Miniworkshop:
Graphene technology for particle physics

Graphene
@ ISOM-UPM

CIEMAT, 13 November 2017

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Group members





- ***Dr. Fernando Calle, Full Professor, Dpto. Ing. Electrónica, ETSI Telecomunicación***
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- ***Dr. Jorge Pedrós, Distinguised Prof. Ramón y Cajal, Dpto. Ing. Electrónica, ETSI Telecomunicación***
- ***Dr. Fátima Romero, Ass. Prof. Juan de la Cierva, Dpto. Ing. Electrónica, ETSI Telecomunicación***
- ***Dr. Alberto Boscá, Ass. Prof., Dpto. Ing. Electrónica, ETSI Telecomunicación***
- ***Antonio Ladrón de Guevara, PhD student, Dpto. Ing. Electrónica, ETSI Telecomunicación***
- ***Rajveer Fandan, PhD student, Dpto. Ing. Electrónica de ETSI Telecomunicación***
- ***Jaime Orellana, Master student, Industrial Design***
- ***Andrés Velasco, Master student, Ing. Materiales***




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Research lines at ISOM-UPM

- **Energy and Environment**
  - *Supercapacitors*
  - *Solar cells*
  - *Illumination*

- **Information and Communication**
  - *Plasmon resonators*
  - *GFET sensors*
  - *G/III-V circuits*

- **Health**
  - *Biosensors*
  - *Transparent electrodes*
  - *Tissues and implants*

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Timeline: Six Year Plan

www.isomgraphene.es

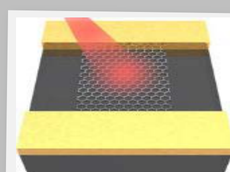
2011 | 2013 | 2015 | 2016 | 2017 | **2018** | 2019 | 2020 | 2021 | 2022 | 2023

2018
Graphene@
ISOM-UPM

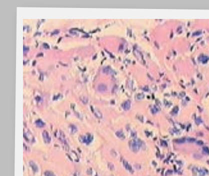
MATERIAL	3D growth	2D growth, laser RGO	2D CVD, LRGO, GNP , 3D foams
PROCESSING	Functionalisation	+ 2D transfer, graphene/III-V	+ Integration, flexible substrates
ASSESSMENT	Electrochemical	Electrical, Optical	Mechanical, Structural
Application	ENERGY	ENERGY+ICT	ENERGY+ICT+HEALTH

01
Supercapacitors
Solar cells
Illumination

02
Plasmon sensors
GFET sensors
Graphene on GaN

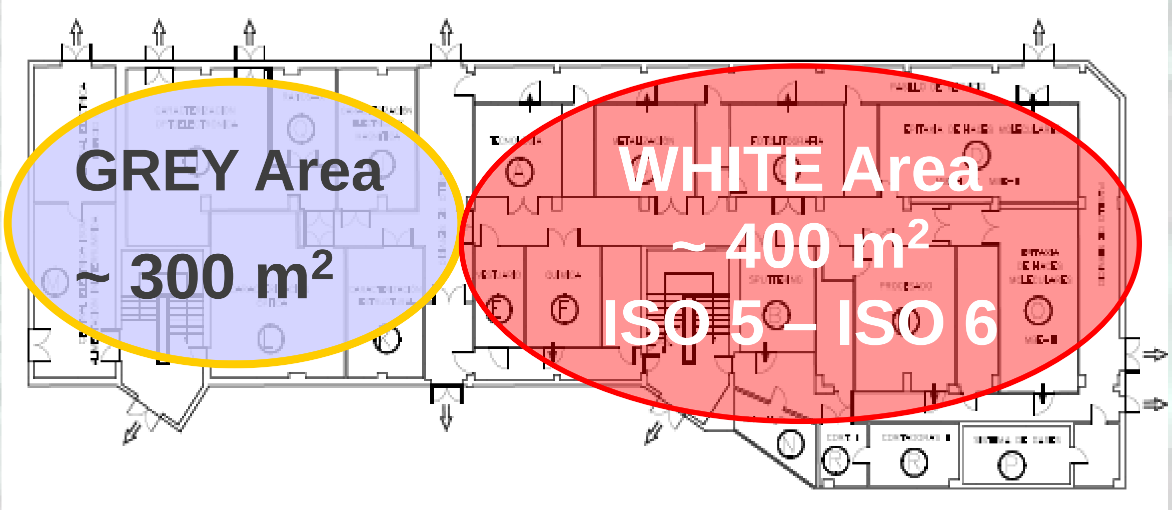


03
Biosensors
Electrodes
Tissues & implants



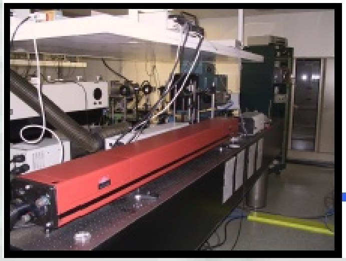
CT-ISOM

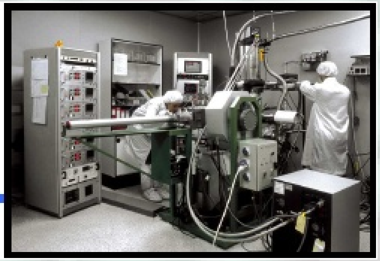
CEI Moncloa



- **Structural characterization labs**
  (HR-XRD, AFM, SEM, Nomarsky)
- **Optical characterization lab**
  (PL, CL, FTIRS, OSA, IF profiler)
- **Electrical/device characterization labs**
  (HF/HP/HT probe stations, VSM, etc)

- **Graphene PE-CVD system**
- **4 MBE systems (III-V)**
- **3 Sputtering ch. (AlN, metals)**
- **6 Joule and e-beam metallizers**
- **CVD system (SiO_2, SiN)**
- **ICP and RIE system, Ar miller**
- **Photo and e-beam lithography**

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Graphene: equipment and facilities

- **Growth**
  - ***PE-CVD (Aixtron BlackMagic Pro)***
  - ***Photoexfoliation*** *(laser reduction)*

- **Processing in ISOM Clean Room**

- **Characterisation**
  - ***Electrical: high frequency, high V-I-P, low-to-high T***
  - ***Structural: FE-SEM, HR-XRD, AFM, etc.***
  - ***Optical: Nomarsky, FTIRS, Raman, etc.***
- **Modeling**

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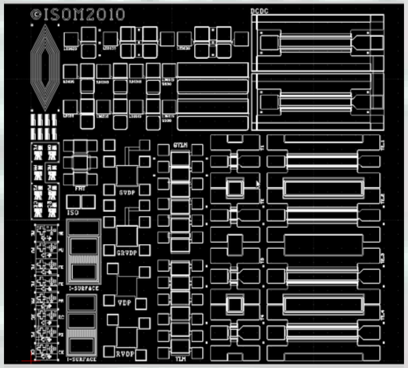
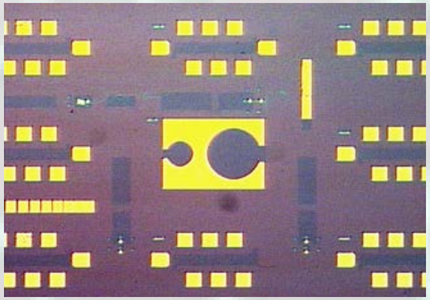
Lithography

- **Photolithography**

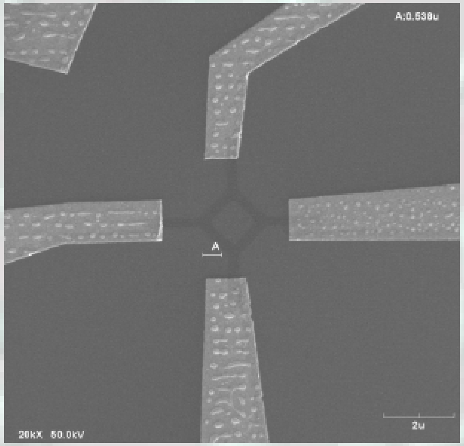


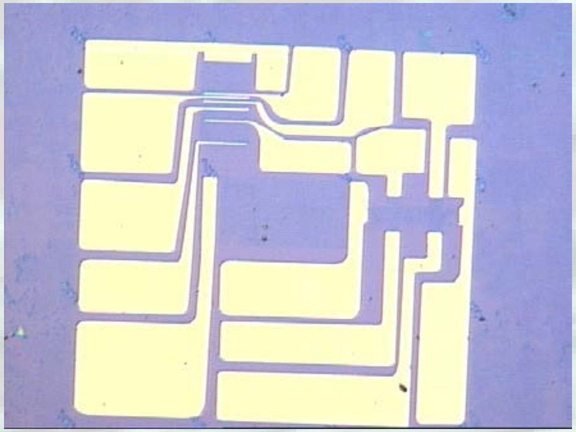
Mask design



Lithography and metallization

- **E-beam lithography**





CRESTEC CABL-9500C
50 KeV e-beam-SEM , 10 nm lithography resolution

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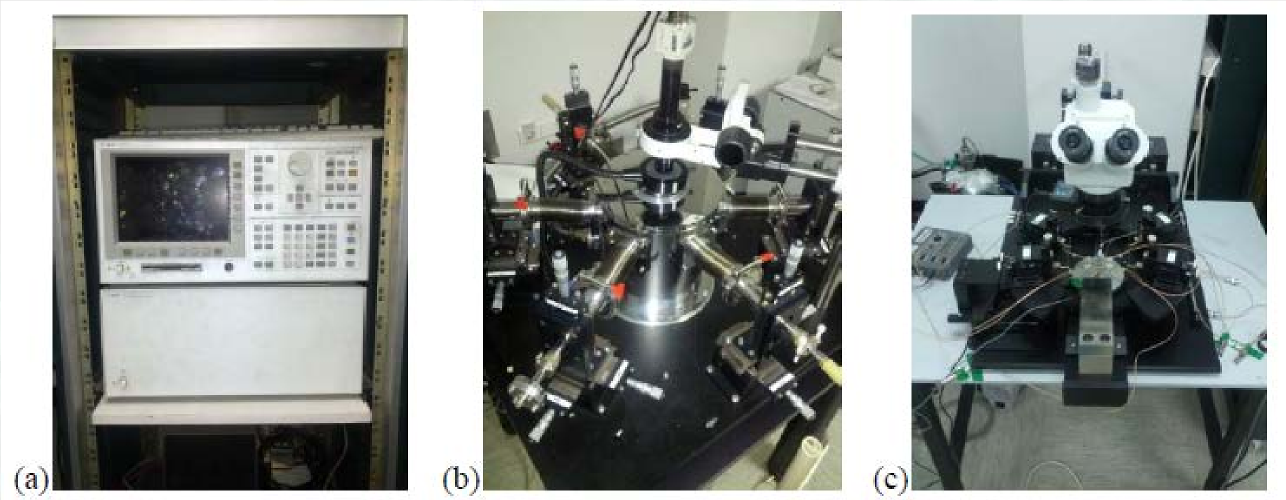
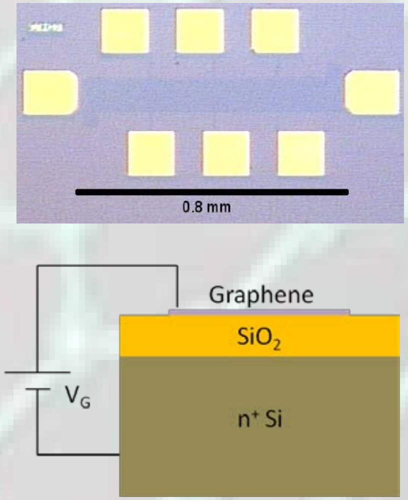
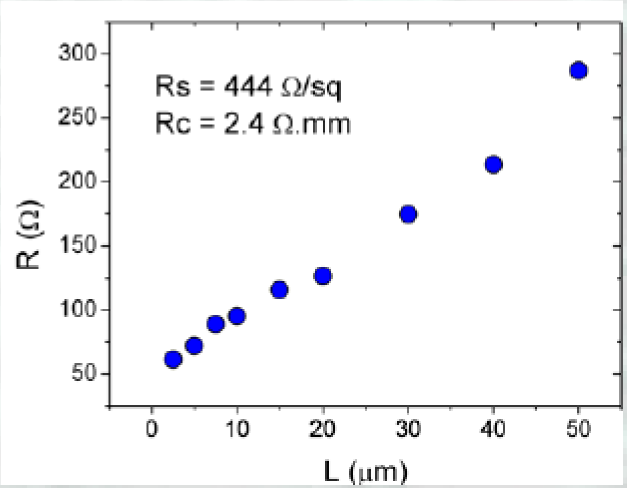
Electrical characterization

