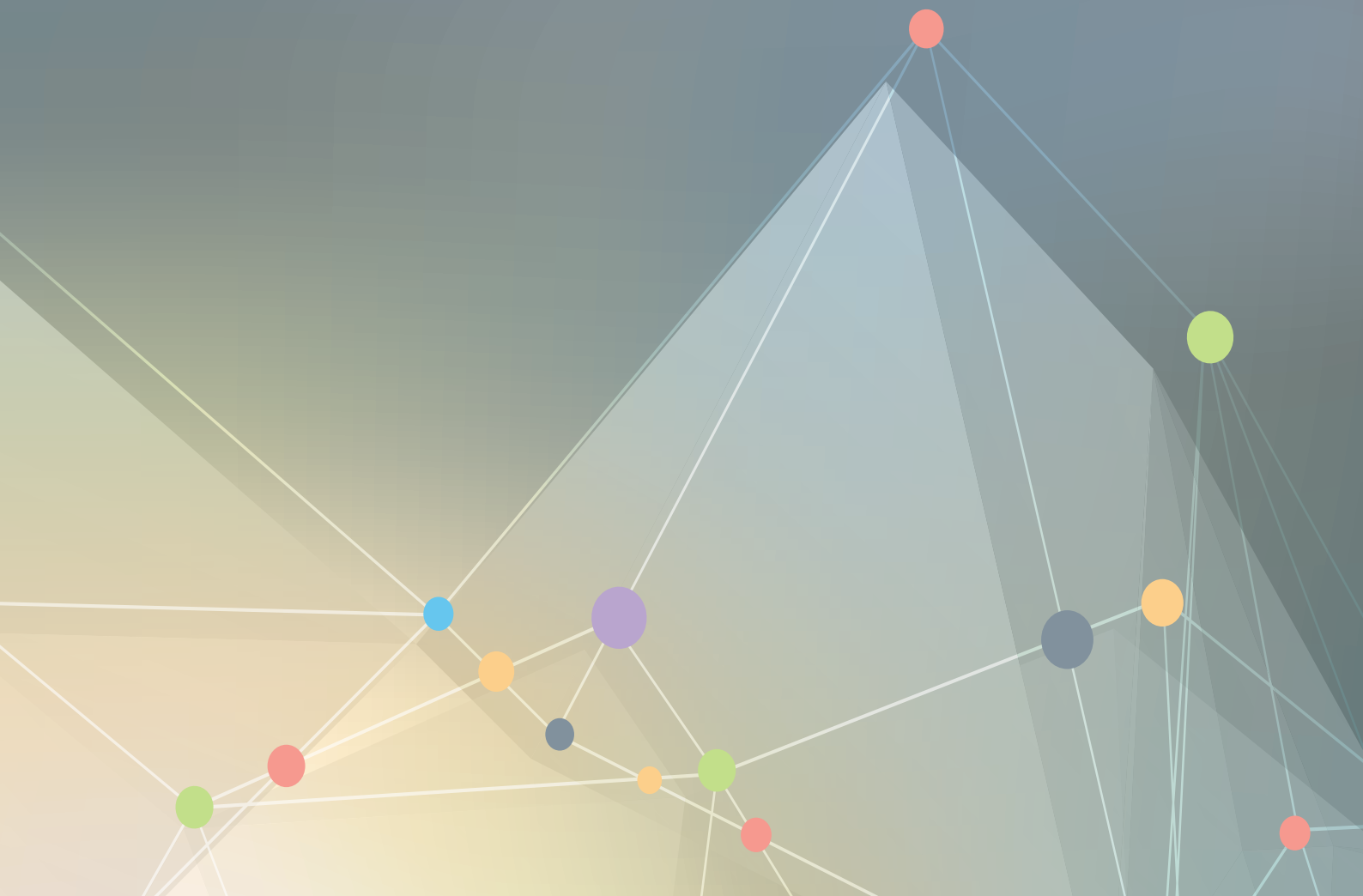
BOOK OF ABSTRACTS

Oral Presentations



C'Nano
THE NANOSCIENCE MEETING
2023

Poitiers
March, 15, 16 and 17

Functional thin films and nanostructures:
growth and properties

(Last update: August 23th, 2022)

Description

Thin films and nanostructures are involved in innumerous technological applications spanning from electronics, magnetism, optics to catalysis, to cite a few. Their targeted properties, that can strongly differ from bulk ones through the overwhelming presence of atoms at surfaces and interfaces, are intimately linked to their atomic structures and morphologies at the nanoscale. In turn, these are governed by the growth processes during which deposition method, epitaxy, stress, interdiffusion, interface reactivity and energetics, substrate patterning, kinetics, environment etc... are driving but intertwined parameters.

The goal of this session is to give an overview of the current understanding at the atomic level of the link between structure/morphology, functional properties and growth processes of inorganic (metals, semi-conductors, oxide, etc...) as well as molecular films. The idea is to gather the broadest scientific community to discuss and present the latest developments and challenges of the field with an emphasis on ***in situ*** characterization techniques and theoretical understanding of involved phenomena.

