CENTRE
D'ÉLABORATION
DE MATÉRIAUX
ET D'ÉTUDES
STRUCTURALES

HIGHLIGHTS 2022

cnrs

CENTRE D'ÉLABORATION DE MATÉRIAUX ET D'ÉTUDES STRUCTURALES

29, rue Jeanne Marvig
BP 94347 - 31055 Toulouse Cedex 4, France

Publication directors:
Alain Couret - Bénédicte Warot-Fonrose

Coordinating editor: *Guy Molénat*

Photo credits:

Graphic Design: Oblique Studio

SUMMARY

EDITO

We are very happy to present you the seventh edition of the significant happenings in CEMES.

In this review, we have presented a selection from the best results obtained by the laboratory in the year 2022. You will note that our work is published in highly renowned international journals. Our published work most often relies on using cutting edge scientific instrumentation in combination with novel modeling approaches to study matter at the limits of spatial, temporal and spectral resolution. Inventing, describing, studying, understanding, modeling, and controlling the structure of molecules, nanoobjects and nanodevices are attributes that are wired into the DNA of the laboratory.

We are very glad to inform you that three projects, *Impress, AddMorePower*, and *COST MecaNano* have been selected for funding from Europe. We also proudly acknowledge our successful collaboration with large industrial actors in the sectors of electronics, aeronautics, and nuclear energy, this owing to our unique knowledge-base and experience in materials sciences. In fact, the renewal of our participation in the priority action of CNRS/STMicroelectronics on the study of GST alloys is a fine example of our successful fruitful collaboration in this area.

The year 2022 saw the arrival at CEMES, of the first CPER equipment and the start of the associated FEDER-REACT projects covering the research areas of electron microscopy and quantum technology. For this, we express our heartfelt thanks to the CNRS, with *l'Institut de Physique* and *la Délégation Régionale d'Occitanie Ouest, the Région Occitanie, Toulouse-Métropole* and the French Govt. We believe that the availability of such advanced equipment will lead us to new progress and breakthroughs and help us to stay on top of the international state-of-the art, principally in the areas of nanooptics, electron holography and metallurgy, the highlights of which are described in this brochure.

With the aim to disseminate research activities to the general public, CEMES has organized many events at the emblematic "Boule" in view of its great popularity originating from its size and its unique spherical shape. The second "NanoCar Race" that was held in the Boule gave us an excellent platform for scientific dissemination. This year, we also had the very popular rappers Bigflo and Oli from Toulouse sing Claude Nougaro's song "O Toulouse" a capella while bursting into spontaneous improvisation — this moment has been captured in the last sequence of the video « Etrange Escale -Toulouse » available on YouTube. Furthermore, in the book « Les Joyaux de Toulouse (The Treasures of Toulouse in the English version) » describing the unique attractions of Toulouse, CEMES finds a special mention along with Airbus, CNES, Midi-Pyrénées Observatory, or the Stade Toulousain rugby team, among others. Lastly, on page 16 of this brochure, you will see a glimpse of the artist Naomi Maury's work, which has been exhibited at the Museum of Modern Art ('Les Abattoirs') in Toulouse. This year, CEMES will continue its support to young people by renewing its offer of "Research apprenticeships" to middle and high school students where they can learn and practice the scientific method and approach.

We hope you enjoy reading this brochure describing the CEMES 2022 highlights!

Alain Couret
Director, CEMES

Bénédicte Warot-Fonrose
Associate director
CEMES

Muriel Rougalle
Secretary General
CEMES

EDITO

Nous sommes très heureux de vous présenter la septième édition des faits marquants du CEMES.

Ce recueil vous dévoile quelques-uns des plus beaux résultats 2022 du laboratoire. Vous verrez que nos travaux sont publiés dans des revues du meilleur niveau international. Très souvent, ils reposent sur des études de la matière à des échelles spatiales, temporelles et spectrales ultimes, sur la base d'une instrumentation scientifique de pointe soutenue par des modélisations originales. Inventer, Elaborer, Etudier, Comprendre, Modéliser, Maîtriser les molécules, les nano-objets et les nano-dispositifs, telle est bien l'ADN du laboratoire.

Nous nous réjouissons de l'obtention cet été de trois projets européens : Impress, AddMorePower et COST MecaNano. Nous nous félicitons aussi du succès de nos collaborations avec les grands groupes industriels des secteurs de l'électronique, de l'aéronautique ou du nucléaire, qui reposent sur nos compétences uniques en science des matériaux. En ce domaine, notre participation renouvelée à l'action prioritaire CNRS/STMicroelectronics sur les alliages GST s'avère emblématique et fructueuse.

L'année 2022 a vu arriver les premiers équipements des CPER et projets FEDER-REACT associés, touchant aux domaines de la microcopie électronique et des technologies quantiques. Nous remercions très chaleureusement de leurs soutiens le CNRS, avec l'Institut de Physique et la Délégation Régionale d'Occitanie Ouest, la Région Occitanie, Toulouse-Métropole et l'Etat. Ces équipements vont nous permettre de nouveaux progrès et de nouvelles avancées, et de demeurer au sommet de l'état de l'art international. Nos activités dans les domaines de la nano-optique, de l'holographie électronique et de la métallurgie sont concernées, autant de domaines qui ont donné lieux à des faits marquants de ce recueil.

S'appuyant sur son emblématique Boule, le laboratoire crée des évènements, pour ensuite communiquer sur sa recherche. La seconde NanoCarRace s'y est déroulée et a offert un beau moment de médiation scientifique. Cette année, nous y avons aussi vu les rappeurs toulousains Bigflo et Oli chanter a capella Ô Toulouse de Claude Nougaro, dans un bel élan de spontanéité, un moment retenu pour la séquence finale de la vidéo « Etrange Escale - Toulouse » disponible sur Youtube. Relevons aussi que le CEMES figure dans le livre « Les joyaux de Toulouse » au côté d'Airbus, du CNES, de l'Observatoire Midi-Pyrénées ou du Stade Toulousain, parmi d'autres. Enfin, vous aurez, page 16 de ces Faits marquants, un aperçu de l'exposition de l'artiste plasticienne Naomi Maury en collaboration avec le Musée des Abattoirs. Cette année, le CEMES renouvelle son offre envers les jeunes publics, en poursuivant le dispositif « Apprentis Chercheur », qui permet à des collégiens et lycéens de pratiquer la démarche scientifique.

Nous vous souhaitons une bonne lecture de ces Faits Marquants 2022 du CEMES.

Alain Couret
Directeur du CEMES

Bénédicte Warot-Fonrose
Directrice Adjointe du CEMES

Muriel Rougalle
Secrétaire Générale du CEMES

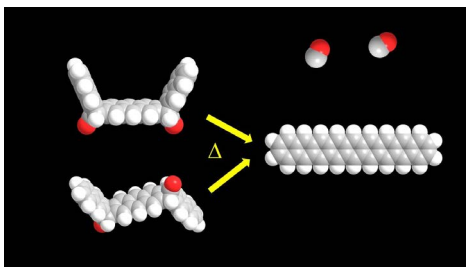
PREPARATIVE-SCALE SYNTHESIS OF NONACENE

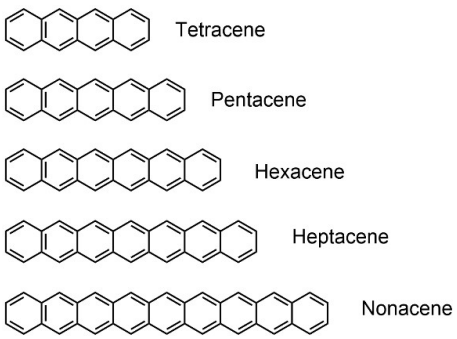
THE LONGER, THE BETTER!

