*(A "creationist" lecture)*

# Graphene and 2D-TMDC materials: the role of chemistry in growth, functionalization and material properties

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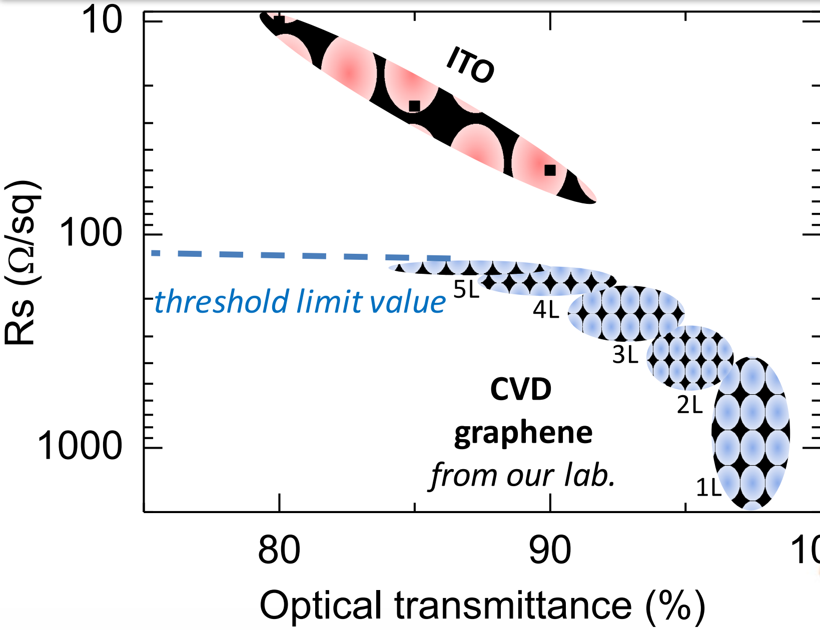
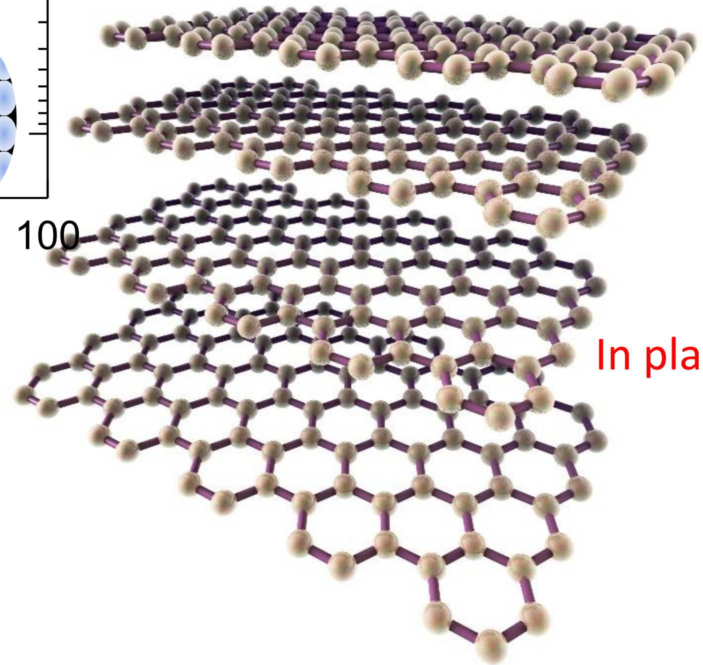
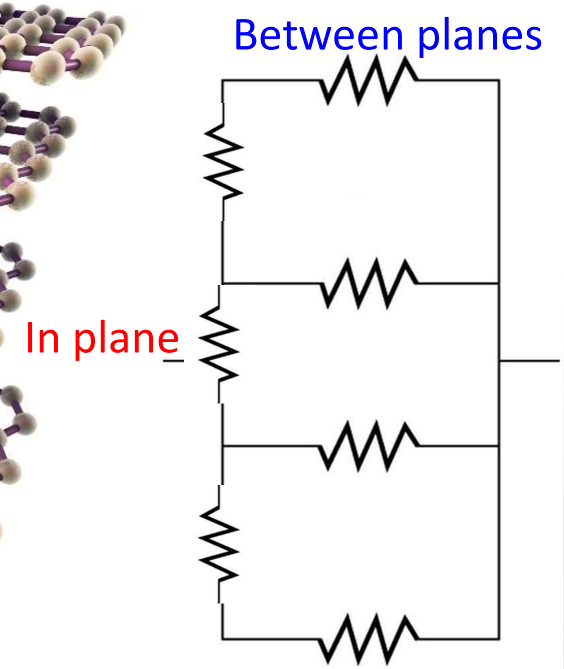
# Driving Motivation




Reduce

- the in-plane resistivity by improving graphene layer quality
- The between-plane resistivity by improving interfacing and stacking of layers

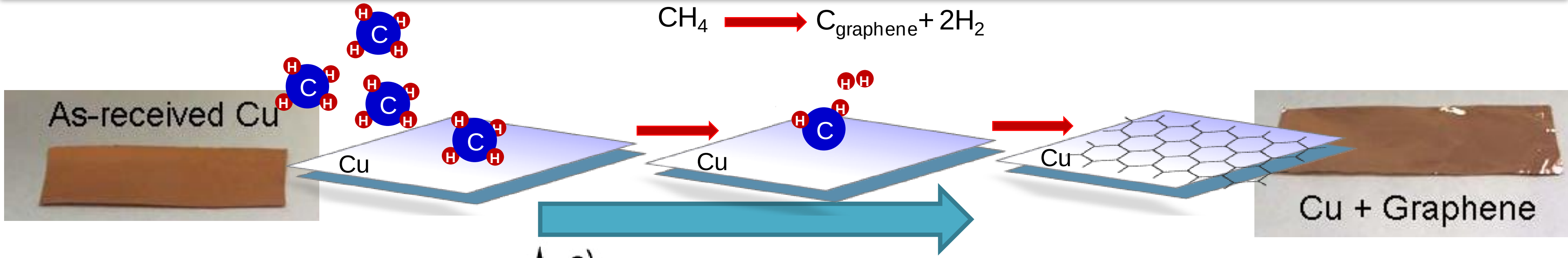


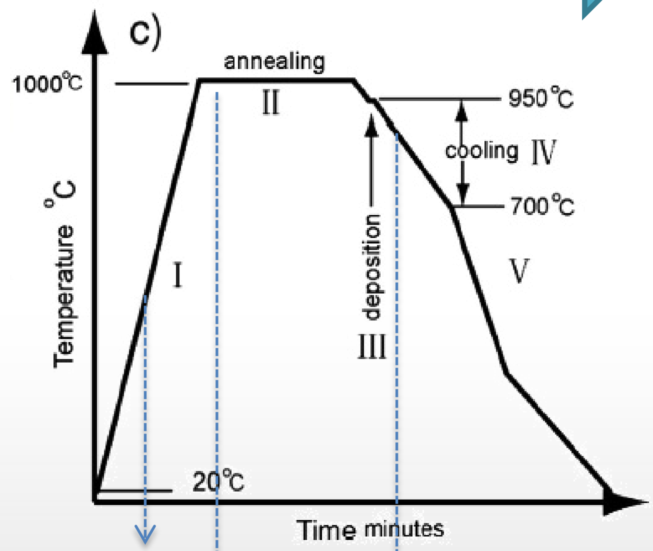


# Outline/Menu

- CVD of Graphene
- Implementation of CVD by $H_2$ plasma
- CVD of TMDs, i.e., $WS_2$
- Doping of Graphene
- Functionalization of Graphene
  - Hydrogenation
  - Fluorination
  - Oxidation
- .........finally play with graphene!!!

# The “Simple” CVD




Need
- catalyst (Cu, Ni),
- carrier gas (Ar, $H_2$ ),
- carbon source ($CH_4$ )
- fast heating/cooling

I. Clean copper foil by heating up to 1000˚C with $H_2$ flowing

II. Add gas flow of $CH_4$ (~170 sccm)

III. Cool down with gas flowing

# CVD Graphene Chemistry: Prehistory & Antiques

"Everything that old is new again"

NATURE November 4, 1961 Vol. 192

## Pyrolytic Carbon Formation from Carbon Suboxide

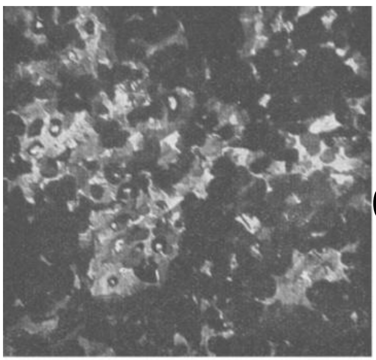
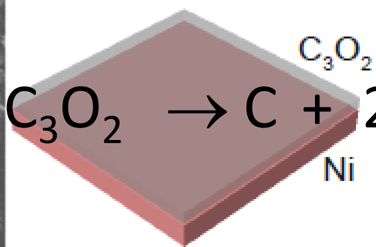
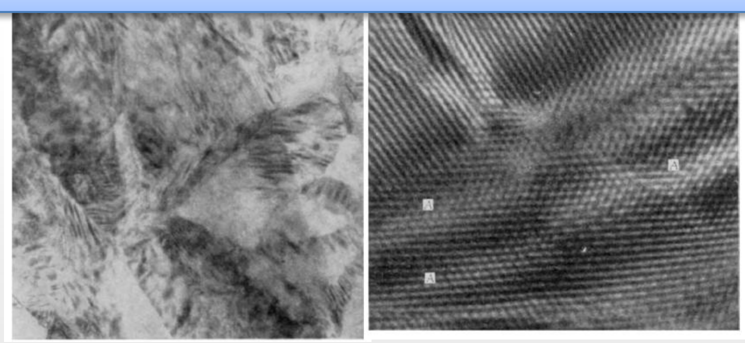


Fig. 2. Transmission electron micrograph of film carbon deposited from $C_3O_2$ on to a nickel substrate at 713° C. (× c. 4,700)




$$C_3O_2 \rightarrow C + 2CO$$

Flaky carbon deposit over Nickel @750°C



Karu & Beer, J. Appl. Phys. (1966)
Irving & Walker Jr., Carbon (1967)
Presland & Walker Jr., Carbon (1969)
...and many others from these times

