



## The growth of carbons on copper from ethanol vapours: a powerful and flexible technique

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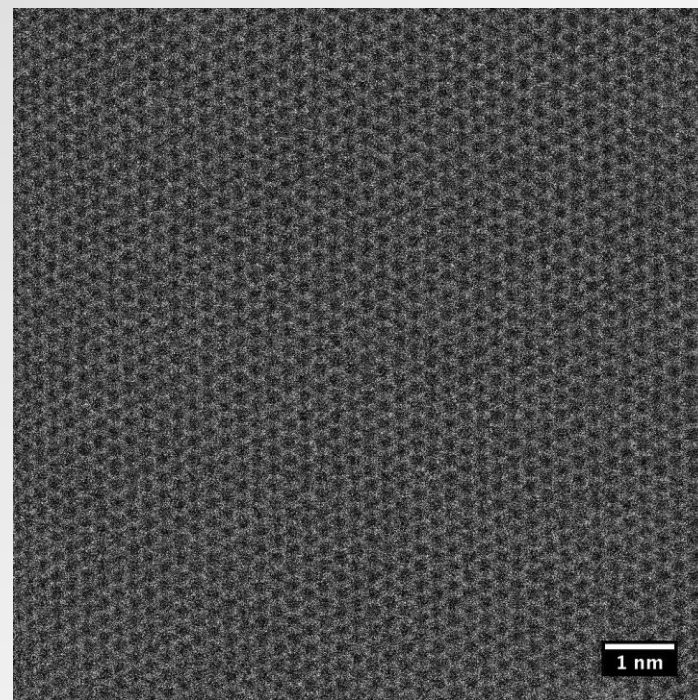
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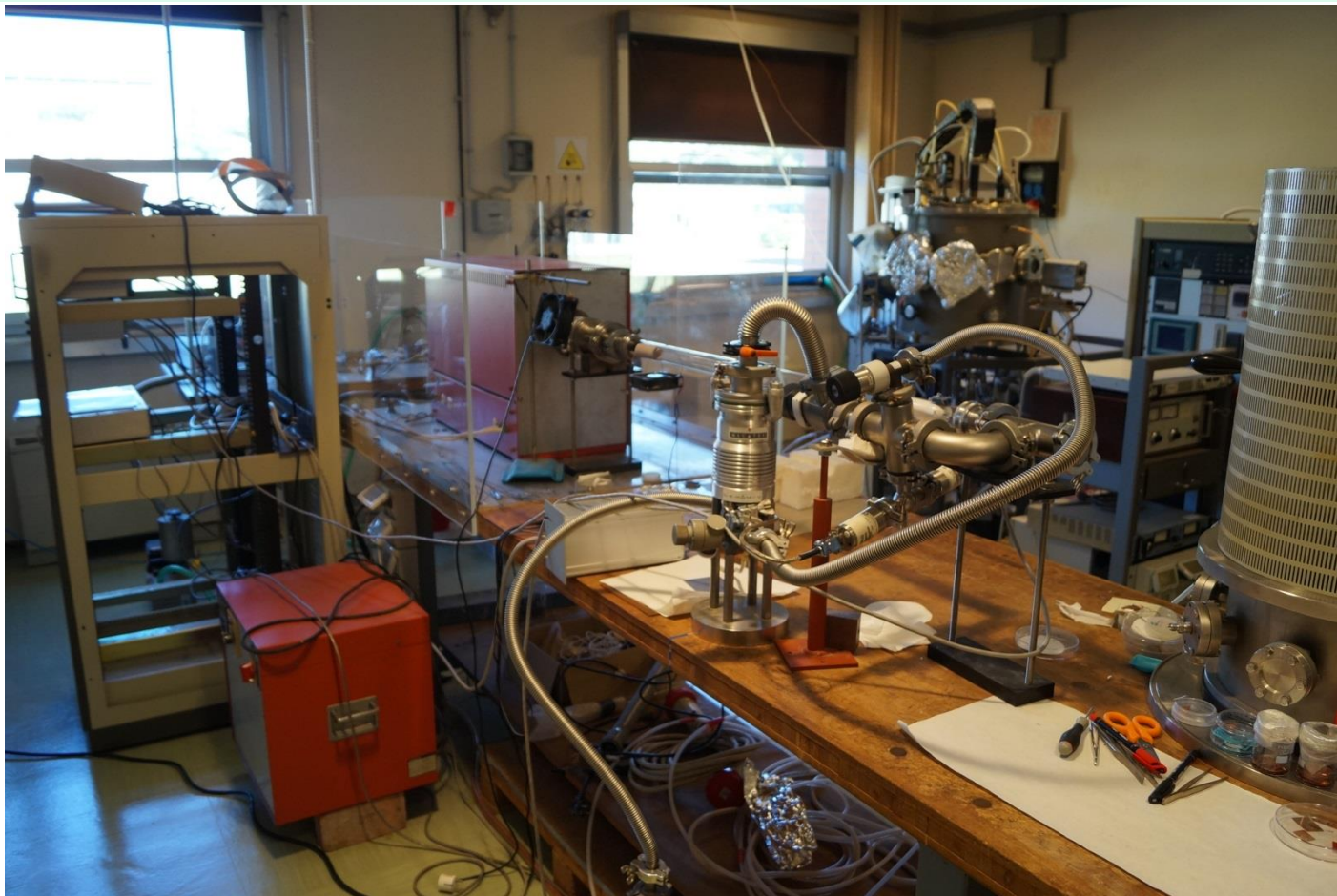
# Outline



1. CVD on copper foils by the decomposition of ethanol
2. High temperature growth of graphene: fast growth and initial stages
3. Low temperature growth: disordered and graphene based derivatives (GBD)
4. Applications to PV

# Graphene studies at ENEA Casaccia: focus

- Graphene and carbons: growth by CVD
- Low temperature, wet, post growth transfer and processing
- Applications mainly to the field of energy technologies

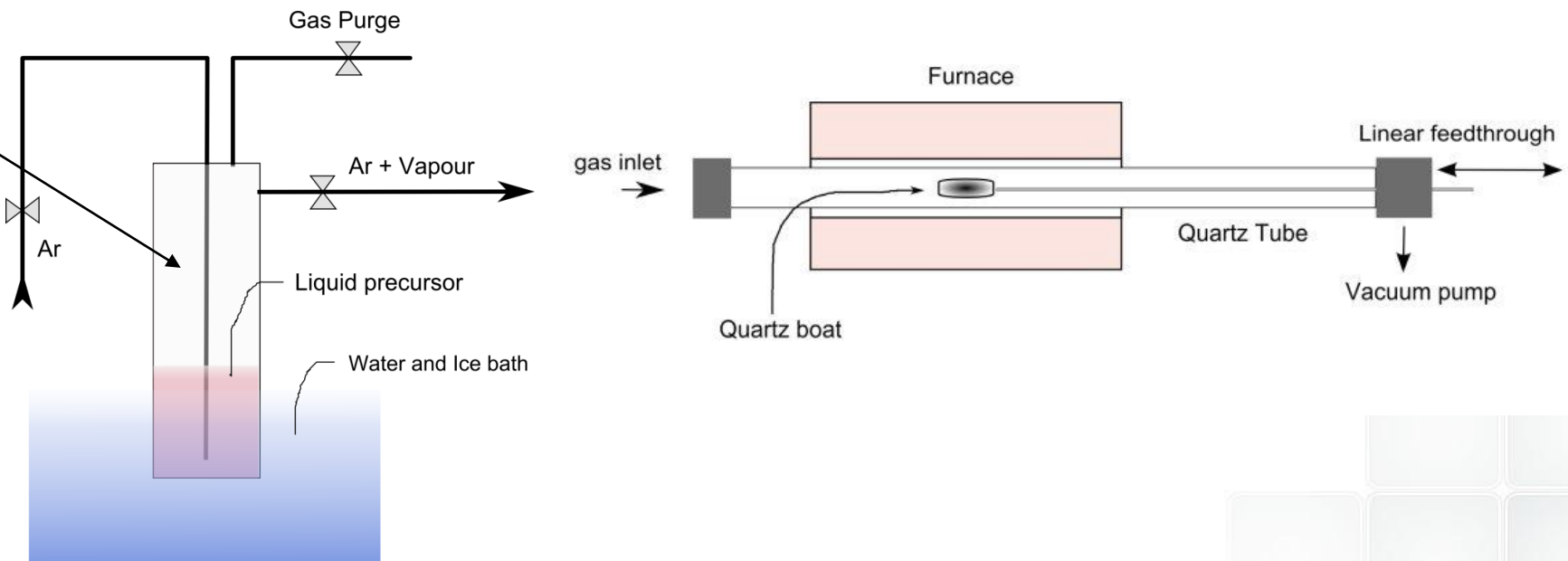


# CVD Graphene growth apparatus: features

1. Samples can be rapidly inserted and extracted from the hot zone (up to 1100°C).
2. The Ethanol vapour is diluted in Ar and H<sub>2</sub> and then fluxed to the vacuum tube furnace and growth substrates.

