Agenzia nazionale per le nuove tecnologie,
l'energia e lo sviluppo economico sostenibile

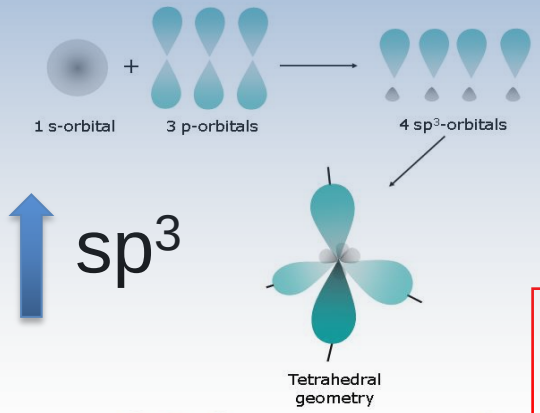
Nano Innovation 2020 Rome, 15-18 September
Conference & Exhibition

graphene based interfaces: characterizations and applications

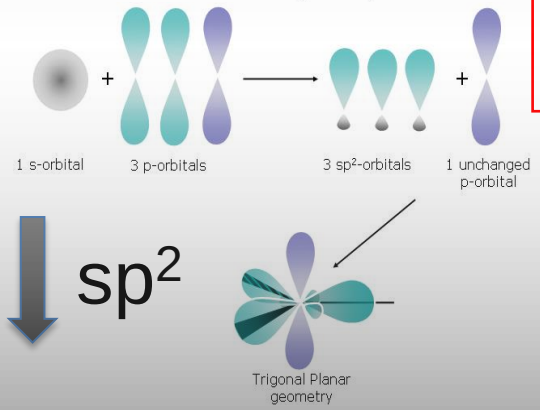
Roma, 16 Settembre 2020

Nicola Lisi / ENEA Casaccia TERIN-PSU-ABI

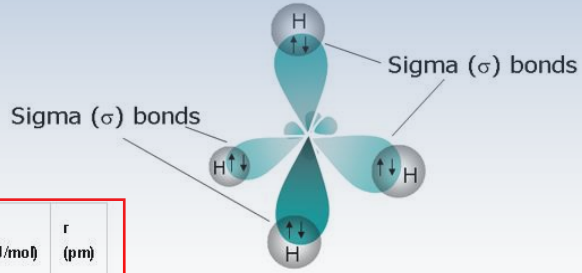
Carbon: orbitals and hybridizations sp^3 e sp^2



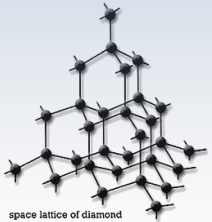
Bond	D (kJ/mol)	r (pm)
C-C	346	154
C=C	602	134
C≡C	835	120



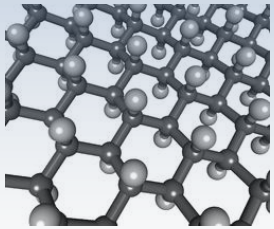
Methane, CH_4



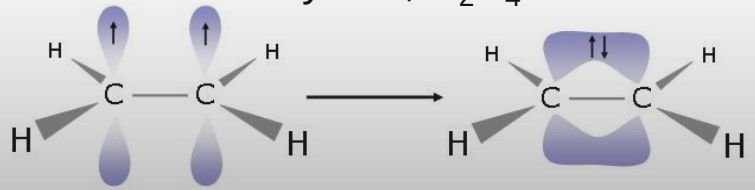
Diamond



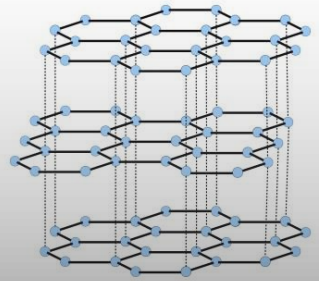
Graphane: 2D fully hydrogenated graphene derivative



Etylene, C_2H_4



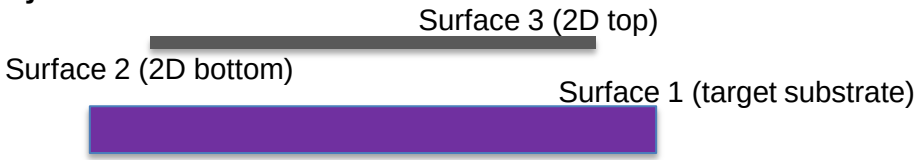
Graphite (here 3 ABA stacked, 2D graphene)



Introduction: graphene's first doom

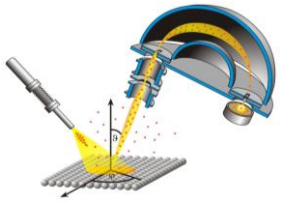
- With the deployment of **each** Graphene, or other **2D material**, **three surfaces are involved**. Graphene is doomed to be always dominated by surface and interface effects, aside when stacked in graphite.

Interfaces, such as surfaces, pose vibrant physical and chemical challenges in their interaction with the environment for practical applications: surface states and contaminations play a major role.



For the reliability of few **nano-scale interfaces**, state of the art (electronic and optical) clean room technology usually applies high **vacuum processing**, applying **ashing, etching and thermal** treatments to recover surfaces. This is usually **not** feasible for "**soft processed**" graphene and 2Ds.

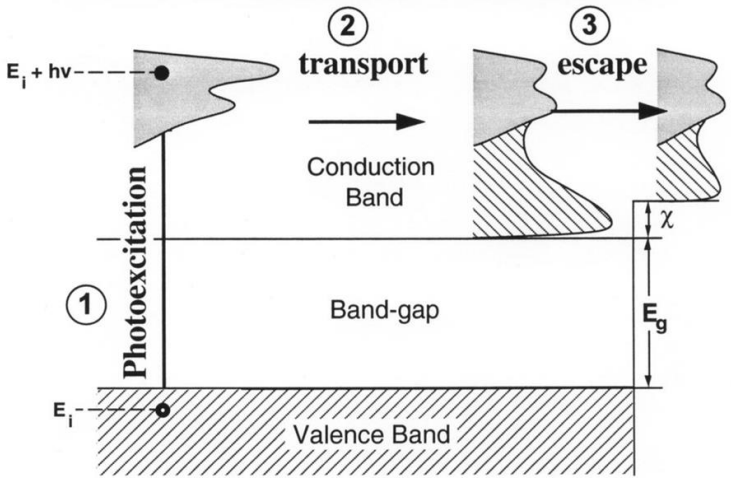
UPS can determine the real* work-function of surfaces