Equipment: high frequency, high V-I-P, low-to-high temperature

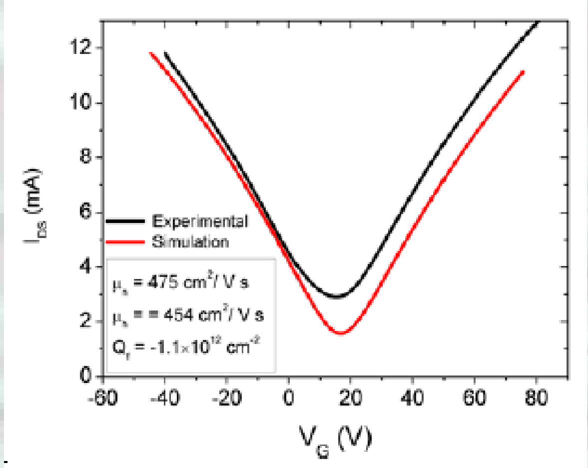




Sheet and contact resistance



Dirac threshold, conductivity



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Projects

- ***Advanced Semiconductor Devices for a Rational Use of Energy, RUE.***
MINECO, Consolider CSD2009-00046 (2010-2015)

- ***Acoustic Waves on Graphene***
PICATA Program, CEI Moncloa (2012-14)

- ***Graphene-based energy storage for EV, SAVE***
Programa Inspire, REPSOL (2012-15) (in col. with ICMM-CSIC, INCAR-CSIC, UCM)

- ***Graphene for energy generation and storage, GRAFAGEN***
MINECO, ENE2013-47904-C3 (2014-2017) (in col. with CIEMAT)

- ***Dynamic electromechanical control of nanostructures by acoustic fields, SAWTrain***
H2020 MSCA ITN 642688 (2015-2019) (coord. P. Santos, PDI Berlin)

- ***Automatic Transfer of 2D Materials to Flexible Substrates and Benchmarking as Chemical Sensors***
MISTI Global Seed Funds (2016-2017) (in col. with MIT, USA)

- ***Graphene NANOcomposites REActors at preindustrial Technology readiness, nanoGREAT***
KIC-EIT Raw Materials. (2016-2018) (coord. M. Zen, FBK-U. Trento)

- ***Graphene-macrophage biomaterials: functional characterization for the use in cardiovascular pathologies***
Fundación Ramón Areces (2017-2019) (in col. with IIB-CSIC/UAM)

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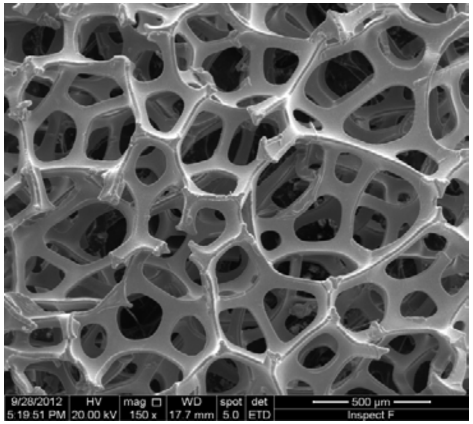
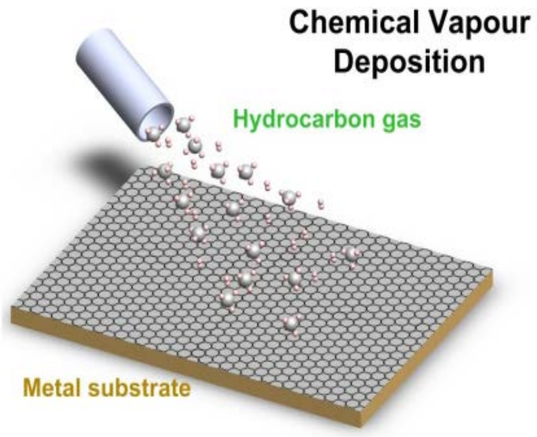
Graphene: growth and processing

Growth
- 2D sheets
- 3D foams

J. Pedrós et al, CVD 3D XXX 2018
A. Boscá et al., CVD 2D XXX 2018
A. Ladrón de Guevara et al, LRGO XXX 2017



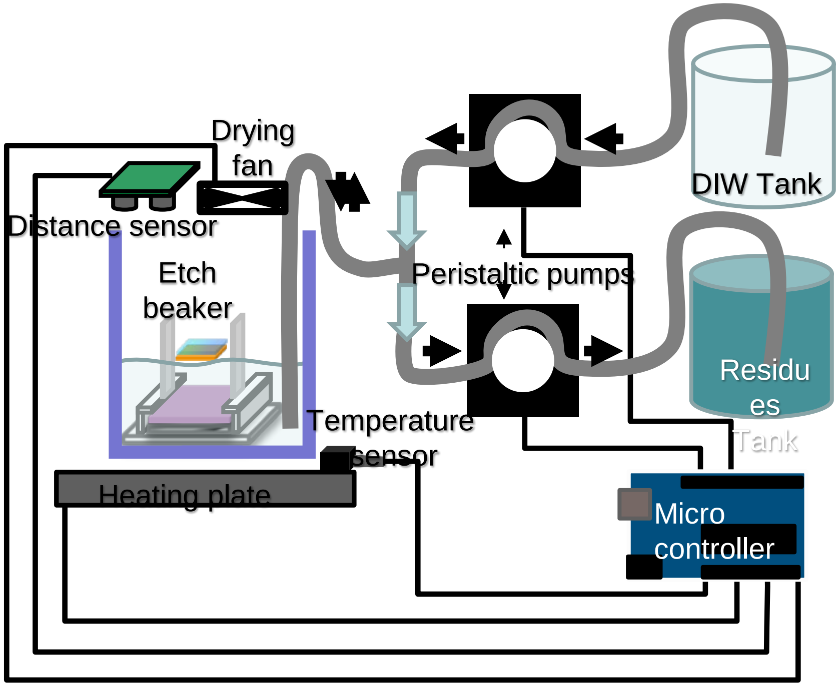


Functionalisation
- Polymerisation
- Electrodeposition

J. Pedros et al. (ISOM), Patent nr. EP14382428.2
V. Barranco et al., Patent EP16382227.3-1375 (2017)
V. Barranco et al., Direct etching foams, XXX (2018)

Automatic transfer
- Self-centering system
- Liquid flow control
- Etch control with temperature

A. Boscá, J. Pedrós, J. Martínez, T. Palacios, F. Calle
Patent ES 2 536 491 B2; PCT/ES2014/070859
A. Boscá et al., Sci.Reports 2016



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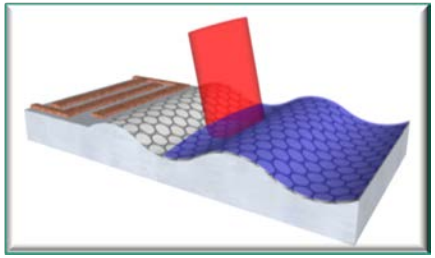
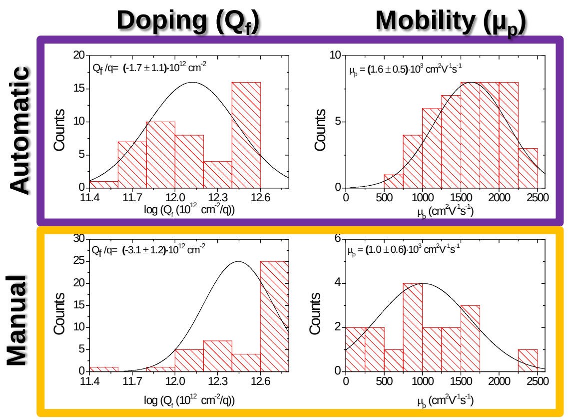
Graphene: applications

ICT

- plasmonic structures
- GFET sensors
- G on GaN-HEMT



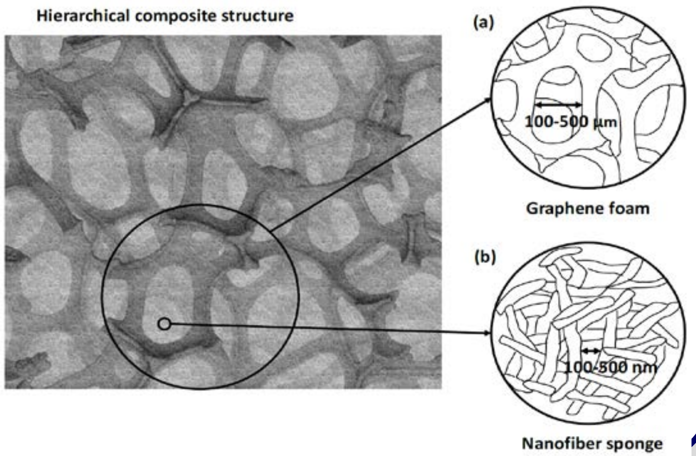
J. Schiefele, J. Pedrós, F. Sols, F. Calle, F. Guinea, Phys. Rev. Lett. (2013)
A. Boscá, J. Pedrós, J. Martínez, T. Palacios, F. Calle, J. Appl. Phys. (2015)
F. Romero, A. Boscá, J. Pedrós, J, Martínez, T. Palacios, F. Calle,EDL (2017)



Energy

- supercapacitors
- batteries

M. Tadjer et al (2014), D.J. Choi et al. (2016)
S. Ruiz et al. (ISOM), Diamond Rel. Mat (2015)
J. Pedros et al. (ISOM), J. Power Sources (2016)
J. Pedros et al. (ISOM), Patent nr. EP14382428.2



