Photoelectron emission microscopy of graphene systems

The Nanocharacterization Platform of MINATEC® center provides the simultaneous measurement of local work function, micron-scale band structure, and chemical state at high spatial and energy resolution for evaluation of graphene based thin films and devices using laboratory X-ray & UV photoemission electron microscopy (PEEM).

Contact: HoKwon KIM, hokwon.kim@cea.fr; Olivier RENAULT, olivier.renault@cea.fr


Study of graphene growth by CVD on Co substrates

- Synthesis of graphene on Co substrate at low temperature and atmospheric pressure.
- Investigation of growth mechanisms: complementary characterizations and in-situ analysis.

Contact: MAYNE-L’HERMITE Martine, martine.mayne@cea.fr

Graphene growth on cobalt substrate by APCVD at low temperature: investigations of synthesis parameters and growth mechanisms, O. Duigou et al., in preparation.
Graphene numbering and analysis

Electron Holography is used to precisely map the amount of Graphene layers at the nanoscale on a graphitic stack.

It can be coupled to various other TEM signals (HAADF - chemistry, EELS - spectroscopy, HREM - atomic resolution...) that are all available through existing TEM facility networks.

Contact: MASSEBOEUF Aurélien, aurelien.masseboeuf@cemes.fr

Surface electrostatic potentials in carbon nanotubes and graphene membranes investigated with electron holography, L. Ortolani et al., Carbon 2011, 49, 1423–1429
Tri-layer of graphene surrounded by potassium (KC\textsubscript{36})

Graphite intercalation compounds with potassium are a route to obtain graphene. By varying the excitation energy from UV to infrared, we observe resonance effects for KC\textsubscript{36} at 2.5 eV.
Unzipping and folding of graphene by swift heavy ions

Individual swift heavy ions were used to cut and fold graphene under grazing angle. The folded patterns have a length of several 100 nm. Defect creation in the graphene as well as the production of hillocks in the support, which push from below on the graphene, are necessary for the patterns.
Graphene synthesis, dispersion & functionalisation

TEM images of FLG (liquid exfoliation – collab. Anadolu Univ., TR) and graphene-like nanocarbons (CCVD synthesis) for functionalisation, dispersion studies, assessment of the environmental impact, toxicity, nanocomposites, nanoelectronics, sensors, etc.

Contact: FLAHAUT Emmanuel, Flahaut@chimie.ups-tlse.fr
P. Wick, E. Flahaut, L. Gauthier, M. Prato, A. Bianco, Angewandte Chemie, 2014, accepted
CVD growth of graphene on AlN templates on silicon

CRHEA works since 2010 on the CVD growth of graphene with propane on semiconductor substrates. One of the specificities of our method is the possibility to hydrogenate the graphene/SiC interface during growth, which finally allows to control and to improve the electronic properties of the graphene film. The good mobilities and the high uniformities of our graphene films allow to observe quantum Hall effect at the centimeter scale which is interesting for metrology.

Contact: Adrien MICHON, adrien.michon@crhea.cnrs.fr
Assessment of the Environmental impact of graphene

The potential environmental impact of graphene and nanocarbons in general is evaluated using different relevant biological models such as amphibian larvae, algae, or plants.

Contact: GAUTHIER Laury, laury.gauthier@univ-tlse3.fr
P. Wick, E. Flahaut, L. Gauthier, M. Prato, A. Bianco, Angewandte Chemie, 2014, accepted
CRHEA works since 2010 on the CVD growth of graphene with propane on semi-conductors substrates. Using an external carbon source allows to grow graphene on SiC, but also on sapphire or on AlN. This work shows the possible integration of graphene both in silicon and in III-nitrides technologies.

Towards arene nanoribbons by organic synthesis.

A new approach to extended arene-oligocarboxylic acid derivatives such as alkylesters and alkylimides has been developed. The carboxylic substituents allow the tuning of the electronic characteristics (donor or acceptor behaviour, band gap) as well as the solubility.