NATURE, VOL. 221, MARCH 15, 1969

## Graphite Formation from Low Temperature Pyrolysis of Methane over some Transition Metal Surfaces

S. D. Robertson* (Pt, Mo, W, Ti, Ta, Ni), @ 1000 °C

$$H_2 + 2^* \rightleftarrows 2H^*$$

$$CH_4 + 2^* \rightleftarrows CH_3^* + H^*$$

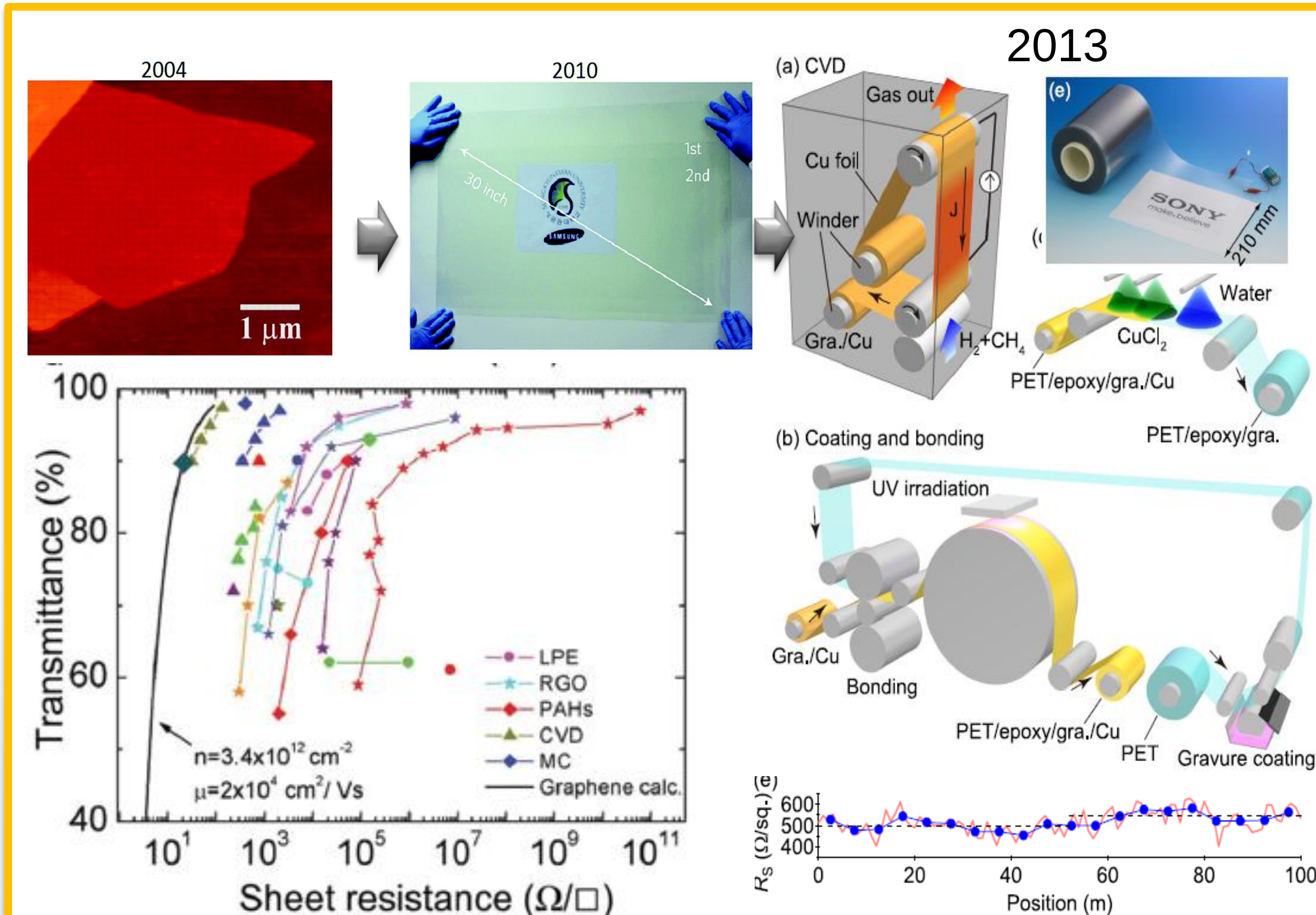
$$CH_3^* + ^* \rightleftarrows CH_2^* + H^*$$

$$CH_2^* + ^* \rightleftarrows CH^* + H^*$$

$$CH^* + ^* \rightleftarrows C^* + H^*$$

# Renaissance (after 2004-2005)...and Industrial Revolution

## What is new about that?



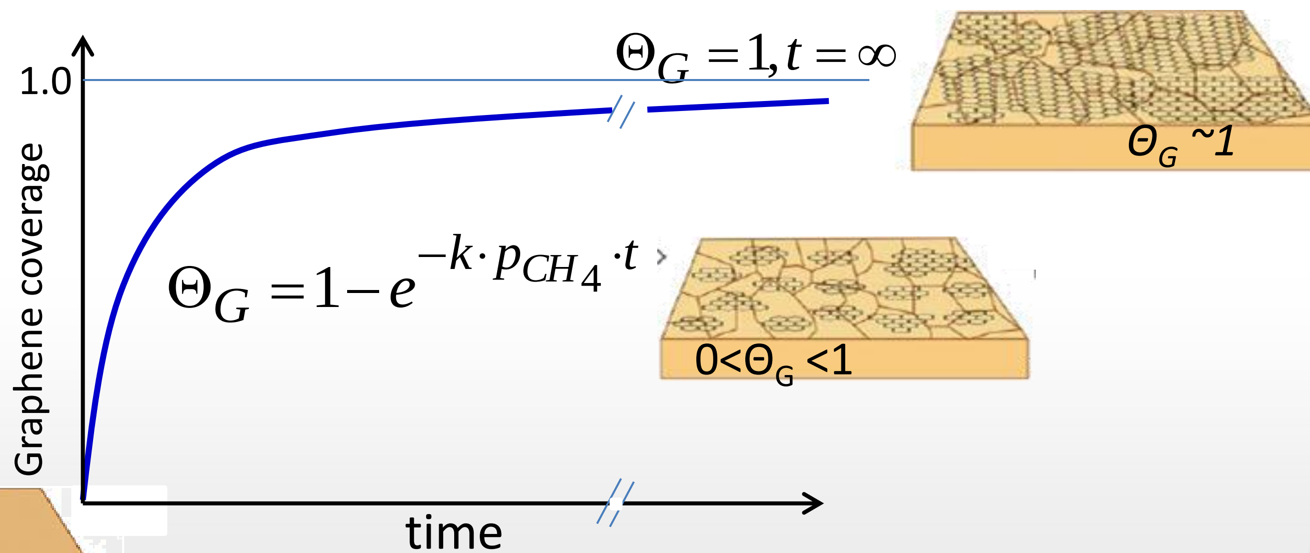
# Graphene CVD Growth: Kinetics

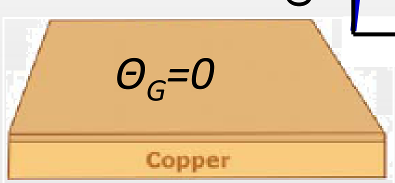
The graphene growth occurs via a **topochemical** reaction:

The rate of graphene formation depends on the free surface area (number of free sites $\Theta_G$) of the Cu catalyst

$$\vec{r}_{graphene} = \frac{d\Theta_G}{dt} = k \cdot (1 - \Theta_G) \cdot p_{CH_4}$$

*Graphene gradually expand on the surface of the copper catalyst, causing the reduction in its activity*

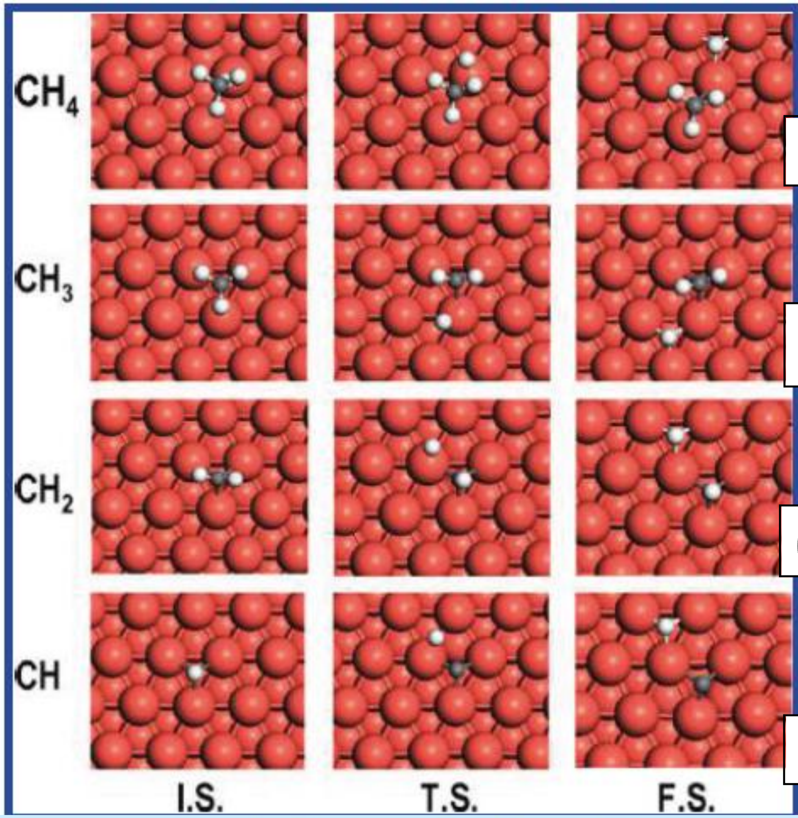



Graphene is a catalyst poison for the decomposition of methane

# $CH_4$ Dehydrogenation on Copper

## $CH_4$ dehydrogenation on Cu (111)



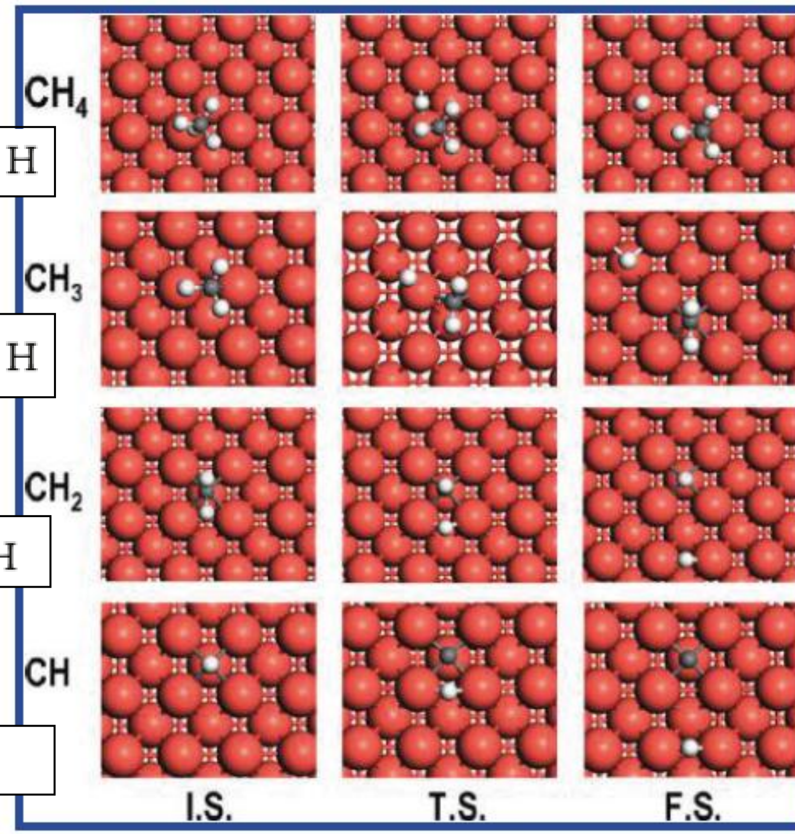

$CH_4 \rightarrow CH_3 + H$

$CH_3 \rightarrow CH_2 + H$

$CH_2 \rightarrow CH + H$

$CH \rightarrow C + H$

## $CH_4$ dehydrogenation on Cu (100)




C mobility /diffuion very unfavorable on the Cu surface

**Atomic Electron Configurations**

$4^{th}$ row elements… The [Ar] $4s^1$ $3d^{10}$ full d configuration of **Cu** is more stable than [Ar] $4s^2$ $3d^9$ (expected)

${}_{29}Cu$ [Ar] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ _ _ _ [Ar] $4s^1$ $3d^{10}$