Long acenes composed of linearly fused benzene rings, have remained for years unreachable compounds despite their high potential interest for applications in molecular electronics, spintronics, and organic electronics. Researchers from the NanoSciences Group in CEMES-CNRS, in collaboration with Hokkaido University (Japan), have found a strategy to prepare nonacene (with 9 rings) and demonstrate its surprising thermal stability in inert conditions.

n-acenes are a class of polyaromatic hydrocarbons consisting of linearly fused benzene rings of formula $C_{4n+2}H_{2n+4}$, where n is the number of rings. These graphene nanoribbon segments exhibit singular electronic properties such as a rapid decay, as a function of n, of the energy gap between the highest occupied and lowest vacant molecular orbitals. This electronic structure induces a diradical character, small optical gaps, low-energy triplet states, low oxidation potentials and high electronic affinity. This explains why the smallest easily accessible acenes such as tetracene (n=4) and pentacene (n=5) are currently being extensively studied for applications in OFET transistors and organic photovoltaic cells, with hole mobilities exceeding than that of amorphous silicon
.
Increasing the number of cycles n should improve these properties, but also increases the chemical reactivity of the molecules. This is why, despite this interest and more than 70 years of research, hexacene (n=6) could only be isolated in 2012, then heptacene (n=7) in 2017, and it was accepted until very recently that it was not certain that longer acenes would be stable enough to be synthesized except under very special conditions of high dilution or ultra-high vacuum, and this, at very low temperature.

Researchers from the Nanosciences Group of CEMES-CNRS have just developed a method for preparing pure nonacene (n=9) and demonstrated its surprising thermal stability in the solid phase. Their strategy, which can be extended to even longer acenes, has been preparation of chemically stable, non-planar and soluble precursors with a large gap, which allows synthesis and characterization by classical methods of organic chemistry (in eleven steps of synthesis in total). These precursors have two bridging carbonyl groups that can be removed in the form of carbon monoxide by solid phase heating at 200 ° C or by ultraviolet irradiation. The nonacene thus formed is a stable black solid, which can be kept under an inert atmosphere for months which will allow its use in organic field effect transistors.





Schematic representation of the precursors used to synthesise the nonacene.

Preparative-scale synthesis of nonacene

Andrej Jančařík, Jan Holec, Yuuya Nagata, Michal Šámal, and André Gourdon.

Nature Communications
13, 223 (2022)

CONTACT

André Gourdon
andre.gourdon@cemes.fr

MAPPING ELECTRICAL PROPERTIES IN WORKING NANODEVICES

STUDY OF NANOCAPACITORS IN WORKING CONDITIONS BY OPERANDO ELECTRON HOLOGRAPHY

The electrical potential distribution in metal-insulator-metal nanocapacitors under working conditions has been investigated using new methodology that combines advanced sample preparation, state-of-the-art electron holography and finite element modelling. Our results demonstrate that electrical properties such as electric field, capacitance and surface charge density of nanodevices directly extracted from production lines can be preserved and studied at the nanoscale.

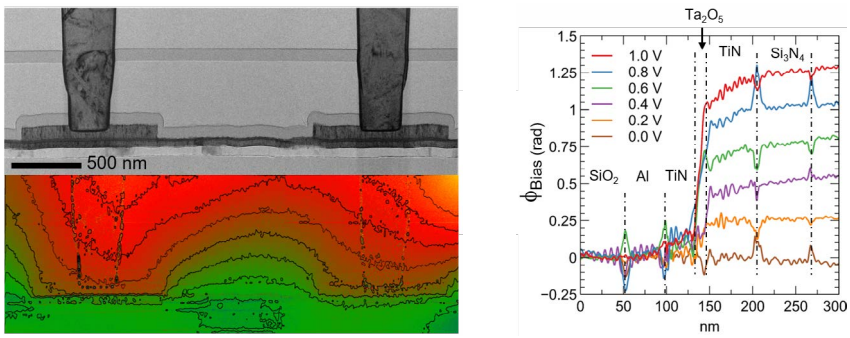
Nano-electronic devices play an essential role in many domains, and their development and improvement attract considerable attention in fundamental and applied research. In collaboration with STMicroelectronics (Crolles, France) and in the framework of the ANR project IODA, we have shown how electric fields in real nanodevices can be studied under working conditions using operando electron holography.

A specific sample preparation method was first developed to bias electron-transparent nanodevices extracted from production lines whilst ensuring their electrical connectivity and functionality without employing dedicated probe-based holders.Using this approach based on focused ion beam (FIB) circuit modification, an array of parallel Metal-insulator-metal (MIM) nanocapacitors extracted from a matrix structure integrated in a STMicroelectronics 28 nm process test chip were prepared for transmission electron microscopy experiments.

Operando electron holography observations performed on the I2TEM microscope allowed the electric potential to be quantitatively mapped in the active areas, and between devices, whilst biasing the devices in situ.

Experimental results were compared with finite element method (FEM) modelling simulations to determine local electrical parameters. We demonstrate that electrical properties such as capacitance and surface charge density can be quantitatively mapped at the nanoscale and have been preserved by our sample preparation methodology when compared to macroscopic measurements.

This work paves the way for mapping the local electrical properties of more complex biased devices such as MOS transistors or spintronic devices by adapting the sample preparation workflow to achieve a successful circuit modification and enable electrical stimulation of the device. This ability to study local electric fields quantitatively in newly proposed devices and devices already in production will help efforts to explore fundamental physical processes as well as to develop and improve current devices.



Left: Amplitude image of both MIM nanocapacitors in parallel and experimental phase image with isopotential contours of the induced electrostatic potential for 0.6V bias applied by the power supply. Right: Phase profiles extracted for different biases. Ta_2O_5 active layer is between the two TiN electrodes.

Mapping electric fields in real nanodevices by operando electron holography

Maria Brodovoi,Kilian Gruel, Aurélien Masseboeuf, Lucas Chapuis, Martin Hÿtch, Frédéric Lorut, and Christophe Gatel.

Appl. Phys. Lett.
120, 233501 (2022)

CONTACT

Christophe Gatel
christophe.gatel@cemes.fr

SILICA, NOT THAT NEUTRAL...

AN «ELECTRON PUMP» WHICH IONISES NANOSILVER!

Amorphous silica is commonly used as a coating matrix to protect metals from oxidation because it is considered to be inert. But is it true? By DFT modelling, we have shown that a silver nanoparticle surrounded by silica becomes cationic. Not only does it form chemical bonds with the silica atoms but it also transfers electrons to silica over a distance of 4 Å. Moreover, if defects are present in silica, they act as «electron pumps» and the nanoparticle loses even more electrons!