Keywords

Inorganic and organic thin films, nucleation and growth mechanisms, functional properties, physical vapor deposition, ***in situ*** characterizations, atomistic simulations, surface science

Scientific committee

Amandine BELLEC (CNRS – MPQ, Paris)
Rémi LAZZARI* (CNRS – INSP, Paris)
Julian LEDIEU (CNRS – IJL, Nancy)
Frédéric LEROY (AMU – CINAM, Marseille)
Anny MICHEL (Univ. Poitiers – Pprime, Poitiers)

** Session Coordinator*

Wednesday March 15th

11.00 am – 1.00 pm

Room 11/12

Program of the session

Chairs: Amandine BELLEC & Rémi LAZZARI

FUNCTIONAL THIN FILMS & NANOSTRUCTURES: GROWTH & PROPERTIES		
11:00	**Origin of the roughness of grain boundaries in 2D materials**	**Olivier PIERRE-LOUIS** • *CNRS – ILM, Lyon – France*
11:30	Kinetic Monte Carlo 3d model for Cu on Cu(001) homoepitaxy: from mounding at normal incidence to ripples orientation transition under GLAD conditions	**Florin NITA** • *Univ. Poitiers - Inst. Pprime, France*
11:45	Atomic scale investigation of deposition of low (W,Mo) vs. high (Ag,Cu) adatom mobility during first stages of silicide interface formation	**Cédric MASTAIL** • *Univ. Poitiers - Inst. Pprime, France*
12:00	Adatom thermomigration on a crystalline surface	**Aurélien ROUX** • *Univ. Paul Sabatier Toulouse - CEMES, France*
12:15	Growth and ferroelectricity of GeTe thin films on Si(111)	**Frédéric LEROY** • *AMU - CINaM, France*
12:30	Two-dimensional dynamic ordering of perylene on Ag(110)	**Laurent GUILLEMOT** • *CNRS - ISMO, France*
12:45	Topological Defects in Smectic A Liquid Crystal Thin Films studied by synchrotron GISAXS measurements	**Jean DE DIEU NIYONZIMA** • *Sorbonne Univ. - INSP, France*
13:00	**Lunch, Posters session & Stand exhibition**	

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Olivier PIERRE-LOUIS

CNRS I Researcher

Light matter institute

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

Biography

Olivier PIERRE-LOUIS is a CNRS Research Director at ILM Lyon. After a PhD in Grenoble and a postdoc at the Univ. of Maryland, College Park, he joined the CNRS in 1998 at Liphy in Grenoble. Since 2009, he develops his research activity at the Institut Lumière Matière in Lyon.
His theoretical research, initially oriented towards crystal growth and electromigration, now includes works in nanosciences, soft matter, biophysics and geophysics. Recently, he has been working on the dewetting of solid-state films, on the growth of nano-confined crystals, on adhesion and confinement of membranes (graphene and lipid bio-membranes), and on the control of the shape of nanoclusters by external fields.

Origin of the roughness of grain boundaries in 2D materials

Grain boundaries in 2D materials are formed by the collision of the edges of the 2D domains during growth. The roughness of these grain boundaries is relevant for the physical properties of 2D materials. This roughness emerges from statistical fluctuations and instabilities during growth. We have modeled these processes using Kinetic Monte Carlo simulations and Langevin models.

Our models suggest that the evolution of the roughness is non-monotonous. While it usually increases during the growth process, the roughness decreases during and after the collision of the edges. This decrease could be used to produce very smooth grain boundaries.

Keywords:

Crystal growth; Grain boundaries; Roughness; 2D materials; Theory and Modeling

References

[1] Growth at high substrate coverage can decrease the grain boundary roughness of 2D materials FDA Reis, B Marguet, O Pierre-Louis, 2D Materials 9 045025 (2022)
[2] Interface collisions with diffusive mass transport B Marguet, FDAA Reis, O Pierre-Louis, Physical Review E 106 (1), 014802 (2022)
[3] Interface collisions
F. D. A. Aarão Reis and O. Pierre-Louis, PHYSICAL REVIEW E 97, 040801(R) (2018)

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Poitiers
March, 15, 16 and 17

Keywords: kMC modelling, Cu homoepitaxy, GLAD
Disciplinary fieldsinvolved : Physics

Kinetic Monte Carlo 3d model for Cu on Cu(001) homoepitaxy: from mounding at normal incidence to ripples orientation transition under GLAD conditions

Florin Nita[1,2], Clarisse Furgeaud[1], Anny Michel[1], Gregory Abadias[1], Cedric Mastail[1]

1. Institut P'- Département Physique et Mécanique des Matériaux, UPR 3346, CNRS-Université de Poitiers-ENSMA, TSA 41123, 86073 Poitiers cedex 9, France
2. National Institute for Research and Development in Microtechnologies, 126A Erou Iancu Nicolae, Voluntari Town, Ilfov County 077190, Romania

Experimental results on Cu on Cu(001) homoepitaxy have shown that the growing interface morphology, roughness and its time evolution are depending on the growth conditions as substrate temperature, deposition rate, deposition angle and incident particle energy. Varying the deposition temperature between 150K and 450K, the interface roughness shows a maximum at a temperature depending on the deposition rate[1] ("reentrant smooth growth"). Pyramidal structures, having more or less square bases, develop at long time deposition. These mounds have the base ledges orientated along <110> directions and face slopes depending on the growth conditions[2]. On the other hand, under GLAD conditions, the characteristic pyramidal mounds developed at normal incidence, become elongated pyramids leading to the ripples formation. The orientation of these elongated pyramids (ripples later) in respect with the incidence plane is depending on the surface temperature and deposition angle[3].

To understand these experimental findings, a rigid lattice 3D-kMC model has been developed. The anisotropy of Cu surface diffusion has been taken into account. The funnelling and steering effects are considered during the deposition event. The angular and energy distributions of the incoming particles are included as well.