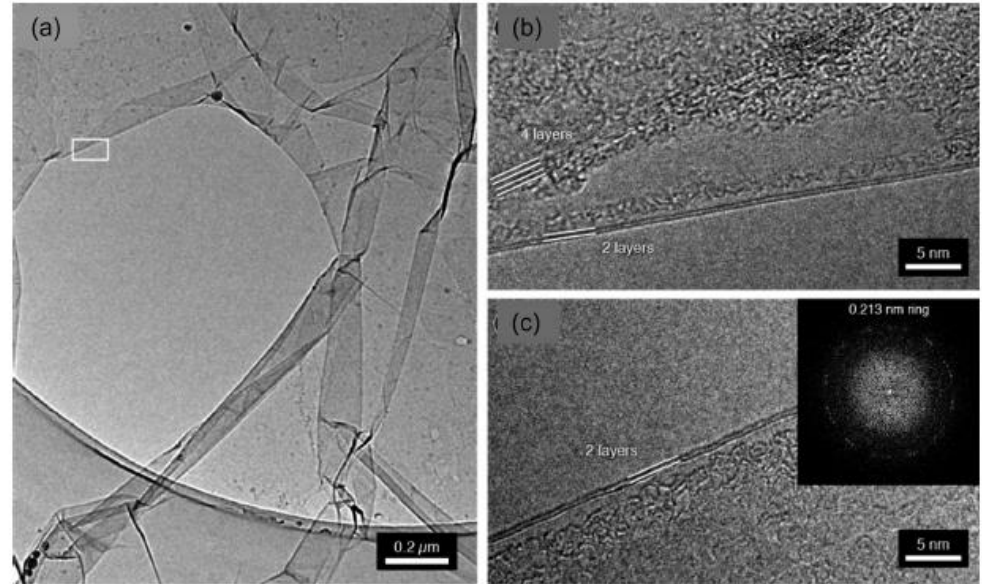
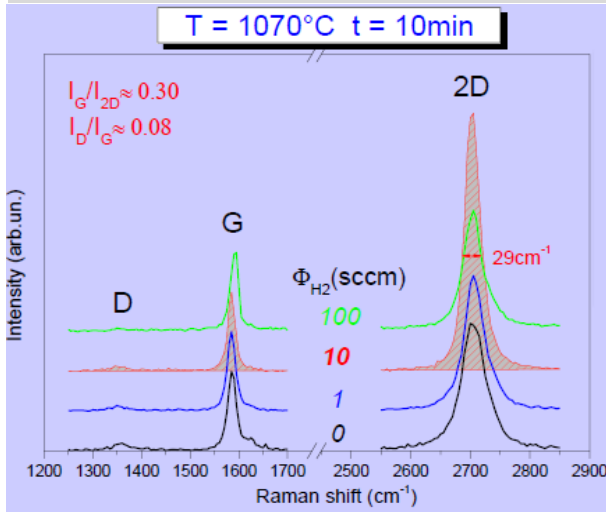
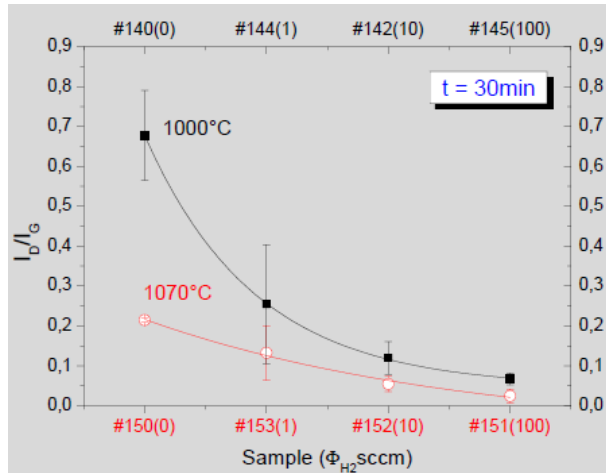
$P_{\text{ethanol}} \sim 15\text{mbar @ } 0^{\circ}\text{C}$ , in equilibrium with 3 Bar of Ar

3. The ethanol enriched Ar flow can be digitally controlled down to a few SCCM  
→ We can study very **short** graphene growths (down to ~10s) under very low ethanol partial pressure ( ~0.05Pa)

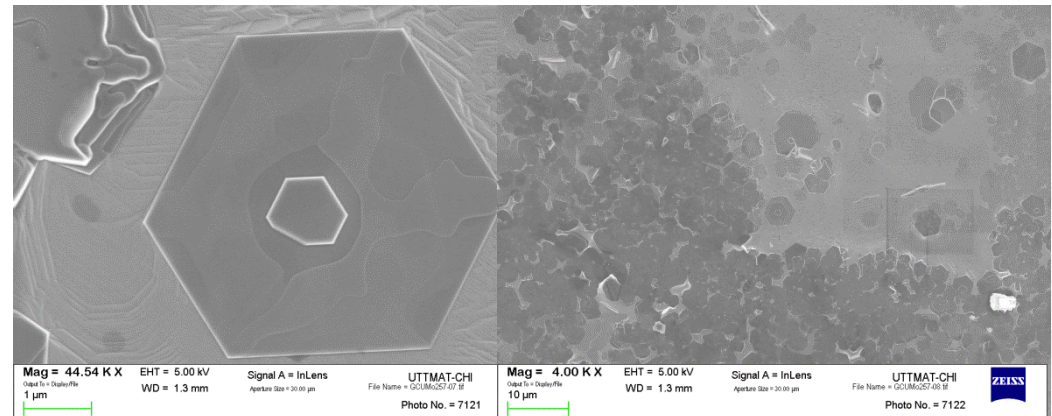


# High temperature (1000°C, 1070°C and above)

At a growth temperature above **1000°C**, at **1070°C**, highly crystalline few layer graphene is produced, comparable to Methane grown.

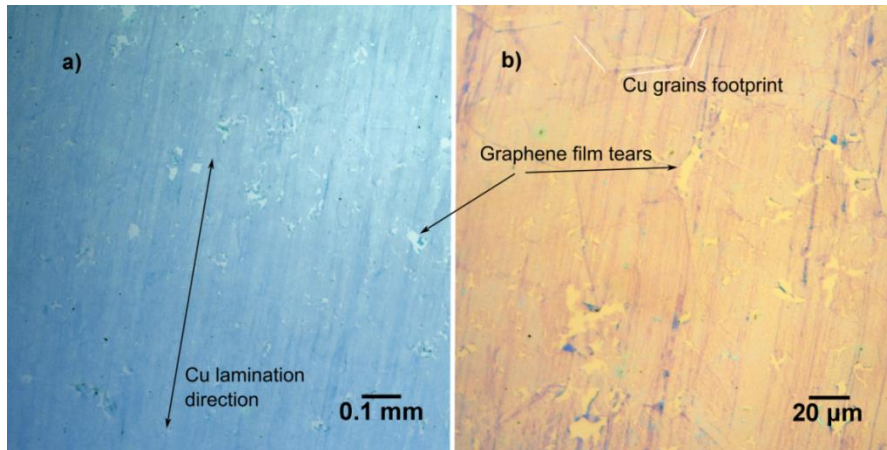


**Above 1084°C**, on molten copper, large single crystals are formed



# Features of ethanol growth: fast coverage

The rapid and efficient growth of high quality graphene is highly desirable. Using ethanol the growth is **faster** and more efficient than using methane or other hydrocarbons.