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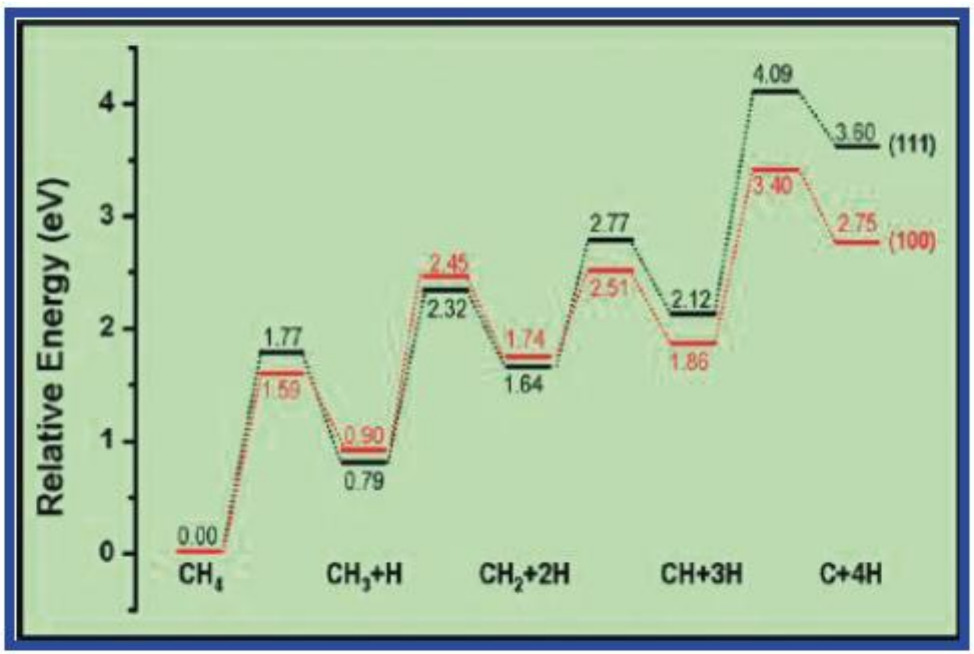
# Energy profile of the dehydrogenation processes of $CH_4$ onCu (111) and (100) surfaces

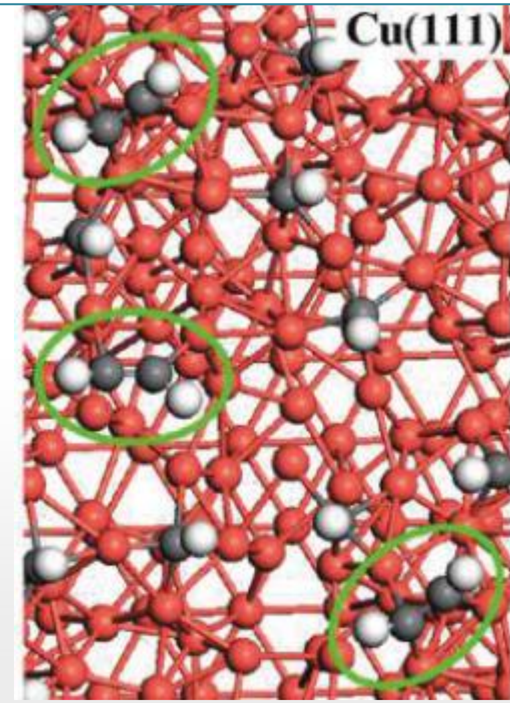
All four dehydrogenation steps are endothermic, and the corresponding activation energy barriers are about 1.02.0 eV. The final product C+4H is already 3.60 eV higher in energy than the adsorbed $CH_4$, which suggests that atomic carbon is energetically very unfavorable on Cu surface

There are possibly more favorable reaction paths to grow graphene compared to a complete dehydrogenation of $CH_4$

$$CH(s) + CH(s) \rightarrow (s)C{=}C(s) + H_2\uparrow$$




since the Cu coordination number of C is higher on the (100) surface

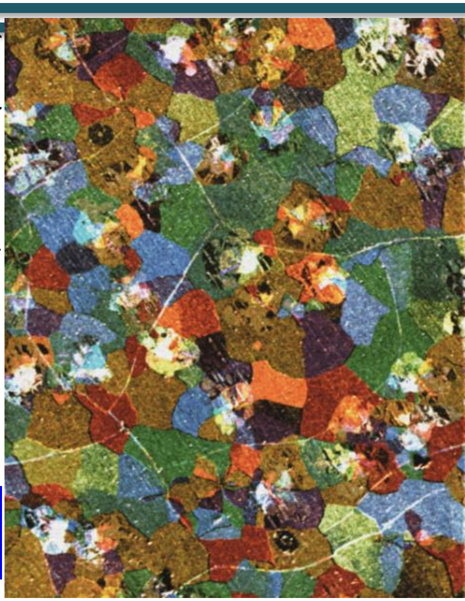



C–C dimers are more stable on all sites of a Cu surface

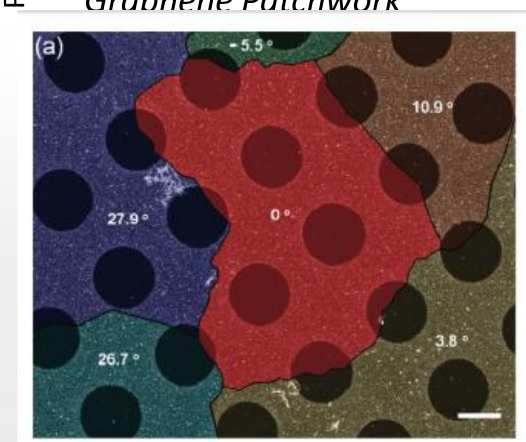
# CVD Graphene on Copper foil: Polycrystallinity!

**Controlling the structure of graphene is needed** | **Tailoring conductivity by GBs**

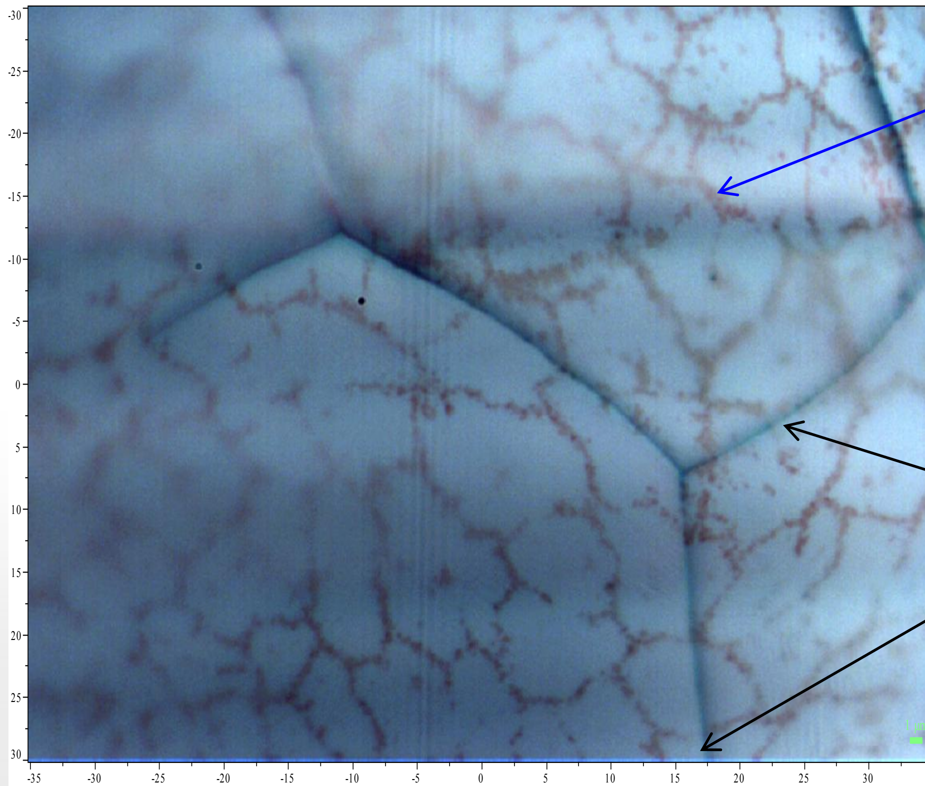
P. Y. Huang et al. Nature 469, 389–392 (2011)



*Graphene Patchwork*




- In all growth methods, **defects are generated in the honeycomb lattice**
- The generation of **grain boundaries drives to poly-crystalline graphene**
- **GBs deeply affects transport properties (as well as mechanical and electronic ones)**




***Graphene GB***

**Cu grain *boundaries***

The problem is not the grain of Cu sincegraphene can grow over it

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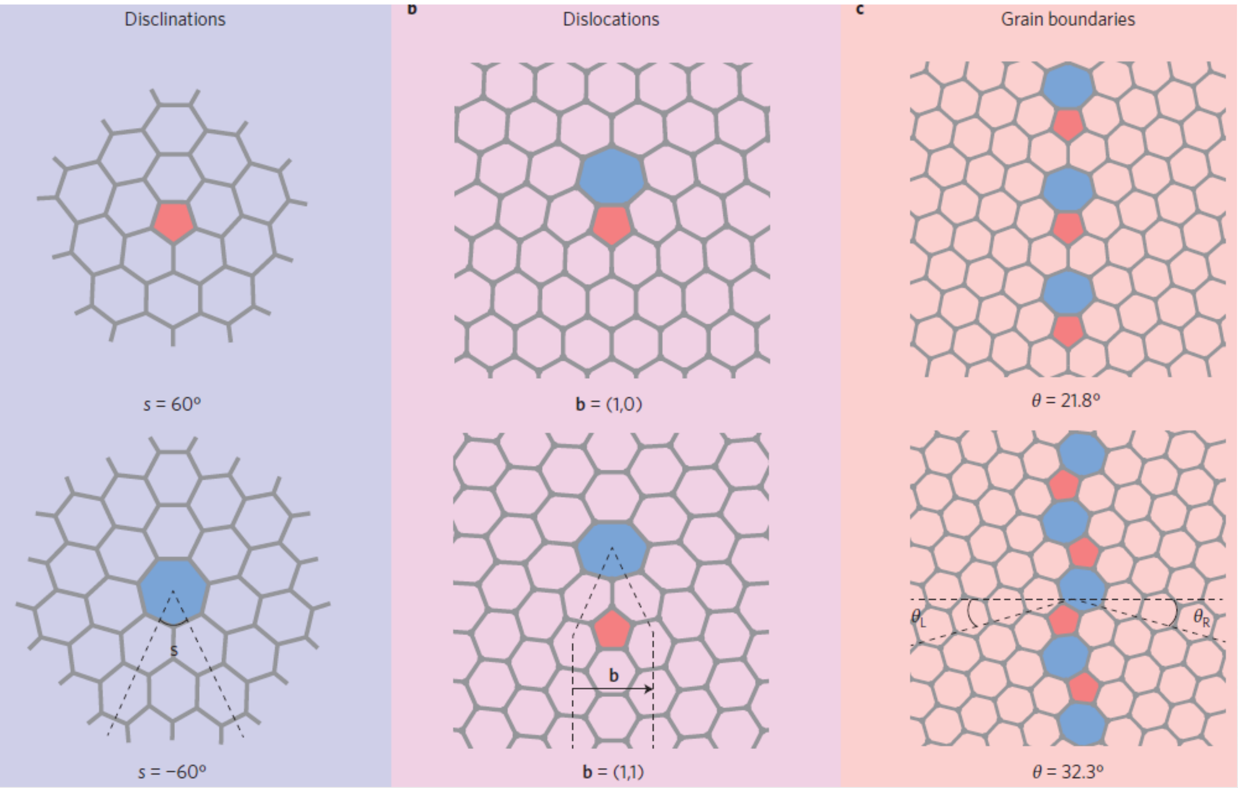
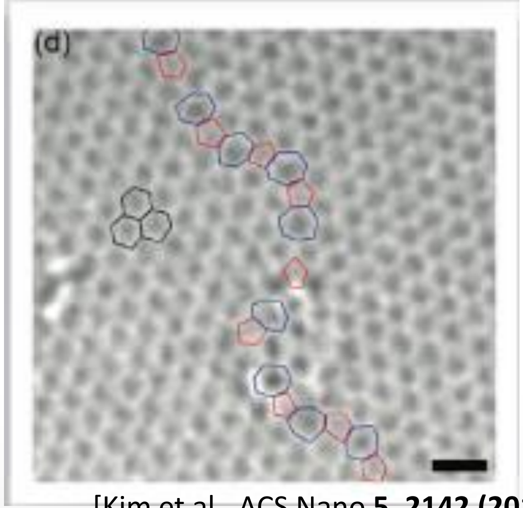
# Defects drive Grain Boundaries in Graphene