The simulation results are in a good qualitative but also quantitative agreement with the experimental results mentioned above.

References:

1 - CE Botez et al., Physical Review B 64(2001)125427
2 - JK Zuo and JF Wendelken, Physical Review Letter 78(1997)2791 3 - FLW Rabbering et al., Physical Review B 81(2010)115425

Acknowledgment: work supported by the French ANR project "INTErface reactivity, microstructure and stressEvolution during thin film GRowth: multi-scALe modelling and experimental validation (INTEGRAL)" (Reference ANR: # ANR-19-CE08-0024-01)

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2023
Poitiers
March, 15, 16 and 17

Keywords: adsorption, physical vapor deposition, atomistic simulations, surface science
Disciplinary fields involved: Physics, material science

Atomic scale investigation of deposition of low (W,Mo) vs. high (Ag,Cu) adatom mobility during first stages of silicide interface formation

Cedric Mastail[1], Vernet Brutus, Florin Nita[1,2], Anny Michel[1], Gregory Abadias[1]

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Existing studies have demonstrated a complex dependence of film microstructure and its properties on the deposition conditions, e.g. the kinetic energy of the deposited particles, and the substrate temperature, as well on the interaction at the film/substrate interface, e.g. adatoms mobility, chemical reactivity.

Computer simulations aim to provide a better understanding on the initial growth and its influence on the evolution of metallic thin film microstructure, grain size and texture and mechanical and physical properties. As part of the INTEGRAL project, the objective is the implementation of a multi-scale computer modelling of the growth of metallic thin films, onto chemically reactive substrates, on realistic time scales based on a kinetic Monte Carlo (kMC) approach.

The present contribution is focused on the first steps of this multi-scale strategy, i.e. a comprehensive study by ab initio calculations of the elementary mechanisms at the atomic level which occur during the growth of a metallic layer onto (100) silicon. The surface reactivity, as well as the diffusion path were examined using the energy adsorption landscape of tungsten (W) and molybdenum (Mo), taken as archetypes of low mobility, and silver (Ag) and copper (Cu), as archetypes of high mobility metals. Even if Cu and Ag have comparable mobility behaviour, the results show that the adatom surface diffusion occurs via alternative mechanisms. Similar results were found in the case of W and Mo. These findings suggest different growth evolution in the early stages of thin film deposition. The formation of an **interfacial silicide layer,** which occurs during the early stages of metal growth under energetic conditions, was also modelled providing useful information to identify relevant mechanisms to the kMC growth model.

Acknowledgment: this work is supported by the French ANR project "INTErface reactivity, microstructure and stress Evolution during thin film GRowth: multi-scALe modelling and experimental validation (INTEGRAL)" (Reference ANR: # ANR-19-CE08-0024-01)

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Keywords: thermomigration, atomic duffusion, molecular dynamics simulation

Disciplinary field involved: Physics

Adatom thermomigration on a crystalline surface

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2. *Auniversité Paul Sabatier, Toulouse, France*

During the particle diffusion in the presence of a temperature gradient, a particle flux along the gradient direction appears. This phenomenon, referred as thermomigration has been studied in gas, liquids and solids. Though less investigated, this physical mechanism also exists at the surface of solids: it has been evidenced experimentally [1] and it has been shown to be involved during the synthesis of nano-objects [2].

We study the thermomigration of an adatom on a surface (111) of FCC crystal using molecular dynamics simulations. We show that the temperature gradient drives the adatom towards cold regions. Examining adatoms trajectories, we calculate the average drift speed induced by the temperature gradient. Besides, we have calculated the thermodynamic potential of the adatom for various temperature gradients. We show that the thermodynamic potential depends on the local temperature and is independent on the gradient. This thermodynamic potential presents an average slope R_{th} responsible of the drift of the adatom towards cold regions and oscillations reminiscent of the diffusion of the adatom on the crystal surface. We study the dependence of both slope R_{th} and oscillations amplitude as a function of adatom binding energy with the surface and adatom mass. Surprisingly, there exists an optimal adatom mass that maximizes the average slope R_{th} of the thermodynamic potential. Finally, we provide a simple model for adatom diffusion on the surface in the presence of a temperature gradient and show that the average thermomigration drift speed is proportional to the gradient of the inverse of the temperature.

References:

[1] A.E Barraj (2019) Growth and Electro-Thermomigration on semiconductor surfaces by Low Energy Electron Microscopy. Université d'Aix Marseille.

[2] Xie, DG., Nie, ZY., Shinzato, S. et al. (2019), Controlled growth of single-crystalline metal nanowires via thermomigration across a nanoscale junction. Nat Commun, 10, 4478.