*Thin Solid Films*, 571 (2014) 139-141

When using ethanol the carbon coverage is much faster than using methane. The optical micrograph shows a graphene film grown for 20s, after its transfer onto a Si/SiO<sub>2</sub> substrate.

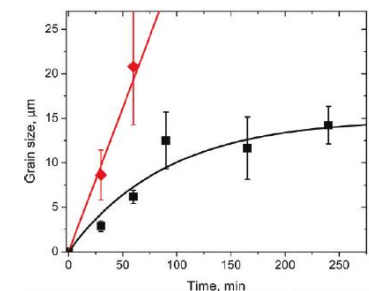
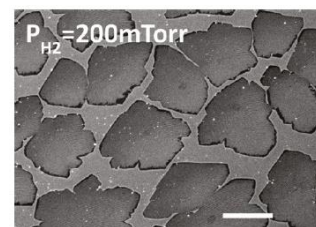
**Also at much lower partial pressure, here 2Pa**

For comparison a typical result using methane

## Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene

Ivan Vlassiuk,<sup>1,\*</sup> Murari Regmi,<sup>2</sup> Pasquale Fulvio,<sup>1</sup> Sheng Dai,<sup>1</sup> Panos Datskos,<sup>1</sup> Gyula Eres,<sup>1</sup> and Sergei Smirnov<sup>3,5</sup>

*ACS Nano*, 2011, 5 (7), pp 6069–6076

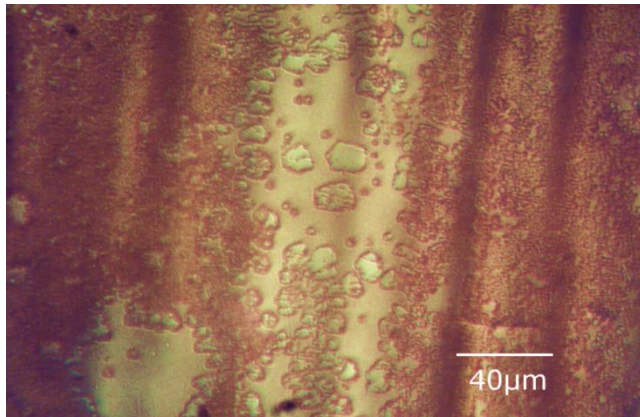


The catalyst coverage time depends on the nucleation density and on the accretion velocity of the graphene nuclei.

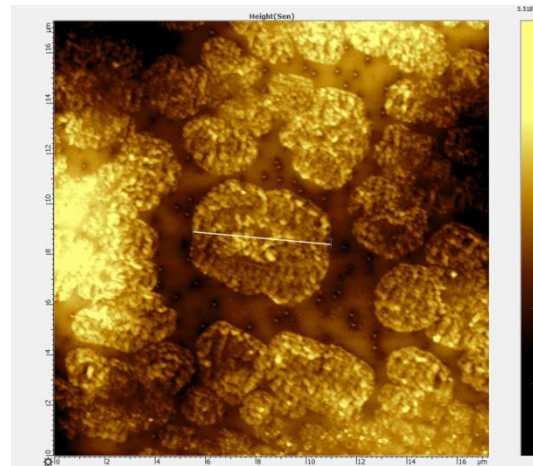
# Initial growth stages with Ethanol

Very recently we succeeded in **observing the initial growth stages of graphene** before the merging of the individual domains, both on Copper and after its transfer on SiO<sub>2</sub>

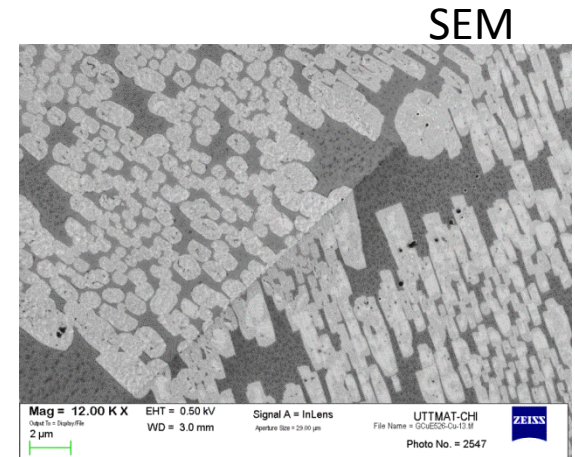
- 15s growth
- decreasing the ethanol partial pressure <0.1Pa
- also Raman D/G improves



Optical Micrograph

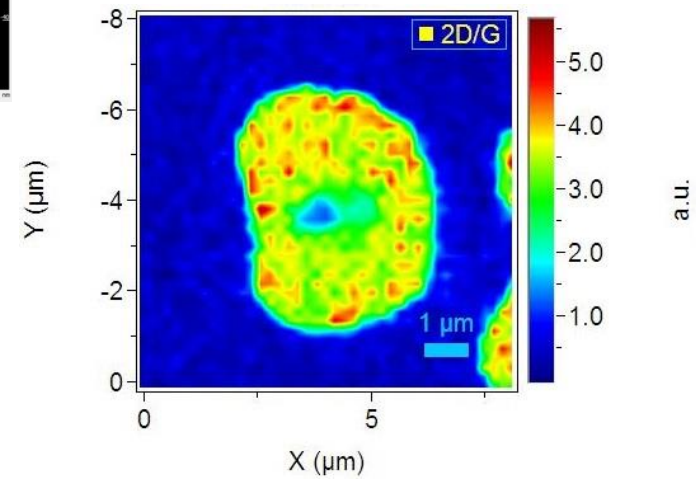


AFM



SEM

Raman Map  
(after transfer on SiO<sub>2</sub>)



The visibility of graphene (optical, scanning and electronic) depends on the “differential” oxidation between covered and uncovered copper regions

# Why is the growth so much faster with ethanol than with hydrocarbons?

At high temperature **ethanol decomposes** into a hydrocarbon radical and an oxygen containing group. There are two main decomposition channels:

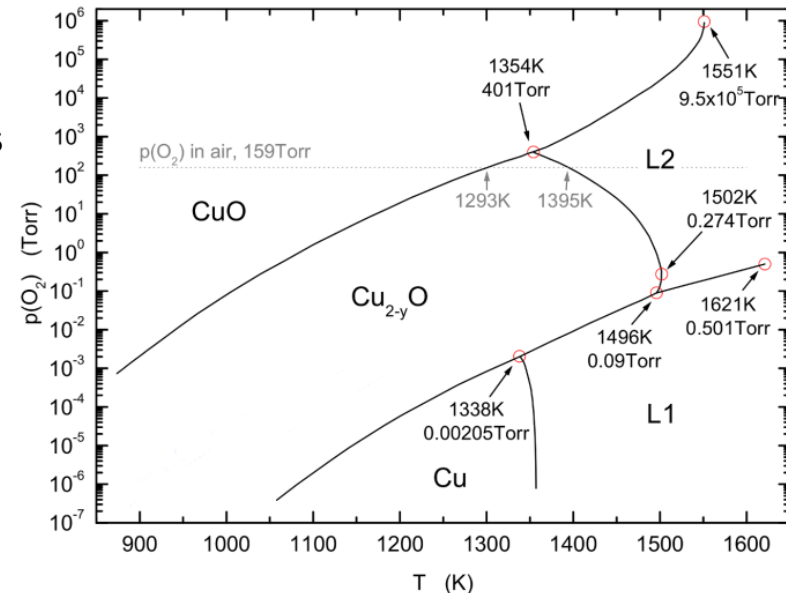


Which is the role of the oxygen?

