for studying the ionic transport across the nanochannels even on the angstrom scale.

References:

- 1) Bocquet, L. Nanofluidics coming of age. *Nature Materials* **19**, 254-256 (2020).
- 2) Secchi, E. *et al.* Massive radius-dependent flow slippage in carbon nanotubes. *Nature* **537**, 210-213 (2016).
- 3) Kavokine, N. *et al.* Fluctuation-induced quantum friction in nanoscale water flows. *Nature* **602**, 84-90 (2022).
- 4) Holt, J.K. *et al.* Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* **312**, 1034-1037 (2006).

Keywords: Graphene Quantum Dots, synthesis, microwaves, luminescence

Disciplinary field involved: Chemistry

Sustainable Development Goals* eventually involved in your research: Responsible Consumption and Production (Goal 12)

From Biomass Wastes toward Gram-Scale Luminescent Graphene Quantum Dots

Philippe Pierrat^{1*}, Pascal Franchetti², Pierre Magri², Jean-Jacques Gaumet²

1. Université de Lorraine, CNRS, L2CM, UMR7053, B.P 95823, 57078 Metz, France
2. Université de Lorraine, LCP-A2MC, EA4632, F-57070, Metz, France

Graphene quantum dots (GQDs) are new fascinating carbon nanomaterials that are attracting great attention according to their outstanding features in comparison with usual organic dyes and heavy metals-based quantum dots. GQDs display chemical inertness, low photobleaching, low cytotoxicity, excellent biocompatibility, wavelength-tunable luminescence, electronic conductivity and a large surface area. As a consequence, GQDs are useful in many applications such as biosensors, solar cells, electrochemical devices, optical sensors and energy storage devices. However, to date, none of these applications reached the industrial level since there was no chemical process allowing to prepare GQDs at a large scale and low costs. In that context, we developed a fast and efficient chemical process allowing to synthesize GQDs at a multigram scale from various biomass wastes (e.g. banana peels, date stones, orange peels, compost,...) which are abundant in our modern society. Our procedure affords GQDs with good homogeneity (in terms of size, chemical constitution and photophysical properties). The GQDs show excitation-dependent photoluminescence ranging from blue to orange emission wavelength in solution. Interestingly, dry films of pure GQDs display white light emission under UV excitation, while aggregation-induced quenching is usually observed in the solid state, opening the way toward OLED applications. We further demonstrated the potential of our GQDs as chemical sensors toward various metal traces such as Hg^{2+} , Fe^{3+} and Sn^{2+} with competitive detection limits through a fluorescence quenching mechanism.

References:

- 1) Philippe, Pierrat*; Jean-Jacques, Gaumet "Graphene Quantum Dots: Emerging Organic Materials with Remarkable and Tunable Luminescence Features" *Tet. Lett.* **2020**, *61*, 49, 152554.
- 2) 29) Noura, Zahir; Pierre, Magri; Wen, Luo; Jean-Jacques, Gaumet*; Philippe, Pierrat. "Recent Advances on Graphene Quantum Dots for Electrochemical Energy Storage Devices" *Energy & Environment Materials* **2022**, *5*, 201-214.

Keywords: Supramolecular chemistry, Nanomaterials structure, DNA nanotechnology

Disciplinary fields involved: Physical Chemistry, Biology, Nanochemistry

On-surface assemblies of DNA-decorated functional nano-objects by supramolecular recognition

Zohreh SAFARZADEH^{1,2,3}, Andre-jean ATTIAS², Christophe PETIT¹, Imad ARFAOUI¹, Christelle MANSUY³

1. MONARIS, UMR 8233 CNRS-Sorbonne Universite, Sorbonne Universite, 4 Place Jussieu, 75252 Paris Cedex, France
2. Building Blocks for FUTURE Electronics Laboratory, UMI 2002, CNRS-Sorbonne Universite'-Yonsei University, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, 03722 Seoul
3. LBM Laboratory, Faculty of sciences, Sorbonne University, Pierre et Marie Curie campus, 75005, Paris, France

Developing new nanostructured materials or devices based on the properties of nano-objects requires the ability to specifically locate them into hierarchical materials on a large scale whatever the size, shape or nature of the nano-object.

With this aim, we propose a new multi-functional platform on Highly Oriented Pyrolytic Graphite (HOPG), based on well-defined supramolecular organic networks hosting guest functional nano-objects organized through biomolecules towards new generation of devices in data storage. To achieve this objective, the new approach we developed, combines (i) organic supramolecular chemistry at surfaces, (ii) inorganic and physical chemistry, and (iii) biomolecules (DNA) chemistry. First, DNA-functionalized gold nanoparticles (AuNPs) have been synthesized and characterized. On the other hand, the surface of a Highly Oriented Pyrolytic Graphite (HOPG) substrate is patterned with a two-dimensional (2D) nanoporous network by on surface supramolecular chemistry to trap into the pores a guest zinc phthalocyanine (ZnPc) complex functionalized with the complementary DNA. The last step consists in the on-surface hybridization in order to organize the AuNPs on the HOPG surface.