C'Nano THE NANOSCIENCE MEETING Poitiers March, 15, 16 and 17 2023

Keywords: thin films, ferroelectrocity, epitaxy, dislocations
Disciplinary field involved: Physics (material science)
Sustainable Development Goals* involved in your research: Affordable and clean energy (Goal 7)

Growth and ferroelectricity of GeTe thin films on Si(111)

Boris Croes[1], Fabien Cheynis[1], S. Curiotto[1], P. Müller[1], F. Leroy[1]

1. *Aix Marseille Université, CNRS, CINAM, AMUTECH, Marseille, France*

Among ferroelectrics, a new class of materials with high potentialities for spintronic applications has been recently introduced and named ferroelectric Rashba semiconductors[1,2]. In particular it has been demonstrated, on α-GeTe thin films, that the reversal of the ferroelectric polarization by an electric field leads to a change of the spin chirality of the band structure[3]. In the perspective of using α-GeTe for spintronics, high quality thin films with a controlled polarization state must be achieved. In this study, we have elucidated the initial stages of GeTe growth on Si(111) by scanning tunneling microscopy and low energy electron diffraction. We demonstrate the presence of an initial 0.35 nm-thick GeTe buffer layer followed by the 2D growth of GeTe via Frank-Read sources of atomic steps. X-ray diffraction, transmission electron microscopy and low energy electron microscopy evidence that numerous mirror domains and in-plane misorientations appear early in the growth process that are gradually buried at the film/substrate interface[4]. Considering the polarization configuration of α-GeTe, we show a major domain with the electric dipole in the ⟨111⟩ direction, i.e. perpendicular to the surface plane and minor ferroelectric nanodomains with in-plane polarization[5]. Using high resolution transmission electron microscopy we show that domain walls are only of 71° type and that the GeTe/Si interface is stabilized by misfit dislocations. The reversible decay of the ferroelectric nanodomains under annealing, as demonstrated by *in situ* LEEM, is attributed to the thermal stress induced by the large difference of linear thermal expansion coefficients of both materials.

References:

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[5] B. Croes, F. Cheynis, Y. Zhang, C. Voulot, K.D. Dorkeno, S. Cherifi-Hertel, C. Mocuta, M. Texier, T. Cornelius, O. Thomas, MI Richard, P. Müller, S. Curiotto, F. Leroy, Phys. Rev. Mat. **5**, 124415 (2021).

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C'Nano THE NANOSCIENCE MEETING 2023
Poitiers March, 15, 16 and 17

Keywords: hybrid interface, epitaxial molecular layer, dynamic ordering, interface thermodynamics

Two-dimensional dynamic ordering of perylene on Ag(110)

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1. ISMO (Institut des Sciences Moléculaires d'Orsay), CNRS/Université Paris-Saclay, Bât. 520, 91405 Orsay

We present a room-temperature STM study of the dynamics of a quasi-liquid perylene monolayer formed on Ag(110) under thermal equilibrium.
We observe that the interplay of site recognition and intermolecular attraction precludes the formation of fixed-bound molecular configurations. The interplay modifies the dynamics of the mobile molecules heterogeneously giving rise to a quasi-liquid state characterized by the collective motion of the molecules distributed into three distinct motion modes. The substrate force field induced a dynamical ergodic–non-ergodic phase transition providing a long-range spatial order to the non-ergodic (−1 2.5 3 2) quasi-liquid state. The single domain epitaxial quasi-liquid state maintains permanently its structure, symmetry, and spatial order. Analysis of the STM topographies shows that the substrate lattice guides the whole molecule ensemble and provides each of the modes with a distinct register. In each mode, the substrate registry forces the transiently immobile molecules to alternate with the transiently mobile ones. Fourier transform of the topographies unravels the long-range spatial correlations and epitaxial character of the quasi-liquid state. Analysis of the short-range mode coupling allows us to understand the mechanism of the long-range mode coupling.

The quasi-liquid state possesses, therefore, dynamics characteristic of a liquid, and long-range order characteristic of a crystalline solid. We anticipate that this duality, unattainable under conventional nanofabrication, opens perspectives to fabricate epitaxial long-range ordered nanostructures of arbitrary
lateral size.

References:

AIP Advances **12**, (2022) in press; doi: 10.1063/5.0099308

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2023

Keywords: Topological defect, Smectic A, Liquid crystal, GISAXS
Disciplinary fields involved: Physics
Sustainable Development Goals* eventually involved in your research: Reduced Inequalities (Goal 10)

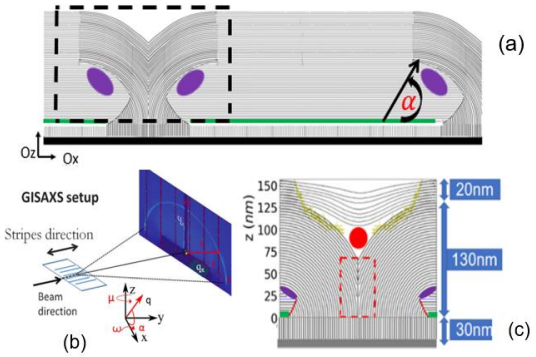
Topological Defects in Smectic A Liquid Crystal Thin Films studied by synchrotron GISAXS measurements

Jean de Dieu Niyonzima[1*], Haïfa Jeridi[1], Charbel Sakr[1], Alina Vlad[2], Alessandro Coati[2], Michel Goldmann[1], David Baboneau[3], Doru Constantin[4], Bruno Gallas[1], Yves Garreau[2], Bernard Croset[1] and Emmanuelle Lacaze[1*]

1. *Sorbonne Université, CNRS, Institut des Nanosciences de Paris, INSP, F-75005 Paris, France*
2. *Synchrotron Soleil, BP 48, L'Orme des Merisiers, 91192 Gif sur Yvette, France*
3. *Université de Poitiers, CNRS, Institut Pprime, Département Physique et Mécanique des Matériaux, UPR 3346 Poitiers, France.*
4. *Institut Charles Sadron (ICS) 23, rue du Lœss 67034 Strasbourg.*

The breaking of continuous symmetry in ordered systems results in topological defects, which are the places where the order melts[1]. Despite of extensive theoretical studies, their structure remains ineffectively known, also because experimental data are still scarce, especially when nanoscale resolution is concerned. Using Grazing Incident Small-Angle X-ray Scattering (setup in Figure (b)) on SIXS beamline at Soleil synchrotron, we have developed unprecedented complementary experimental and theoretical methods to explore the intimate structure of distorted thin smectic-A films of 4-n-octyl-4'-cyanobiphenyl (8CB). They are made of an array of flattened hemicylinders composed of superimposed and periodic rotating smectic layers (seen in side view on Fig (a))[2].