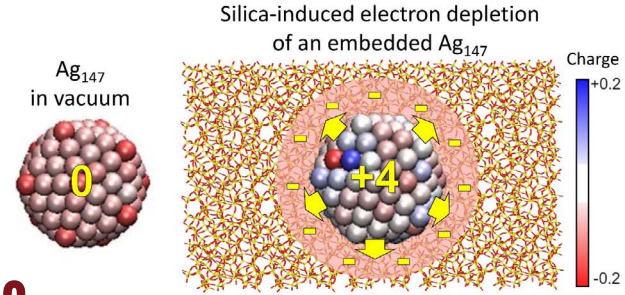
Silver nanoparticles (AgNP), extensively studied in recent years due to their remarkable biological and optical properties, find many applications in sensing, optoelectronics and as antimicrobials. However, because of their toxicity and their high propensity for oxidation and sulfidation, these nanoparticles require to be incorporated into a matrix for many applications. Nevertheless, despite their frequent use, the effect of the matrix on the nanoparticle properties remains largely unknown.

By means of dispersion-corrected Density Functional Theory (DFT) calculations, we have examined the effect of an amorphous silica matrix on the structure and charge distribution of 55- and 147-atom AgNPs. We observe that covalent bondings between the AgNP and the matrix occur at the interface involving the breaking of Si–O bonds, which systematically leads to the formation of Ag–Si bonds, and in some cases, to the formation of Ag–O ones. Interestingly, these interface reconstructions are accompanied by electron depletion of the nanoparticles, a substantial number of electrons being transferred from the two outer shells of the AgNP to the surrounding silica medium. The electrons lost by the nanoparticles are captured by the Si atoms involved in the interface bonds, but also, unexpectedly, by the atoms of the silica network inside a few angstroms spherical shell around the AgNP, this electronic extension going beyond that attributable to the AgNP spill-out. The numbers of interface bonds and electrons transferred to the surrounding silica shell appear to be proportional to the surface area of the AgNP. Another noteworthy point is the electron pump effect of the undercoordinated silica atoms when silica is defective. The presence of additional electrons in the matrix, especially on defects, is consistent with the experimental literature.

Implications of this finding are important for the AgNP chemical, electrochemical and optical properties, in particular for its surface reactivity which drives the AgNP dissolution mechanisms. In addition, the presence of electrons trapped on defects in the matrix predicted by our simulations will impact the conduction properties of such nanocomposite devices.

This work is part of a transverse project between the NeO and SINAnO groups in collaboration with J. Puibasset (ICMN, Orléans).

It is supported by the ANR BENDIS “Interaction of biological targets with solid dielectric layers consisting of silver nanoparticles embedded in silica matrices: Towards tailored antimicrobial surfaces”.



Atomic charges on a 147-atoms silver nanoparticle in vacuum (left) and embedded in silica (right).

Silica-induced electron loss of silver nanoparticles

Magali Benoit, Joël Puibasset, Caroline Bonafos, and Nathalie Tarrat.

Nanoscale
14, 7280 (2022)

CONTACT

Magali Benoit
magali.benoit@cemes.fr

Nathalie Tarrat
nathalie.tarrat@cemes.fr

Caroline Bonafos
caroline.bonafos@cemes.fr

SPIN MANIPULATION AND DETECTION AT THE SINGLE-MOLECULE SCALE

TOWARDS A NEW CONCEPT OF DEVICE IN MOLECULAR SPINTRONICS

Achieving size-compact and energy-efficient control and detection of magnetism are paramount for the development of future spintronic devices. Using single molecules as quantum units opens a new pathway to reach the physical limits of miniaturization. However, due to the very large number of possible material combinations, there is an urgent need for fundamental understanding and guiding concepts to search for new smart, functional molecular designs. A novel concept has been proposed, enabling all-electrical spin manipulation and detection in molecular spinterfaces.

"Smaller, faster, lower energy consumption" are some of the keywords for next-generation information and communication technologies. Currently, spintronics devices are mainly operated via either an external magnetic field (e.g., tunnel magnetoresistance devices), which is high power consumption.

Researchers from CEMES-CNRS associated with physicists from the Technical University of Denmark and SPEC-CEA theoretically (i.e., ab initio + quantum transport theory) proposed a new way to achieve a full-electrical control of molecular spintronic devices without relying on external magnetic fields. An experimentally feasible three-terminal quantum transport setup (see Fig. a) is proposed, where an iron porphyrin (FeTPP) molecule is deposited on B-doped graphene (BG). Notably, a reversible spin switching between S=1 to S=3/2 spin states is achieved by a gate voltage, tracing their origin to a strong hybridization between Fe-d_{z2} and B-p_z orbitals due to perfect orbital symmetry-matching as shown in Fig. b.

These results show a "writing" operation at the atomic scale. The authors further demonstrate how the in-plane quantum transport for the BG, which is non-spin polarized, can be modified significantly by FeTPP, yielding a significant transport spin polarization near the Fermi energy (>10% for typical coverage, see Fig. c). Such a large spin-polarized signal can be probed by current state-of-the-art experimental techniques such as shot noise measurements. These complementary results show that it is, therefore, not only possible to write but also to read the spin.

The novel concept proposed in this work outlines both a general and an effective design principle required for successful all-electrical operations of molecular spintronic devices. This work could lead to the development of next-generation spintronic devices with ultralow-power consumption.

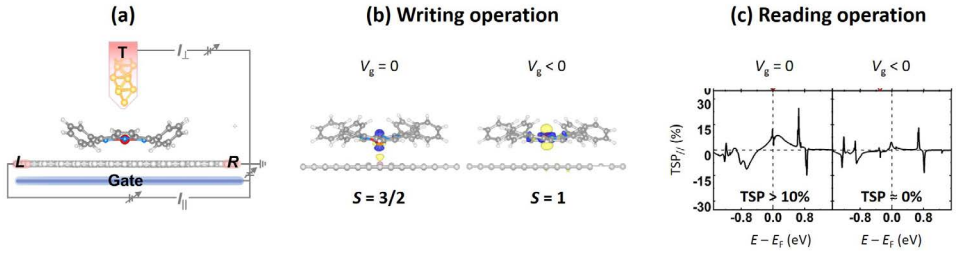


Figure: (a) Schematic view of a single FeTPP absorbed in substituted graphene with an STM tip and a back-gate plane. The proposed three-terminal device allows an out-of-plane and an in-plane transport. (b) The molecular spin states can be reversibly switched between S=1 and S=3/2 via a simple gate voltage. (c) The absorption of the molecule on BG changes the quantum transport behavior of the BG sheet dramatically from nonmagnetic to magnetic, which can be easily read out as "0" and "1".

Proposal for all-electrical spin manipulation and detection for a single molecule on boron substituted graphene

Fei Gao, Dongzhe Li, Cyrille Barreteau, and Mads Brandbyge.