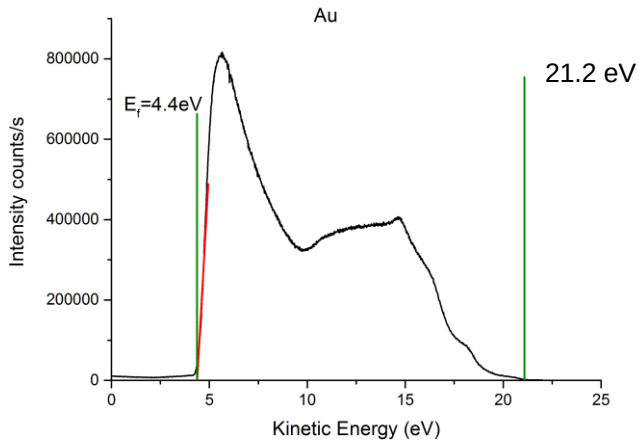


*real= that determines surface electronic exchange properties

In UPS WF is measured by simple physics: it is the **low** kinetic **energy** at which the secondary emission is **cut off**.
No matter how hard we try, after air exposure Au **work-function** never reaches the correct value of 5.3-5.4eV.
(after O2 plasma ashing we managed to reach 5.0eV)

He I line 21.2 eV





Heterogeneous surfaces (further reading suggested)

On **heterogeneous surfaces**, low work-function areas screen those with higher work-function. The consequence is that **contaminants** have a **dominant** effect on charge exchange at surfaces.

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Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/apsusc

Invisible high workfunction materials on heterogeneous surfaces

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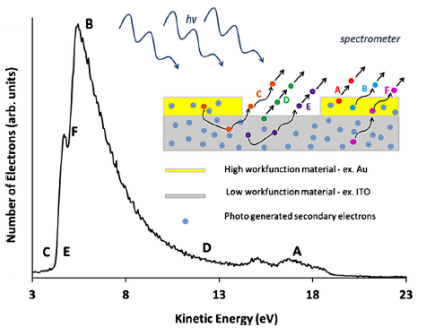

Fig. 4. A schematic depicting potential photoemission processes during a UPS experiment and the labels indicate their contributions to an experimental spectrum for a Au-ITO heterogeneous surface prepared using TEM grid of mesh size 300.

FULL PAPER

Photoelectron Spectroscopy

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Reliable Work Function Determination of Multicomponent Surfaces and Interfaces: The Role of Electrostatic Potentials in Ultraviolet Photoelectron Spectroscopy

*Thorsten Schultz, Thomas Lenz, Naresh Kotadiya, Georg Heimel, Gunnar Glasser, Rüdiger Berger, Paul W. M. Blom, Patrick Amsalem, Dago M. de Leeuw, and Norbert Koch**

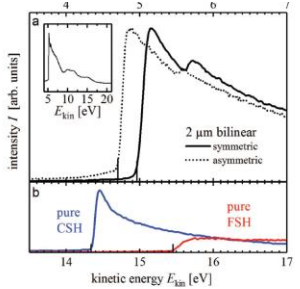
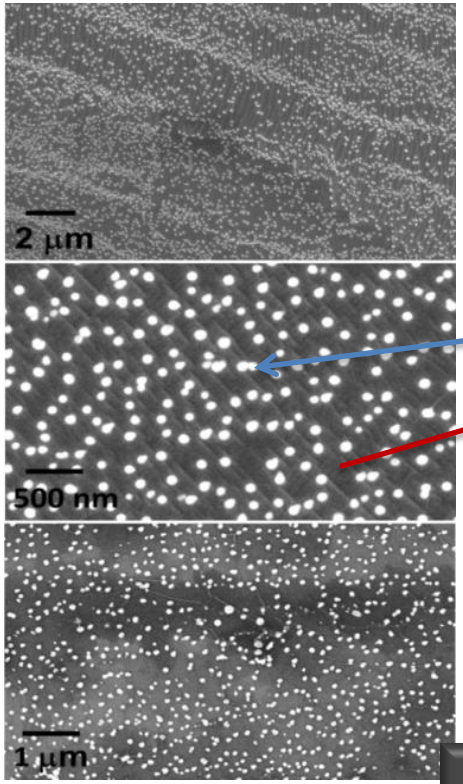
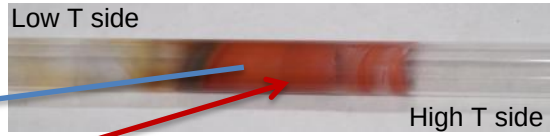


Figure 2. a) SECO spectra of symmetric and asymmetric 2 μm samples. The low kinetic energy cut-off is clearly shifted compared to pure CSH (reference spectra of pristine SAMs shown to scale in b)), whereas the high kinetic energy cut-off is at the same position as the one from the pristine FSH. For the asymmetric sample (larger CSH area), the low kinetic energy cut-off is shifted to lower kinetic energies. For detailed fitting, see Figure S2 in the Supporting Information. The full-range spectrum is shown in the inset in (a). The cut-off features are clearly sharper than the valence band features. A −10 V bias was applied for all measurements.