Both integrated intensity and wave vector transfer q data in function of the angle α that characterizes the orientation of the smectic layers (Fig. (a)) allowed us to reconstruct the smectic layer geometry. We evidence 3 types of topological defects in one given smectic hemicylinder, all oriented parallel to the hemicylinder axis (see Fig. (c)). They are 2 dislocations (puple ellipses) of Burger vector 4; 1 disclination (red point) with a core of size around 30 nm together with a 2D ribbon-like topological (green line). Having elucidated the nature and size of the topological defects, we are now able to rationalize the stability of these thin smectic films with a large defect density.



We also study how the defects change in presence of nanoparticles confined in the core defects, these last features allowing to create original oriented organization of nanoparticles [3].

References:

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Acknowledgment: This thesis is funded by both CNRS and French Government through its embassy in Rwanda.

Thursday March 16th

3.30 pm – 6.30 pm

Room 13/14

Program of the session

Chairs: Anny MICHEL & Frédéric LEROY, Julian LEDIEU & Rémi LAZZARI

FUNCTIONAL THIN FILMS & NANOSTRUCTURES: GROWTH & PROPERTIES		
15:30	**Unveiling the growth pathways of manganese germanides and silicides**	**Lisa MICHEZ** • *AMU – CINaM, Marseille – France*
16:00	Effect of O2 addition on the film growth mechanism of sputtered Ag thin films	**Ramiro ZAPATA** • *SGPM RECHERCHES - INSP/SVI, France*
16:15	Real-time study of ultrathin Ag growth: role of additives	**Grégory ABADIAS** • *Univ.Poitiers - Inst. Pprime, France*
16:30	Microstructure behavior of nitride-based multilayer coatings under He ion irradiation	**Nicolas SÉNICOURT** • *Univ.Poitiers - Inst. Pprime, France*
16:45	Innovative process of micro-nanostructure of titanium nitride (TiN) by association of a photostructurable titanium oxide (TiO2) and a rapid thermal annealing (RTA)	**Victor VALLEJO-OTERO** • *Univ. Jean Monnet - LabHC, France*
17:00	Coffee & tea break	
17:30	Growth of Metallic Nanostructures Embedded in Dielectrics for Quantitative Surface-Enhanced Raman Spectroscopy	**Emmanuel DE LOS SANTOS VAZQUEZ** • *Univ. Nantes - IMN, France*
17:45	From Chemical Solution Processes to Transparent Nanostructured Thin Films: Oxide Nanocrystals or Octahedral Metal Atom Clusters	**Fabien GRASSET** • *CNRS - ISCR, France*
18:00	Tio2 and ti-cu-o thin films deposited by aa-mocvd for marine antibiofouling applications	**Lisa DEBLOCK** • *CNRS - LMGP, France*
18:15	Recrystallization of thin 4H-SiC films deposited by PVD techniques, a way for new emerging fields	**Enora VUILLERMET** • *UTT - L2n, France*

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Lisa MICHEZ

University of Aix-Marseille I Professor

CINaM

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Biography

Lisa MICHEZ carried out her PhD in the Condensed Matter at Leeds University, supervised by Bryan Hickey and Jim Morgan. From 2002 and 2005, she was a postdoctoral fellow with Christopher Marrows at Leeds University. In 2005, she joined the CRMCN lab at Aix-Marseille university as an assistant professor. She holds now a professorship at CINaM in the field of materials science and spintronics. She is the leader of the 'Si/Ge-based Heterostructures' team in the Nanomaterials department.

Her research activities are mainly focused on the study of the epitaxial growth of nanostructures and heterostructures based on Group-IV elements and their related structural, chemical and magnetic properties, in particular for spin injection into semiconductors. Since recently, she has been investigating the spin-to-charge conversion in unconventional antiferromagnetic materials.

Unveiling the growth pathways of manganese germanides and silicides

Silicon- or Germanium-based systems attract a great deal of attention due to their high compatibility with the mainstream technologies and the abundance of these elements in the earth crust. When alloyed with manganese, these compounds exhibit fascinating properties that are induced by their exotic magnetic structures [1-3].

We will focus here on the epitaxial growth of Mn5Si3 and Mn5Ge3 thin films on Si(111) and Ge(111), respectively. Both Mn5Si3 and Mn5Ge3 compounds crystallize in the hexagonal D88 structure (P63/mcm space group). Despite the similarities of the heterostructures in terms of crystal symmetry and lattice mismatch, the growth mechanisms in both systems are drastically different. Whereas the Mn5Ge3 growth on Ge(111) can be implemented using different techniques such as solid phase epitaxy [4] and reactive deposition epitaxy [5], there is no report to date on the formation of a sole Mn5Si3 thin film directly grown in epitaxy on Si(111). We will show how the growth pathways and the structural properties of the manganese silicides and germanides can be rationalized in terms of reactions maximizing the free-energy lowering rate [6-7]. In addition, different types of defects have been identified in these thin films. They play a central role in the phase formation and the film relaxation [8].