Health

- biosensors
- biocompatibility
- tissue implants and regeneration

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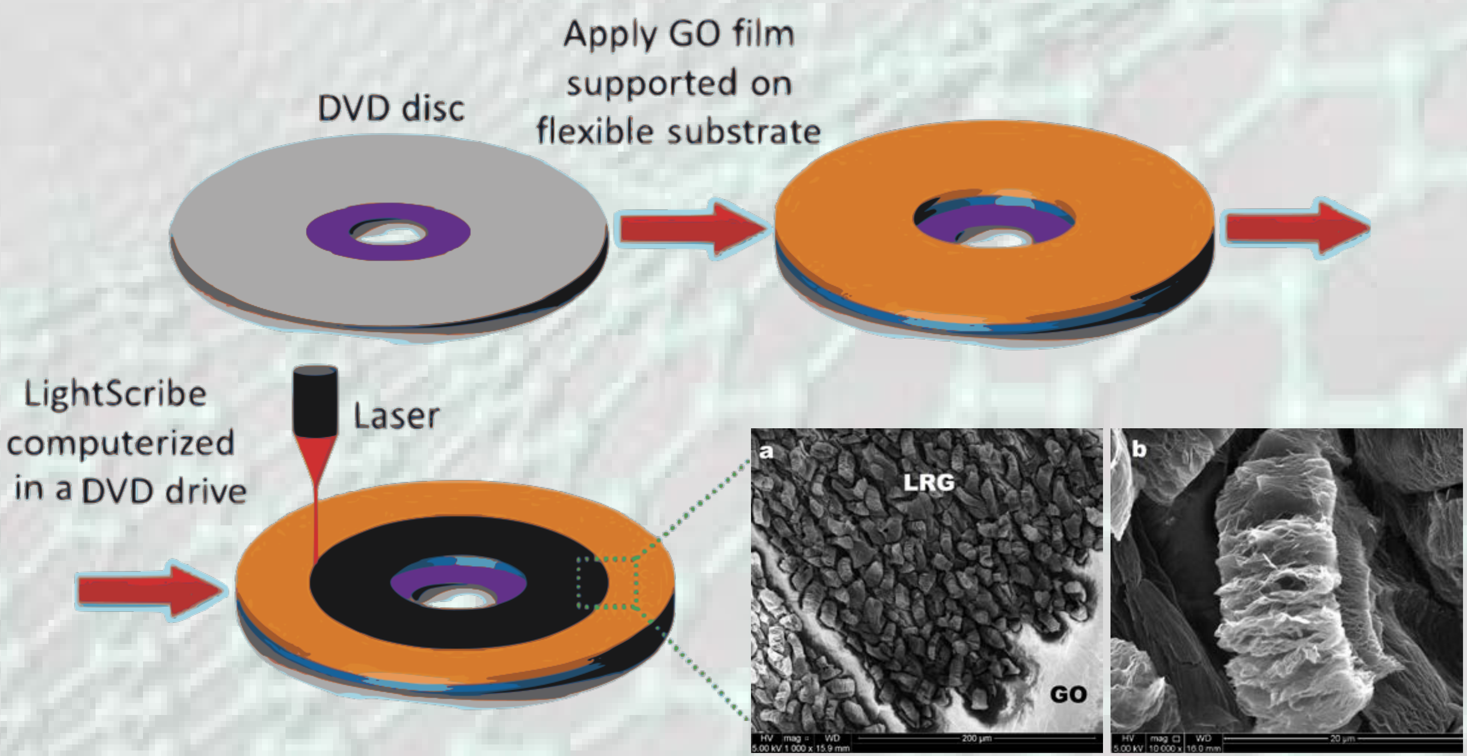
LRGO-based energy storage



- **Supercapacitors electrodes based on LRG**
  - ✓ Good electronic conductivity (< 1 KΩ/sq)
  - ✓ Large and accessible specific area (1520 m^2/g) [1]
  - ✓ Open network accessible for the electrolyte

$C_{esp\ LRGO} \approx 82$ F/g

(ESR ≈ 400 Ω)

[1] M.F. El-Kady, R.B. Kaner, Nature communications (2013)

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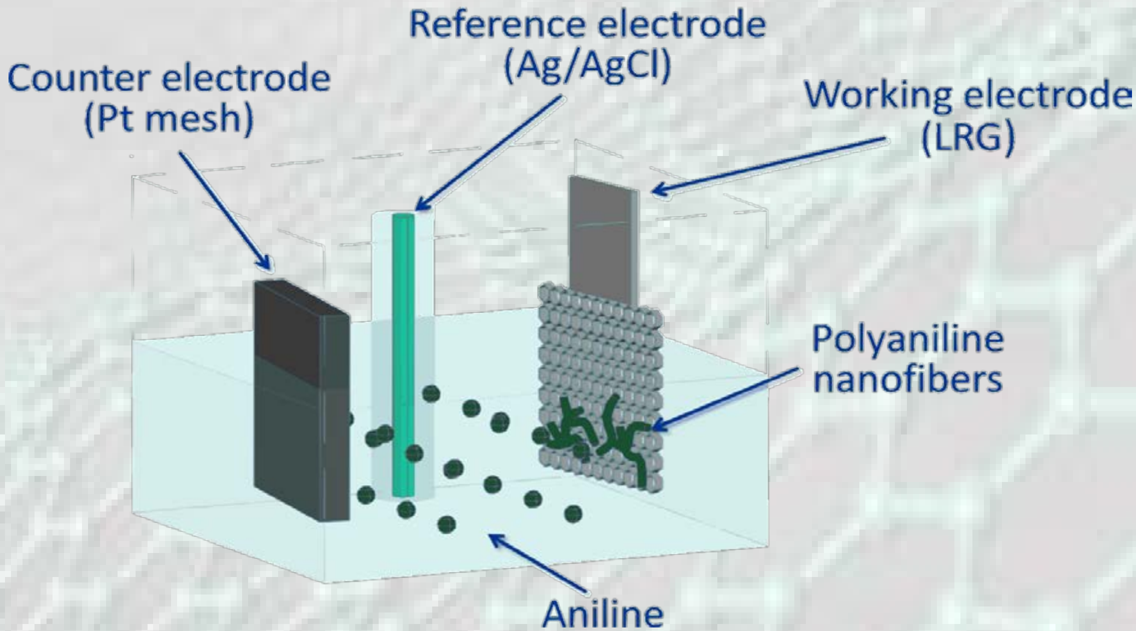
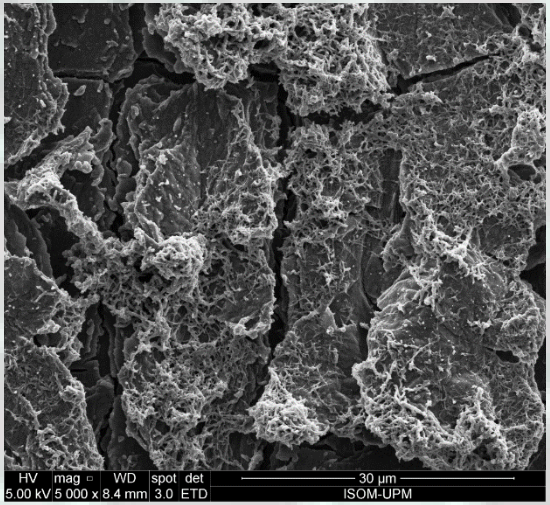
LRGO - PANI Supercapacitors





LRGO:
Light weight
High conductivity

+

PANI
Large specific area
High pseudocapacitance

=

$C_{esp\ LRGO\_PANI} \approx 440$ F/g

ESR ≈ 10 Ω

⇨ PANI nanofibers / LRGO flakes composite:

outstanding material for high-performance electrochemical capacitors

[1] A. Ladrón de Guevara et al. (ISOM, to be published

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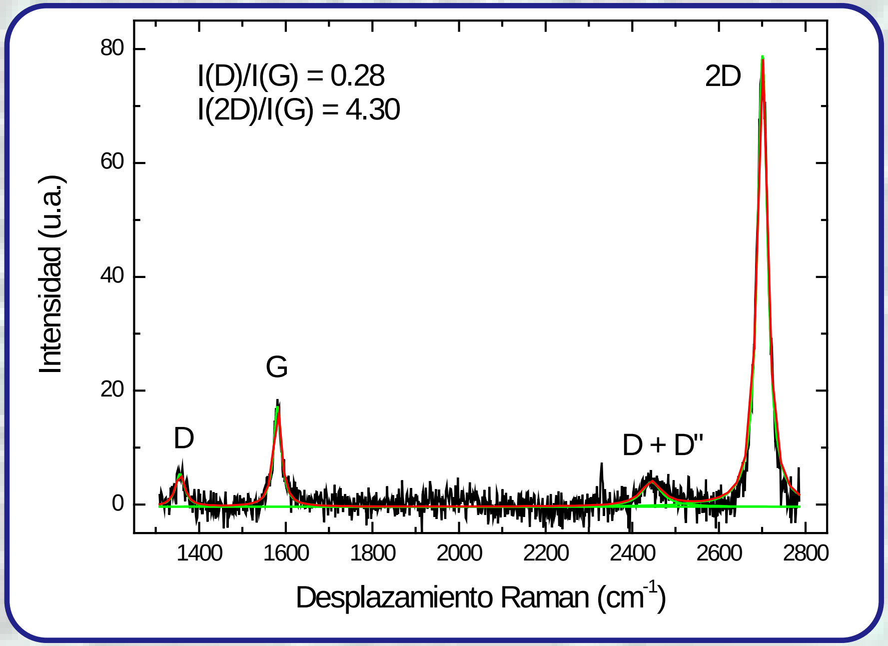
CVD of single layer graphene

Growth optimisation

- Wafer substrates of Cu foil and Cu/SiO2/Si(111), 4 inches
- Narrow growth window, around 935ºC @ 25 mbar
- Gas mixture: Ar: H2: CH4 (C2H2)
- ➢ Result: single layer graphene, defect free



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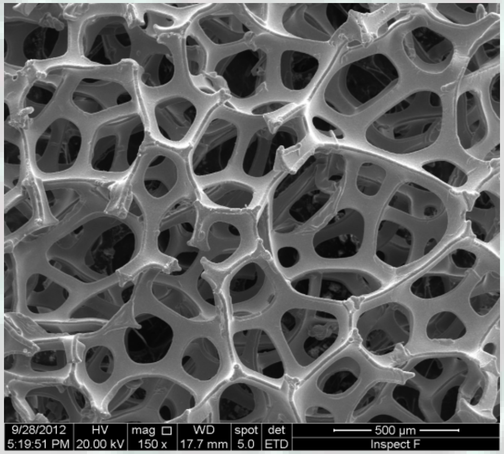
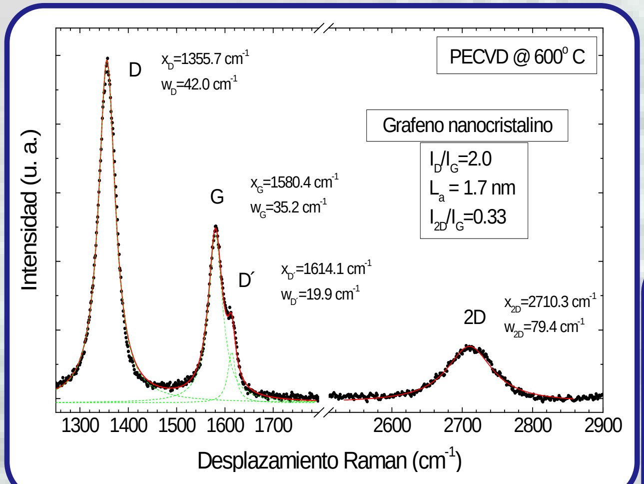
PECVD on metal foams: Raman

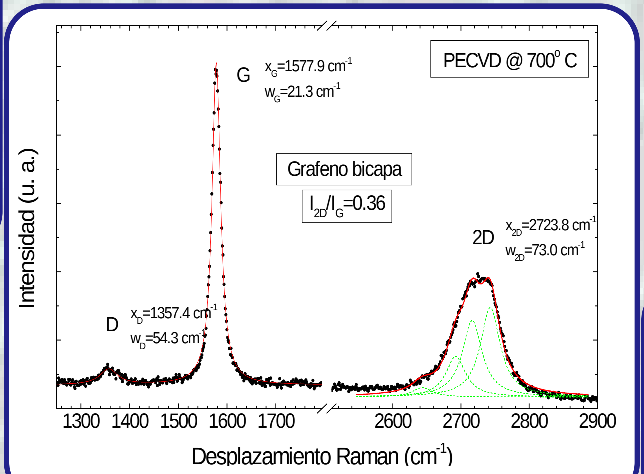
Optimization of graphene on Ni foams



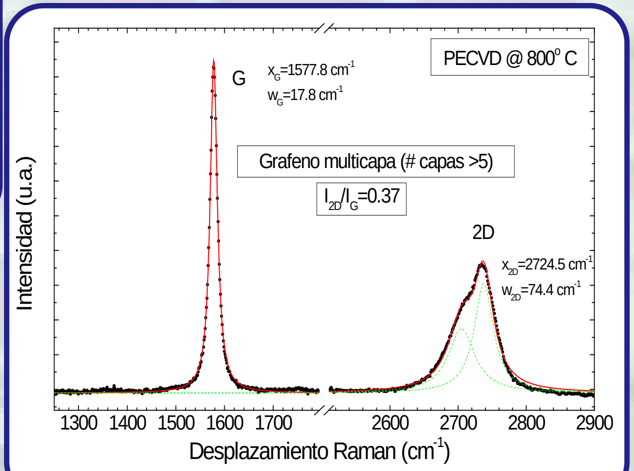
PECVD, 600ºC



PECVD, 700ºC



PECVD, 800ºC



- 600ºC: nanocrystallites
- 700ºC: BLG
- 800ºC: FLG (>5 layers)