For CVD graphene, contamination issues already appear during growth. Copper surfaces are well clean and reconstructed at 1000°C but… , the white dot issue



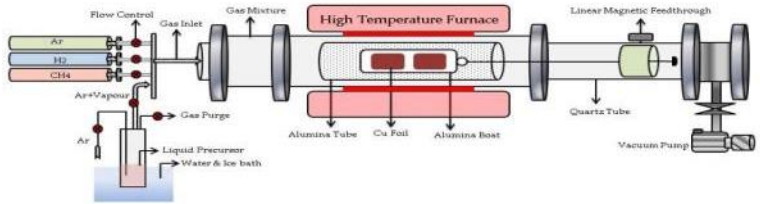
After prolonged high-temperature usage SiO is released by the reactor tube vessel as Cu migrates into the quartz bulk and results in severe **graphene contamination** (which alters graphene and the growth process itself)

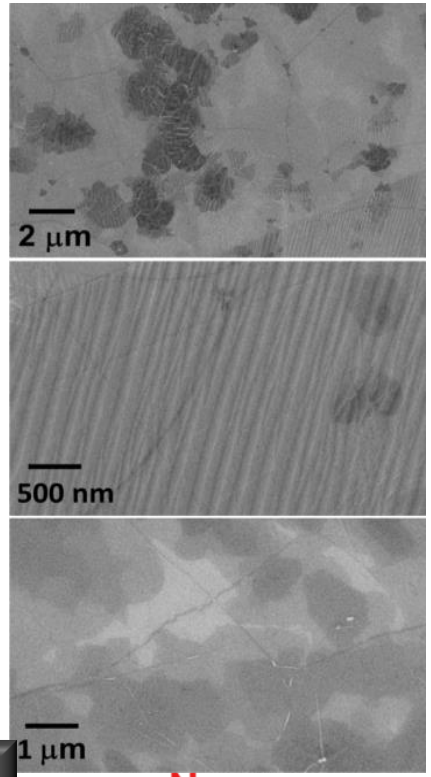


SiO

Cu

novel reactor geometry with screens for vapours (Cu and SiO)





Growth of (heavily) contaminated and clean graphene

graphene’s second doom

An incredibly **broad** range of applications od 2Ds as a functional layers have been proposed; however the deployment of graphene into **devices**, between two different materials or between a material and the environment, has revealed a **challenging** task.

It requires **accurate characterization** and **repeated** assessments during all the fabrication **steps** in order to target a successful integration with diverse fabrication technologies ad survival in the deployment environment.

- We must bear in mind that **graphene does not chemically bind to surfaces**.

In the next few slides interfacial graphene acts as a conductor or as an optical absorber.

Graphene transfer is still a big issue: PMMA approach

NANO LETTERS

2009
Vol. 9, No. 12
4359-4363

Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes

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Received August 11, 2009; Revised Manuscript Received September 18, 2009

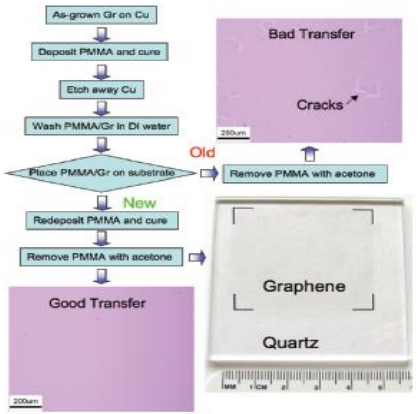

Figure 2. Processes for transfer of graphene films ("Gr" = graphene). The top-right and bottom-left insets are the optical micrographs of graphene transferred on SiO_2/Si wafers (285 nm thick SiO_2 layer) with "bad" and "good" transfer, respectively. The bottom-right is a photograph of a 4.5 × 4.5 cm^2 graphene on quartz substrate.

APPLIED PHYSICS LETTERS **102**, 091602 (2013)

Procedure of removing polymer residues and its influences on electronic and structural characteristics of graphene

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(Received 1 November 2012; accepted 25 February 2013; published online 6 March 2013)

Procedure of removing polymer residues by post-annealing and the effect on electronic properties of transferred monolayer graphene grown by chemical vapor deposition method are investigated using X-ray photoelectron spectroscopy and Raman spectroscopy. It is found that breaking the polymerization backbone bond induces effective removal of poly(methyl methacrylate) on the graphene surface by depolymerization, and decomposition of the carboxyl functional group involves reducing the level of p-doping of the graphene, while the annealing process leads to an increase in defects, and consequently, to oxidation that transforms the graphene into p-doped material. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794900]

NANO LETTERS

Letter

pubs.acs.org/NanoLett

Graphene Annealing: How Clean Can It Be?

dx.doi.org/10.1021/nl203733r | *Nano Lett.* 2012, 12, 414–419

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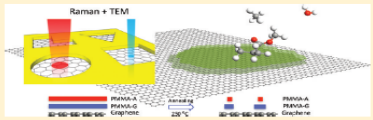
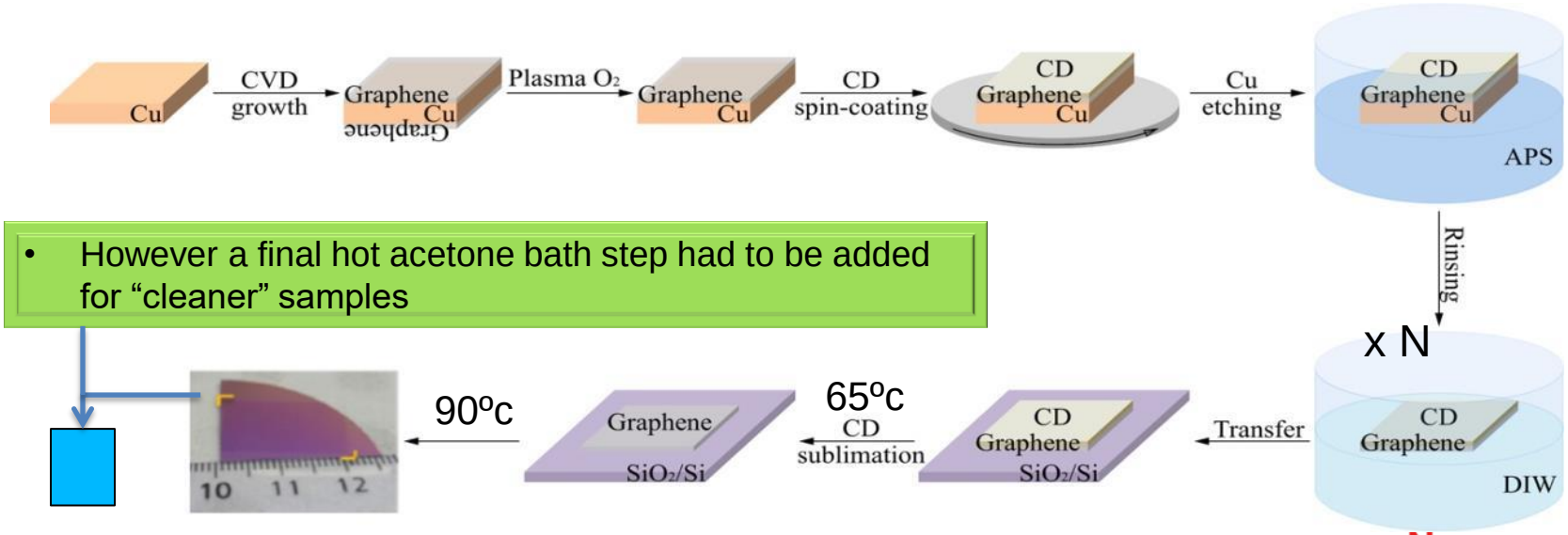
Supporting Information