Interestingly, this D88 crystal structure contains two crystallographically independent sets of manganese atoms: Mn1 atoms, in the 4d-sites, form long chains parallel to the c-axis whereas Mn2 atoms occupy the 6g-positions in an octahedral arrangement. Such structures have a nearly unique ability to bind different heteroatoms in the preformed octahedral cavity formed by Mn2 atoms, which modifies profoundly their physical properties. As an example, the incorporation of C atoms in these specific positions leads to enhanced magnetic properties [4] while increasing the phase stability [8, 9]. Our works also evidence for a selective fulfillment of the available cavities by carbon, leading to a highly ordered superstructure [10].

In summary, these examples illustrate how molecular beam epitaxy can be used for the controlled growth of epitaxial films in the search of emerging materials for nanoscaled electronic and magnetic devices.

Keywords:

Epitaxial growth; Mn compounds; Magnetic properties; Phase formation and stability

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Keywords: magnetron sputtering, silver thin films, film growth, *in situ*, real-time measurements
Disciplinary fields involved: Chemistry and Physics
Sustainable Development Goals eventually involved in your research: Affordable and Clean Energy (Goal 7) – Energy-efficient buildings

Effect of O_2 addition on the film growth mechanism of sputtered Ag thin films

Ramiro Zapata[1,2], Rémi Lazzari[1], Hervé Montigaud[2], Matteo Balestrieri[2], Iryna Gozhyk[2]

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Production of low-emissivity (energy-efficient) glazing products involves the deposition of complex thin film stacks on glass surfaces, using magnetron sputtering. Nanometer-thick Ag thin films are included in these stacks to reduce heat transfer by reflecting IR radiation. Their efficiency is ultimately dependent on the Ag film electrical conductivity, which is a parameter that is intimately related to the microstructure of this metallic film. Careful control of the deposition physical parameters is therefore key for mastering the Ag film growth mechanism. In this work, the effect of O_2 addition to the deposition vessel during magnetron sputtering deposition on the growth mechanism of Ag thin films was scrutinized using a custom experimental setup, which couples sputter deposition with real-time and *in situ* measurements. Real-time electrical resistance and Surface Differential Reflectance Spectroscopy (SDRS) provided information on different stages of the 3D (Volmer-Weber) film growth mechanism (growth, coalescence, and film percolation stages) while *in situ* X-Ray Photoelectron Spectroscopy (XPS) was used for surface chemical characterization – namely to detect and quantify the formation of oxidized Ag species. Three different regimes as a function of the incoming O_2 flux will be discussed.

References:

Pliatsikas, N.; Jamnig, A.; Konpan, M.; Delimitis, A.; Abadias, G.; Sarakinos, K. Manipulation of Thin Silver Film Growth on Weakly Interacting Silicon Dioxide Substrates Using Oxygen as a Surfactant. J Vac Sci Technol A J Vac Sci Technol A 2020, 38 (4).

C'Nano
THE NANOSCIENCE MEETING
2023
Poitiers
March, 15, 16 and 17

Keywords: Growth, in situ monitoring, ultrathin films, morphology
Disciplinary field involved: Physics

Real-time study of ultrathin Ag growth: role of additives

G. Abadias[1], D. Babonneau[1], B. Krause[2], A. Jamnig[1], A. Michel[1], K. Solanki[1], M. Kaminski[2], A. Resta[3], A. Vlad[3], A. Coati[3], K. Sarakinos[4]

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Noble-metal ultrathin films, with nominal thickness smaller than ~15 nm, are ubiquitous in a wide range of plasmonic devices and other optoelectronic applications. Silver (Ag) layers are interesting candidates for use as transparent conductive electrodes (TCE) in flexible devices. However, the growth of Ag on weakly interacting substrates proceeds in a 3D fashion. Strategies to produce fully continuous, ultrathin and ultrasmooth Ag layers without compromising their electrical conductivity have lately been deployed. Among them, the use of gaseous additives, such as N_2 or O_2, or template layers appears to be an efficient route to shift the continuous film formation thickness to lower values [1]. However, understanding the entire evolutionary growth regime requires the implementation of *in situ* and real-time diagnostics.

In the present work, the impact of N_2 or Ge addition on the morphological and structural evolution of ultrathin Ag layers is investigated by coupling complementary *in situ* and real-time diagnostics. Lab-scale studies include wafer curvature, surface differential reflectance spectroscopy and electrical resistivity to determine morphological transition thicknesses such as percolation threshold and onset of continuous film formation [2]. These results are further comprehended using real-time X-ray synchrotron studies (SIXS beamline at SOLEIL) in which the grazing incidence diffraction and small-angle scattering signals are simultaneously recorded, together with stress evolution. This enables us to explore the influence of Ge and N_2 on island shape, texture and stress development.

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Acknowlegdments: This work is part of the IRMA project funded by the ANR and DFG (reference ANR-21-CE09-0041-01). It also pertains to the French Government programs "Investissements d'Avenir" EUR INTREE (reference ANR-18-EURE-0010) and LABEX INTERACTIFS (reference ANR-11-LABX-0017-01).