References:

1. R. Brisse, I. Arfaoui, S. Sagan, C. Petit, A. J. Attias et al., *Chem Commun.*, 2018, 54, 10068
2. B. Kim, I. Arfaoui, C. Petit, A. J. Attias et al., *Materials Horizons*, 2020, DOI: 10.1039/D0MH00950D

Keywords: MXenes, molybdenum carbide, titanium carbide, 2D materials

Disciplinary fields involved: Chemistry, Material Science

Sustainable Development Goals* eventually involved in your research: Climate Action (Goal 13)

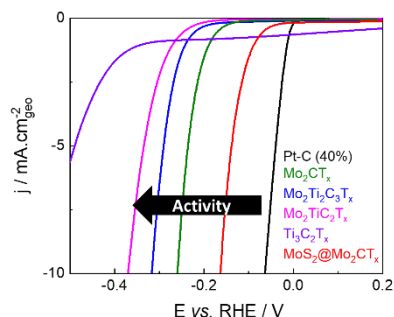
Synthesis, characterization and surface chemistry of 2D Mo/Ti solid solution based MXene. Application to hydrogen evolution reaction in alkaline media

Lola Loupias¹, Christine Canaff¹, Patrick Chartier², Cláudia Morais¹, Vincent Mauchamp², Aurélien Habrioux¹ and Stéphane Céliérier¹

1. IC2MP, SAMCat (From the Active Site to the Catalytic Material), Poitiers University, Poitiers, France
2. Pprime Institut, Physics and mechanics of materials, Poitiers University, Poitiers, France

In 2011, the scientific world discovered MXenes, 2D materials obtained by etching of the A-element from $M_{n+1}AX_n$ 3D precursors called MAX phase (M = transition metal, A = element from columns 13 or 14 of the periodic table, X = C and/or N and n = 1 to 3) a family of about 150 different members [1]. To date, more than 40 different compositions have been synthesized [2], making MXenes the largest 2D materials family. Thus, the high versatility of the MXene composition and their related properties leads to their study in numerous fields such as electromagnetic interference shielding, batteries, biosensors among others [3]. Because of their excellent electronic conductivities, MXenes could be ideal candidates as substrate or co-catalysts for hydrogen evolution reaction (HER) [4].

In this work, we first focused on the synthesis and characterization (XRD, XPS, SEM) of 4 pure MXenes: $Ti_3C_2T_x$, $Mo_2TiC_2T_x$, $Mo_2Ti_2C_3T_x$ and Mo_2CT_x with T standing for terminal group (T = O, OH and/or F). Then, we studied the influence of M element on the MXene HER activity. Thus, among the studied MXenes, Mo_2CT_x is the most promising one. Indeed, according to electrochemical tests, molybdenum would facilitate the adsorption of hydrogen which would increase the electrocatalytic performance of this material [5]. Finally, by topotactic growth of MoS_2 on Mo_2CT_x MXene, a very active $MoS_2@Mo_2CT_x$ composite can be obtained [4].



Linear polarization curves of different MXenes recorded in a nitrogen-saturated 1 mol.L⁻¹ KOH electrolyte with different MXenes using a rotating disk electrode set at 1600 rpm and a scan rate of 5 mV.s⁻¹.

References:

- [1] M. Sokol, V. Natu, S. Kota, and M. W. Barsoum, "On the Chemical Diversity of the MAX Phases," *Trends Chem.*, vol. 1, no. 2, pp. 210–223, 2019, doi: 10.1016/j.trechm.2019.02.016.
- [2] M. Naguib, M. W. Barsoum, and Y. Gogotsi, "Ten Years of Progress in the Synthesis and Development of MXenes," *Adv. Mater.*, vol. 33, no. 39, pp. 1–10, 2021, doi:10.1002/adma.202103393.
- [3] M. Khazaei, A. Mishra, N. S. Venkataramanan, A. K. Singh, and S. Yunoki, "Recent advances in MXenes: From fundamentals to applications," *Curr. Opin. Solid State Mater. Sci.*, vol. 23, no. 3, pp. 164–178, 2019, doi: 10.1016/j.cossms.2019.01.002.
- [4] M. Benchakar *et al.*, "On a Two-Dimensional MoS₂/Mo₂CTx Hydrogen Evolution Catalyst Obtained by the Topotactic Sulfurization of Mo₂CTx MXene," *J. Electrochem. Soc.*, vol. 167, no. 12, p. 124507, 2020, doi: 10.1149/1945-7111/abad6e.
- [5] L. Loupiau, "Synthèse et caractérisation de matériaux à base de MXène : application à l'électrolyse de l'eau en milieu alcalin," Université de Poitiers, 2022.