Contact: Fabien DUROLA, durola@crpp-bordeaux.cnrs.fr
Fluorination of graphene using either atomic or molecular fluorine

Fluorine chemistry to prepare graphene materials using exfoliation or fluorination/defluorination of fluorinated (nano)carbons

Contact: Nicolas BATISSE, nicolas.batisse@univ-bpclermont.fr
Organic nanomaterials and delivery

Design and development of new advanced carbon-based materials (carbon nanotubes, graphene, and adamantane) via their chemical functionalisation with different classes of molecules towards biomedical applications (i.e. therapy, imaging and diagnostics). Impact of these nanomaterials on health and environment.

Contact: ALBERTO BIANCO, a.bianco@ibmc-cnrs.unistra.fr


Growth of 13C graphene by high energy carbon implantation

The mechanism of thin layers graphite (TLG) synthesis on monocrystalline nickel films on MgO(111) has been investigated by $^{13}$C implantation followed by annealing at 600 °C. Carbon implanted may migrate either to the surface or to the interface according to the implantation energy.

Contact: Francois LE NORMAND, francois.le-normand@unistra.fr

Channel engineering of graphene transistors: nanomesh and strain

We explore two strategies of channel engineering to improve GFET performance: introducing a Graphene Nanomesh (GNM) section to open a bandgap or using a strained/unstrained junction to generate a transport gap. It allows enhancing strongly the \( I_{on}/I_{off} \) ratio and other parameters \( (g_D, f_{max}) \).
Single and bilayer graphene was grown by Si-flux assisted molecular beam epitaxy (MBE) on the C-face of SiC. The SiC substrate induces a strong doping by charge transfer, with a Dirac point located 320 meV (resp. 190 meV) below the Fermi level for monolayer (bilayer) graphene. An energy band gap is also observed, whose width is inversely dependent on the thickness.
The fabrication and RF characterization of graphene nanoribbon field-effect transistors are investigated. Graphene is obtained from the thermal decomposition of (0001) 4H-SiC. A structure with an array of GNR connected in parallel was fabricated by e-beam lithography. The best intrinsic current gain cut-off frequency of 60 GHz and maximum oscillation frequency of 30 GHz were achieved.

Contact: Pr. Henri HAPPY, Henri.Happy@iemn.univ-lille1.fr

Modelling doped and defective nanocarbon

DFT Modelling of new carbon nanostructures (cones, scrolls, fullerenes) to understand and control edge behaviour, defect structure, chemical tuning and new nanocarbon forms.

Contact: CHRIS EWELS, chris.ewels@cnrs-imn.fr  www.ewels.info

Low-energy termination of graphene edges via the formation of narrow nanotubes, Phys. Rev. Lett. 2011, 107, 065502

Graphene redox Chemistry

Controlling graphene-based electrode materials through chemical functionalisation to improve supercapacitance and Li-ion storage capabilities.
Chemically converted graphene

The researches conducted aim at synthesizing graphene from the oxidative exfoliation of graphite and then to study its reduction, functionalization and N-doping to produce samples of potential interest as catalyst (ORR) and Li-ion battery anode materials.
Growth and grafting of epitaxial graphene

The research deals with the optimization of the 6H-SiC sublimation protocol in order to achieve high-quality graphene samples for fundamental studies of the physical properties of graphene related to the functionalization with specific molecules and to the superconducting proximity effect.

Contact: G. BIDAN, gerard.bidan@cea.fr

Atomic scale study of graphene flower defects

Aberration corrected (AC) TEM imaging of flower-like defects formed inside a CVD grown large single crystal domain; low-pass filtered images (maximum filtered in insets) reveal a formation of isolated islands in combinations with several types of defects.

Contact: Hanako OKUNO, hanako.okuno@cea.fr
Reference 1: H. Okuno, P. Pochet, A. Tyurnina and J. Dijon, publication in preparation
Freestanding graphene monolayers are immune from substrate-induced perturbations, and allow investigations of graphene’s intrinsic properties. By means of spatially-resolved Raman spectroscopy, we have demonstrated that freestanding graphene layers are quasi-undoped and exhibit only small built-in strain, below 0.1%.