C'Nano THE NANOSCIENCE MEETING 2023
Poitiers March, 15, 16 and 17

Keywords: Thin films, Growth, Interfaces, Multilayers, Irradiation
Disciplinary field involved: Physics

Microstructure behavior of nitride-based multilayer coatings under He ion irradiation

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The development of advanced nuclear reactors drives the search for more radiation-tolerant materials. Structural materials are indeed subjected to high He fluences leading to the introduction and accumulation of point defects that can drastically modify the mechanical properties of the materials. Multilayer systems offering a high density of interfaces, thus allowing the recombination of point defects, are among the solutions considered. Previous works have mainly focused on immiscible metallic multilayer systems [1]. Recently, systems combining amorphous and crystalline materials have been shown to be a promising route. In particular, immiscible multilayers of the MeN/ SiN_x type (Me being a transition metal), present interesting properties: good mechanical and thermal stability and tolerance to irradiation [2,3]. In addition, they offer sharp interfaces allowing the detailed study of their interfaces.

This work focuses on the study of the effect of interfaces and grain boundaries on the radiation tolerance of MeN/SiN_x multilayer systems, with a period between 8 and 50 nm, and Me=Ti or Zr. The different systems were grown by reactive magnetron sputtering at 300°C from Zr, Ti and Si_3N_4 targets. Reference monolithic layers (TiN, ZrN and SiN_x) were also synthesized for comparison purpose. Prior to implantation, the MeN layers are polycrystalline, while the SiN_x layers are amorphous. Interfaces are relatively sharp with a roughness < 0.5 nm. After He implantation (30 keV, $7x10^{16}$ ions/ cm^2), swelling of all the layers is observed but the presence of cavities is only revealed in the amorphous a-SiN_x layers. The influence of period, microstructure and grain size on the radiation tolerance of the materials will be discussed.

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March, 15, 16 and 17

Keywords: Titanium nitride, Micro-nanostructure, Nitridation, Optical lithography
Disciplinary fields involved: Material Sciences, Optics
Sustainable Development Goals* eventually involved in your research: Responsible Consumption and Production (Goal 12)

Innovative process of micro-nanostructure of titanium nitride (TiN) by association of a photostructurable titanium oxide (TiO_2) and a rapid thermal annealing (RTA).

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The titanium nitride (TiN) is usually used for its thermal, mechanical, electrical and optical properties. Its micro-nanostructure allows to use it in a wide range of applications especially in the area of optic [1] and photocatalysis [2]. These properties combined make this material a promising alternative of gold and silver for optical applications at high temperature or in extreme environment.

The fabrication of microstructured or nanostructured surfaces in TiO_2 and in TiN on large substrates with plane or complex geometry is a challenge. Due to their high thermal, chemical and mechanical stability, TiN layer are difficult to micro-nanostructure by etching or engravement after their deposition. An alternative route is to micro-nanostructure titanium oxide film (TiO_2) before converting it into TiN by a nitridation process [3,4].

In this presentation, a new method of elaboration of micro-nanostructured TiN layer from a TiO_2 photostructurable sol-gel by rapid thermal annealing (RTA) will be presented. This sol-gel is photostructurable by optical lithography and nano-imprint lithography (NIL), allowing an easy and quick production of micro-nanostructure TiO_2 layers (figure 1). These layers can then be converted into micro-nanostructure TiN layers thanks to an RTA of few minutes under ammonia flux. The micro-nanostructured films have been characterized by X-ray diffraction, Scanning Electron Microscopy (SEM), Spectroscopy RAMAN... The optical and electrical properties have been studied and a plasmonic application will be presented.

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Keywords: Surface Plasmon Resonance, Ag nanoparticles, Raman spectroscopy, reusable sensors.

Disciplinary fields involved: Physics and chemistry

Sustainable Development Goals* eventually involved in your research: Sustainability. Responsible Consumption and Production (Goal 11)

Growth of Metallic Nanostructures Embedded in Dielectrics for Quantitative Surface-Enhanced Raman Spectroscopy

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Chemical sensors are valuable tools in various fields, such as chemical processes, environmental and industrial safety applications [1,2]. Sensors based on approaches such as surface-enhanced Raman spectroscopy (SERS) allows for the detection of molecules via the amplification of their Raman signal using noble metal nanostructures, which exhibit Surface Plasmon Resonance (SPR) for a specific range of wavelengths. SERS is usually associated with the presence of intense electromagnetic hot-spots arising in the gaps between these nanostructures due to near-field plasmonic coupling when excited by light close to the SPR wavelength.

Here, we will show that quantitative SERS sensors can be produced by oblique-angle ion-beam sputtering deposition of silver on nanorippled alumina surface. Under certain growth conditions, self-aligned Ag nanoparticles (NPs) with tunable interparticle gaps in the range from ~2 to 20 nm can be created, thus assuring a high density of hot spots and fine control of the near-field enhancement properties over a wide spectral range [3,4]. Additionally, these systems possess original dichroic properties, reflected in a polarization-dependent excitation of their SPR, which can be exploited for the quantitative detection of bipyridine used as a probe test molecule. Moreover, the Ag NPs can be covered with a thin dielectric layer (order of a few nm) that protects the sensor from the environment, but also prevents selective adsorption and direct interaction between the NPs and the probed molecules. These features allow building a cleanable and reusable sensor, therefore ensuring a long operational lifetime, reproducibility and durability [5].