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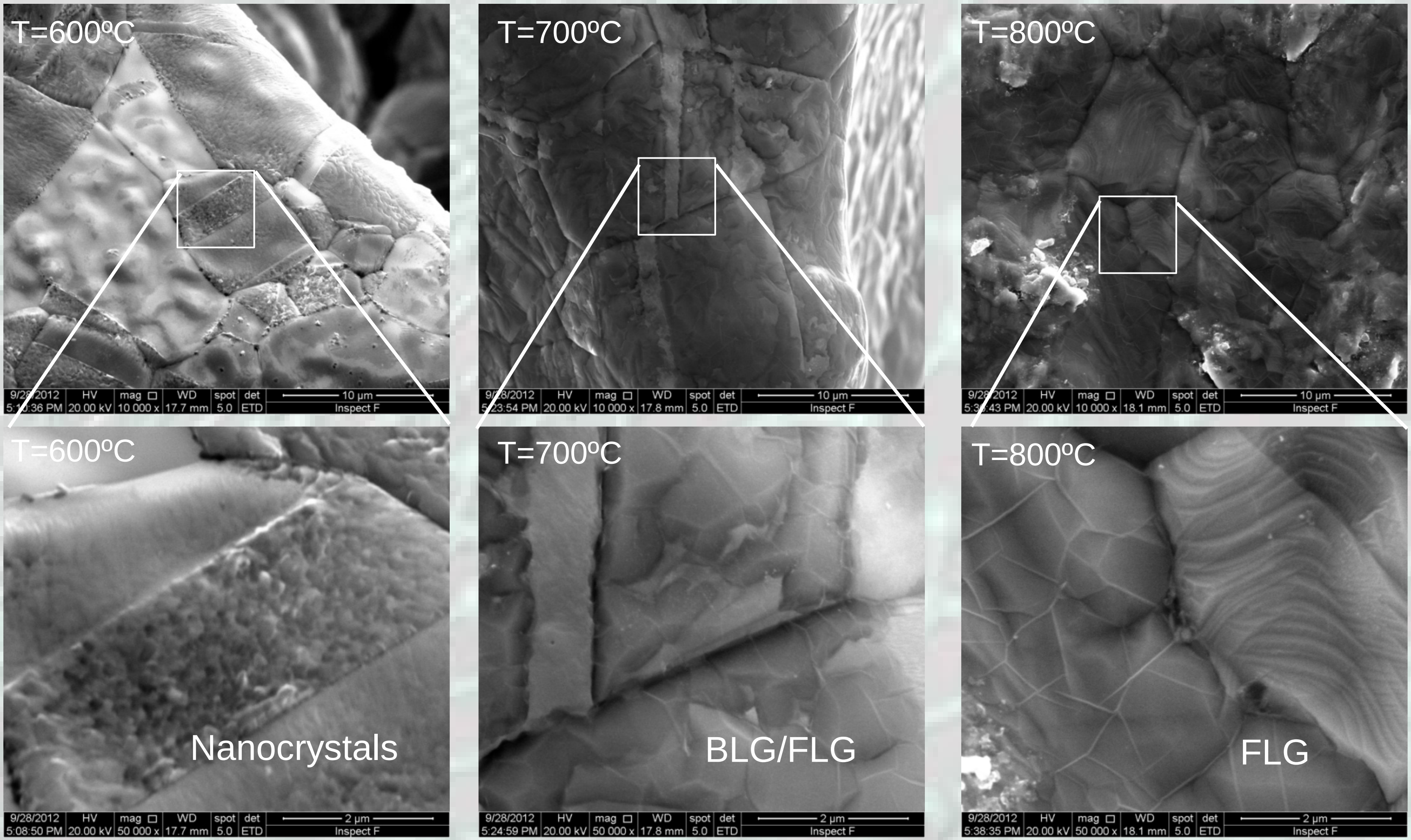
PECVD on metal foams: SEM

Optimization of graphene on Ni foams: SEM



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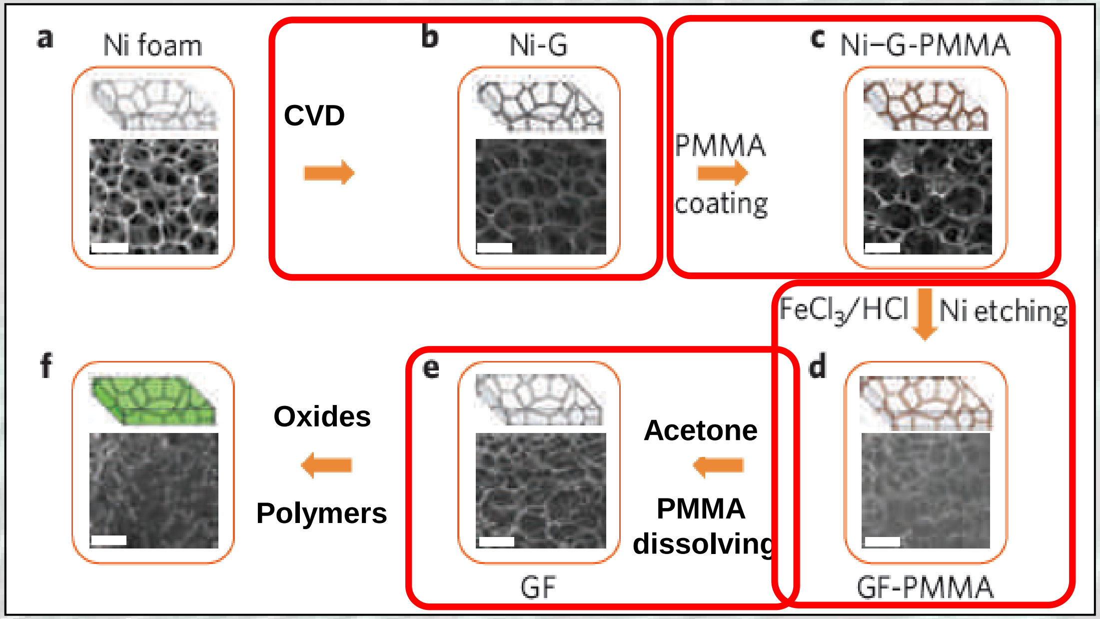
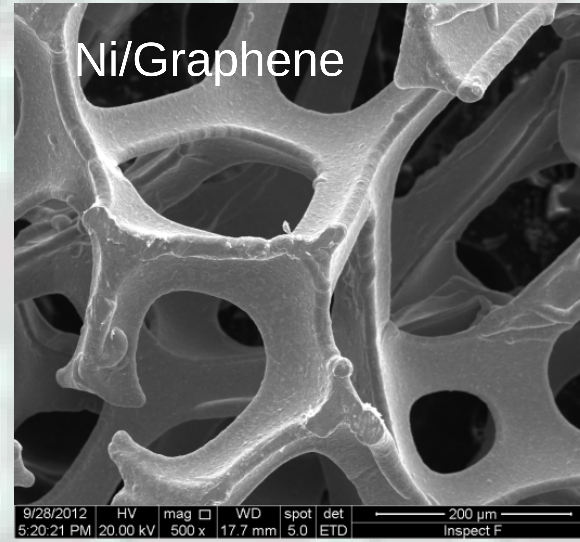
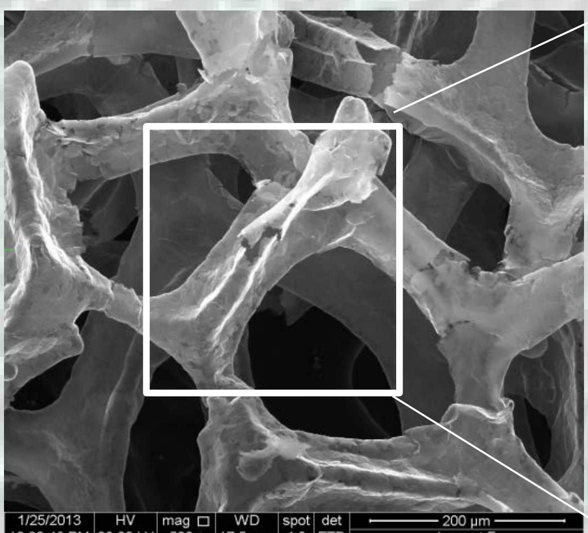
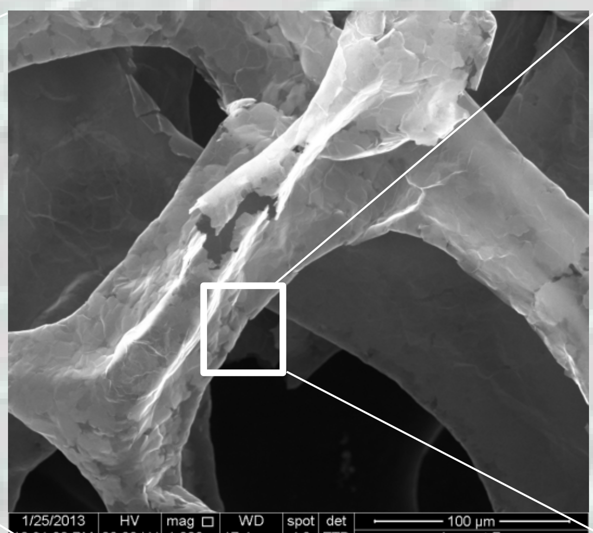
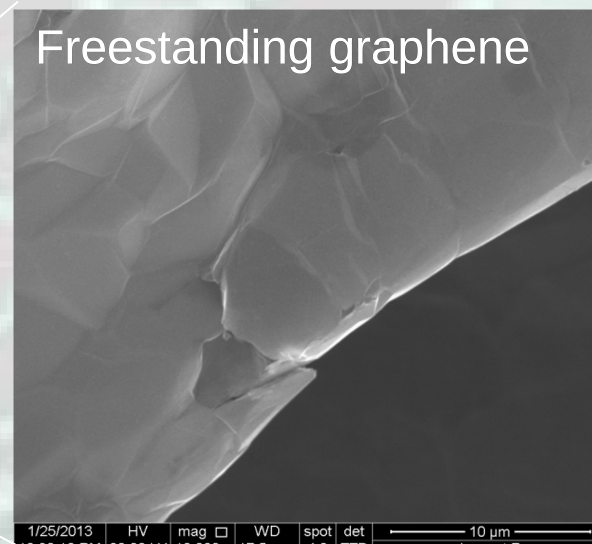
Free-standing graphene network