References:
1) S. Berciaud et al. Nano Letters (2009) 9, 346
3) S. Berciaud et al. Nano Letters (2013) 13, 3517
Epitaxy of MgO magnetic tunnel barriers on epitaxial graphene

AFM images of ferromagnetic (FM) electrodes after annealing and Au capping. (a) Fe, (b) permalloy and (c) Co. The smaller clusters are attributed to Au capping deposited at room temperature after annealing. The average mesa height is close to 30-35 nm as shown on profiles in insets. (d) Micro-Raman spectrum of graphene obtained on the sample with Fe, after annealing.

Contact: D. Halley (halley@ipcms.unistra.fr) & J-F Dayen (dayen@ipcms.unistra.fr)

References: F. Godel et al. Nanotechnology (2013) 24, 475708
Resist-Free fabrication of CVD graphene FETs

(a) Stencil mask pattern used to define the graphene device shape. 
(b) Optical image of the cross-bar shaped graphene device with width 30 µm and length 250 µm. 
(c) 2D Raman map showing the \( I_D / I_G \) peak ratio of the device central portion. 
(d) Magnetoconductance (\( \Delta \sigma (B) - \Delta \sigma (0) \)) curves of the device shown in (c) with at various temperatures.

Contact: Bernard DOUDIN, bdoudin@unistra.fr
References: A. Mahmood et al., to be submitted
Generating Long Supramolecular Pathways with a Continuous Density of States by Physically Linking Conjugated Molecules via Their End Groups, R. Shokri et al., JACS, 2013, 135, 5693.

STM investigation of the molecular fastener effect of TTF molecules deposited on Graphene, M.N. Nair et al., submitted.

Graphene-Molecule Interface

* A perfect substrate in order to obtain structurally and electronically homogeneous self-assembled molecular layers.

*Direct visualization of Molecular Orbitals.

*Possible doping of Graphene while preserving its electronic properties. Transfer of charge from/to molecule depending on its conformation.
Graphene functionalized by intercalation of Au

Modifications of the band structure of graphene while preserving its electronic properties:
*no doping
*increase of Fermi velocity
*extension of van Hove Singularity

Single Au atoms intercalate above Buffer layer. They decouple Graphene from SiC substrate and induce standing waves on Graphene.

Contact: Laurent SIMON, laurent.simon@uha.fr

High van Hove singularity extension and Fermi velocity increase in epitaxial graphene functionalized by intercalated Au clusters, M.N. Nair et al., PRB, 2012, 85, 245421.
Superlattice of resonators on ML graphene created by intercalated Au nanoclusters, M. Cranney et al., EPL, 2010, 91, 66004.
Reversible covalent chemistry for the exfoliation of graphene

Graphite is exfoliated in a variety of solvents using only a low-power sonication bath by using a reversible Diels-Alder cycloaddition that, unlike oxidation, does not generate permanent defects.
Graphene by PLD as a SERS platform

Diamond-like Carbon film grown by pulsed laser deposition has been converted to fl-graphene and further decorated with gold nanoparticles. The textured fl-graphene films with nanoscale roughness were highly beneficial for SERS detection. The detection at low concentration of a commercial pesticide was demonstrated.
Sp2 materials: from selection to growth mechanisms

Understanding possible strategies to select the sp2 sector of the configuration space of new 2D materials is of particular importance. This question has been addressed in the case of boron fullerenes for which the polymorphism lead to a glassy-like behavior in the potential energy surface.
Large Scale Production of Few Layer Graphene

A low cost, versatile catalytic fluidized bed CVD technique has been developed for the large scale production (10g/h on laboratory scale) of high quality few layer graphene (FLG) powder. The process can be adapted to produce CNT+FLG hybrids in the desired composition.

Contact: Serp, Philippe - philippe.serp@ensiacet.fr

Structural and optical properties of exfoliated h-BN layers

Top Left panel: Atomic Force Microscopy images of exfoliated h-BN layers on SiO₂

Top Right panel: Cathodoluminescence spectra of the same samples

Bottom Left panel: High Resolution Transmission Electron Microscopy image of an exfoliated BN sheet

Bottom Right Panel: Valence electron Energy Loss spectroscopy spectrum of the TEM sample.