Keywords: MAB phases, MBenes, MXenes, molten salts, in situ

Disciplinary field involved: Chemistry

Probing *in situ* the reactivity in molten salts of carbides and borides: synthesis of layered compounds, etching, and tuning of their composition

David Portehault,¹ Fernando Igoa,^{1,2} Emile Defoy,¹ M. Baron,¹ A. Ghoridi,¹ A. Séné,^{1,3} S. Célérier,³ Pierre-Olivier Autran,⁴ Dominique Thiaudière⁵

1. *Laboratoire de chimie de la matière condensée de Paris, Sorbonne Université, CNRS, Paris, France*
2. *Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, CNRS, MNHN, IRD Paris, France*
3. *Institut de Chimie des Milieux et Matériaux de Poitiers, Université de Poitiers, CNRS, Poitiers, France*
4. *European Synchrotron Radiation Facility (ESRF), Grenoble, France*
5. *Synchrotron SOLEIL, Gif-sur-Yvette, France*

Inorganic molten salts are non-volatile liquids stable at high temperatures, often up to 1000 °C and beyond. Performing chemical reactions in inorganic molten salts is a way to trigger reactivity in liquids at temperatures that usually pertain to solid-state reactions. This enables syntheses of unprecedented materials, such as nano-objects of strongly covalent materials, like metal borides.[1] Recently, these media have been demonstrated to enable selective etching of A elements (A=Al, Si, Ga) into MAX phases, thus delivering carbide and nitride MXenes[2,3] with new terminations. This reactivity is however poorly understood and its applicability to other families of layered materials, like borides, is still to be demonstrated.

We are tackling the reactivity of layered materials into molten salts by developing *in situ* methods, in order to understand and control their synthesis and their delamination. In this presentation, we will first show how to perform the synthesis of layered metal borides (so-called 'MAB' phases[4]) into molten salts, how this method yields specific reactivity and then compositions. We will then discuss how galvanic replacement and delamination reactions of MAX and MAB phases can be triggered in molten salts and we will assess their mechanisms by using synchrotron-based *in situ* X-ray diffraction and X-ray absorption spectroscopy with a newly developed sample environment.

References:

- [1] Portehault *et al.*, *Chem. Soc. Rev.*, 2022, **51**, 4828-4866
- [2] Li *et al.*, *J. Am. Chem. Soc.*, 2019, **141**, 4730-4737
- [3] Kamysbayev *et al.*, *Science*, 2020, **369**, 979-983
- [4] Zhou *et al.*, *Science*, 2021, **373**, 801-805

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Keywords: 2D transition metal carbides, ion implantation, electrical and optical properties, (S)TEM-EELS

Disciplinary fields involved: Physics, chemistry

Tuning the optical and electrical properties of 2D $Ti_3C_2T_x$ MXenes: an ion implantation approach

A. Benmoumen^{1,2}, S. Hurand¹, E. Gautron², L. Loupias³, S. Célérier³, S. Tangui¹, P. Moreau², M.L. David¹ and V. Mauchamp¹

1. Université de Poitiers, ISAE-ENSMA, CNRS, PPRIME, Poitiers France.
2. Nantes Université, CNRS, IMN, Nantes, France
3. Université de Poitiers, CNRS, IC2MP, Poitiers, France

MXenes are a family of 2D layers obtained from the exfoliation of MAX phase materials [1]. Due to the chemical diversity of the MAX phase precursors [2], MXenes are probably the richest family of 2D materials in terms of chemical variety and physical properties. Their chemical formula is $M_{n+1}X_nT_z$, with M a transition metal, X C and/or N, T_z surface terminations (e.g. O(H), F) and $n = 1, 2$ or 3 (Fig. 1-a). Thanks to their hydrophilicity, these materials are easily processed into thin films with various applications, including transparent conductive electrodes [3].

Aside from the M and X elements, inherited from the parent MAX phase, the functional groups T_z have a very strong influence on MXene physical properties [4]. Among the several (physico)chemical approaches proposed to act on this lever, ion irradiation is a very promising route [5]. In this work, we demonstrate the efficiency of He^+ irradiation in tuning the optical properties of $Ti_3C_2T_z$ spin coated thin films (Fig. 1-b). The introduction of a controlled amount of structural defects into the MXene layers, by tuning the irradiation fluence, allows for the increase of the thin films transparency while preserving the electrical conductivity. The modification of the properties is rationalized using a combination of structural, electronic and optical characterization methods including (S)TEM-EELS, thereby giving insights on the correlation between structural defects and modification of the Ti-d bands, which are responsible for the optical/electrical properties in this system.

References:

- [1] M. Naguib et. al. Adv. Mater. 23, 4248-4253, (2011)
- [2] M. Sokol et al., Trends in Chem., 1, 210 (2019)
- [3] S. Abdolhosseinzadeh et al., Materials Today 48, 214 (2021).
- [4] A. VahidMohammadi et. al. Science, 372, eabf1581 (2021).
- [5] H. Pazniak et. al. ACS Nano, 15, 3, 4245-4255 (2021).

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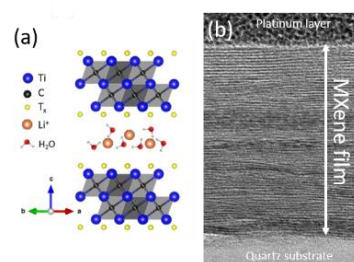


Figure 1 : (a) schematic representation of $Ti_3C_2T_x$ crystal structure, (b) HR-TEM micrograph of $Ti_3C_2T_x$ cross section