- The gaseous environment is overall reducing.

During the CVD process oxygen dynamically attaches (adsorption / desorption) to the copper surface (forming  $Cu_2O$ ). **The oxidized surface states can enhance the dehydrogenation of the hydrocarbon molecule**, thus the formation of graphitic carbon, promoting the growth kinetic.

- After the growth, XPS reveals that the surface is entirely **metallic** below the graphene.

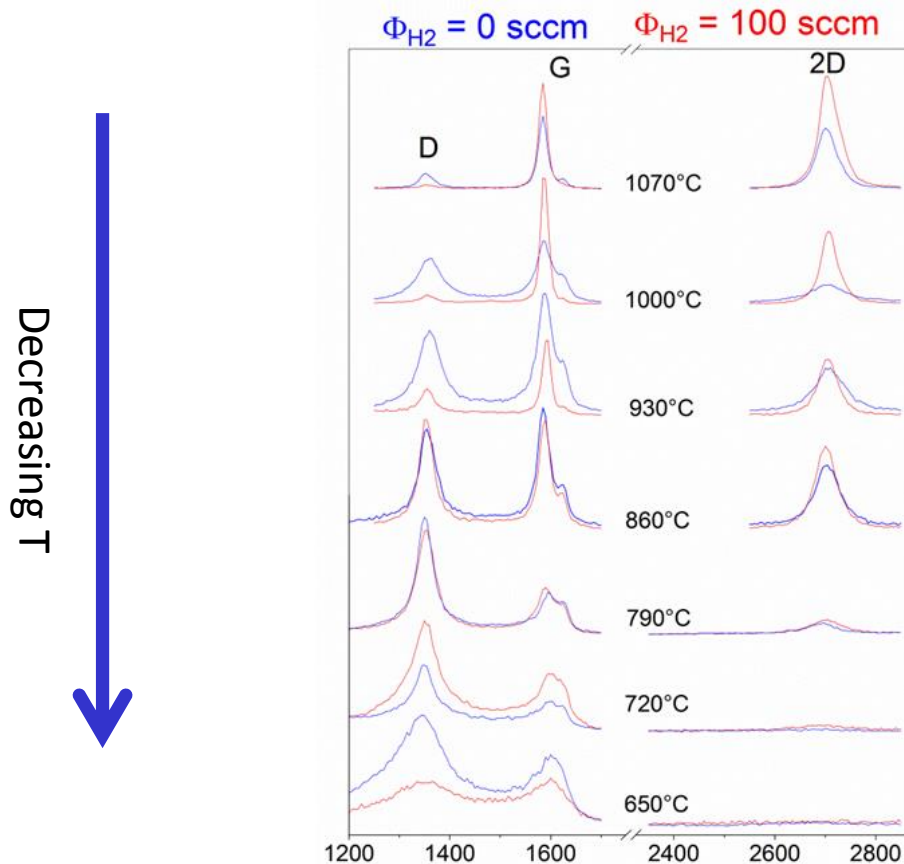


The copper oxygen phase diagram



# The growth on copper below 1000°C

If we decrease the growth temperature below 1000°C, thin and transparent carbonaceous films continue to grow down to much lower temperatures (600°C and below). The films progressively lose their graphitic character and appear to head towards amorphous phases.

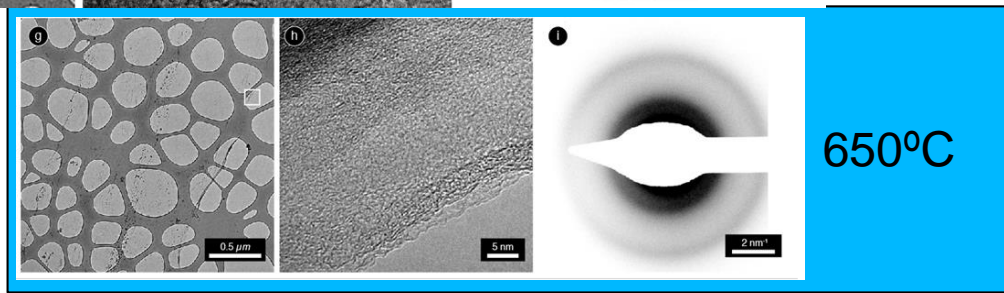
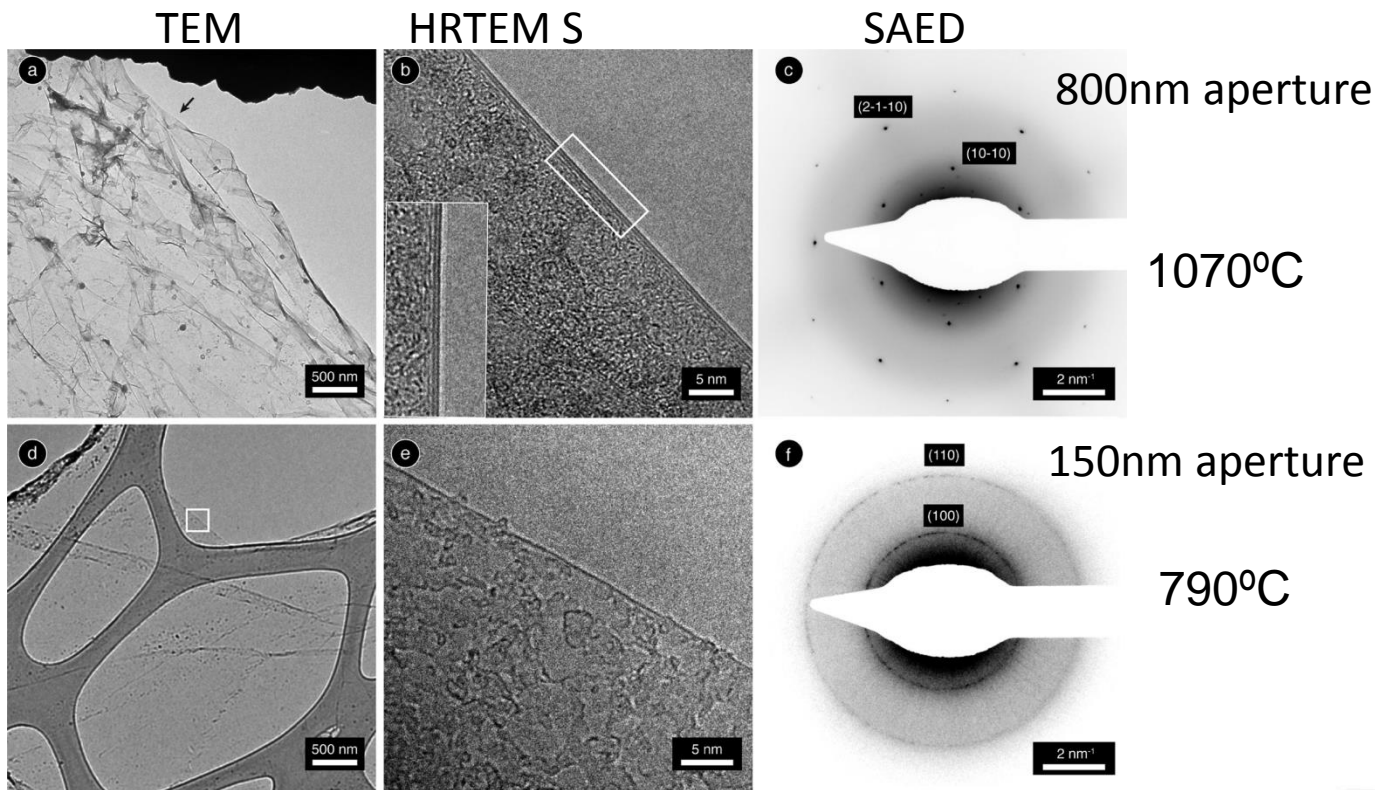


Raman spectra of the carbonaceous growth at decreasing temperatures

Films are grown on copper and transferred onto Si/SiO<sub>2</sub> (300nm) for Raman analysis