ABSTRACT: Surface contamination by polymer residues has long been a critical problem in probing graphene's intrinsic properties and in using graphene for unique applications in surface chemistry, biotechnology, and ultrahigh speed electronics. Poly(methyl methacrylate) (PMMA) is a macromolecule commonly used for graphene transfer and device processing, leaving a thin layer of residue to be empirically cleaned by annealing. Here we report on a systematic study of PMMA decomposition on graphene and of its impact on graphene's intrinsic properties using transmission electron microscopy (TEM) in combination with Raman spectroscopy. TEM



Scheme of the *Cyclododecane* (CD) assisted transfer. CD sublimates in air at room temperature (no solvent)

- Less solvents are required: green processing
- Low temperature processing: transfer on heat sensitive and solvent sensitive substrates (also bio-systems)



- However a final hot acetone bath step had to be added for “cleaner” samples

Test Devices: Silicon Graphene Schottky solar cells

Solar cells are “no-nonsense devices”, all interfacial defects emerge as a reduced PE.

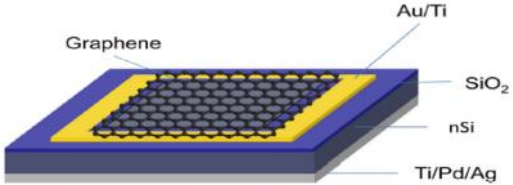
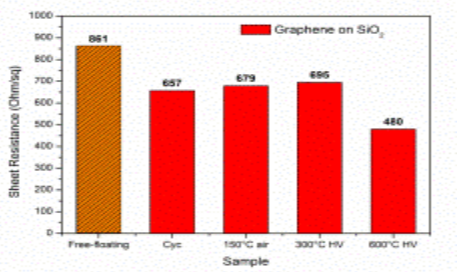
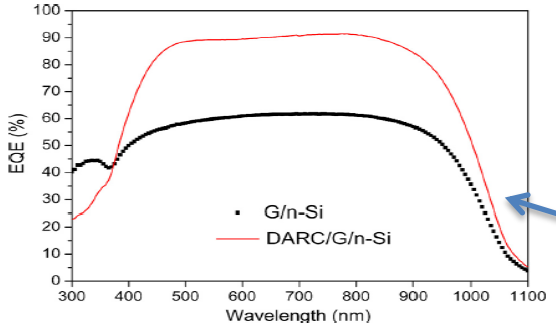


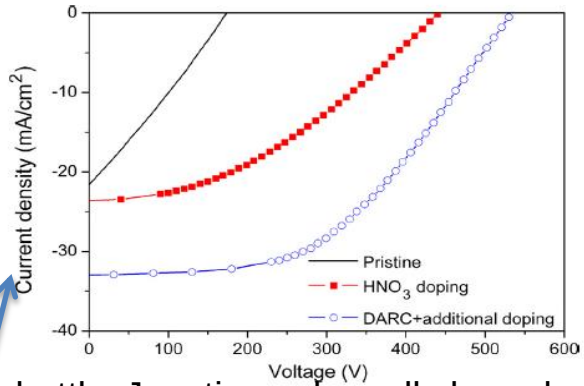
Fig. 2. Schematic illustration of the G/n-Si SBSC.

Cell based on silicon and ML Graphene transferred using cyclododecane

Type n-Si absorber
Resistivity: r=0.7 – 1.3 Wcm







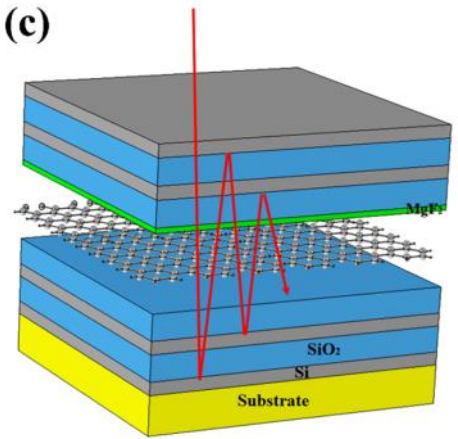
Schottky Junction solar cells based on few layer graphene: effects of molecular doping (changes the WF) and AR coatings

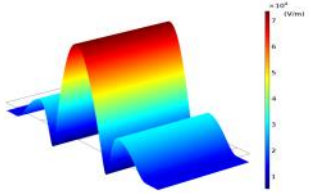
PCE at 8.5% and heading **towards 10%**

QY is 90% with double anti reflection coating (DARC) evaporated directly on top of graphene

Optical test device, a perfect graphene absorber: embedding in a Fabry-Perot cavity and integration with sputtering deposition technology

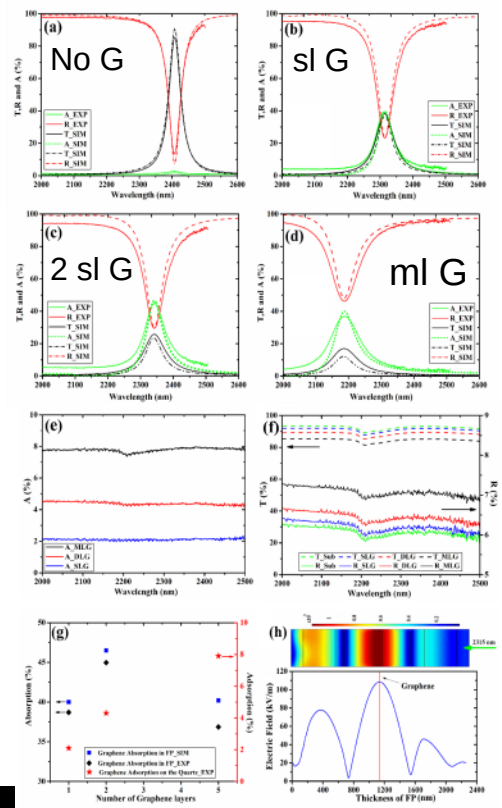
Si and SiO_2 layers thickness is $\lambda/4n$, n refractive index