Phys. Rev. Lett.
129, 027201 (2022)

CONTACT

Dongzhe Li
dongzhe.li@cemes.fr

CRYSTALLIZATION OF GE-RICH GeSbTe ALLOYS

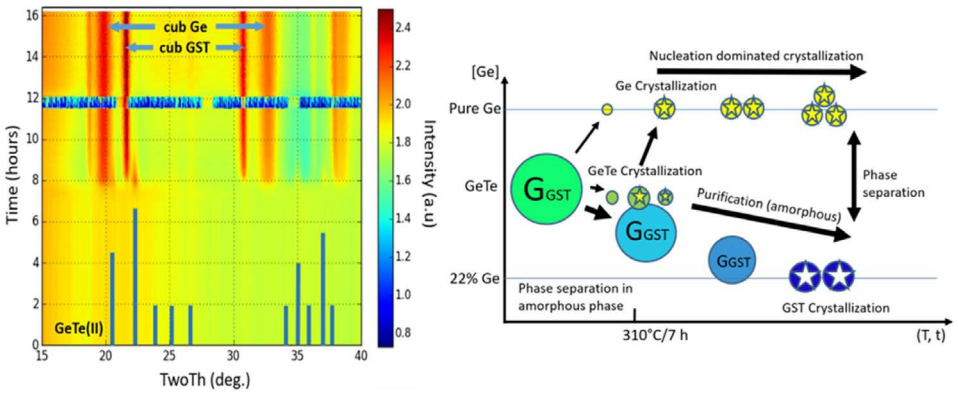
THE RIDDLE IS SOLVED

Ge-rich GeSbTe (GST) alloys are of considerable interest for embedded digital memories and neuromorphic devices. Up to now, the mechanisms by which such alloys crystallize remained unclear and very controversial. Using in situ synchrotron X-ray diffraction during isothermal annealing and advanced TEM techniques, we unveiled the mechanisms leading to the overall crystallization of such alloys.

Our previous ex situ XRD studies have shown that the incubation time, i.e. the time after which the onset of crystallization is observed, is of about several tens of minutes at 330°C. We decided to investigate the 310-330°C temperature range in detail, in an effort to slow down and decompose the different mechanisms which intervene in the crystallization process. The great angular and temporal resolution offered in diffraction by the synchrotron allow us to characterize these different steps.

During in-situ annealing at 310°C, the initially homogeneous and amorphous material undergoes a progressive phase separation leading to the formation of Ge-rich regions of different compositions. During this decomposition, first formed GeTe embryos crystallize and trigger the heterogeneous crystallization of the Ge cubic phase. As the phase separation proceeds, these embryos dissolve and the Ge phase gradually builds up through the nucleation of small grains. Only when this Ge cubic phase is largely formed, the remaining amorphous matrix may locally reach the $Ge_2Sb_2Te_5$ composition at which it can crystallize as large grains. Our density functional theory calculations confirm that the quite exotic Pnma GeTe structure we have experimentally identified is more stable than the regular R3m structure at nanometric sizes.

These results unveil the intriguing characteristics of the three-step crystallization of Ge-rich alloys and close a long-lasting controversy concerning the order and the scenario of crystallization in these alloys.



Left: Synchrotron X-ray diffraction map obtained during in-situ isothermal annealing at 310°C on a Ge-rich GST sample as a function of annealing time.
Right: Graphical representation of the crystallization process of Ge-rich GST alloys proposed from both experimental and calculation investigations.

Crystallization of Ge-Rich GeSbTe Alloys: The Riddle Is Solved

Eloïse Rahier, Sijia Ran, Nicolas Ratel Ramond, Shuangying Ma, Lionel Calmels, Sabyasachi Saha, Cristian Mocuta, Daniel Benoit, Yannick Le Friec, Minh Anh Luong, and Alain Claverie.

ACS Appl. Electron. Mater. 4, 6, 2682 (2022)

CONTACT

Alain Claverie
alain.claverie@cemes.fr

Eloïse Rahier
eloise.rahier@cemes.fr

MEASURING LOCAL CHARGE DENSITIES ON AN ACTIVE METAL-OXIDE-SEMICONDUCTOR DEVICE

EXTREME MEASUREMENTS BY ELECTRON HOLOGRAPHY ON A BIASED CAPACITOR

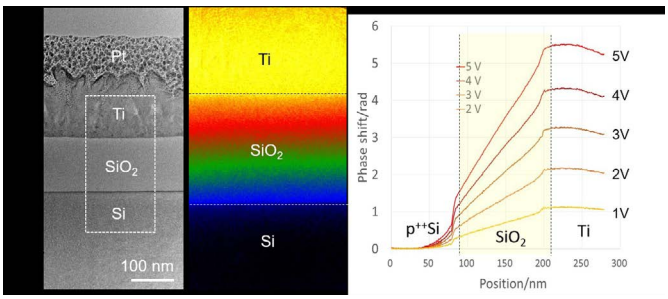
Everything is considered known about the humble capacitor, especially one made of silicon dioxide on silicon extremely used in semiconductor devices. It is surprising therefore that the electric field within a such capacitor has never been mapped out at the nanoscale. Using operando electron holography, the electric potential across a working MOS nanocapacitor has been measured with unprecedented sensitivity and revealed unexpected charged layers at the interfaces with electrodes.

MOS capacitors are widely used in many advanced devices whose performance is dependent on their miniaturization and operation (field-effect transistor, flash memory, dynamic random-access memory and active regions of image sensors). While new materials for the dielectric are constantly being explored from high-K materials to ferroelectrics and negative capacitance ferroelectric stacks, silicon dioxide is still the most widely used dielectric material and feature prominently in textbooks on semiconductor physics. By applying bias across the two electrodes, charge is stored at the two interfaces. In reality, the physics is rich and complex, ranging from band-bending, depletion regions and inversion layers in the semiconductor substrate to charge trapping in the dielectric oxide and at the interfaces.

Charge trapping changes the capacitance and performance of real devices by modifying the threshold voltage and frequency response and is a major concern for dielectric breakdown. The uncertainty concerning their location arises from the fact that the majority of the characterisation techniques are based on indirect measurements.

CEMES researchers have explored whether electron holography combined with finite element modelling simulations can be used as a new way of studying these systems. They succeeded in mapping the electric field, with nanometre spatial resolution and very high sensitivity, in a nanocapacitor whilst applying bias. Surprisingly, the electric field is not uniform in the dielectric layer: a much higher electric field prevails in a region which extends to over 5 nm close to the electrodes. This region corresponds to a zone of uniform space charge, opposite in sign to that on the electrode. Whilst charge trapping is known in silicon dioxide capacitors, it is totally unexpected to find charges over 5 nm from the interface. Furthermore, these experiments show that these dielectric charges are at thermal equilibrium, appearing only when the capacitor is biased. Needless to say, the consequences are important for the capacitance and others electrical features of the device.

These results both demonstrate the extreme sensitivity of the measurement technique (device capacitance of 80 atto-Farad, electrical potential resolved to 9 mV, charge measurements down to 50 elementary charges).



Left: TEM image of the metal (Ti) - oxide (SiO2) - seminconductor (Si) device Middle: Projected electric potential under a 5V polarisation measured by electron holography in the I2TEM microscope Right: Phase shift profile for different applied potentiel as a function of the position in the stack.

Extended Charge Layers in Metal-Oxide-Semiconductor Nanocapacitors Revealed by Operando Electron Holography

Christophe Gatel, Roberto Serra, Kilian Gruel, Aurélien Masseboeuf, Lucas Chapuis, Robin Cours, Leifang Zhang, Bénédicte Warot- Fonrose, and Martin J. Hÿtch.