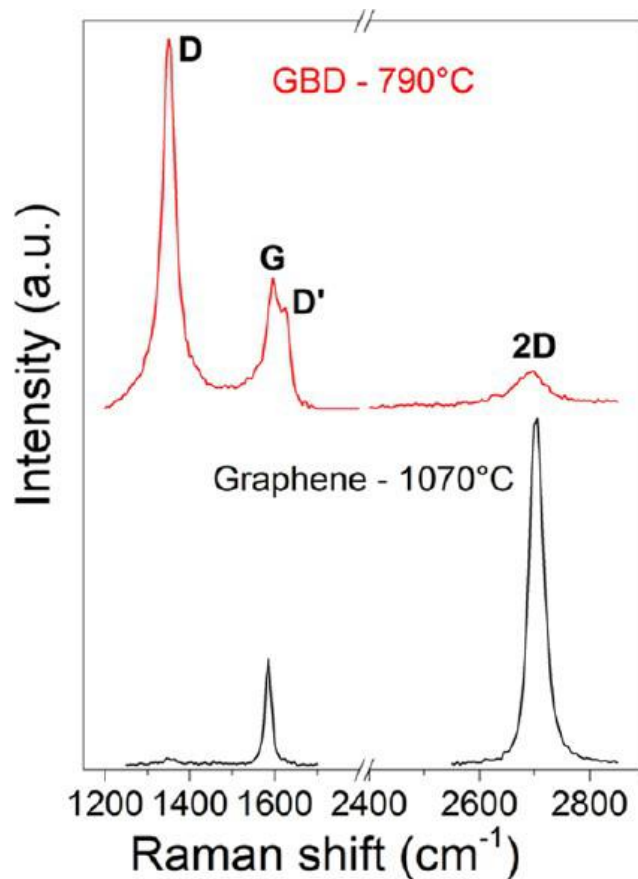
# The microstructure, single layer at 790°C

The temperature of 790°C was selected based on Raman and TEM evidence, and the film was further investigated to determine its structure.



# Comparing TEM with the Raman spectrum

By counting the number of dots on the 150nm SAED we can estimate the domain size to be around **20-25nm**, but not smaller

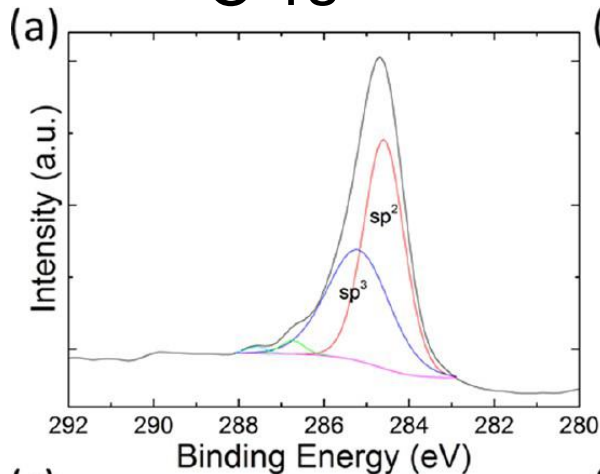


On the contrary the Raman spectrum tell us of a highly defective graphene, with an inter-defect distance in the **1nm** range. Observing these highly defective “stage 2 type” Raman spectra, no hypothesis can be made on the defects, whether vacancies, points or edges. But also functional groups inserted at  $sp^3$  sites, contribute to the D band as discontinuities of the  $sp^2$  lattice

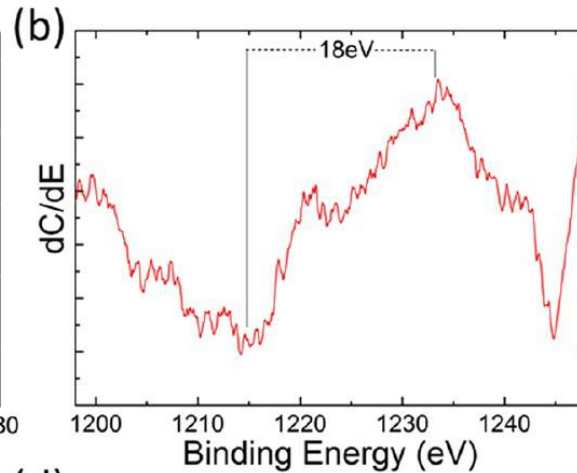
There seems to be a discrepancy

# Determining the type of carbon bonding by XPS

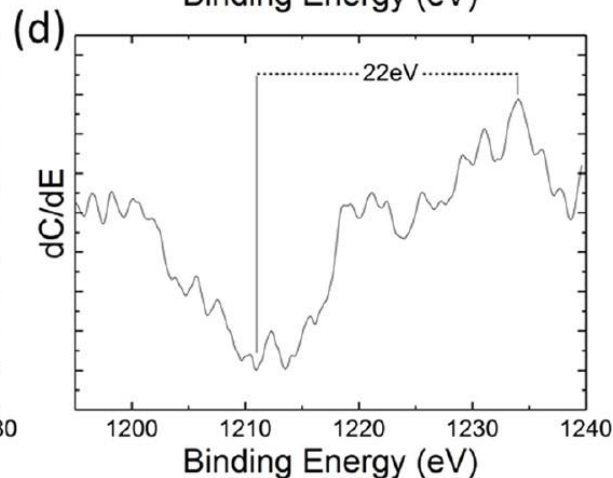
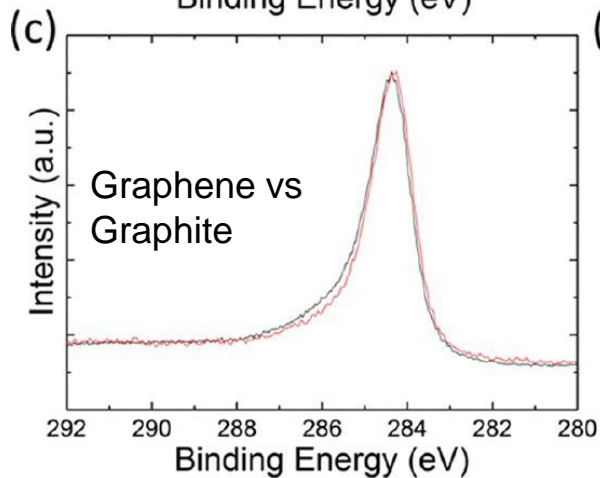
## C 1s



## Auger KLL edge diff. and parameter

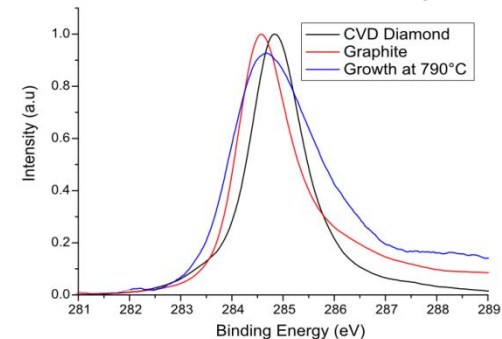


790°C



1070°C

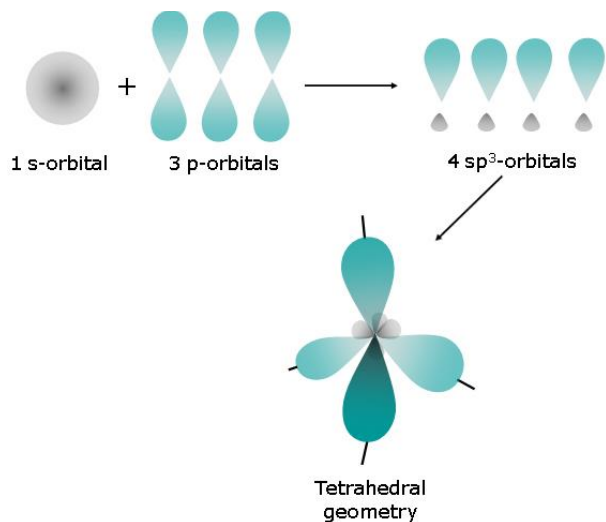
## C 1s comparison at a glance



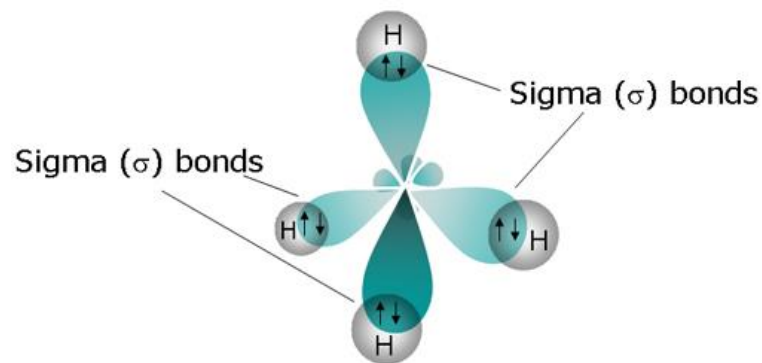
The growth at lower T has a significant sp<sup>3</sup> fraction. **No Oxygen is detected!**