Contact: LOISEAU, annick.loiseau@onera.fr

Atomic-scale study of graphene

Top panel: STS spectra and STM image of doped graphene with N

Bottom panel: Growth of graphene from Ni surface (Monte Carlo simulations)

Contact: LOISEAU, annick.loiseau@onera.fr


3D graphene network by CVD on nickel foam

Wt. percentages as high as 15 % of 3D multi-layers graphene networks have been produced from ethylene at 750 - 850°C. Such graphene masses largely exceed the weights corresponding to carbon solubility into nickel at these temperatures, involving the existence of a continuous mechanism of graphene formation.

Contact: Brigitte Caussat, Brigitte.Caussat@ensiacet.fr

Graphene-based Heterojunctions for Photovoltaics

2D materials present extraordinary sunlight absorption although transparent at the nanoscale. Such a high optical absorption with respect to the thicknesses involved makes this route appealing for energy conversion. We are interested in the recombination characterization and the modulation of the electronic properties in 2D heterojunctions.

Contact: Boutchich, Mohamed

Graphene sheets by liquid phase exfoliation for electrical contact applications

Graphene is a material with very high potential for technological innovation through its electrical, mechanical and thermal exceptional properties. Obtention of graphene sheets by liquid phase exfoliation has been known for some years; we are interested in tuning the exfoliation conditions to obtain sheets with dimensions and structural properties suitable for spray-deposition on the metallic substrates used for electrical contacts. Electrical properties are investigated at various scales.

Contact: Noel Sophie
We developed a new strategy to form thickness-adjusted and ultra-smooth films of very large and unwrinkled graphene oxide (GO) flakes. We also proposed a new localized reduction method of GO by electrogenerated naphthalene radical anions followed by selective functionalization of the patterns.
Flexible Gigahertz Transistors Derived from Solution-Based Single-Layer Graphene

We conducted the first study of solution-based graphene transistors at GHz frequencies, and show that graphene ideally combines the required properties to achieve high speed flexible electronics on plastic substrates. It demonstrates the advantages of graphene inks over printable organic materials.

Contact: Derycke Vincent, vincent.derycke@cea.fr
CVD Growth of Graphene on Platinum coated Si Wafers

CEA Liten is currently developing graphene growth on Si wafers using Pt coating. The objective is to develop a green technology with reusable substrate to make high quality graphene layer. We are making Single Layer Graphene at relatively low temperature (700°C) and are going to upscale the process in an industrial microelectronic reactor.
Reversible lithium storage capacities vs. cycle number for Fe2O3, GNs, Fe2O3/GNs and Fe2O3@C/GNs electrodes.

Contact: Jinbo Bai, jinbo.bai@ecp.fr

Synthesis and evaluation of carbon-coated Fe2O3 loaded on graphene nanosheets as an anode material for high performance lithium ion batteries, G. Wang, H. Wang, S. Cai, JT. Bai, ZY. Ren, JB. Bai, Journal of Power Sources, 239, 2013, 37-44
Quantum Hall Effect in mono-, bi-, and tri-layer graphene

By using high-magnetic fields (up to 60 T), we observe compelling evidence of the integer quantum Hall effect in trilayer graphene. The magnetotransport fingerprints are similar to those of the graphene monolayer, except for the absence of a plateau at a filling factor of $v=2$. 

Contact :ESCOFFIER Walter, walter.escoffier@lncmi.cnrs.fr
Unveiling the Magnetic Structure of Graphene Nanoribbons

We perform magnetotransport measurements in lithographically patterned graphene nanoribbons down to a 70 nm width. We bring evidence that the magnetic confinement at the edges unveils the valley degeneracy lifting originating from the electronic confinement. Quantum simulations suggest some disorder threshold at the origin of mixing between chiral magnetic edge states and disappearance of quantum Hall effect.
Magnetic fields for science

The LNCMI is one of the few large scale facilities in the world that generate high magnetic fields. They are used as a powerful experimental tool in physics, chemistry and biology.

Graphene and other two-dimensional materials are studied at the LNCMI with optical spectroscopy and electronic transport methods.