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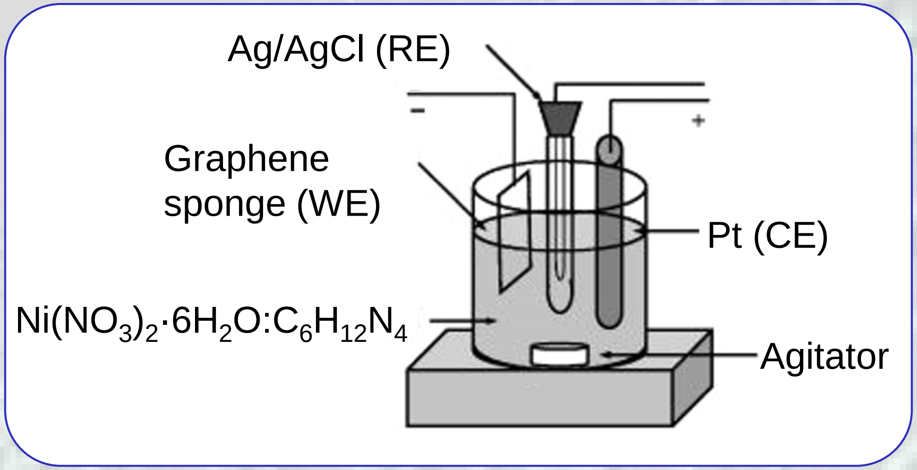
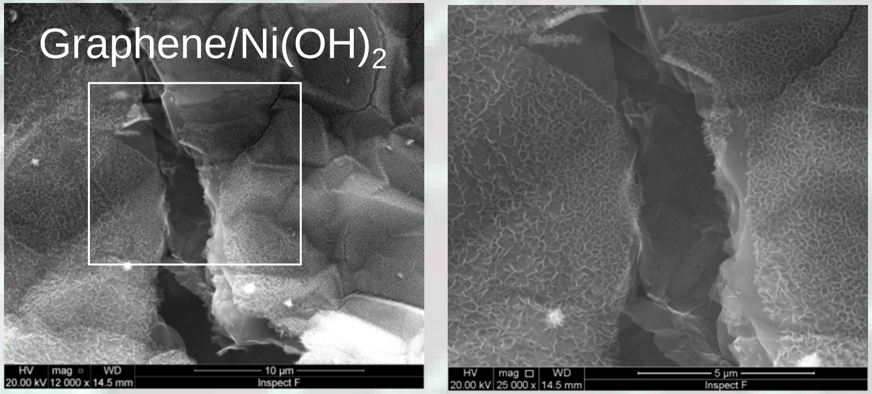
Functionalization procedures

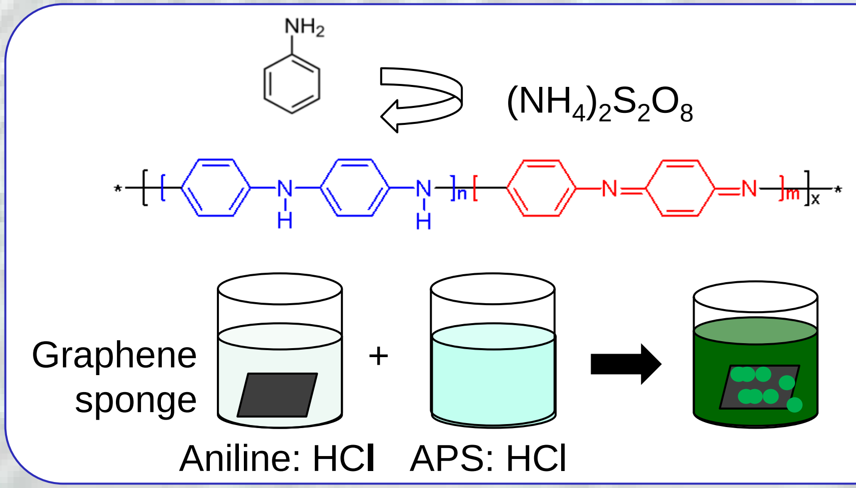
(A) Oxides: electrodeposition ($Ni(OH)_2$) or sol-gel (MnO_2)

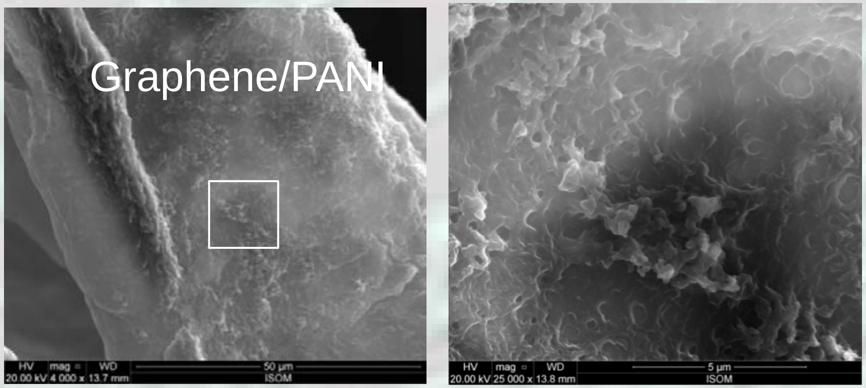




S. Ruiz *et al.* (ISOM), Diamond Rel. Mat (2015)

(B) Polymers: In-situ polymerisation or electrodeposition: PANI





J. Pedrós *et al.* (ISOM), J. Power Sources (2016)

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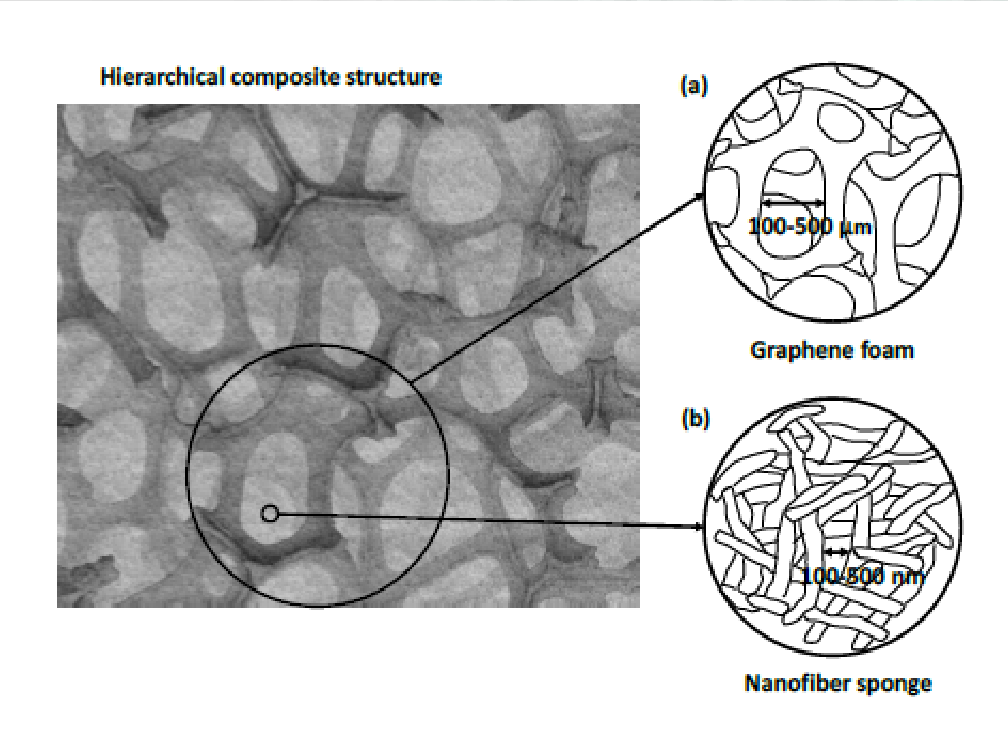
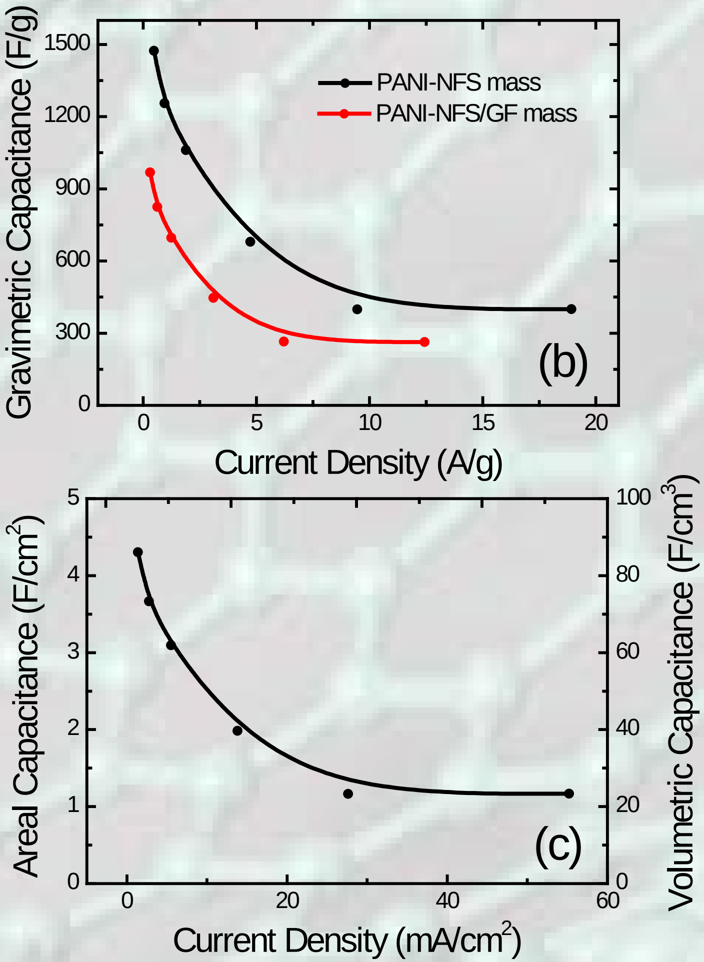
G Foam - PANI Supercapacitors





- ☑ Large specific & volumetric capacitance
- ☑ Electrode with integrated collector
- ☑ Good cyclability

J. Pedrós, A. Boscá, J. Martínez, F. Calle, S. Ruiz-Gómez, L. Pérez, V. Barranco, A. Páez, and J. García, WO/2016/066843

J. Pedrós, A. Boscá, J. Martínez, S. Ruiz-Gómez, L. Pérez, V. Barranco, and F. Calle, J. Power Sources 317, 35 (2016)

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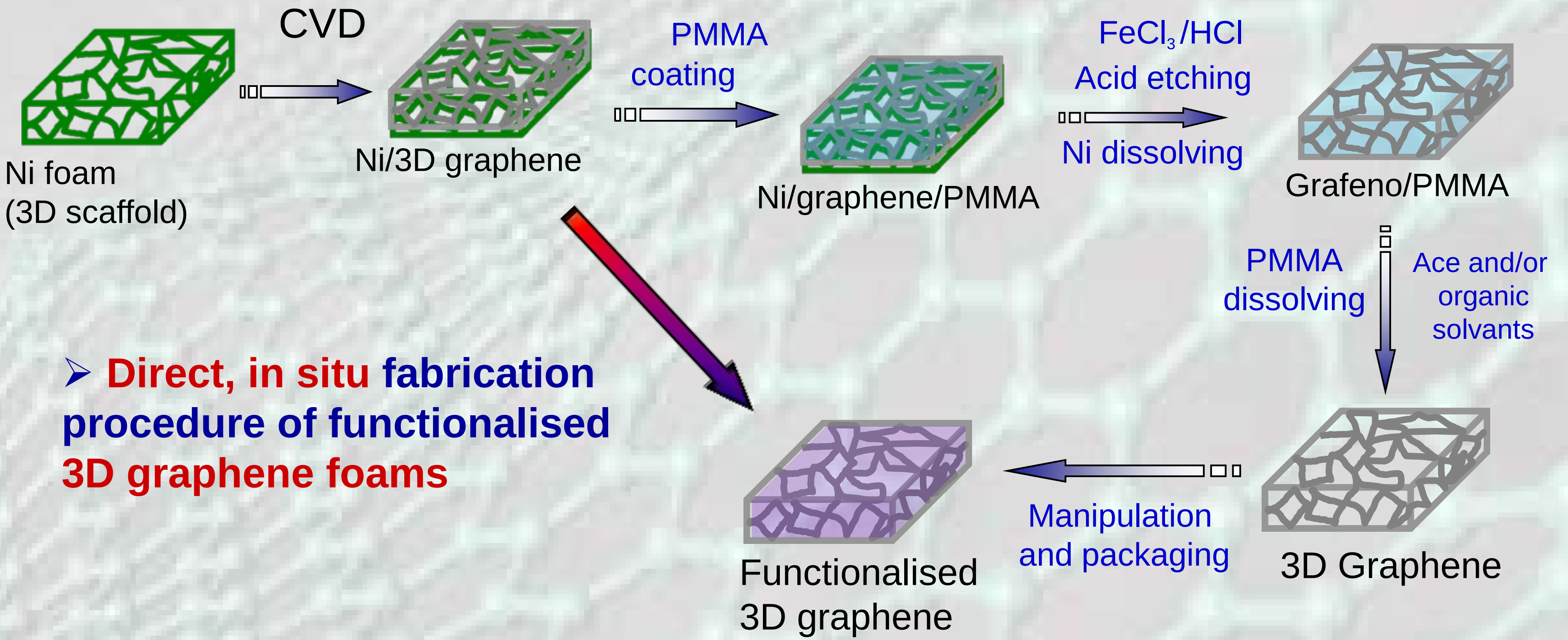
In situ controlled substrate removal