# Carbon: $sp^2$ and $sp^3$

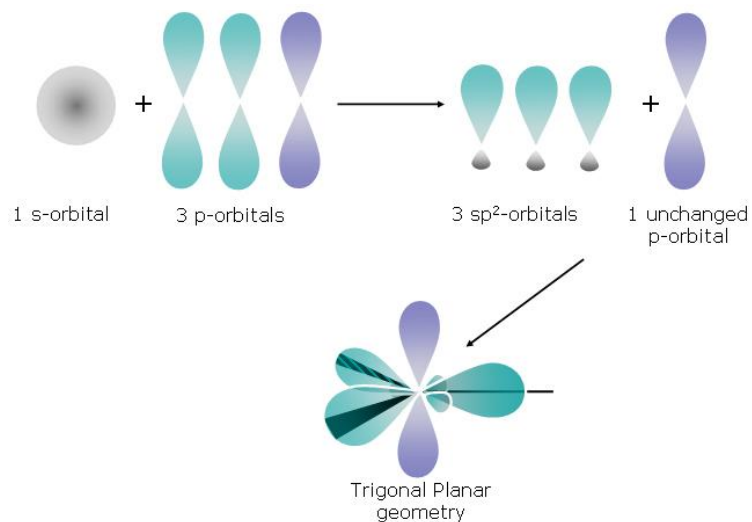
$sp^3$



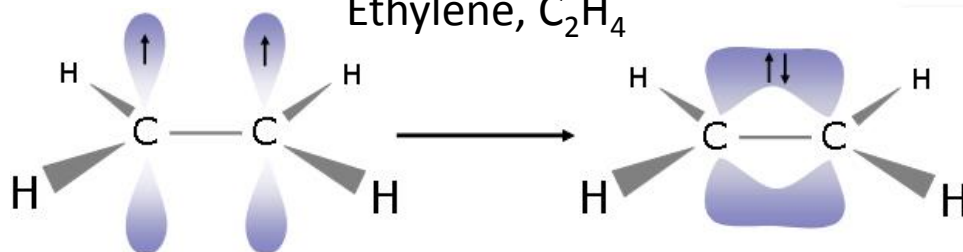
Methane,  $CH_4$



$sp^2$



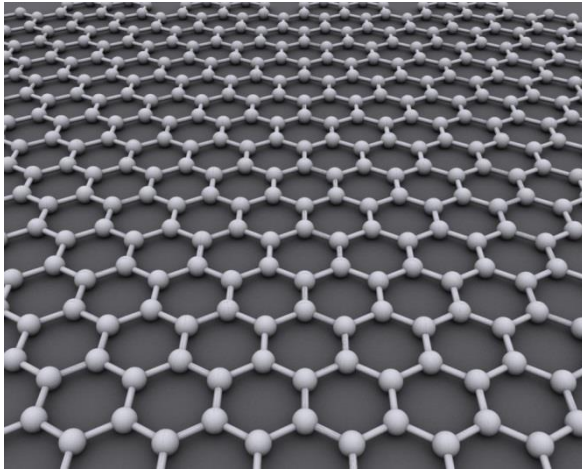
Ethylene,  $C_2H_4$



# Graphene and its derivatives

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

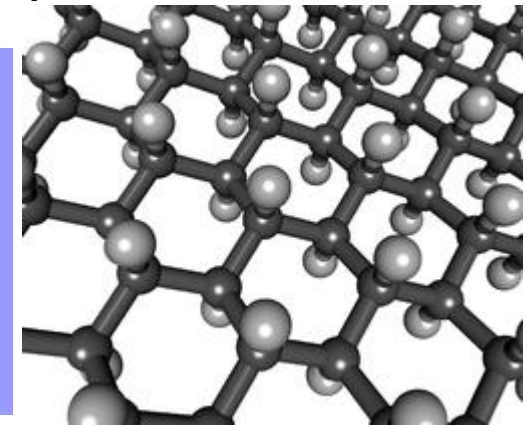


## periodic Graphene Based Derivatives

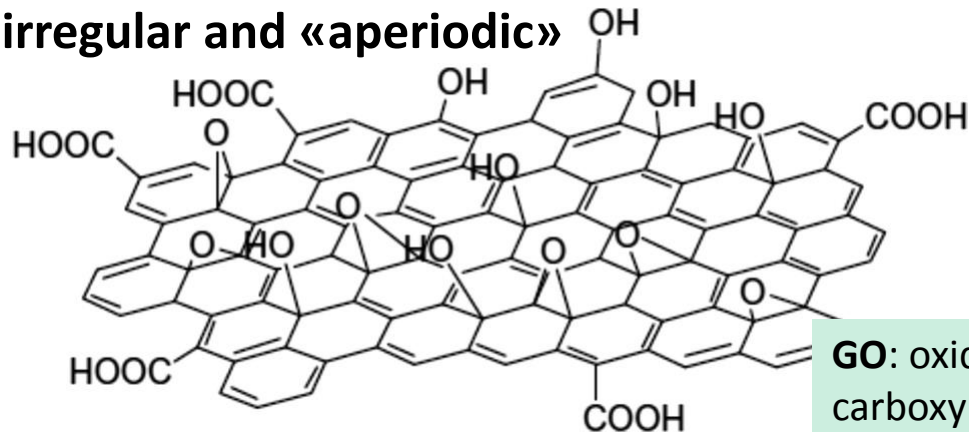
**Graphane:** all carbons are  $sp^3$  and bonded to hydrogen