Contact: Marek POTEMSKI, marek.potemski@lncmi.cnrs.fr

Quantum Hall effect metrology in graphene

We explore the Hall resistance quantization accuracy, expected to be robust, even at $10^{-9}$, to develop a convenient quantum resistance standard operating in conditions accessible to industrial end-users ($B<4T$, $T>5K$). High quality material ($\mu>10000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, $n<10^{11}\text{cm}^{-2}$) is required on large area.

Contact: W. Poirier, wilfrid.poirier@lne.fr

QHE in exfoliated graphene with charged impurities: Metrological measurements, J. Guignard et al., PRB, 2012, 85, 165420
Monolayer epitaxial graphene on SiC(0001)

We directly demonstrate the importance of saturating the Si dangling bonds at the graphene/SiC(0001) interface to achieve high carrier mobility. Upon successful Si dangling bonds elimination, carrier mobility increases from $3000 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ to $>11000 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at $0.3 \, \text{K}$.
Graphene-capped InAs/GaAs quantum dots

Uncapped as well as capped graphene InAs/GaAs QDs have been studied. We gather from this that the average shifts $\Delta \omega$ of QDs Raman peaks are reduced compared to those previously observed in graphene and GaAs capped QDs. The encapsulation by graphene makes the indium atomic concentration intact in the QDs by the reduction of the strain effect of graphene on QDs and the migration of In atoms towards the surface.

Contact: Ali MADOURI - ali.madouri@lpn.cnrs.fr

Improved efficiency of graphene transferred on hetero structures of InAs/GaAs quantum dots. R. Othmen1, K. Rezgui, A. Cavanna, H. Arezki, F. Gunes, H. Ajlani, A. Madouri, M. Oueslati. Accepted at JAP
Epitaxial Graphene on SiC(0001) Grown under Nitrogen Flux: Evidence of Nitrogen-Doped Graphene

The Nitrogen-doped graphene exhibits large n-type carrier concentrations of about 4 times more than what is found for pristine graphene. This in-situ doping method is highly attractive for the efficient incorporation of doping species into the graphene lattice.

Contact: Abdelkarim OUERGHI, abdelkarim.ouerghi@lpn.cnrs.fr
Scanning tunneling microscopy of doped graphene

Scanning tunneling spectroscopy is used to probe the electronic structure of graphene at the atomic scale. On nitrogen doped graphene, the shift of the Dirac point and the formation of localized states has been revealed.

In-place, transfer-free, low-temperature, (nano)graphene layers growth

Pioneer of the synthesis of graphene at the interface between a catalytic metal layer and the substrate, NanoMaDe team at LPICM succeed to obtain centimeters scale, uniform nanocrystalline-graphene layers at temperatures as low as 250°C on various substrates including glass. The synthesis capacity will be extended in 2014 to substrates up to 4 inch.

Contact: Costel Sorin COJOCARU, costel-sorin.cojocaru@polytechnique.edu

Carbon 66 (2014) 1-10; Nanotechnology 23 (2012) 265603; Nanotechnology 22 (2011) 085601

Epitaxial graphene nano-ribbon ballistic transport

Nanoribbons 40nm wide epitaxially grown on sidewalls of silicon carbide are single-channel room temperature ballistic conductors on a length scale greater than 10µm, owing to their annealed smooth edges. Transport is dominated by two modes, possibly reflecting ground state properties of neutral graphene.
First direct observation of a nearly ideal graphene band structure

ARPES (Angle Resolved Photoemission Spectroscopy) measured band structure of a 10-layer C-face graphene grown on the 6H-SiC. The sample temperature is 6K. Three linear Dirac cones are visible corresponding to the outermost decoupled graphene sheets.

Contact: A. Taleb Ibrahimi - amina.taleb@synchrotron-soleil.fr
Nitrogen doping of graphene is of great interest for both fundamental research to explore the effect of dopants on a 2D electrical conductor and applications such as lithium storage, composites, and nanoelectronic devices. The electronic properties of graphene are modified thanks to the introduction, during its growth, of nitrogen-atom substitution in the carbon honeycomb lattice.