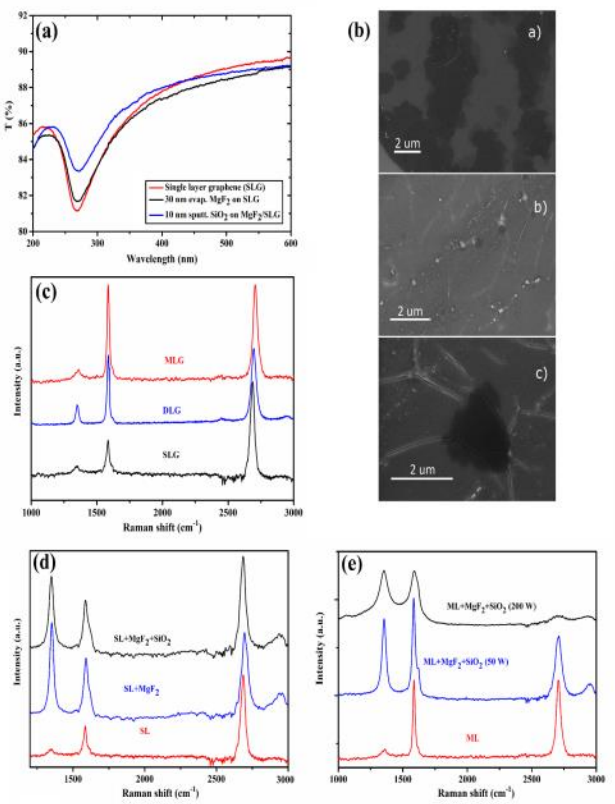
The Electric field **E** is maximum at the cavity centre, where graphene is placed.

Light is reflected between two Bragg reflectors and hits graphene several times.
The light travels inside a FP a number of times equal to the finesse of the FP $\Gamma = \frac{\pi\sqrt{R}}{1-R}$ R of our mirrors is 0.86. F indicates the width of the transmission band of the FP.

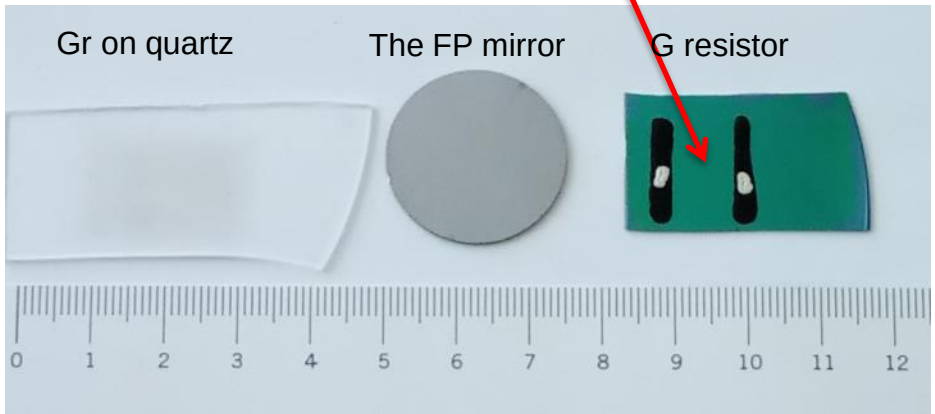


Absorption increases from 2 to 40%

Graphene embedded in a Fabry-Perot cavity, graphene protection with evaporated MgF_2

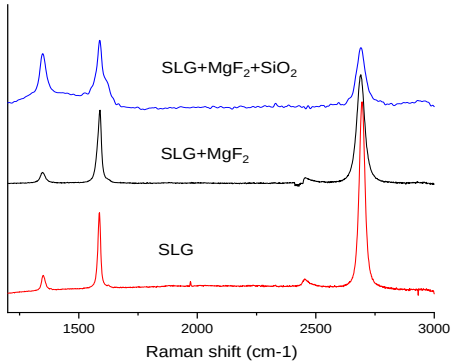


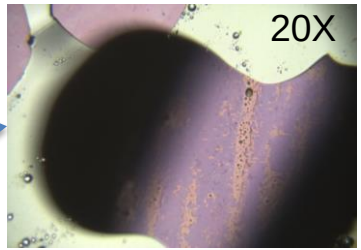
- We succeeded in using sputtering techniques to deposit oxides on top of graphene, by applying first an thin evaporated MgF_2 buffer layer
- Tested on Si, SiO_2 and thermally oxidized Si
- The MgF_2 alters Raman but does not impair graphene's electrical resistance



Towards a perfect graphene absorber

- Also after the sputtering deposition of SiO2 (or of other oxides) graphene maintains it's mostly crystalline structure
- Improved MgF_2 deposition process leads to negligible changes of graphene Raman spectrum
- A new resonant structure grants 85% absorption from a single layer CVD graphene (SLG) with important applications to optoelectronics and photonics. It is possible to apply the same technology to other 2D materials.
- However the device is **locally** subject to **peeling**, mainly at the edges… again issues are arising from the **lack of binding** of graphene to the device (graphene-dielectric interface)





graphene's third doom

Tuning of graphene structure and **adding functional groups** allows it to implement a broader range of functionalities (we have already seen the molecular doping effect of HNO3 in Shottky barrier solar cells that changes the WF and decreases the sheet resistance).

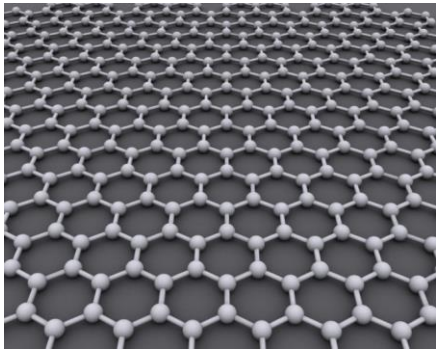
Functionalised graphene requires **extra-careful and repeated investigations** by applying spectroscopic and microscopic techniques during the various processing steps of such delicate, one atom/molecule thin, evanescent coatings.