Phys. Rev. Lett.
129, 137701 (2022)

CONTACT

Christophe Gatel
christophe.gatel@cemes.fr

Martin Hÿtch
martin.hytch@cemes.fr

JOINING EACH OTHER: A SOLUTION TO AN OLD METALLURGY CONUNDRUM

THE PUZZLING ANOMALOUS SLIP OF DISLOCATIONS IN BCC METALS IS FINALLY SOLVED

We have deformed niobium samples at -170°C in a transmission electron microscope, and observed in real time the corresponding microscopic mechanisms. Some extremely fast dislocation movements correspond to the "anomalous slip" first reported 50 years ago, but never elucidated until now. Atomistic simulations are in good agreement with observations and allow us to understand the frequency of occurrence of this phenomenon in various body-centered cubic metals.

Crystal strength and plastic flow are controlled by the motion and interaction of dislocations, the line defects carrying atomic shear increments. While, in most crystals, deformation develops in the crystallographic planes where the glide force acting on dislocations is maximum, plasticity in body-centred cubic (BCC) metals is more complex. Slip systems where the resolved shear stress is not the highest can dominate at low temperature, leading to the so-called anomalous slip, first observed in 1969, but never elucidated at the microscopic scale.

Using in situ tensile tests at -170°C in a transmission electron microscope, we can observe the motion of dislocations, in niobium samples and in real time, and determine all their different properties. Here we show that anomalous slip arises from the high mobility of multi-junctions, i.e. junctions between more than two dislocations (4 dislocations in the present case), which glide at a velocity several orders of magnitude larger than single dislocations. These multi-junctions result from the interaction of a simple binary junction with a gliding dislocation.

Although elasticity theory predicts that these binary junctions should be unstable in crystals with a weak elastic anisotropy like tungsten, both experiments and atomistic simulations reveal that such junctions can be created under dynamic conditions, in agreement with the existence of anomalous slip in almost all BCC metals, including tungsten.

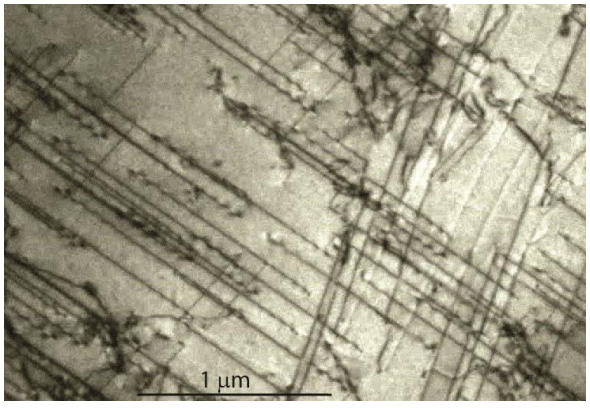


Image of in situ electron microscopy at -170°C, showing mobile dislocations during the plastic deformation of niobium

Anomalous slip in body-centred cubic metals

Daniel Caillard, Baptiste Bienvenu, and Emmanuel Clouet.

Nature
609, 936 (2022)

CONTACT

Daniel Caillard
daniel.caillard@cemes.fr

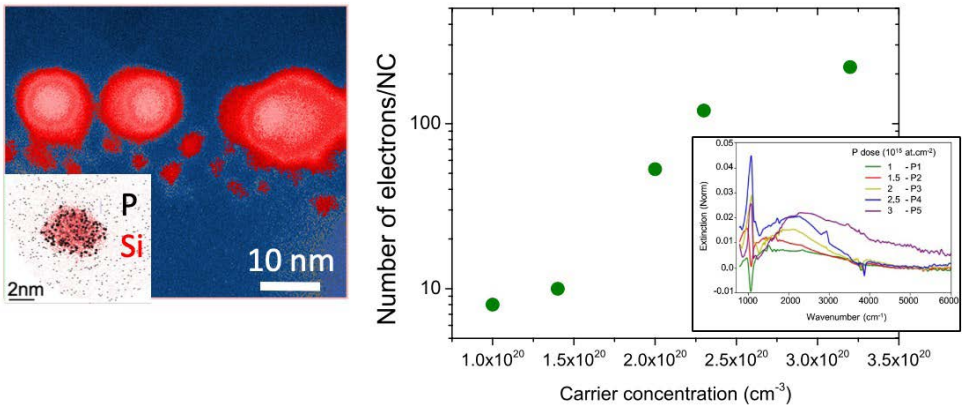
ULTRASENSITIVE OPTICAL PROBES MADE FROM DOPED SI NANOCRYSTALS

SILICON STANDS FOR PLASMONICS

Plasmonics, which uses the collective oscillations of free electrons localized in doped metallic or semiconductor nanostructures (plasmon resonances), allows for the manipulation of light on a much smaller scale than its wavelength, down to nanometric dimensions.

Researchers from CEMES collaborated with four other French laboratories to demonstrate in a recently published study the appearance of surface plasmon resonances carried by small (10 nm) silicon nanocrystals doped with phosphorus and embedded in a silica matrix. These Si nanocrystals were fabricated in the lab using low energy ion implantation, and their plasmon resonance was measured using Fourier Transform IR spectroscopy in the mid-infrared (IR) (4-7 µm). This resonance can be tuned across a wide spectral range by simply adjusting the free carrier concentration via phosphorus doping.

By comparing these experimental results to numerical simulations, we were able to demonstrate a coupling between this plasmon mode and the IR phonons of the surrounding silica matrix. We also demonstrated that only ten free electrons inside the nanostructure are enough to generate a plasmon. Finally, the nanocrystals' small size, well below the mean free path of electrons, drastically reduces their mobility, resulting in a broadening of the plasmon signature. The formation of phosphorus aggregates inside the nanocrystals exacerbates this phenomenon for high doping. This work was funded by the ANR DONNA (Doping at the Nanoscale, ANR-18-CE09-0034).



Left: Energy filtered electron microscopy (EFTEM) image of P doped SiNCs. Inset, atom probe tomographic image showing the distribution of P atoms (black) within a SiNC (red).
Right: Number of free electrons/NC as a function of the carrier concentration. Inset: FTIR measurements of the surface plasmon resonance for different implanted P doses.

Infrared nanoplasmonic properties of hyperdoped embedded Si nanocrystals in the few electrons regime

Meiling Zhang, Jean-Marie Poumirol, Nicolas Chery, Clément Majorel, Rémi Demoulin, Etienne Talbot, Hervé Rinnert, Christian Girard, Fuccio Cristiano, Peter R. Wiecha, Teresa Hungria, Vincent Paillard, Arnaud Arbouet, Béatrice Pécassou, Fabrice Gourbilleau, and Caroline Bonafos.

Nanophotonics
11 (15), 3485 (2022)

CONTACT

Caroline Bonafos
caroline.bonafos@cemes.fr

Jean-Marie Poumirol
jean-marie.poumirol@cemes.fr

ASYMMETRIC EXCITONIC TRANSPORT IN $MoSe_2$-WSe_2 LATERAL HETEROSTRUCTURE EVIDENCED BY TIP-ENHANCED OPTICAL SPECTROSCOPY

TOWARDS A 2D EXCITONIC DIODE

The growth of lateral heterostructures with two different TMD materials is important for the fabrication of new strictly planar devices. Using tip-enhanced optical spectroscopies allowing sub-40 nm spatial resolution, it is shown the nonsymmetric diode-like behavior of a $MoSe_2$/WSe_2 lateral heterostructure. Thus, excitons created under the tip in the $WeSe_2$ part can migrate through the junction and recombine in the $MoSe_2$ area. Contrary, excitons created in the $MoSe_2$ part are blocked at the interface due to the energy barrier.