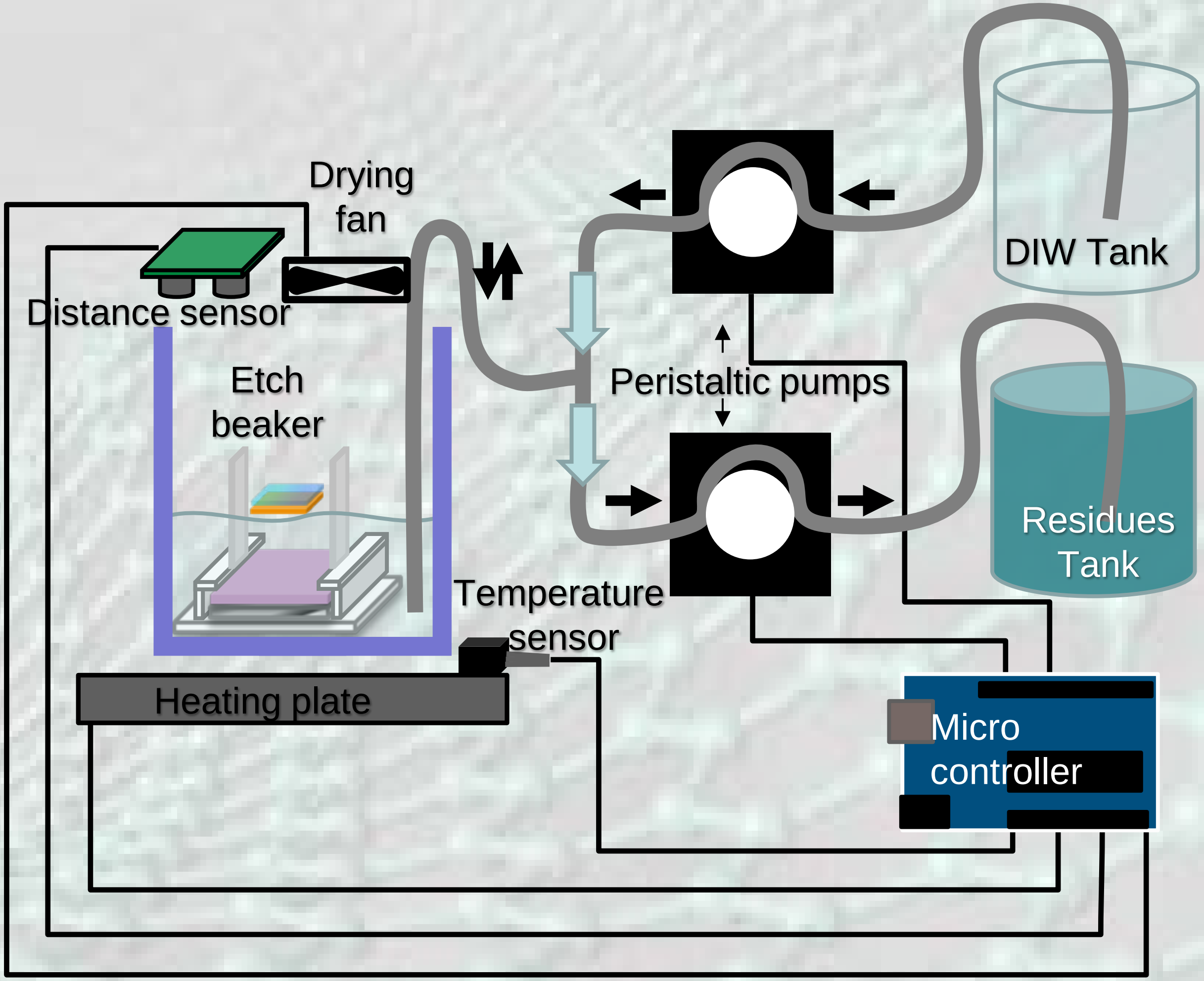


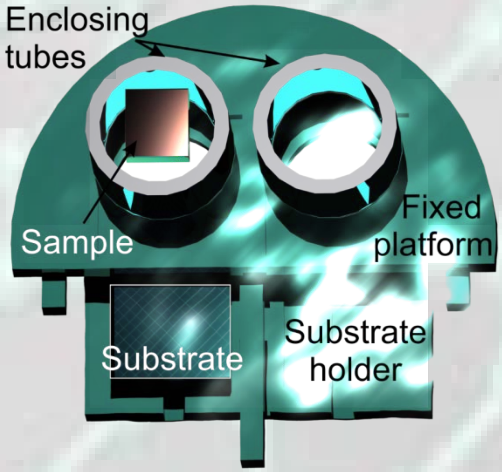
- **Direct, in situ fabrication procedure of functionalised 3D graphene foams**

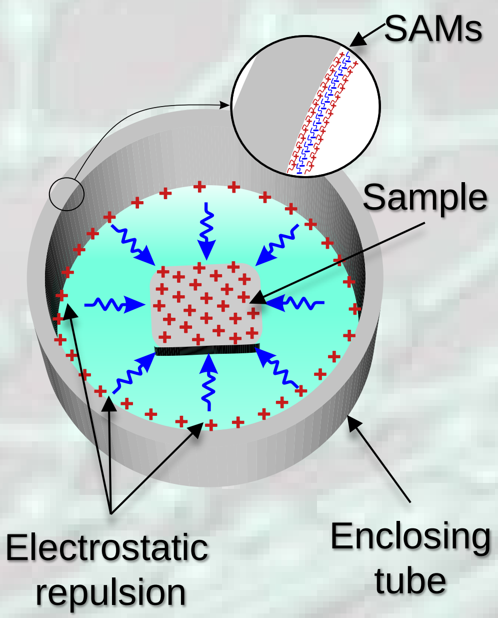
- The procedure may include one or two steps in the same chamber
  - Partial or total dissolving of metal scaffold
  - Oxide functionalisation of the graphene foam

EPO (ICMM, ISOM, REPSOL)
Direct process for in-situ fabrication of functionalized 3D graphene foams

Automatic system: components







A. Boscá, J. Pedrós, J. Martínez, T. Palacios, F. Calle (ISOM-UPM and MIT)

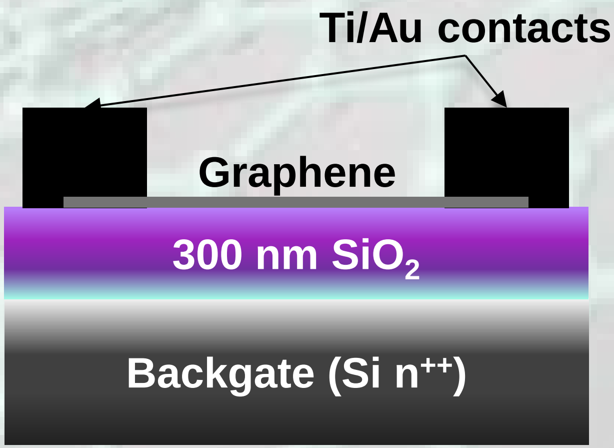
Patent 201331701, ES2536491
Sci. Rep. (2016)

System test: Comparison with GFETs

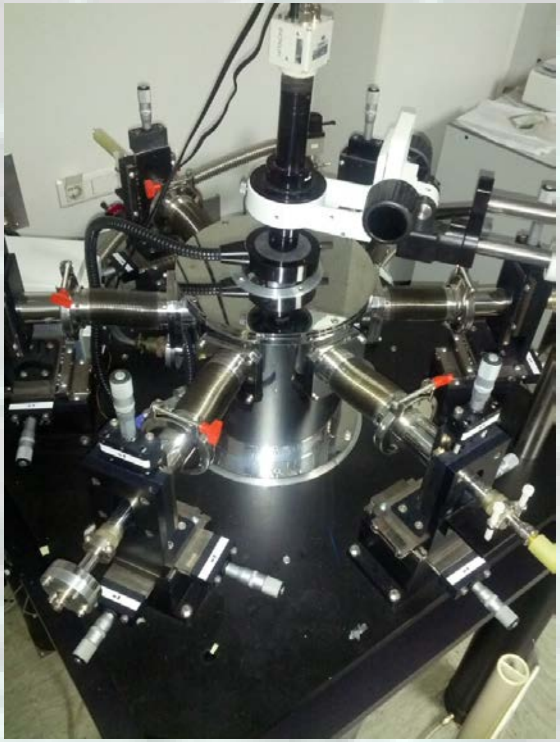
- **GFET fabrication for automatic *vs.* manual transfer comparison**

- **Measurement**
  - ***Vacuum annealing***
  - ***Monitoring of Dirac point displacement***
  - ***3-terminal characterization***
  - ***Method to estimate electrical parameters: Q, μ [1]***

[1] A. Boscá, J. Pedrós, J Martínez, F. Calle J. Appl. Phys., vol. 117, (2015), p. 044504