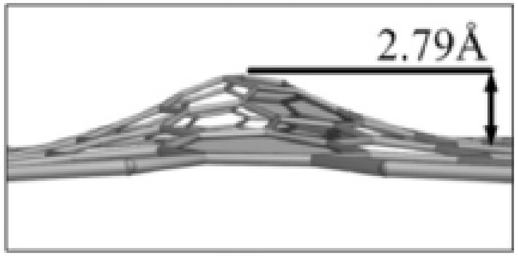
The changes of the lattice orientation are accommodated by the presence of topological defects. There are three types of topological defect relevant to 2D materials — disclinations, dislocations and GBs




GBs are characterized by a **sequence of pentagon-heptagon rings**



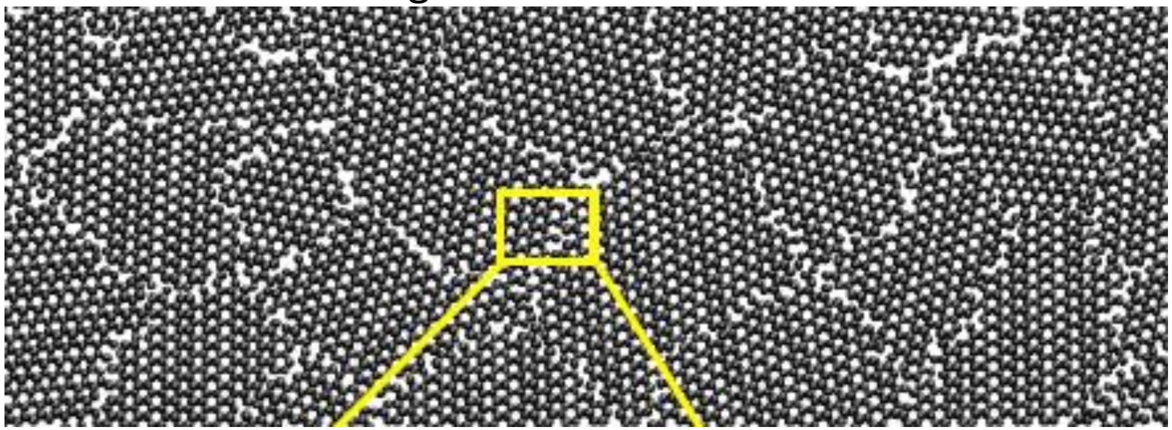

[Kim et al., ACS Nano **5, 2142 (2011)]**

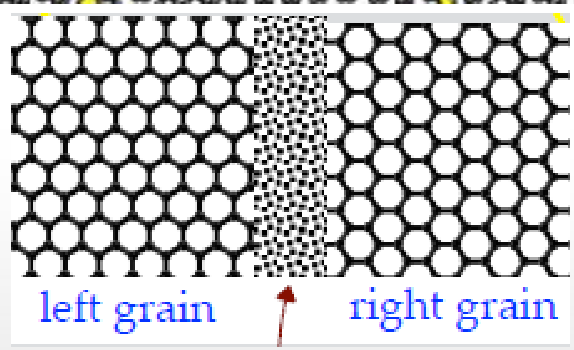


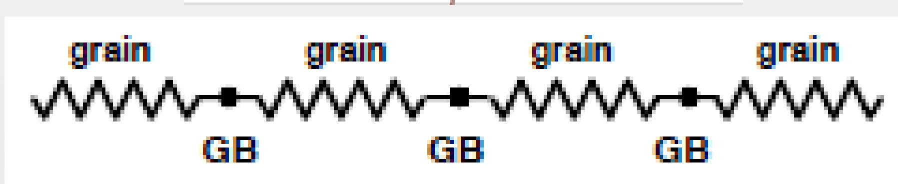

GBs results in highly non-planar structures_out of plane currugation

# Grain Boundaries

Grain boundaries can be regarded as a connection in series of resistances

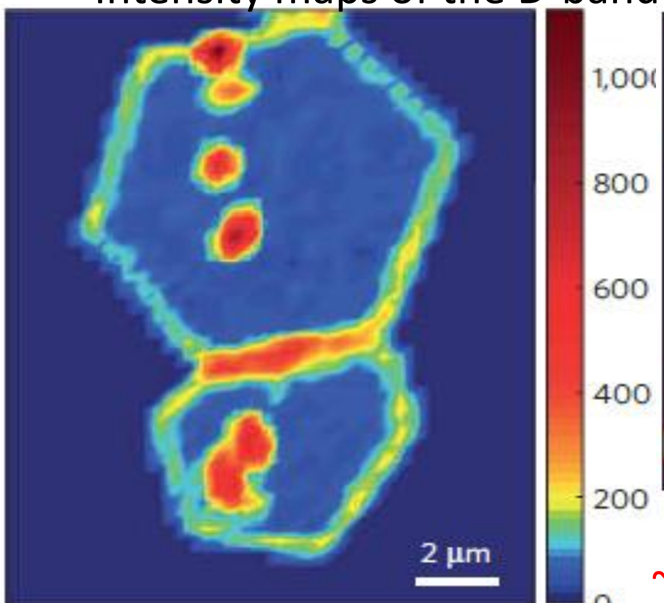


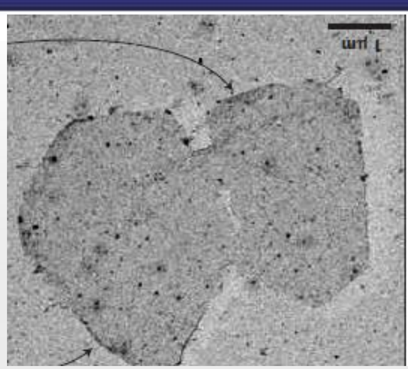


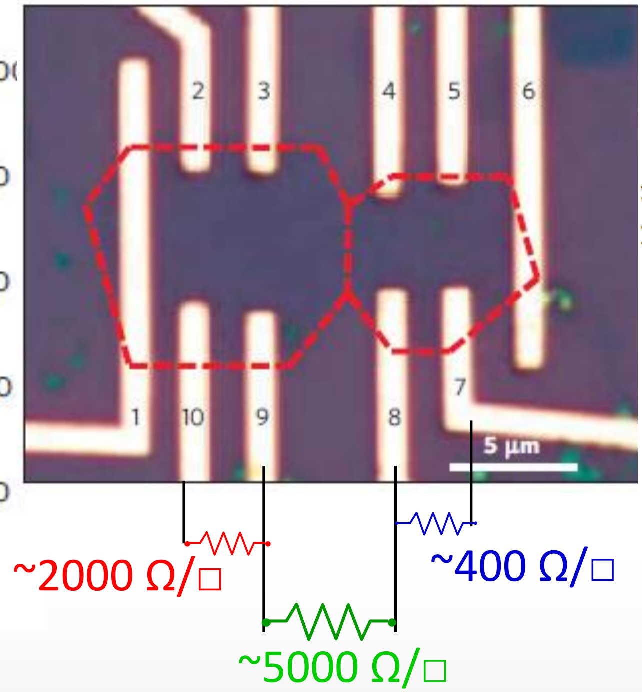



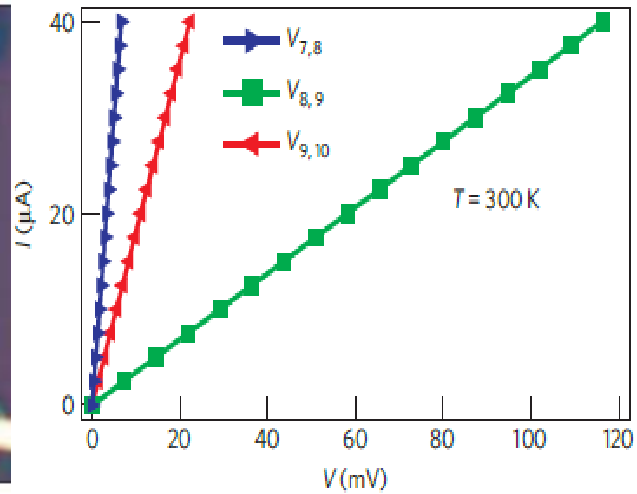
# Grain Boundaries Resistivity

Intensity maps of the D-band



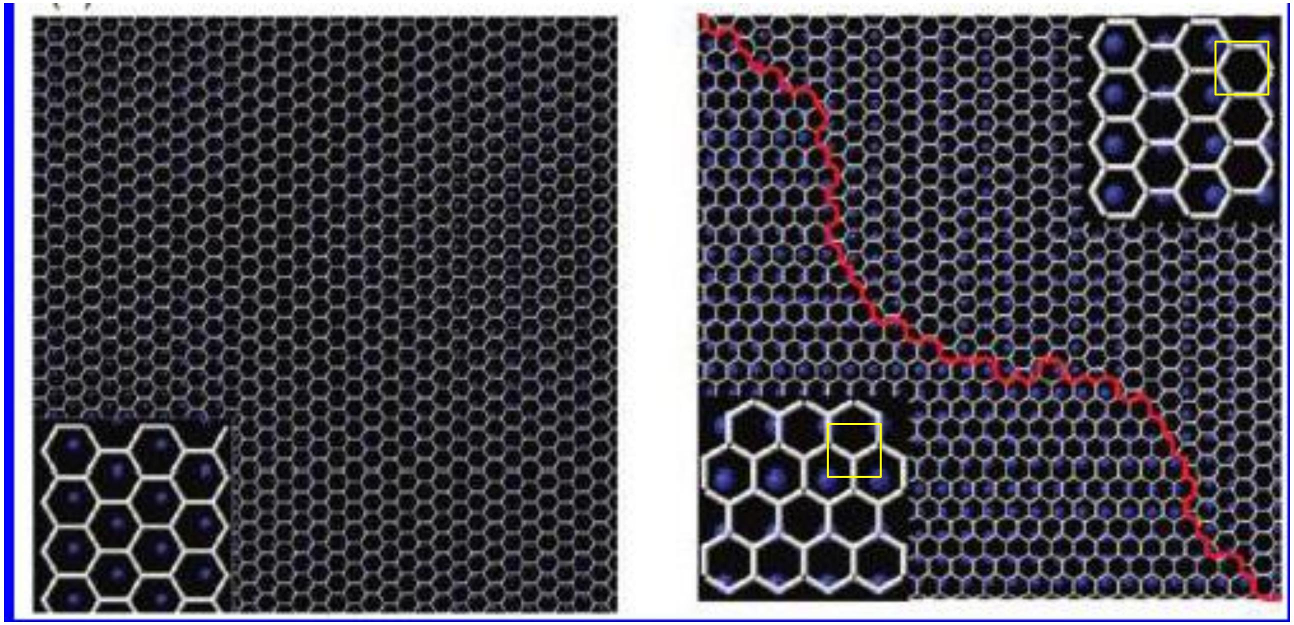






Q. Yu et al. Nature Material 10, 443 (2011)