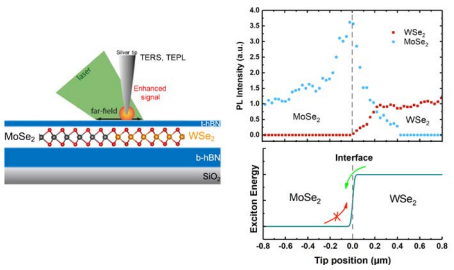
Monolayers of transition metal dichalcogenides (TMD) are extensively studied for their unique optoelectronic properties. TMD heterostructures were initially obtained by stacking two monolayers of two different TMDs, for instance $MoSe_2$ and WSe_2. Recently, pure 2D lateral heterostructures (see fig.) have been obtained by chemical vapor deposition by Tuchanin's group in Iena, then transferred on a substrate encapsulated between h-BN layers, and characterized in the framework of an international collaboration, including researchers from LPCNO and CEMES in Toulouse.

At CEMES, the heterojunction was studied by tip-enhanced Raman spectroscopy (TERS) and tip-enhanced photoluminescence spectroscopy (TEPL), allowing a spatial resolution of 40 nm, about 10 times better than with a standard confocal microscope. The excitation laser is focused on the silver-coated tip, locally enhancing the electric near-field, hence the creation of excitons (an electron-hole pair) in the TMD layer. The PL due to electron-hole pair recombination and the Raman signal are detected and analyzed in each point of the sample. In fact, the sample is raster scanned while recording spectra sequentially with the tip in contact with the surface, and 30 nm above the surface. The near-field contribution is then obtained by taking the difference between both recorded signals.

The TERS mappings delimit the very sharp boundary between both materials with a resolution of about 40 nm, equivalent to the tip diameter at its apex. The TEPL spectra are fitted using a combination of the exciton contributions of $MoSe_2$ and WSe_2. The first important result is that a $MoSe_2$ contribution can be detected when the tip is on the WSe_2 side, proving that excitons created even far from the interface (up to 400 nm) can diffuse and recombine in the $MoSe_2$ region. In contrary, when the tip is in the $MoSe_2$ region, even close to the interface, no WSe_2 contribution is ever detected.

This asymmetric exciton transport behavior, schematically shown in the figure, proves that the lateral heterojunction acts as an excitonic diode, with unidirectional transfer of excitons from WSe_2 to $MoSe_2$.

This work was partly funded by projects ANR HiLight (ANR-19-CE24-0020-01) and EUR NanoX 2DLight (ANR-17-EURE-0009). Tip enhanced optical spectroscopies were performed during H. Lamsaadi's master internship.



Left: scheme of the tip-enhanced spectroscopy set-up scanning the lateral heterojunction. The improved spatial resolution (40 nm) compared to standard laser spot size (500 nm) is due to the local field enhancement around the tip.

Right: (top) Photoluminescence intensity line scan showing that $MoSe_2$ emission (blue dots) can be detected even when the excitation occurs in the WSe_2 region, while WSe_2 emission (red dots) is forbidden when the excitation stays in the $MoSe_2$ region. This proves the nonsymmetric excitonic transport due to the energy barrier (bottom) and the lateral heterojunction abruptness.

Exciton spectroscopy and unidirectional transport in MoSe2-WSe2 lateral heterostructures encapsulated in hexagonal boron nitride

Dorian Beret, Ioannis Paradisanos, Hassan Lamsaadi, Ziyang Gan, Emad Najafidehagani, Antony George, Tibor Lehnert, Johannes Biskupek, Ute Kaiser, Shivangi Shree, Ana Estrada-Real, Delphine Lagarde, Xavier Marie, Pierre Renucci, Kenji Watanabe, Takashi Taniguchi, Sébastien Weber, Vincent Paillard, Laurent Lombez, Jean-Marie Poumirol, Andrey Turchanin, and Bernhard Urbaszek.

npj 2D Materials and Applications
6, 84 (2022)

CONTACT

Jean-Marie Poumirol
jean-marie.poumirol@cemes.fr

Vincent Paillard
vincent.paillard@cemes.fr

CONTROLLED COUPLING OF QUANTUM EMITTERS TO HIGH-INDEX DIELECTRIC NANOANTENNAS

ENHANCED SINGLE PHOTON SOURCES FOR QUANTUM COMMUNICATIONS

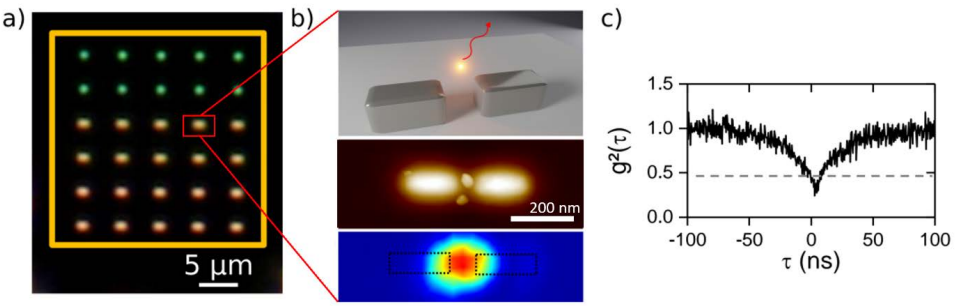
Researchers in CEMES, in collaboration with LPCNO, LAAS and CEA-Leti, have used AFM nanoxerography for large-scale positioning of quantum nanoemitters in the near field of high-index silicon nanoantennas. They demonstrate the increase of the nano-source brightness as a function of the resonances of the nanoantennas. This collaborative work opens the way to new planar architectures of arrays of efficient single photon sources for quantum technologies.

With the emergence of quantum technologies for information transfer, a major stake is the handling of quantum sources of light at the nanoscale and the control of their far-field emission. An approach based on optically resonant nanostructures has demonstrated the capability to control and enhance the emission of quantum emitters accurately positioned in their optical near field. In this context, CMOS-compatible high-index dielectric nanostructures hosting Mie resonances in the visible offer very promising opportunities, since they allow to manipulate, concentrate or redirect light, with low losses.

Researchers from CEMES, in collaboration with LPCNO, LAAS and CEA-Leti, have demonstrated that AFM nanoxerography makes possible the fast, robust and repeatable positioning at large-scale of model quantum emitters (nanodiamonds hosting NV centers) in the gap of silicon nanoantennas with dimer geometry.

By tuning the parameters of the nanoxerography process, the number of deposited nanodiamonds can be statistically controlled, yielding configurations down to a unique single photon emitter, with a high selectivity, and enhanced brightness induced by a near-field Purcell effect. Numerical simulations are in very good quantitative agreement with time-resolved photoluminescence experiments, and a multipolar analysis reveals in particular all the aspects of the coupling between the dipolar emitters and the Mie resonances in these simple nanoantennas. This proof of principle opens the path to a genuine and large-scale spatial control of the coupling of quantum nanoemitters to arrays of optimized nanoantennas. It paves the way to future fundamental studies in quantum nano-optics and to future integrated devices for quantum technologies.