- However accurate are processing and characterisation, more than for graphene itself, **functionalised** graphene's properties are dominated by **interaction with the environment**!

Graphene and its derivatives (covalent functionalization)

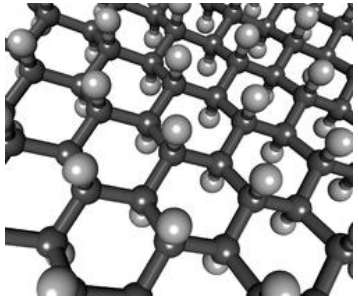
In the fully sp^2 hybridized 2D lattice, some carbons can be altered into the sp^3 hybridization while bonds pop out to become available out of the plane

Graphene

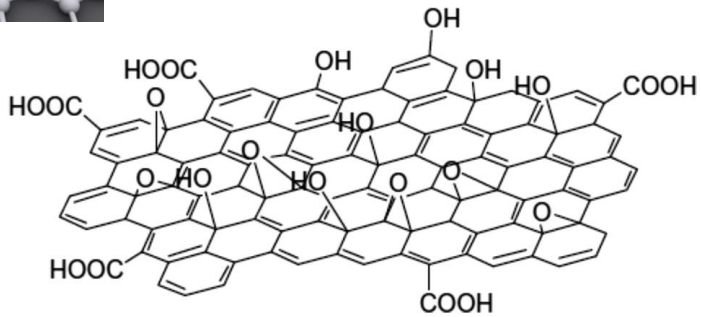


Graphane: all carbons are sp^3 and bonded to hydrogen
Fluorographene: the same structure with fluorine
Graphone: hydrogen only on the top

periodic Graphene Based Derivatives

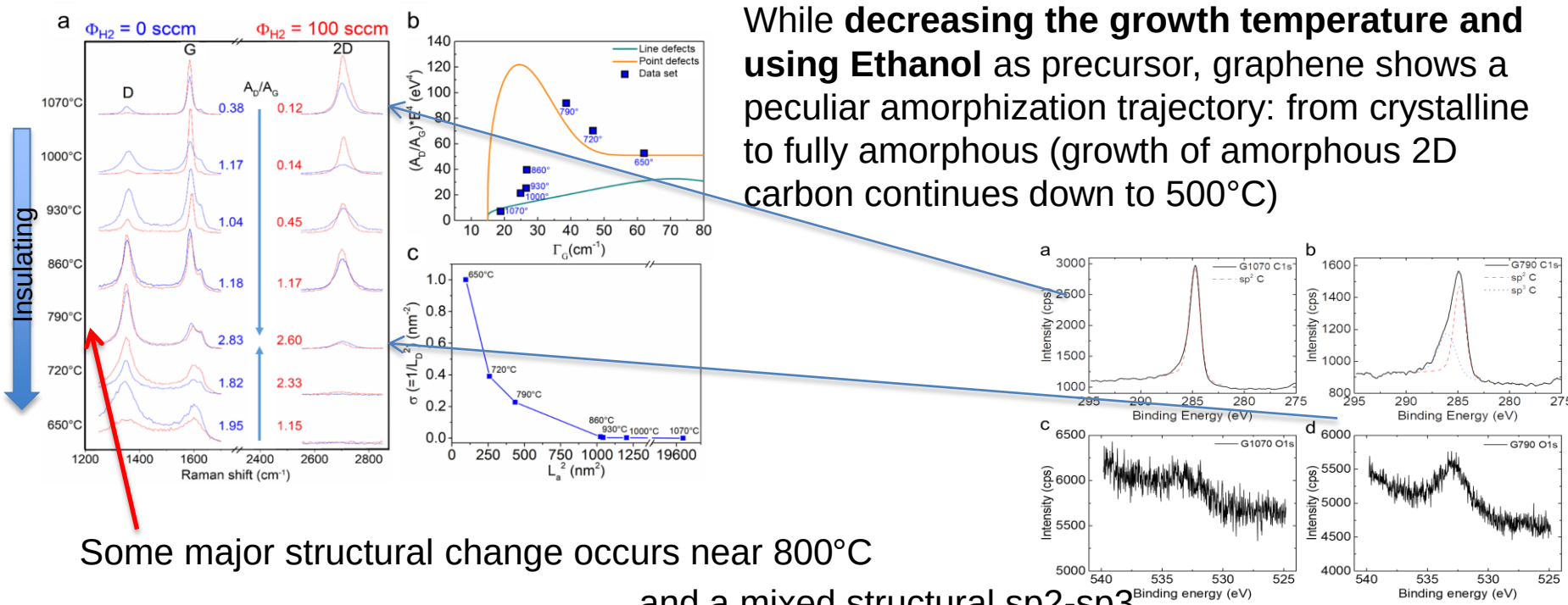


irregular and «aperiodic» (GO)



Also fully sp^3 GOH structures are possible: hydrogenated, epoxide, hydroxyl mix are predicted are possible

Interfaces based on modified CVD graphene



While **decreasing the growth temperature and using Ethanol** as precursor, graphene shows a peculiar amorphization trajectory: from crystalline to fully amorphous (growth of amorphous 2D carbon continues down to 500°C)

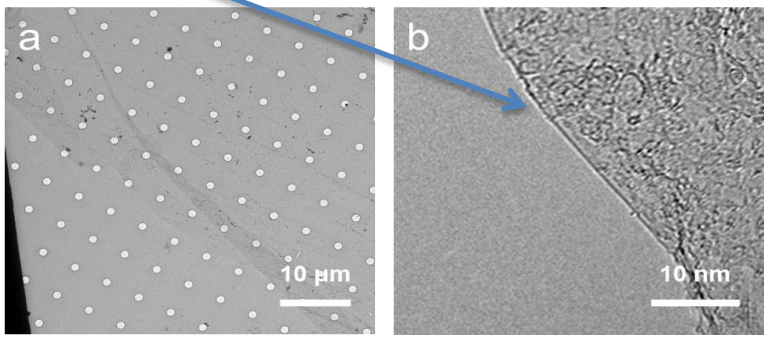
Some major structural change occurs near 800°C