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Keywords: Chemical Solution Process, Thin Films, HfO_2, ZnO, Metal Atom Clusters
Disciplinary fields involved: Chemistry
Sustainable Development Goals eventually involved in your research: Affordable and clean energy (Goal 7), Industry, Innovation & Infrastucture (Goal 9)

From Chemical Solution Processes to Transparent Nanostructured Thin Films: Oxide Nanocrystals or Octahedral Metal Atom Clusters

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Transparent thin films or coatings, with thickness ranging from nanometres to micrometres, are playing an important role in daily life. Recently, the demand of robust, low cost and friendly-environmental functional nanocomposite thin films with high transparency for applications is strongly increasing. Moreover, the use of chemical solution disposition (CSD) processes is highly desirable in order to reduce the cost and waste and that can enable fabrication method for flexible devices. This presentation will summarise our works on the synthesis of functional nanostructured or nanocomposite thin films based on oxide nanocrystals (NCs) or metal atom clusters (MC) by CSD processes (spin-coating, dip-coating or electrophoretic deposition (EPD)).[1-5] We will demonstrate that CSD processing of inorganic nanocolloidal solutions is highly flexible in terms of precursor composition, targeted substrate and coating procedures at ambient pressures, and thus can be complementary of physical-based deposition routes while providing materials with matching or even superior properties. The first part will focus on oxide colloidal solutions.[1-2] The second part will be devoted on octahedral MC and highly transparent thin films in the visible.[3] Transparent films with prominent photoactive or antibacterial properties were obtained by using specific Mo_6 MC whereas UV and NIR filters were realised by using Ta_6 and Nb_6 MC.[3-4] We will particularly emphasise that the EPD process appears a performant CSD strategy to fabricate highly transparent and coloured nanocomposite thin films for optical, biological and energy applications.[5]

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Keywords : Biofouling, interface, marine, nanostructure, photocatalysis
Disciplinary fields involved : Chemistry, material science, Biology
Sustainable Development Goals* eventually involved in your research: life below water (Goal 14) Conserve and sustainably use the oceans, seas and marine resources

TiO_2 AND TI-CU-O THIN FILMS DEPOSITED BY AA-MOCVD FOR MARINE ANTIBIOFOULING APPLICATIONS

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Since 2003, the use of tributyltin (TBT) in antifouling coatings is prohibited because of its toxicity towards marine environments(1). The last decade has seen the emergence of a new research area : environmental-friendly antifouling coatings. Combined with a non-toxic, time and corrosion-resistant character, the photocatalytic properties of TiO_2 make this oxide a good eco-friendly antibiofouling alternative for marine environments(2). But even if it is showing promising results in *in vitro* experiments(3), the limited exposure to sunlight in the sea and the restricted absorbance range (UV) of TiO_2 in the solar spectrum are important issues. To enhance the antibiofouling properties, a combination of morphological and physico-chemical properties of TiO_2 is investigated.

In this context, TiO_2 thin films have been synthesized using Aerosol Assisted Metal Organic Chemical Vapour Deposition (AA-MOCVD). Using precise parameters, nanometric petal assembly (forming microflower-like structures) are obtained, enhancing the reactive specific surface of the material and thus its photocatalytic properties. By tuning some deposition parameters , it is possible to vary the size and density of the flowers, and to investigate their influence on both the photocatalytic and antibiofouling properties of the thin films.

The film morphologies, composition and photocatalytic performances are going to be investigated using SEM, DRX and a photocatalysis test, as well as their antifouling properties during *in vitro* experiments and marine immersion.

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Keywords: Raman spectroscopy, razing XRD, 4H-SiC, recrystallization
Disciplinary fields involved: Physics, Chemistry
Sustainable Development Goals* eventually involved in your research: Industry, Innovation and Infrastructure (Goal 9)

Recrystallization of thin 4H-SiC films deposited by PVD techniques, a way for new emerging fields.

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Nowadays, localized growth of homoepitaxial silicon carbide (SiC) is limited utilizing usual CVD methods [1]. In this paper, we present 4H-SiC layers obtained by more classical PVD techniques, opening a way to design new SiC devices. Amorphous thin SiC layers (from 0.15 to 1.15µm thick) are deposited by electron-beam evaporation or sputtering techniques on commercial 4°-off axis 4H-SiC substrates and then recrystallized by high temperature annealing at 1400 and 1700°C. The crystallinity of the SiC layers is studied by Raman spectroscopy and razing XRD. Raman analysis shows that the thin films partially recrystallize in 4H-SiC (Figure 1) confirming the homoepitaxial growth. An electrical conductivity of the layers is also determined which seems to be related to nitrogen *n*-type doping activation. SIMS measurements in SiC with N-profiles will be done for the conference date.

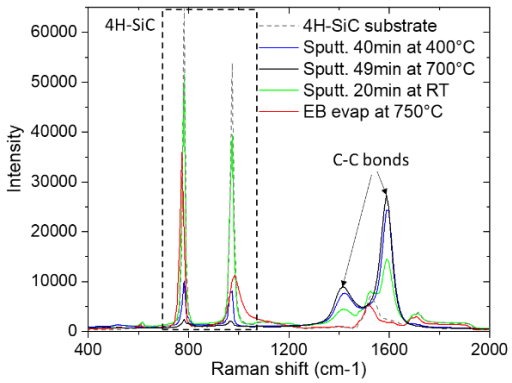

Fig. 1: Raman under laser excitation of 325nm spectra of SiC layers after annealing at 1700°C for 30min. Raman peaks of 4H-SiC are identified [2].

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