# Density of Grin Boundaries relates to Cu Orientation

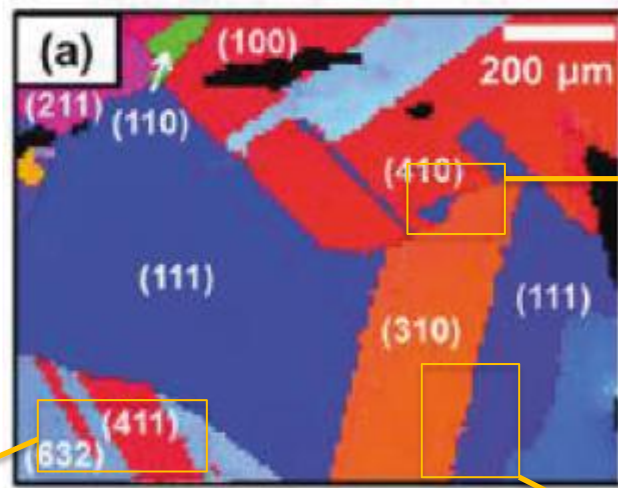


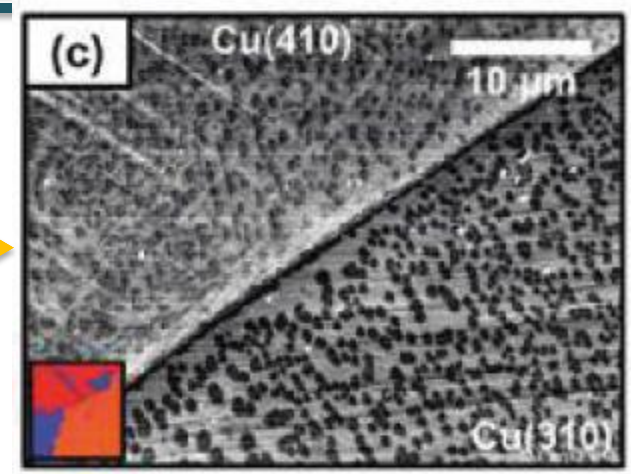
(111) planes symmetry matched with the graphene structure with single orientation

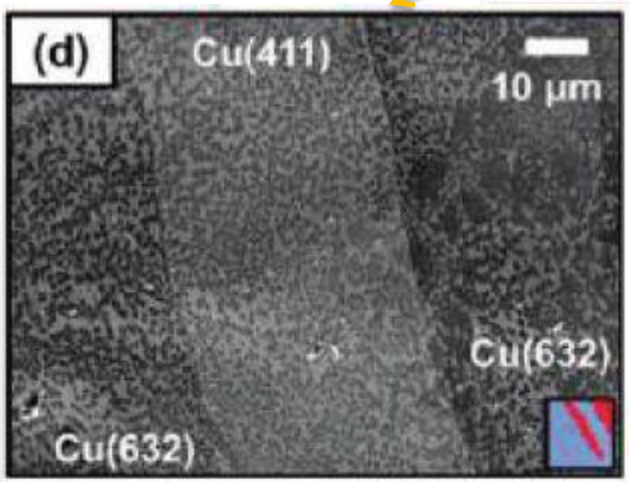
the graphene on Cu(100) exhibits a clear multidomain structure with two preferential domain orientations rotated by 30°, reflecting the mismatch of the lattice symmetry of graphene (6-fold symmetry) and the Cu(100) lattice (4-fold) symmetry.

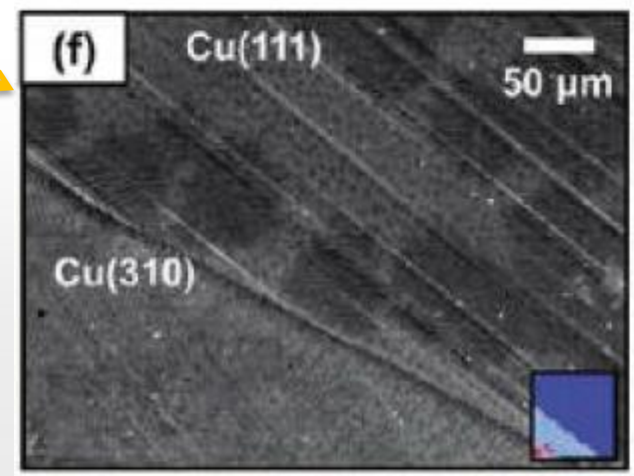
# Effects of Polycrystalline Cu Substrate on Graphene CVD Growth

The challenge is the different orientation of Cu grains



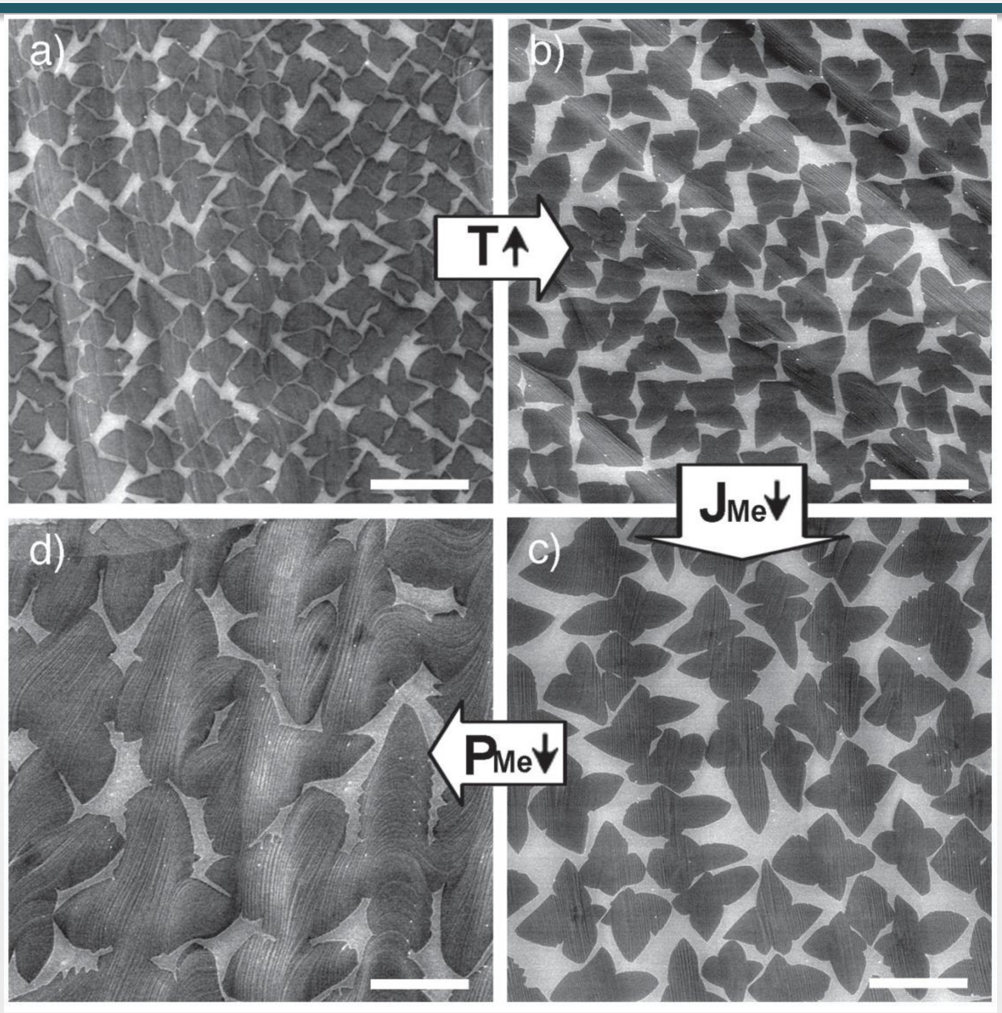




Nano Lett. 2011, 11, 4547–4554

# Shape of Graphene Nucleation and Density of GBs

Grain boumdaries/area graphene LOWEST

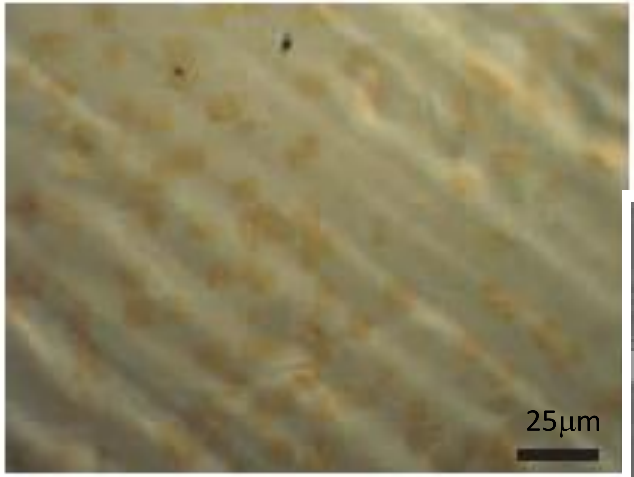



….. the optimized growth conditions are still high temperature and low pressure…….