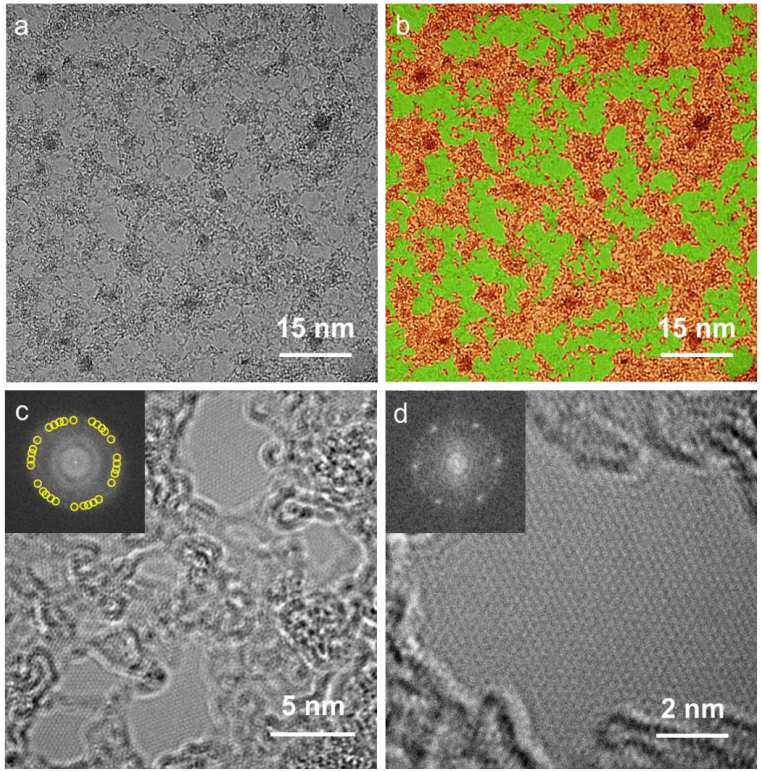
and a mixed structural sp2-sp3 phase does appear

TEM is always relevant: 790°C growth

TEM allows he direct observation of atoms and gives **direct proof of the structure** inferred by other analytical techniques: crystalline structures in an amorphous matrix

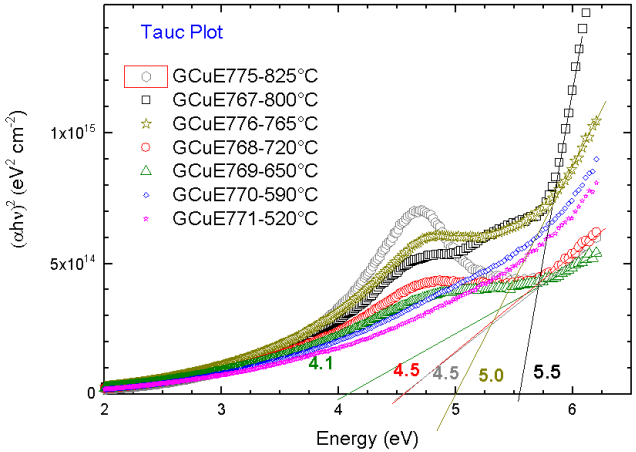
2D

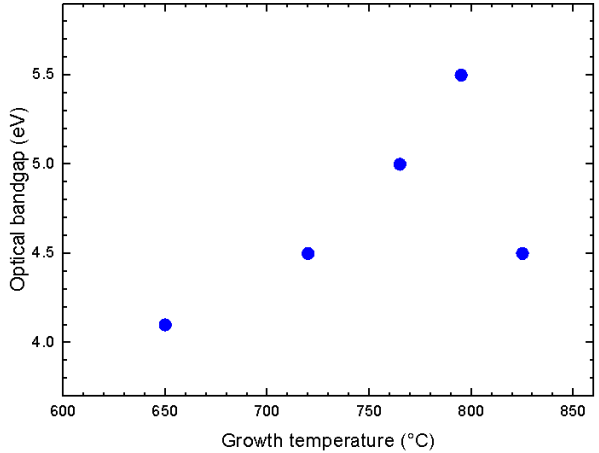




The elusive gap of graphene grown at low temperature

UV-Vis absorption measurements showed that an optical gap in the UV appeared, in correspondence with the structural change and with the rise of the sp3 component

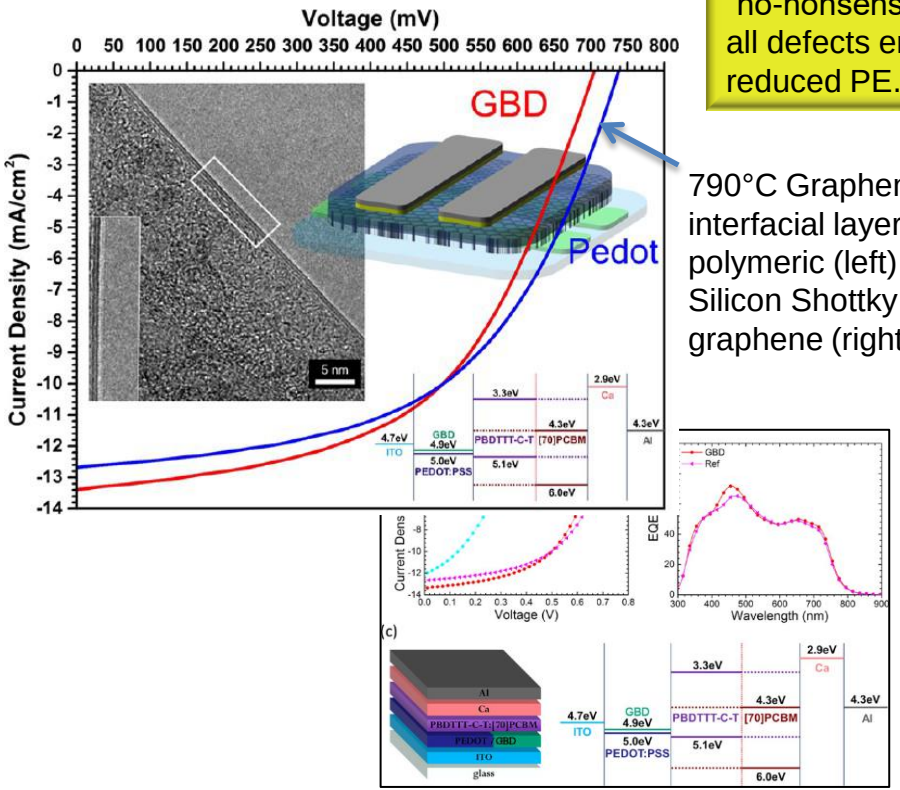




However all these optical features **do not survive acetone** rinsing!