This work has been funded by the projects NanoX MILO (ANR-10-LABX-0037-NEXT), ANR HiLight (ANR-19-CE24-0026-HiLight), IQO-MILO and CALMIP P1107



(a) Darkfield image of an array of silicon nanoantennas with different sizes (inducing different perceived colors). (b) Top: artistic view of a single dimer antenna coupled to a quantum emitter. Middle: AFM image of the antenna in (a) (red square) with nanodiamonds positioned in the gap. Bottom: corresponding photoluminescence image. (c) Autocorrelation function measured from the dimer antenna in (a) (red square).

Large-scale controlled coupling of single-photon emitters to high index dielectric nanoantennas using AFM nanoxerography

Mélodie Humbert, Romain Hernandez, Nicolas Mallet, Guilhem Larrieu, Vincent Larrey, Frank Fournel, François Guérin, Etienne Palleau, Vincent Paillard, Aurélien Cuche, and Laurence Ressier.

Nanoscale
Advance Article (2023)

CONTACT

Aurélien Cuche
aurelien.cuche@cemes.fr

NAOMI MAURY
THE SONG OF PARTICLES IN SOLAR WIND

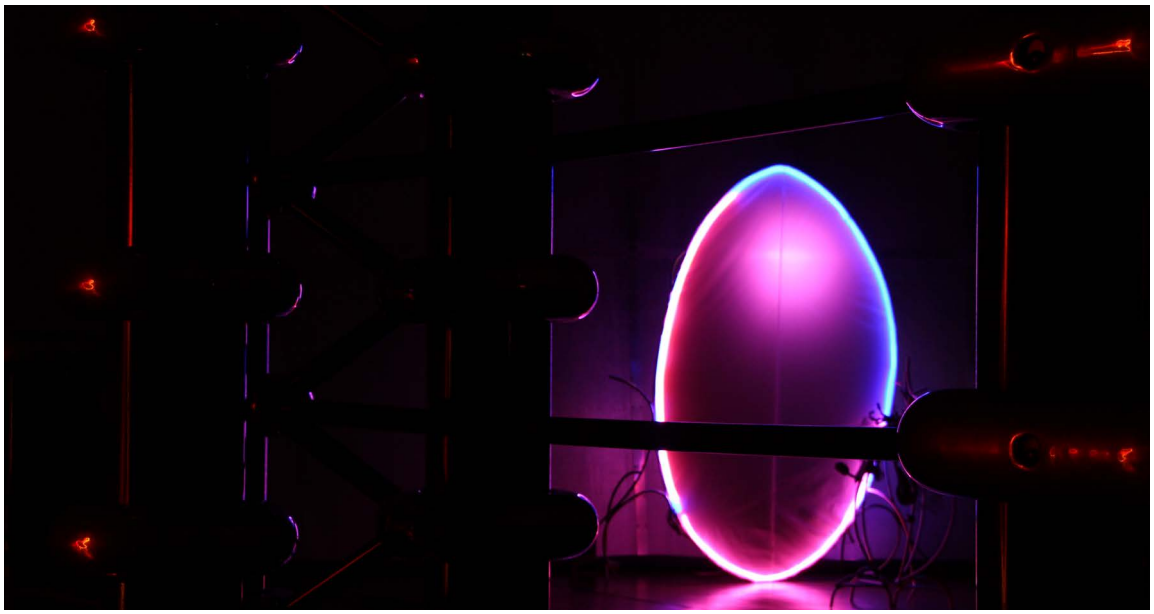
Following the installation of the artist Johan Decaix's works in 2020 in the Boule, CEMES hosted those of Naomi Maury in the Fall of 2022. This exhibition, inaugurated during the "Fete de la science" and co-organized by Toulouse Museum of modern art (Les Abattoirs), the Regional delegation of CNRS, and CEMES, was visited by close to 1100 people, among which 200 were preschool and primary school children of the locality. Each Saturday, a specialist expert in modern art was present to explain the works to the visitors.

Naomi Maury, a plastic artist, lives and works in the town of Sète. In 2021 she was awarded the Mezzanine prize at the museum of modern art in Toulouse where she presented her art installation, that was both sensory and immersive. In 2022, she won the "*Occitanie-Medicis*" prize and was a resident at the Villa Medicis at Rome.

Naomi Maury's interest is in the rapport that human beings have with non-humans (plants, animals, machines). For her sculpture, she carefully selects her material, be it natural or industrial. She then creates objects to reveal various aspects concerning the interconnection and interdependence between species and leads the viewer to empathize with others' suffering. The subject of Prosthesis—the symbiosis between the living and non-living is at the heart of her work.

CONTACT

Guy Molénat
guy.molenat@cemes.fr



Following the exhibition, the artist was invited to stay at CEMES that gave her the opportunity to immerse herself in its surrounding where she could meet researchers and learn about their interactive experience in the study of matter. The collection exhibited at the Boule comprised three original works inspired entirely from these meetings and created especially for CEMES.

«At the center of the Boule, are erected the mushrooms (electron accelerators) like the remains of a world in the making. The shimmering and Science Fiction-like atmosphere becomes a new space for light reflections. For this space, I have created a sort of movement with the help of light halos. Bathed in the light of these halos are ceramic relics of microscope parts along with sculptures of prostheses.

This environment is a sort of excuse offered by matter to the infinitely small particles that we are made of, that surround us and which may be us one day. How can we change ourselves to be more appreciative of our vital interdependence towards other human beings? Could this change help us to rethink the interactions of us humans to the non-humans?» Naomi Maury

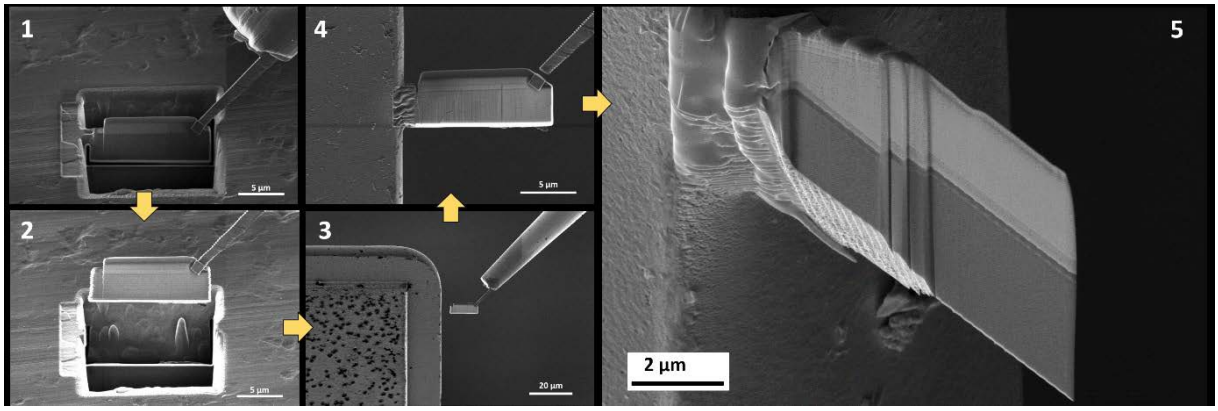
FIB
SERVICE UNIT

At CEMES, we have two microscopes equipped with ion beam columns, commonly known as the “Focused Ion Beam (FIB)” using which, abrasion of materials at the scale of tens of nanometers can be achieved. The ion beam is created at a tungsten tip wetted by liquid gallium, by applying a high electric field to ionize the gallium atoms. Ga+ ions are then accelerated under a voltage of 1–30 keV and focused using electrostatic lenses. The focused ion beam impinges on the sample with an energy that is sufficient to extract atoms from the sample surface. This controlled etching allows to create trenches at nanometer precision; for an acceleration voltage of 30 keV, the resolution of FIB is around 10 nm.