**Fluorographene:** the same structure with fluorine

**Graphone:** hydrogen only on the top



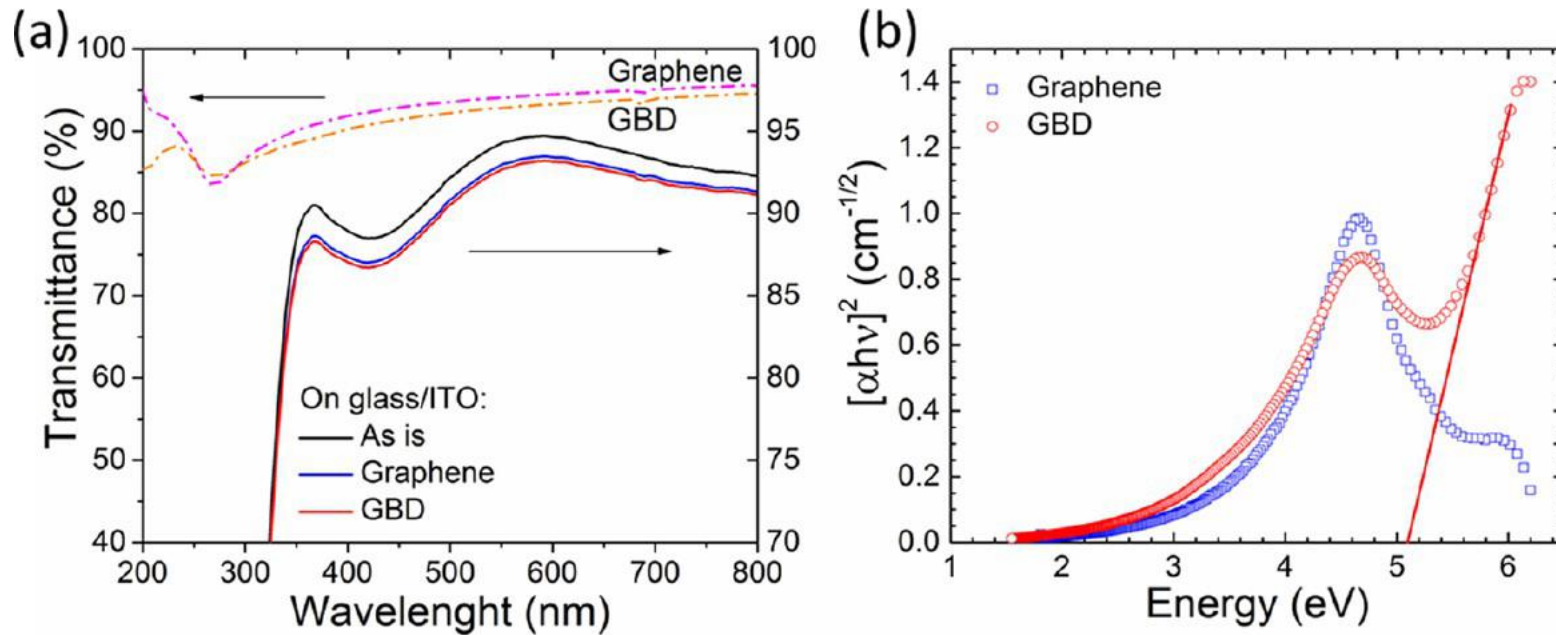
## irregular and «aperiodic»



**GO:** oxidised graphene. Epoxide, carboxyl and hydroxyl

Also fully  $sp^3$  GOH structures are possible: hydrogenated, epoxide, hydroxyl mix are predicted to be possible. Buonocore this conf.

# Optical and electrical properties at 1070°C and 790°C



Optical properties. (a) Transmittance of 1070°C and 790°C transferred on quartz substrates (top curves, left axis) and on glass/ITO substrates (bottom curves, right axis). (b) Tauc plot of graphene and GBD on quartz. An **optical gap around 5.1eV** was found by extrapolation.

The sheet resistance increases from **400 ohm/sq** to **400kohm/sq** by lowering the temperature from 1070°C to 790°C

# In conclusion: CVD growth of a graphene based derivative



In summary, what we know that the film grown on copper at 790°C:

- 1) it is mainly made of single layer, well formed and crystalline.
- 2) its Raman spectra appear not coherent with its crystallinity.
- 3) a large fraction of carbon is  $sp^3$  bonded, but no oxygen can be detected by XPS (it is not GO!).
- 4) it is electrically insulating and it has an optical gap at 5.1 eV.

Our conclusion is that we have produced a **graphene based derivative closely related to graphane**, although we only have indirect evidence.

The chemistry of ethanol on copper is very **effective** for producing carbonaceous growth, possibly with a role for the exchange of oxygen on the metal surface.

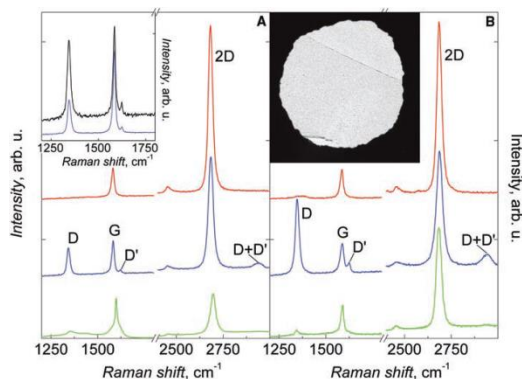
We presume that radicals are inserted into the lattice while not fully dehydrogenated, but we should also bear in mind similarities to the **hydrogenation** reaction of alkenes onto transition metal surfaces, at lower temperature.



# Graphane synthesis

1. Graphane is regarded by the theorists as an extremely stable molecule, more stable than benzene, it is electrically insulating and its optical gap was computed between 5.4-6.1eV.
2. Probably stoichiometric graphane and fluorographene have not been synthesized yet, despite early claims.
3. Hydrogenated graphene is usually produced by exposing graphene to hydrogen plasmas, in a non-equilibrium post growth process (which probably generate metastable phases).
4. The thermal CVD process occurs at equilibrium and it can be expected to produce stable phases.

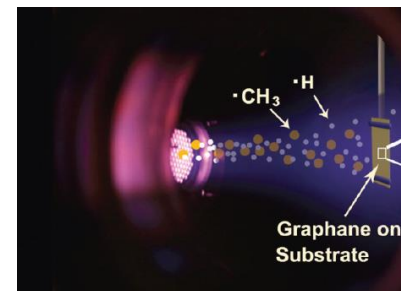
Early report on graphane



- (A) Graphene on SiO<sub>2</sub>  
(B) Free-standing graphene.

Elias et al 2009 Science 323 610

Only one work reports on the growth of Graphane by plasma enhanced CVD



Wang et al 2010 ACS Nano 4 6146

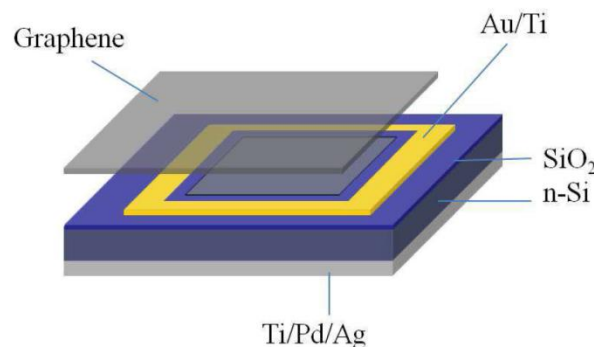
# Graphene applications: Silicon-Graphene Schottky junction solar cells. **Graphene acts as a thin conductor.**

A test device was jointly developed at Portici and Casaccia ENEA labs.

Silicon-Graphene Schottky junction solar cells. Based on a junction between a silicon absorber and a **low sheet resistance multilayer graphene** film. Graphene was transferred on the active area using a temporary **Cyclododecane** supporting layer. The cell was topped with a double layer AR coating (**DARC**)