JANIS high T/ low T vacuum probe station



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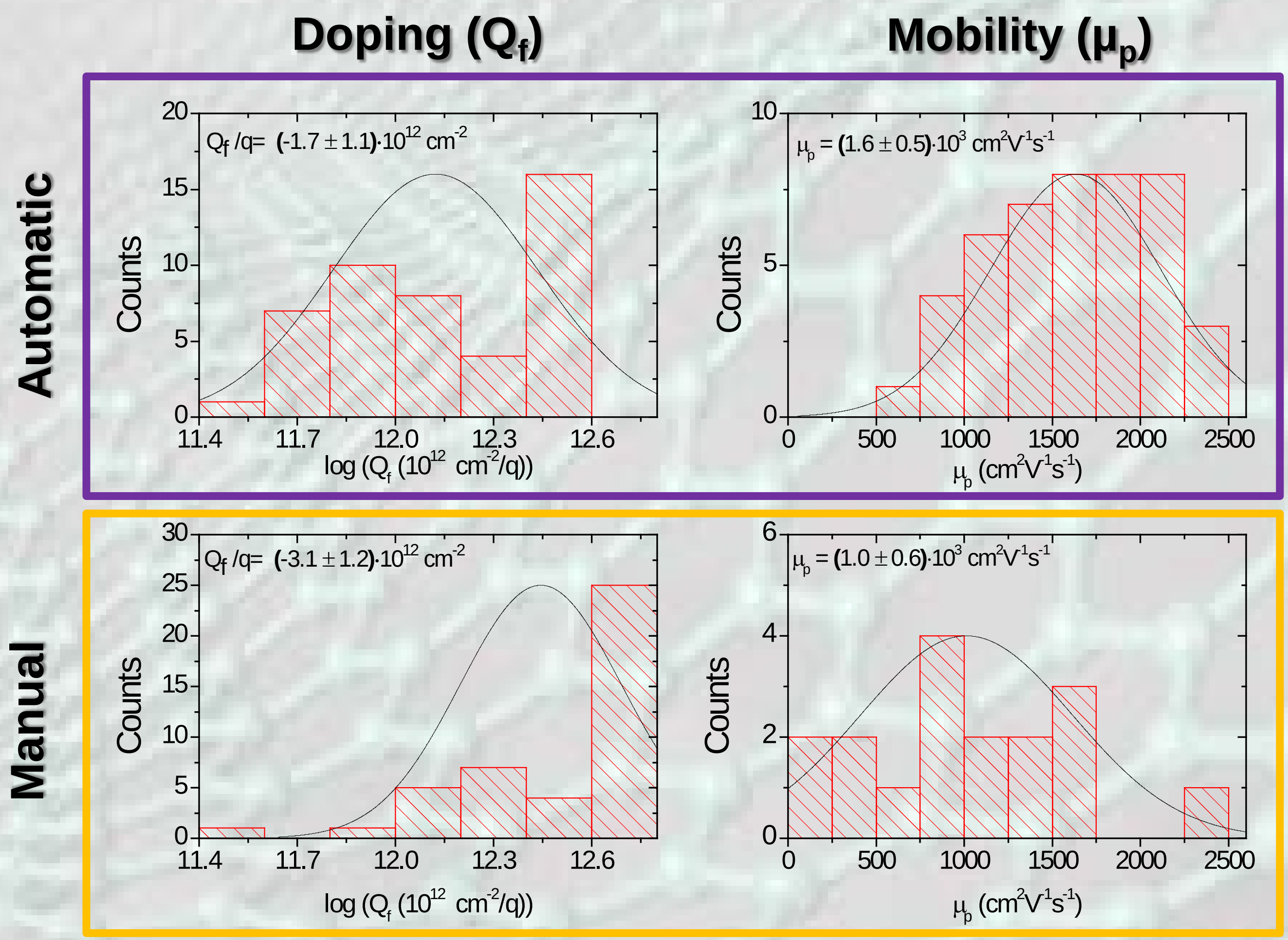
System test: Results



- Higher charge impurities concentration using manual transfer
- Higher mobility for automatically transferred samples

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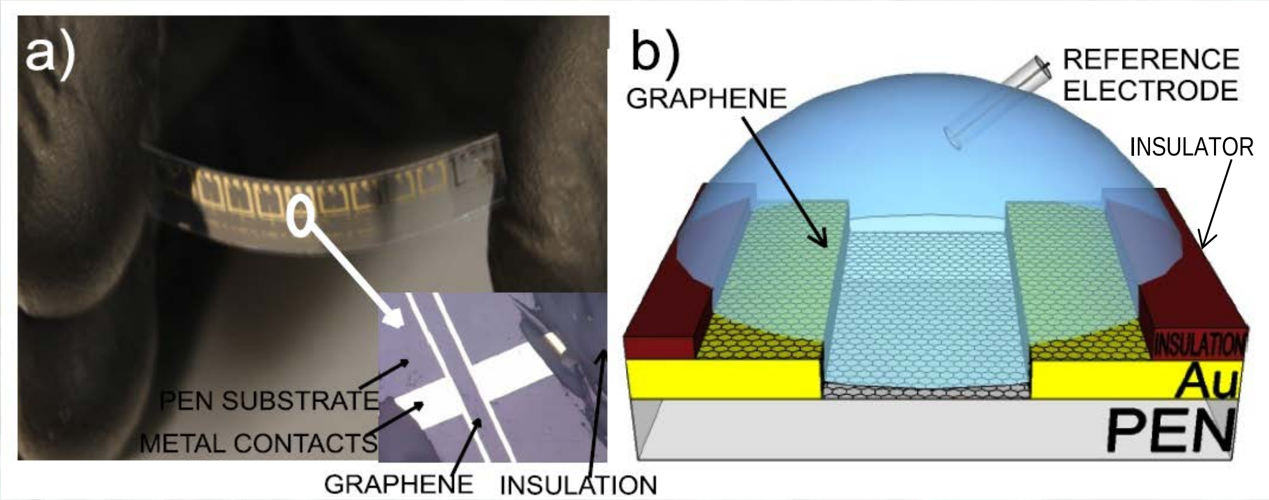
GFET arrays



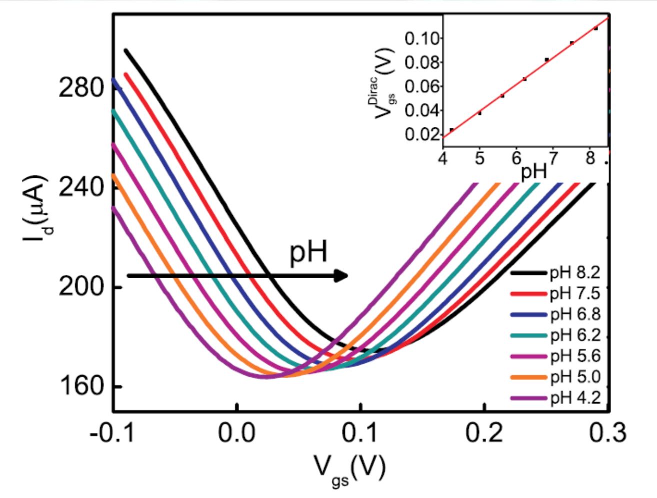
a) Array of graphene chemical sensors on plastic substrate.

b) Scheme of a graphene-on-PEN solution-gated FET.

Transfer characteristics of a 50x100 μm^2 graphene-on-PEN SGFET at a constant V_{ds}=50 mV for different pH values.

Inset: linear relation between the Dirac point shift V_{gs}^{DIRAC} and the pH.

B. Mailly-Giacchetti et al., T. Palacios (MIT), JAP 114 (2013)



➢ **Issue: Large dispersion of values and lack of uniformity**

MISTI project MIT-ISOM

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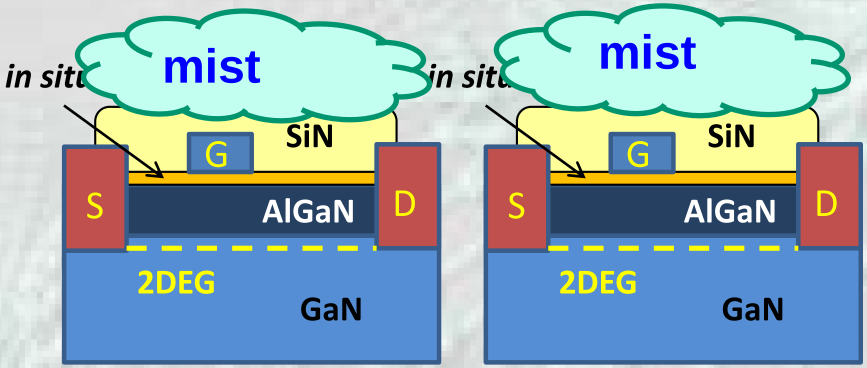
Objectives and Method

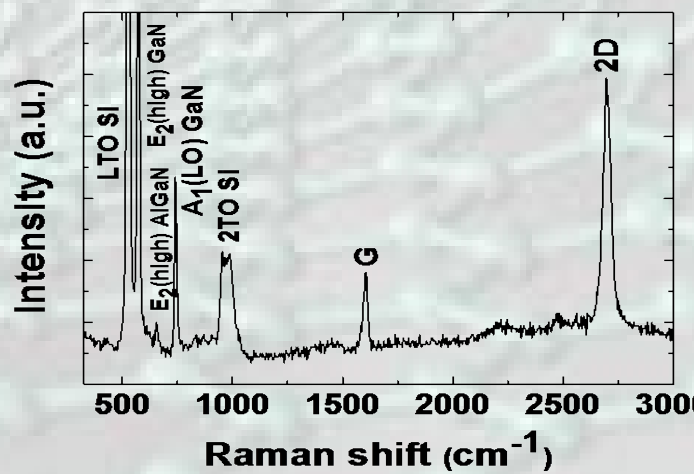
Use a top-layer of graphene in combination with the SiN layer passivation, to prevent efficiently the trapping effects → water-related in AlGaN/GaN HEMT



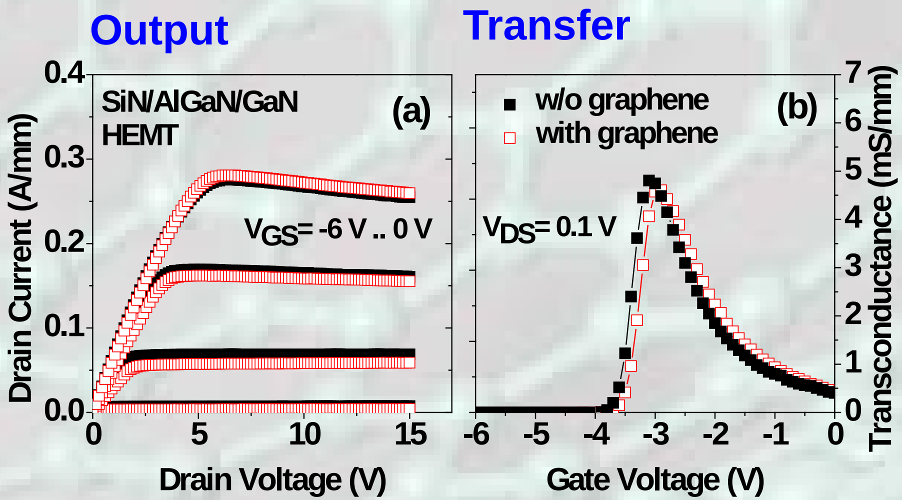
Reference

With Graphene

Transferred CVD SLG from Cu [1]



[1] Boscá et al. *Sci. Rep.* 6 (2016)



No significant changes were observed after the graphene transfer

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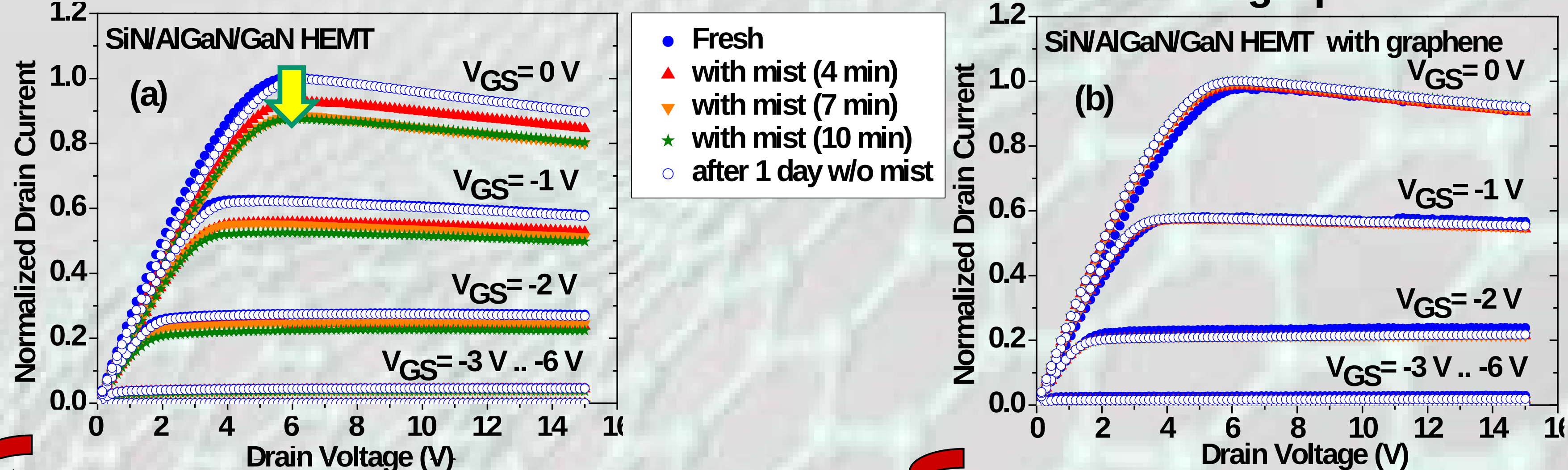
I-V (during mist exposure)