The ion beam columns are often combined with scanning electron microscopes (SEM) to form DualBeam or Cross-Beam microscopes, which in turn can be equipped with other accessories to enable material deposition, moving objects, or for chemical or crystallographic characterization, all on the submicron scale.

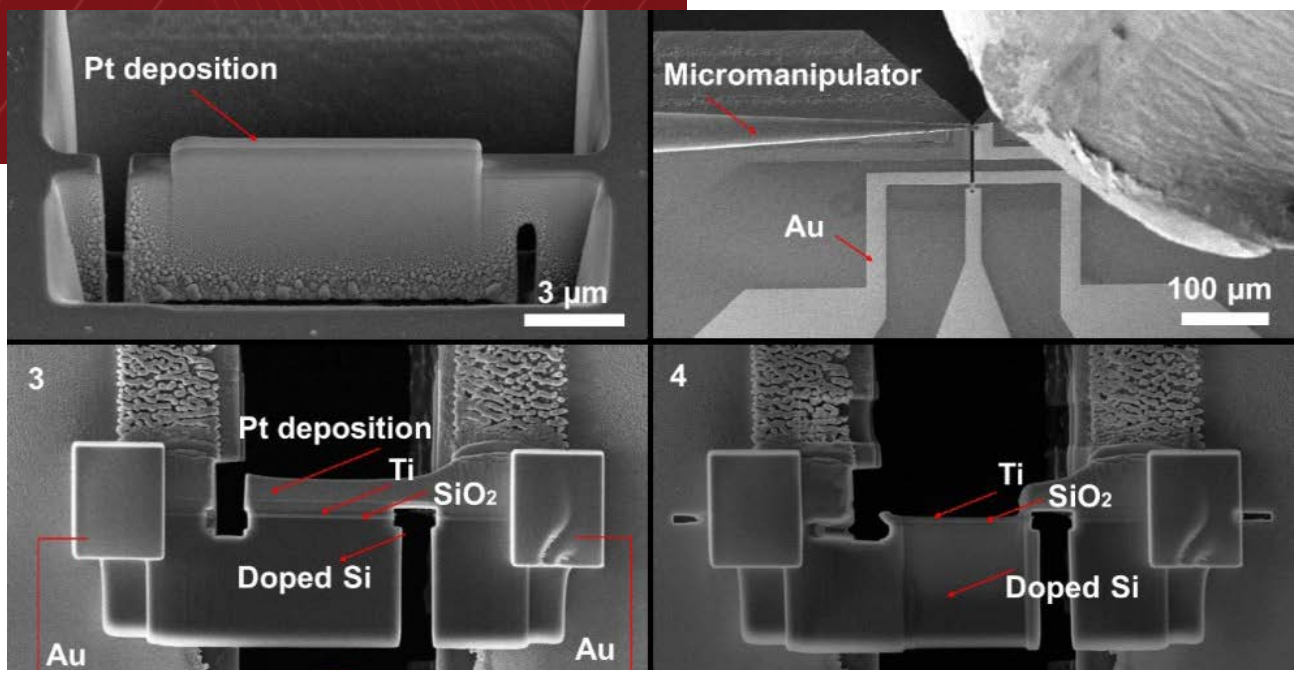
In CEMES, such machines are used on a daily basis to prepare ultrathin lamellas of different types of materials for TEM observation: semiconductors, metals, ceramics or glass. Moreover, the versatile nature of these microscopes allows them to be used in many different experiments including EDS or EBSD analysis, milling pillars and beams for in situ compression and bending tests, etching stencil networks on Si3N4 membranes, depositing metals at specified location for electrical contacting, etc…

Below are three examples of experiments that we carry out in CEMES using our Dualbeam ThermoFisher Helios NanoLab 600i FIB.



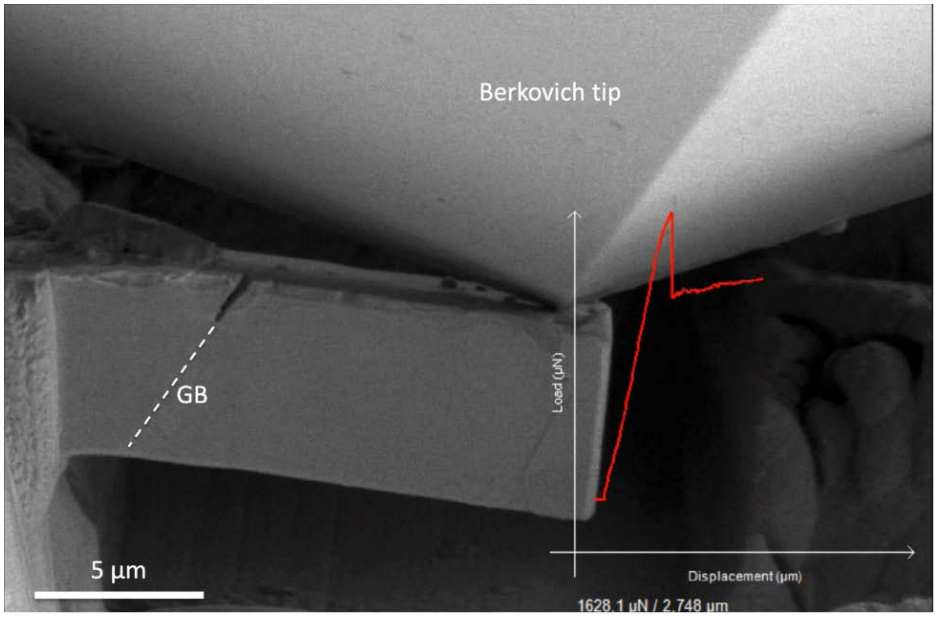
Preparation of thin lamellas for Transmission electron microscopy (TEM)

We use FIB to cut out a zone of a few µm² area of the sample, which is then lifted out with the help of a micromanipulator (photos 1 and 2). This relatively thick slice is pasted onto a support that is adapted to the TEM instrument (photos 3 and 4). The slice is then thinned down to tens of nanometer thickness to render it transparent to the electron beam of the TEM (photo 5).



Using FIB to prepare dielectric or ferroelectric nanocapacitors for operando electron holography in TEM

The preparation protocol is complex comprising the following steps: 1. Extracting the cross section, 2. Mounting it a Si_3N_4 support containing gold contacts, 3. Connecting the electrodes on the lamella to the gold contacts on the support, 4. Final thinning to make the lamella transparent to electrons.



In situ bending test on a steel beam

In situ bending test inside a FIB-SEM carried out on a micro-beam that was etched using ions and containing an oxidized grain boundary (GB). The superimposed red curve shows the force as a function of the displacement of a diamond tip (Berkovich Tip). We note that the force reaches a peak followed by a slip that corresponds to a rupture of the weak oxidized part of the boundary. This test was carried using the nanoindentor NMT04 from Femtotools.

CONTACT

Robin Cours
robin.cours@cemes.fr

CEMES - CNRS

29, rue Jeanne Marvig
BP 94347
31055 Toulouse Cedex 4
France

@cemes_cnrs

www.cemes.fr