Type: n-Si, Resistivity:  $\rho=0.7 - 1.3 \Omega\text{cm}$

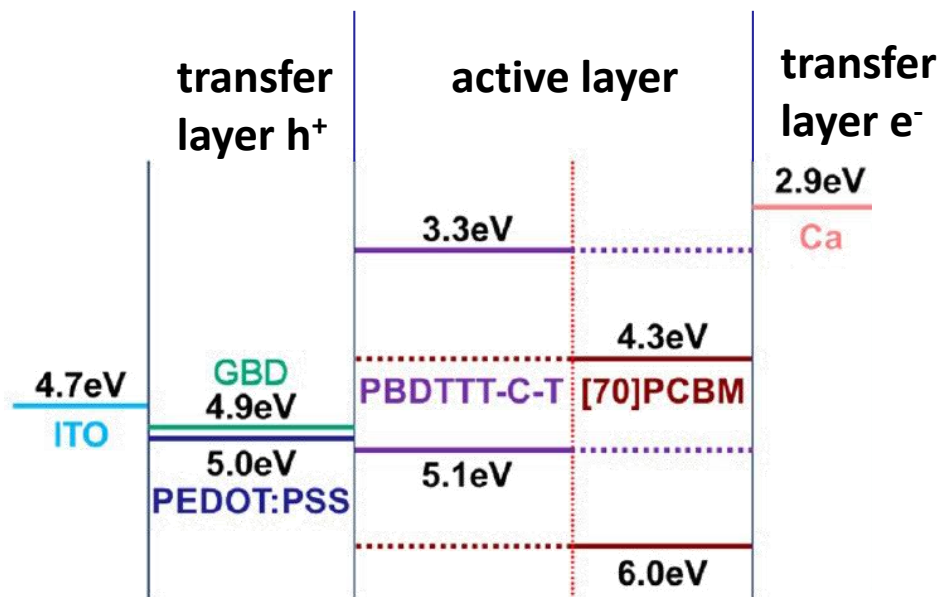
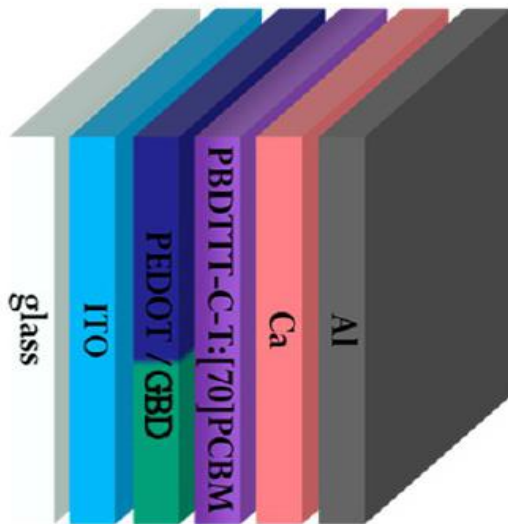


Cell schematic, about 3mm side active area

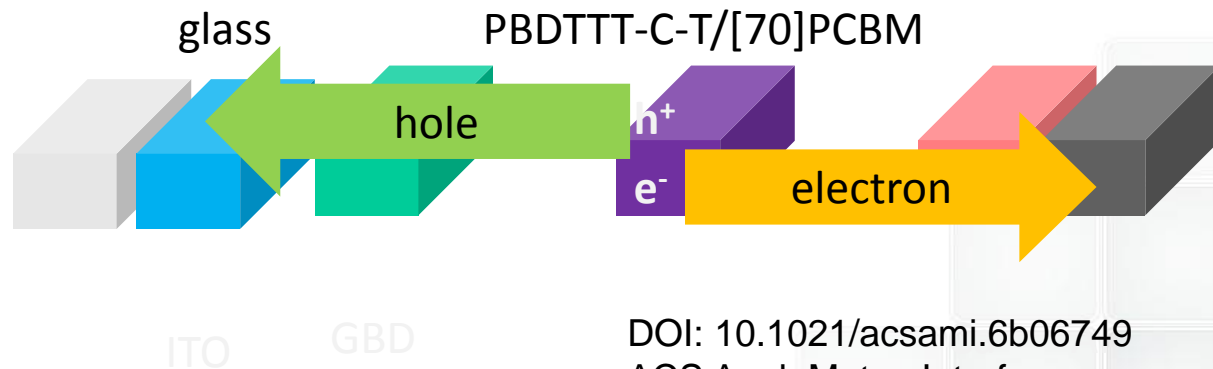
**Latest PE 8.5% and QY 90% with AR coating**

*Solar Energy 2015, Lancellotti et al.*

# Graphene Based Derivative as HTM for organic photovoltaics. The GBS acts as a matching barrier.



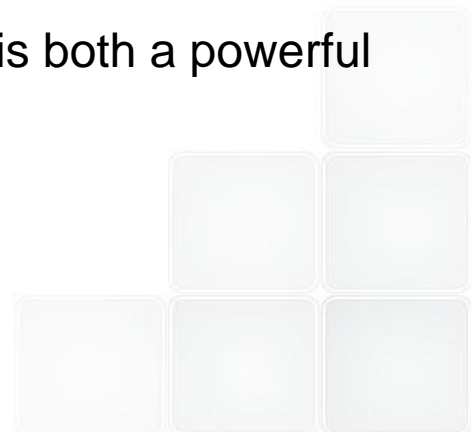
- The cells attained a maximum power conversion efficiency of 5%, matching reference cells made with state-of-the-art PEDOT:PSS as the hole transport layer, with the advantage that GBD should not corrode the ITO electrode.



# Conclusions



- The macroscopically large 2D carbon lattices of graphene offer a unique opportunity to be covalently functionalized by the conversion of carbons from the  $sp^2$  to the  $sp^3$  configuration.
- We believe that graphene based derivatives can be directly grown by thermal CVD processes by employing the opportune precursors and processes.
- Graphene and its derivatives can be transferred by wet chemical methods to top arbitrary surfaces
- Graphene at present does not succeed in its ambitious objectives for high conductivity “in-plane” electronic applications.
- Graphene derivatives offer the opportunity of «a platform» to alter the functional properties of surfaces and interfaces.
- We have demonstrated that the CVD from ethanol on copper is both a powerful and flexible technique



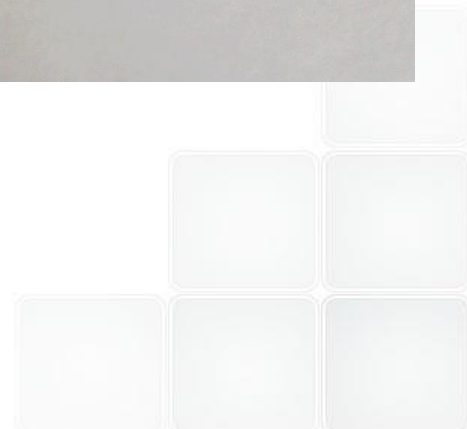
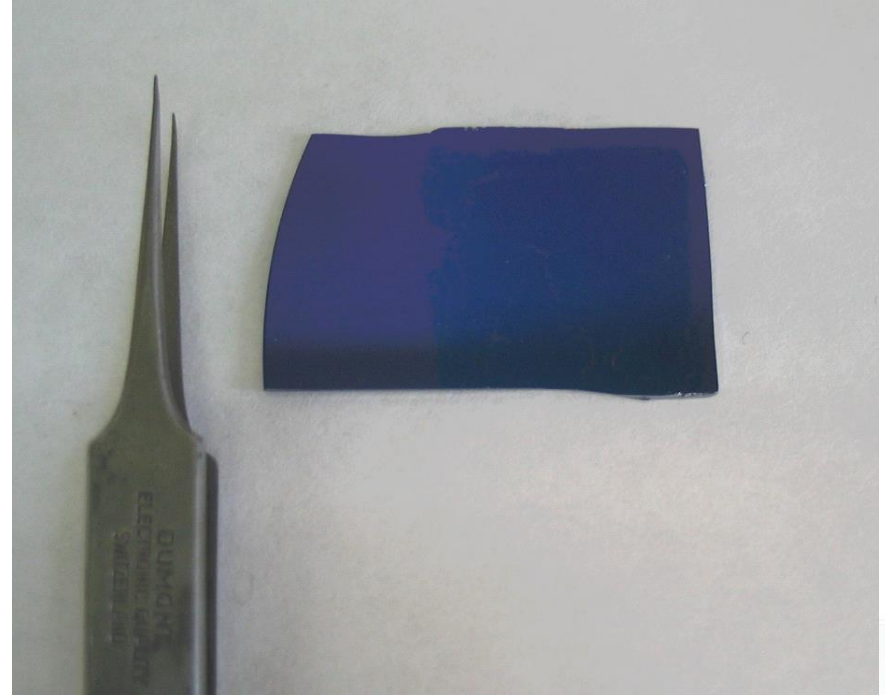
# 2D Materials Handling: Transfer

Graphene must be separated from the copper substrates for the subsequent use.

The etching of copper is most frequently performed using protective layers for graphene, such as PMMA. **Removing the protective layer is not easy.**

This is even truer for **chemically functionalized**, graphene based derivatives.

An innovative way for graphene transfer was employed for this study, making use of a **cyclododecane** resist, a compound which **sublimates** at ambient temperature.



# Cyclododecane based transfer

Scheme of the post growth processing method developed at ENEA, based on a cyclododecane temporary protective layer