Contact: F. Sirotti fausto.sirotti@synchrotron-soleil.fr

Epitaxial Graphene on 4H-SiC(0001) grown under Nitrogen flux: evidence of low Nitrogen-doping and high charge transfer.
Velez-Fort, E. et al., ACS Nano, 2012, 6(12), 10893–10900
Increasing graphene production up to industrial scale

The exceptional electrical properties of graphene have been discovered only 5 years ago, but today the yield of total production of different types of graphene is greater than 15 tons per year. Scientists have created single large polycrystalline graphene sheets by a simple synthesis method and comprehensively characterized them using “Nano Angle Resolved Photoelectron Spectroscopy”.

Contact: J. Avila jose.avila@synchrotron-soleil.fr

Superconducting graphene grown on Rhenium

A very efficient way to induce superconductivity in graphene consists in growing it directly on top of rhenium, a superconductor below 2K. Scanning tunneling microscopy and spectroscopy performed at 50 mK unveiled a moiré pattern and a homogeneous superconducting state.

Contact: CHAPELIER Claude, claude.chapelier@cea.fr

Graphene devices
Towards high frequency electronics & optoelectronics

Thales R&T, Palaiseau, France

Collaborations

Concentric transistors

Dual gate transistors

Towards high frequency devices

Funding

Contact: Pierre.Legagneux@thalesgroup.com
Graphene spintronics

Spintronics is a paradigm focusing on electrons spin as information vector. Two properties of graphene are particularly promising for spintronics: the transport of spin information with high efficiency and the passivation of ferromagnetic electrodes against oxidation.

Contact: Pierre SENEOR, pierre.seneor@thalesgroup.com

Highly efficient spin transport in epitaxial graphene on SiC, Dlubak B., Martin MB et al., Nature Physics, 2012, 8, 557

Graphene-passivated nickel as an oxidation-resistant electrode for spintronics, Dlubak B., Martin MB et al., ACS Nano, 2012, 6, 10930
Reactivity of carbon multivacancies in graphene studied with the DFT method.

Periodic DFT calculations have been performed to study the reactivity with respect to atmospheric oxidants (O$_2$, H$_2$O, O$_3$ and atomic oxygen) of multivacancy structures created in graphene sheet by removing adjacent carbon atoms (illustration here with the adsorption of O$_2$ on a trivacancy site).

Contact: PICAUD Sylvain, sylvain.picaud@univ-fcomte.fr

Synthesis of few-layer graphene by solvothermal reaction

This work aims for the synthesis of large few-layer graphene (FLG) samples by a solvothermal reaction between ethanol and sodium, then a pyrolysis\(^1\). The material obtained is a mixture of amorphous carbon and FLG. The influence of some reaction parameters on this material is studied.

Left: TEM micrograph of the few-layer graphene obtained (incident beam 80 keV)
Right: EFTEM micrograph (mode zero-loss) of the same sample (incident beam 80 keV)

Contact: Sébastien FONTANA, sebastien.fontana@univ-lorraine.fr

Reversible optical doping of graphene

Charge carrier density of graphene exfoliated on a SiO₂/Si substrate is finely and reversibly tuned between electron and hole doping with visible photons. This photo-induced doping happens under moderate laser power but requires hydrophilic substrates and vanishes for suspended graphene.

Contact: Erik DUJARDIN, erik.dujardin@cemes.fr

Transport in perfect edged graphene nanoribbons

Using a scanning tunnelling microscope, the electronic structure of a long and narrow graphene nanoribbon, which is adsorbed on a Au(111) surface, is spatially mapped and its conductance then measured by lifting the molecule off the surface with the tip of the microscope.

Contact: Christian JOACHIM, joachim@cemes.fr

Voltage-dependent conductance of a single graphene nanoribbon, M. Koch, F. Ample, C. Joachim, L. Grill
Nature Nanotechnology 2012, 7, 713-717
Integrated graphene nanoribbon electronics

Intrinsic electronic properties of graphene nanoribbons are obtained by patterning suspended graphene into crystalline edged nanoribbons with a new non-amorphizing non-contaminating e-beam induced etching technique.

Contact: Erik DUJARDIN, erik.dujardin@cemes.fr