However, ….. the copper substrate pre-treatment serves several important functions that ensure high quality graphene deposition

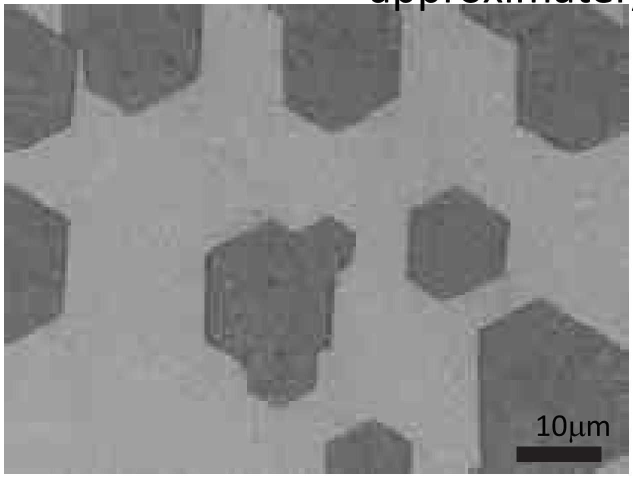
*Adv. Mater.* ***2016, 28, 6247–6252***

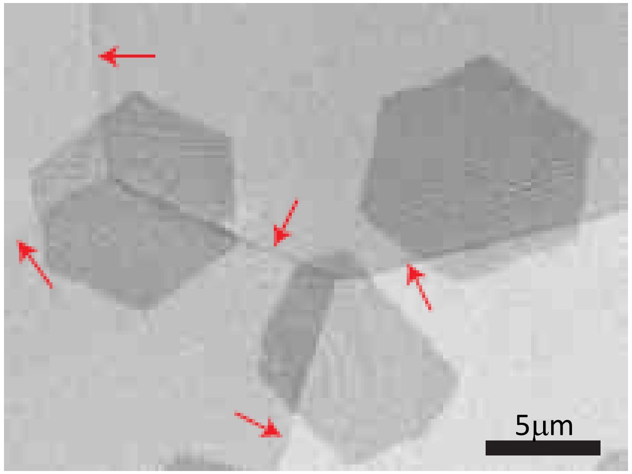
# Hexagonal Graphene Nucleation




as-grown, mostly hexagonally shaped graphene grains on Cu

as-grown grains whose edge orientations are approximately aligned with each other

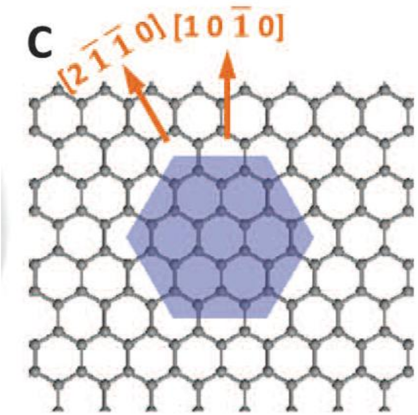


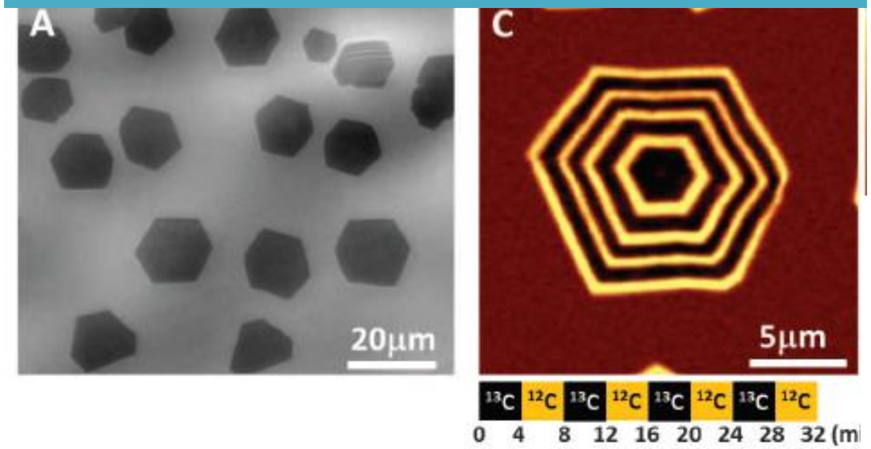

hexagonally-shaped graphene grains can be grown continuously across Cu crystal grain boundaries

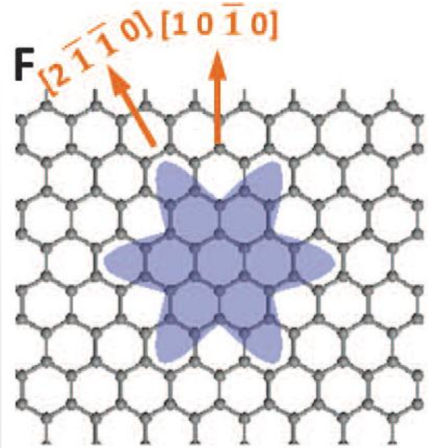
Q. Yu et al. Nature Material 10, 443 (2011)

# The role of Oxygen in CVD of Graphene

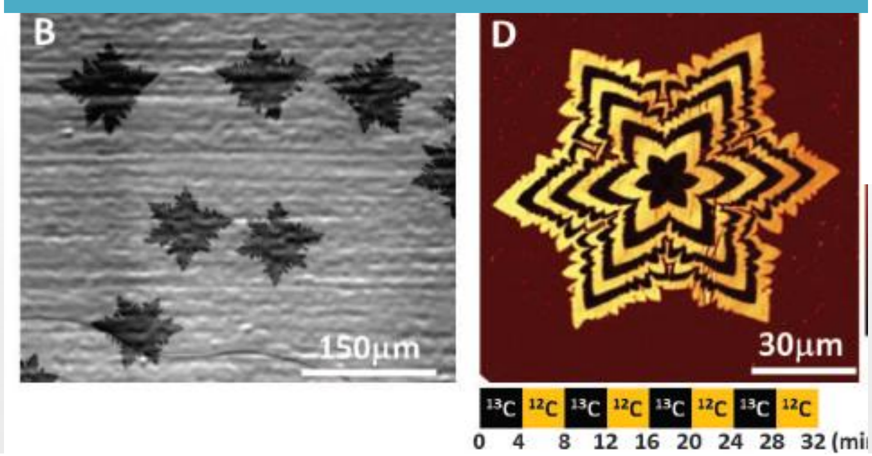



## O-Free Cu: hexagonal



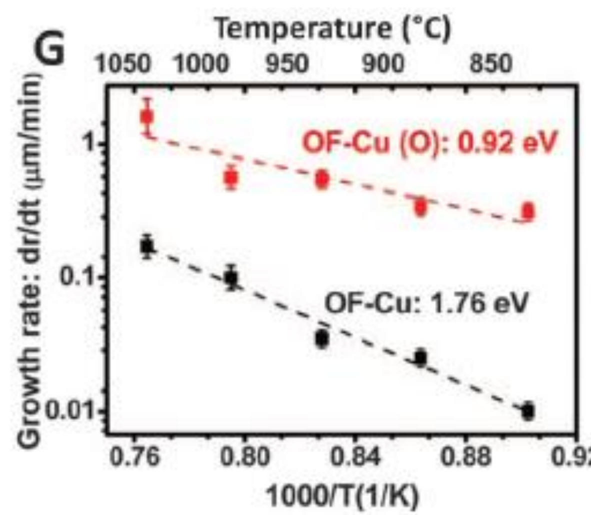

## O-Rich Cu: multibranched and dendritic




Arrhenius plot_

Growth rate of graphene domain

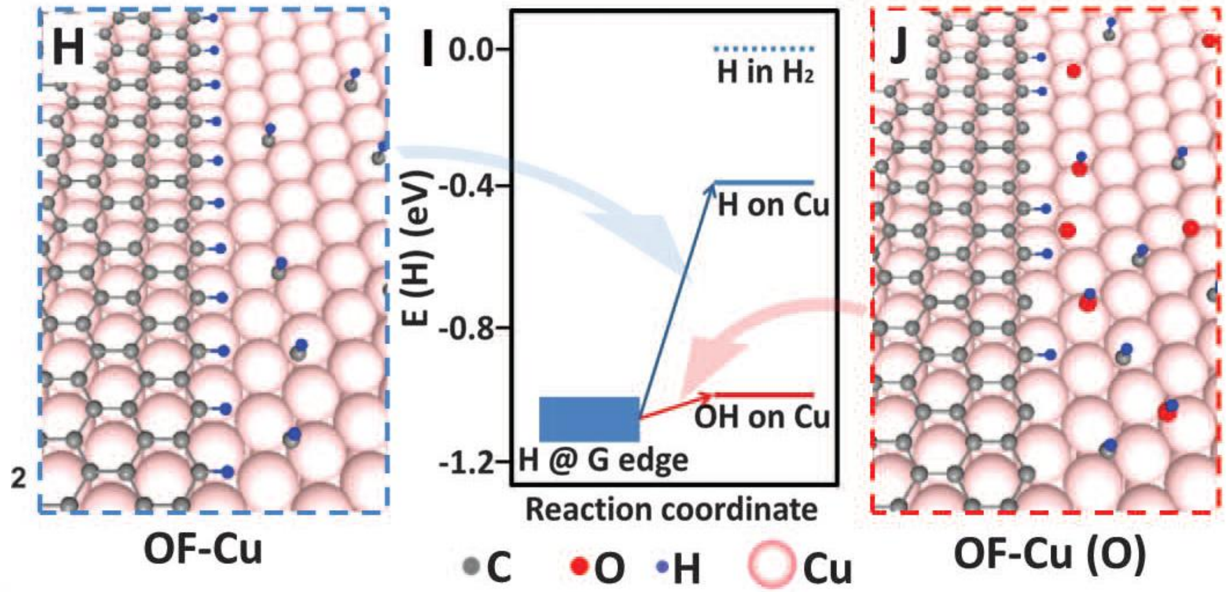
$$d\bar{r}/dt \propto \exp(-E_a/k_B T)$$




R.S. Ruoff Science, 720, 342 (2013)]

# The role of Oxygen in CVD of Graphene

**O-Free Cu: hexagonal** | **O-Rich Cu: multibranched and dendritic**




The H-terminated graphene edge on Cu is more energetically favorable than the bare graphene edge on Cu

Thus, C species edge attachment and lattice incorporation require dehydrogenation e.g.,

$CH_x \xrightarrow{Cu} CH_{x-1} + H$ (x = 4, 3, 2, 1)

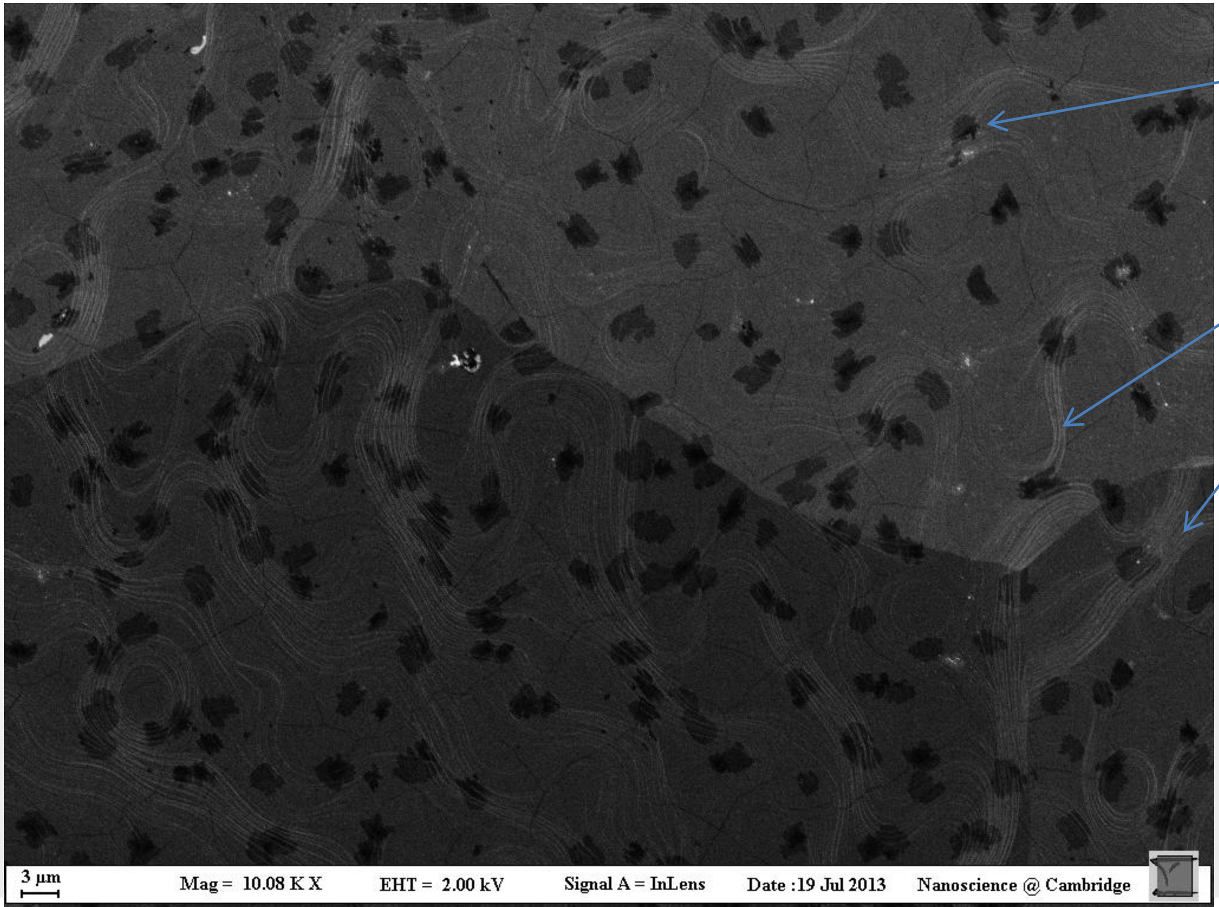
Preadsorbed O on the Cu surface can enhance the dissociation of hydrocarbons through the reaction

$CH_x + O \xrightarrow{Cu} CH_{x-1} + OH$ (x= 4, 3, 2, 1)

DFTcalculations have shown that the energy of H in the form of an OH group on Cu is lower than that of H-on-Cu by 0.6 eV/H

# Cu foil pretreatment: role of Cu morphology

The morphology of the copper surface strongly influence the dynamics of the growth: lamination lines, stripes structures and microporisity of the copper foil induce the formation of IWC.