Reference | **With graphene**

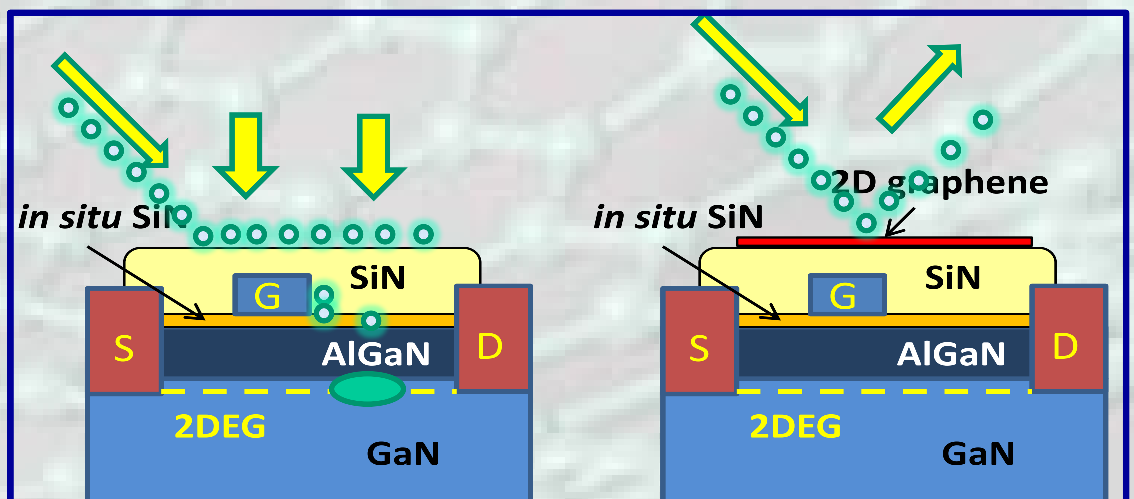


$I_{D,max}$ and $g_{m,max}$ decreased gradually up to 23% and 10%, respectively, as the mist exposure time increased

No significant changes in $I_{D,max}$ and $g_{m,max}$ during the mist exposure

Also HEMTs with graphene keep GLR stable, with no gate lag

In HEMTs with graphene → avoid water-related trapping effects that affect the AlGaN surface during mist exposure [1]



[1] M.F. Romero et al. *IEEE EDL*. 28 (2017)

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Surface plasmons on graphene

- Graphene can sustain surface plasmons from MIR to THz frequencies
  ⇨ basis of nm-size devices that combine electronic functions with optics.

- **Procedures of light interaction with graphene plasmons:**

➢ **Patterning the material** to couple photons to the electronic oscillation,
  ✓ It prevents tunability.
  ✓ It also causes energy loss due to scattering off the imposed structures

➢ **Mechanical actuator** to excite a sheet of graphene
  ✓ Flexural waves on the sheet coupled to the plasmon field establish the grating pattern to have energy flow from incident light into surface plasmons.

Exciting Graphene Surface Plasmon Polaritons through Light and Sound Interplay
M. Farhat et al, Phys. Rev. Lett. **111**, 237404 (Dec 2013)

➢ **Surface acoustic waves (SAW)**
✓ The graphene sheet is placed on a piezoelectric substrate
✓ Electrically induced SAW on the graphene set up the modulation matching the photon and plasmon phases.
✓ Devices: chemical detection, light to electricity conversion, nanooptoelectronics.

Coupling Light into Graphene Plasmons through Surface Acoustic Waves
J. Schiefele, J. Pedrós, F. Sols, F. Calle, F. Guinea, Phys. Rev. Lett. **111**, 237405 (Dec 2013)

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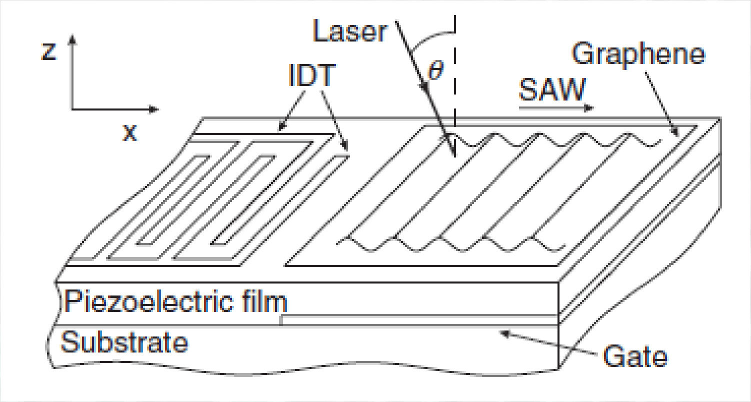
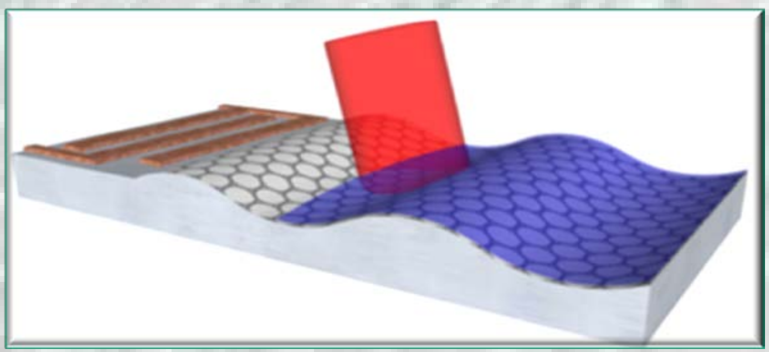
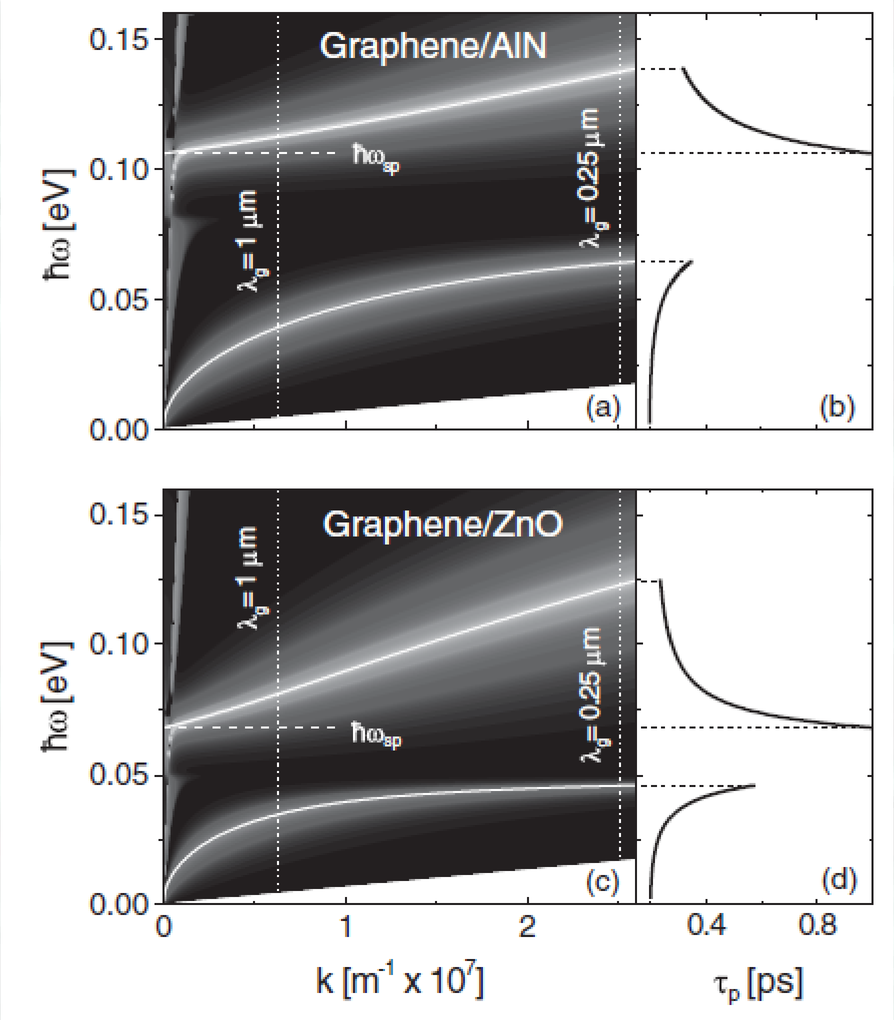
Graphene Plasmons SAW







- ☑ Simple far-field optics
- ☑ Simple device fabrication
- ☑ Propagating plasmons
- ☑ Scalable & integrable
- ☑ Active control

J. Schiefele, J. Pedrós, F. Sols, F. Calle, and F. Guinea, Phys. Rev. Lett. 111, 237405 (2013)

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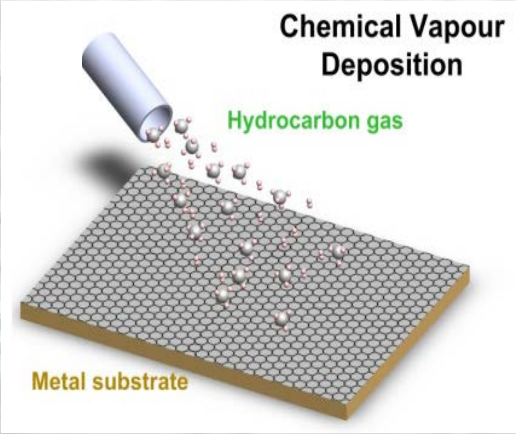
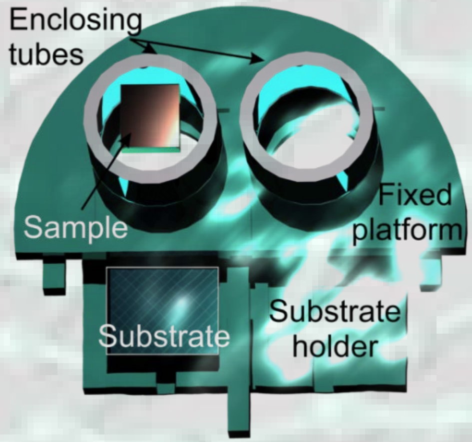
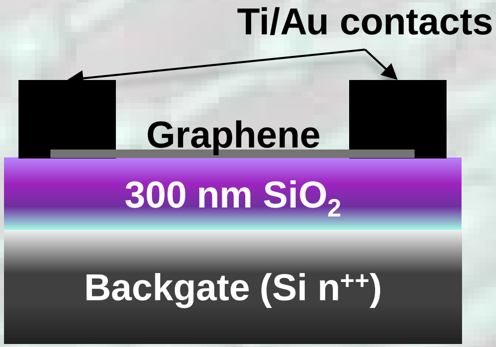
Graphene for neutrino detection

- **Ultrasensitive detection is a must**
- **It requires**
  - ***Very high crystal quality, low defect density 2D graphene***
  - ***High performance and reproducible transfer***
  - ***Reliable GFET processsing***
  - ***Excellent structural and electrical characterization***







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