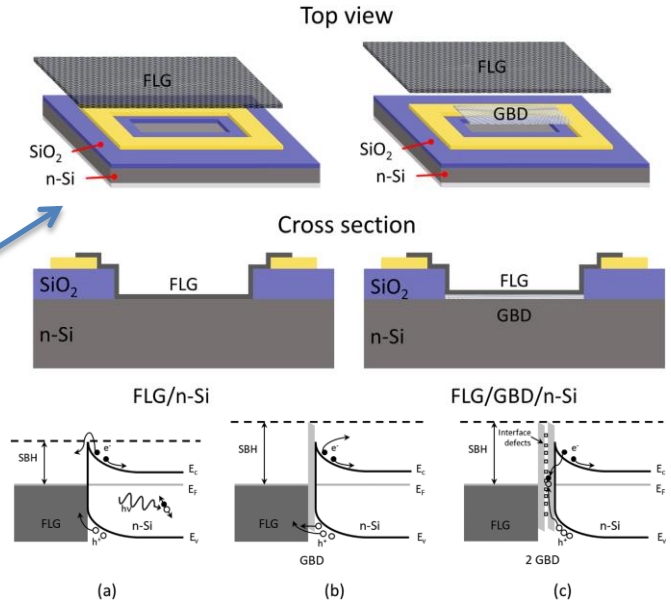
Absorption is due to trapped Cyclododecane, structural changes helps to capture organic contaminants (a vital task indeed!)

Interfacial layer for solar cells: selective HTL/ETL



"no-nonsense" in solar cells: all defects emerge as a reduced PE.

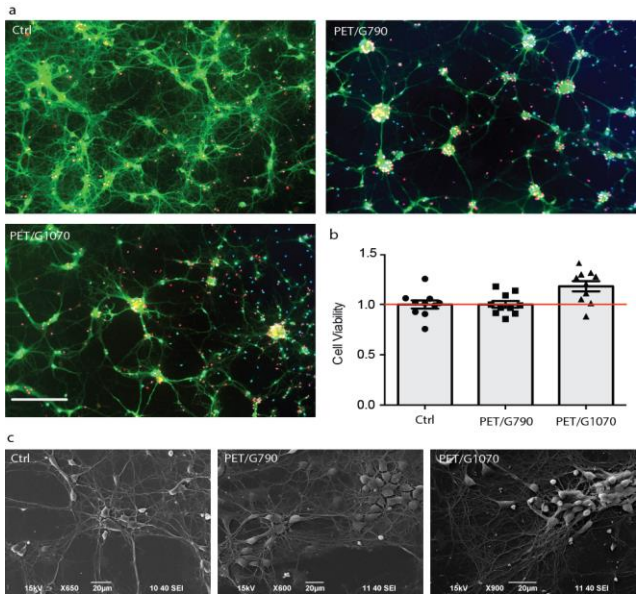
790°C Graphene (GBD) as interfacial layer for solar cells: polymeric (left)
Silicon Shottky barrier with graphene (right)



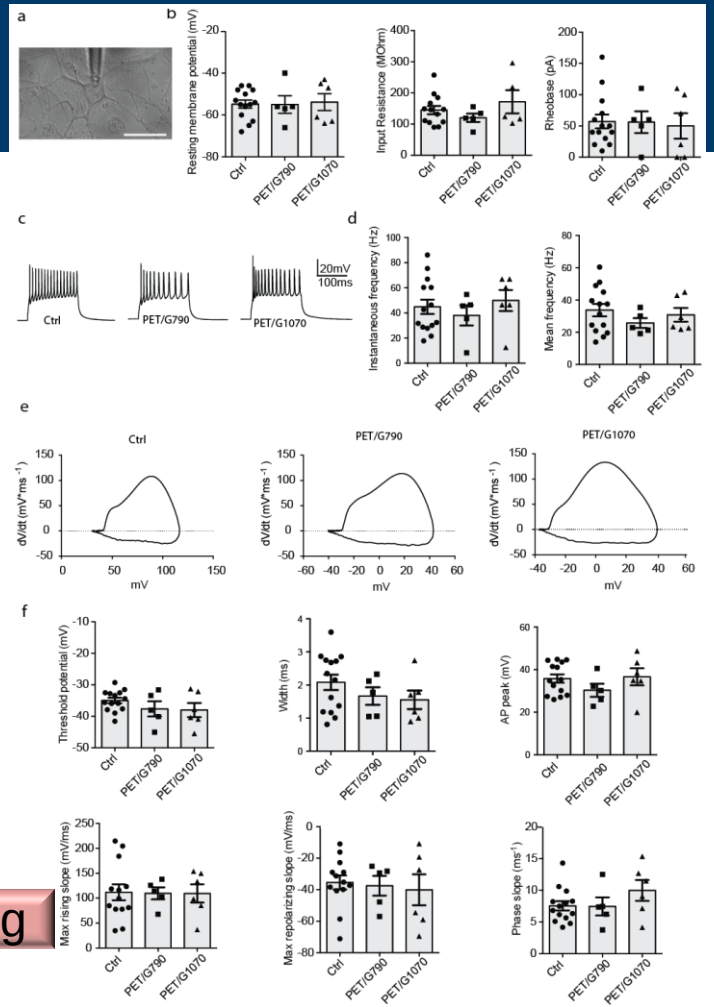
In conclusion interface defects, mostly related to processing play an important role.
Huge reproducibility issues for devices based on stacked 2D materials!!

Neuronal interfaces G1070 and G790

Neuron viability does not change



Bio applications are more forgiving



neither PET/G790 nor PET/G1070 alter the physiological growth of primary neurons and the development of an excitable network.

Both G790 and G1070 can serve as efficient and biocompatible neuronal interfaces.

Highly conductive graphene is not necessary

Conclusions

- **2D, always a surface, always an interface**
- **No binding when deployed**
- **Worse for functionalized graphene or derivatives**

All the above pose serious challenges for 2D applications: repeated characterizations and assessment during fabrication and application.

Is soft processing any good, beyond bio-systems?

Many thanks for your attention!

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and many more.