# Cu foil pre-treatment: *wet cleaning & annealing*

**Improving the crystalline quality of the metal films is the enabling key**

The pre-treatment of the copper foils has been found to be important in obtaining large graphene domains in the as-deposited product.

Wet chemical pre-treatment by dipping in acetic acid partially remove $Cu_2O$
*(K. L. Chavez and D. W. J. Hess, J. Electrochem. Soc., 2001, 148 )*

$$2 \bullet CH_3COOH + Cu_2O \rightarrow 2 \bullet Cu^+CH_3COO^- + 2 \bullet H_2O$$

Annealing in a $H_2$ reducing atmosphere @ 1000°C remove CuO
*(C Y. N. Z. Trehan, Z. Anorg. Allg. Chem., 1962, 318, 107 )*

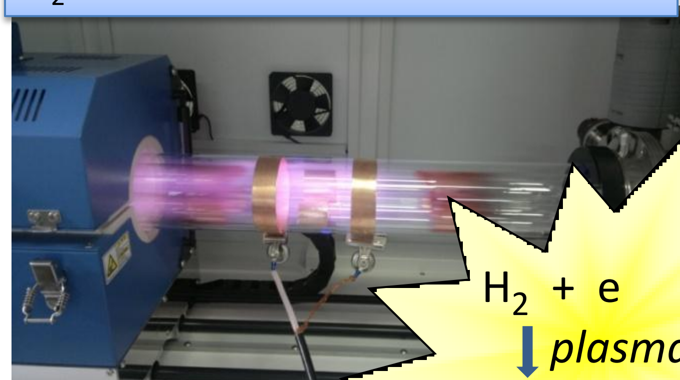
$$CuO + H_2 \rightarrow Cu + H_2O$$

Annealing stage (1000°C, 30 min) prior to deposition is also important for increasing the Cu grain size and rearranging the surface morphology

*(J.D. Wood et al, Nano Lett. 2011, 11, 4547–4554; Chem. Mater. 2013, 25, 871)*

# $H_2$ Plasma Implementation of CVD of Graphene

$H_2$ Plasma for native oxide removal



$H_2 + e$

↓ *plasma*

$2H + e$

Cu-Surface

Cu- bulk

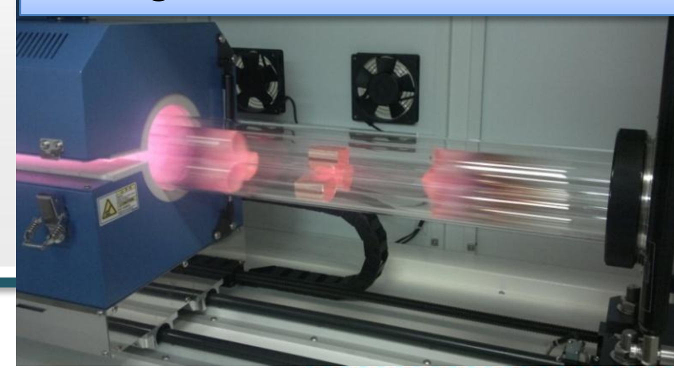
Cu foil Annealing and graphene growth

Reduction of Cu-oxides and ablation of C-contaminants

$CuO, Cu_2O + H \rightarrow Cu + H_2O \uparrow$

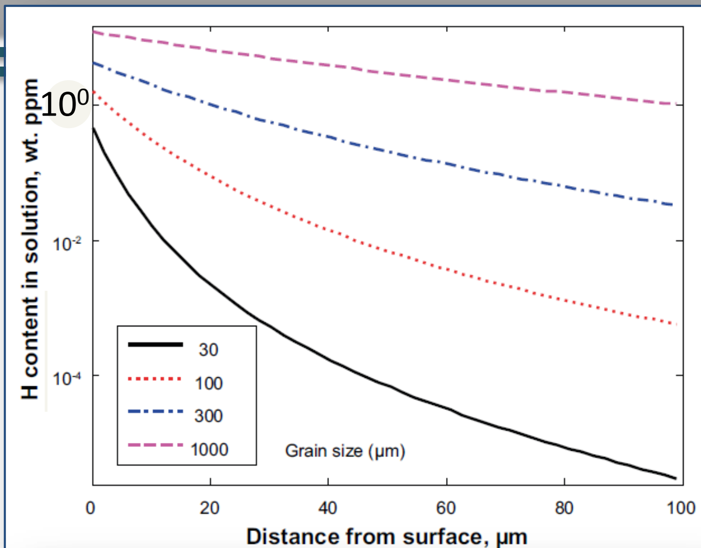
$\text{amorph-C} + H \rightarrow C_nH_{2n+2} \uparrow$

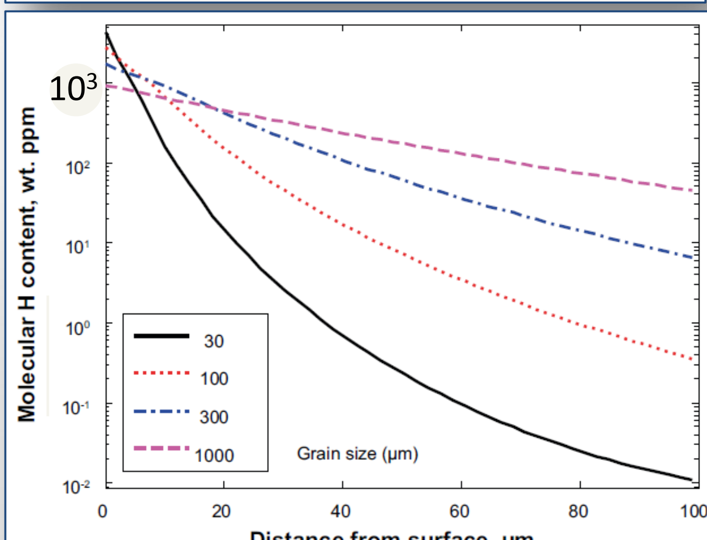
Cooling from 1000°C to RT



Cu foil covered with graphene

# H-plasma vs $H_2$ Annealing




- C is soluble in Ni and not in Cu
- $H_2$/H is soluble in Cu and not in Ni [*]

- The equilibrium solubility of hydrogen in copper increases with increasing temperature.

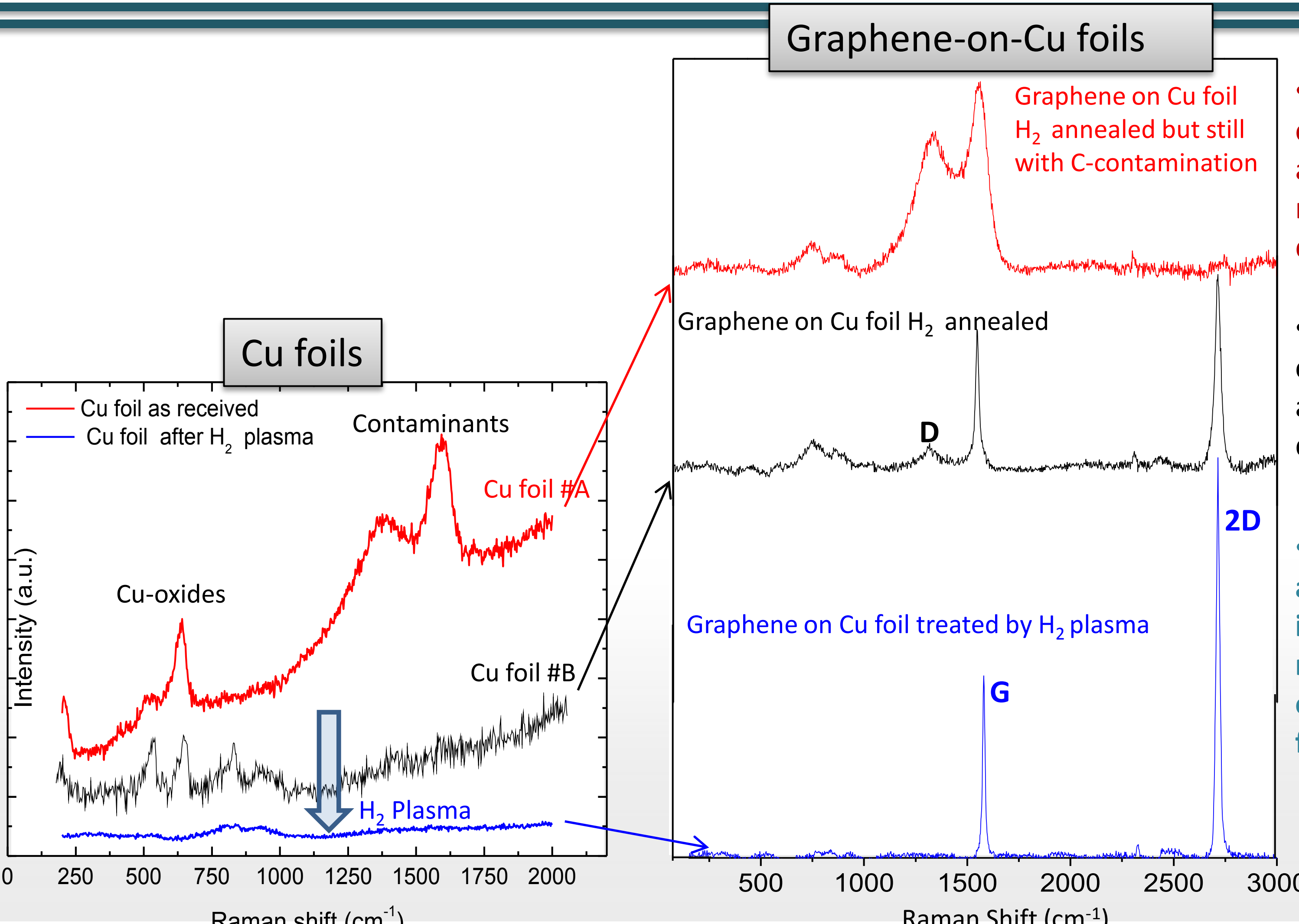
- Hydrogen is stored in the material in two forms:
  - atomic hydrogen, H, in solid solution and
  - molecular hydrogen, $H_2$, in bubbles

- The amount of $H_2$ in bubbles from annealing is several orders of magnitude higher than H-atoms from plasma in solid solution.

- This bubbles also have a role during Cu dissolution forming wrinkles in graphene

- **H-plasma results in a less incorporation of hydrogen into Cu**

# H-Plasma and $H_2$ Annealing: Impact on Graphene Growth



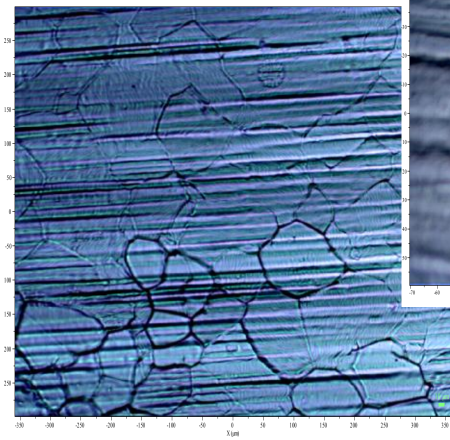

- Residual Carbon-contamination from annealing results in mainly in Csp3 deposition
- Residual oxide-contamination from annealing results in defective graphene
- **H-plasma passivating and reducing all impurities and defects make possible growth of graphene on any Cu foil**

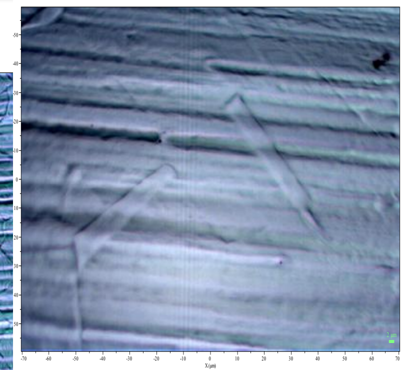
# Cu foil $H_2$ plasma pretreatment: Cu reflow by *H-atoms*

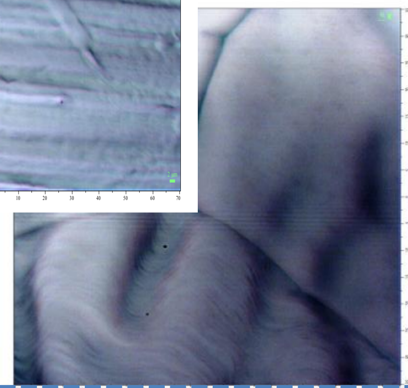
Another problem is related to the morphology of the copper surface: lamination lines and microporisity of the copper foil strongly influence the dynamics of the growth

**$H_2$ Annealing**

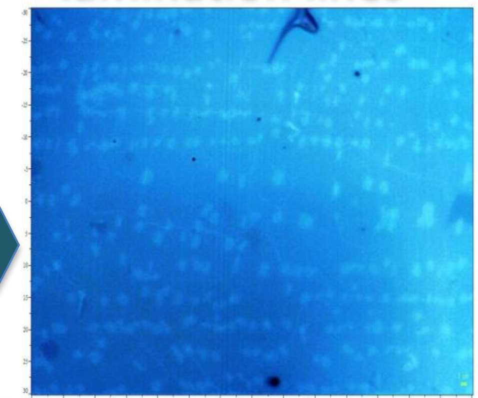

Lamination lines



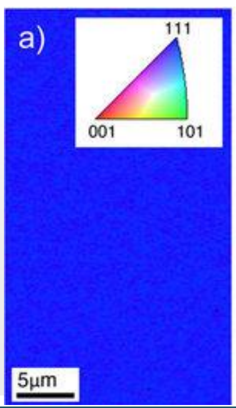




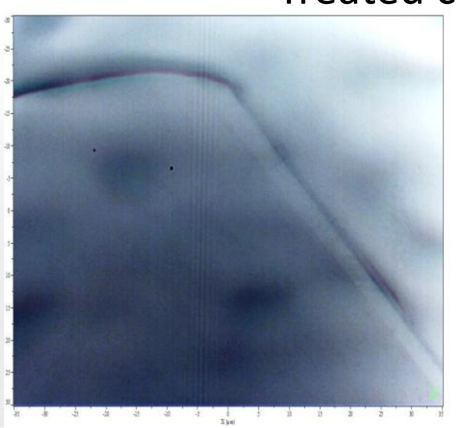
IWC growth along lamination lines

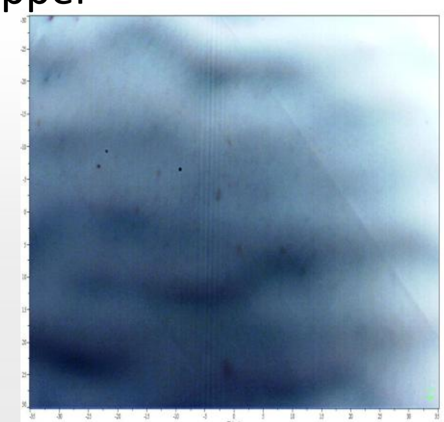


**H-plasma**

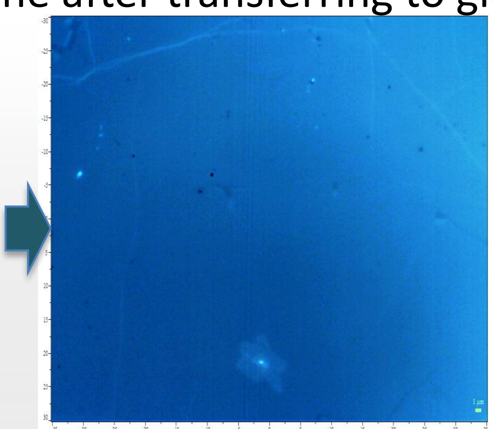



Treated copper



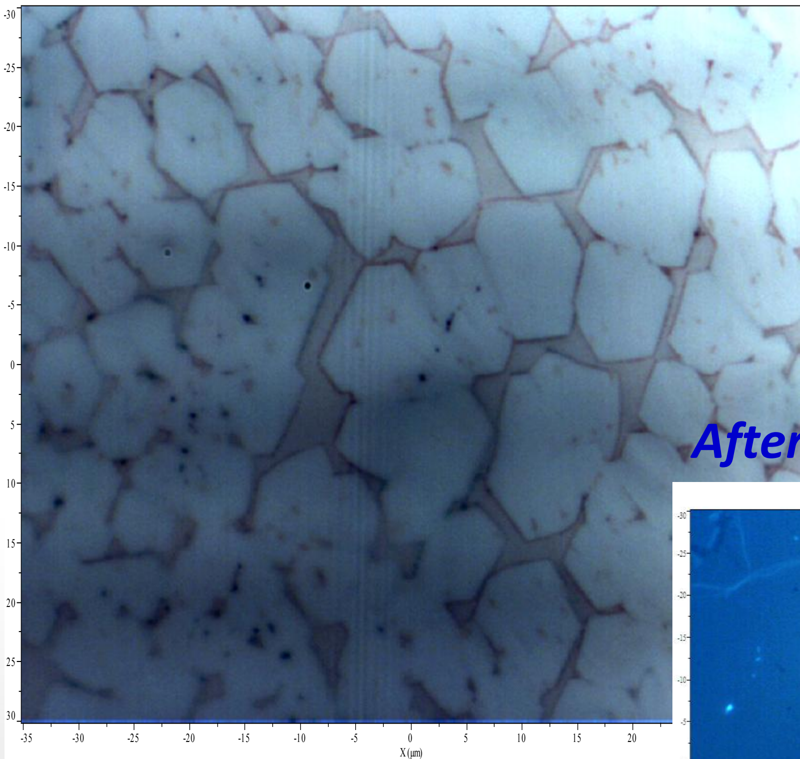


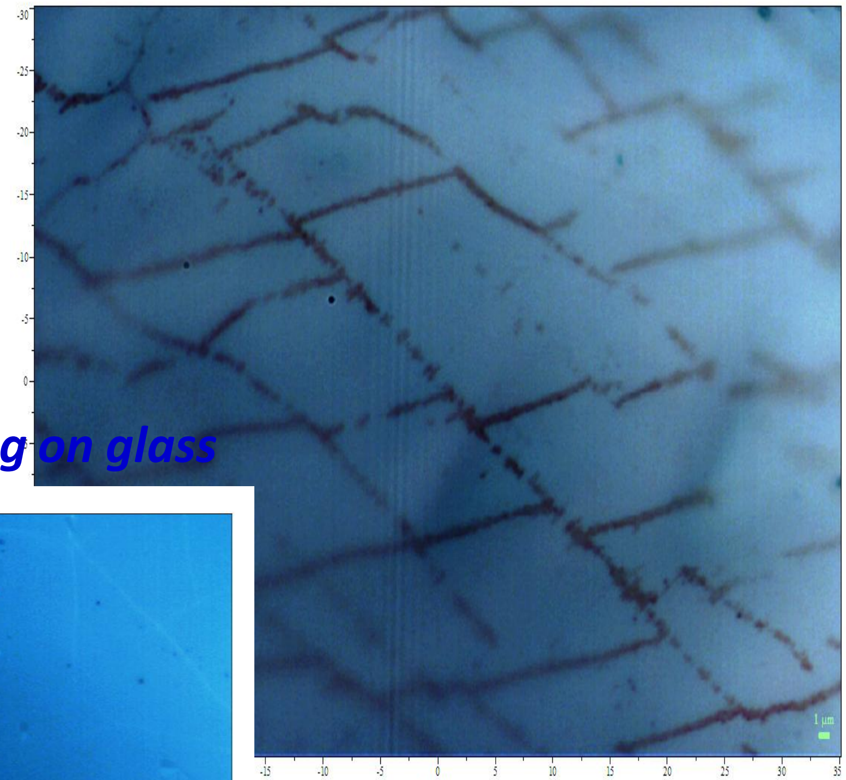
Graphene after transferring to glass



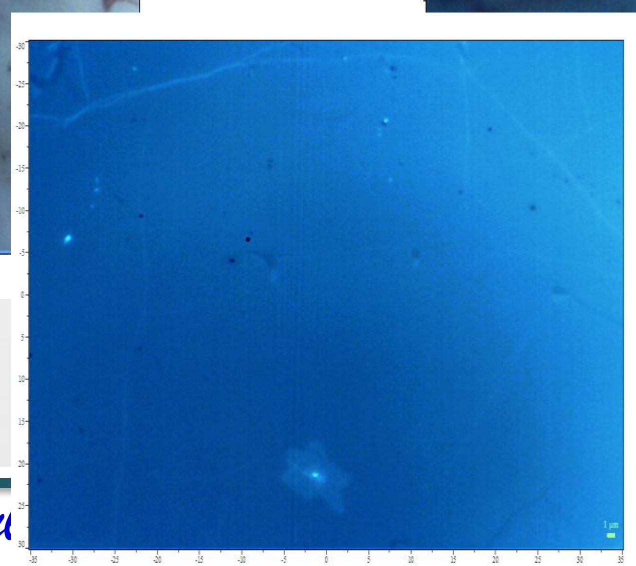
# Cu foil pretreatment: *growth morphology*

Typical graphene hexagonal/square structures on $H_2$ –plasma treated Cu-foil



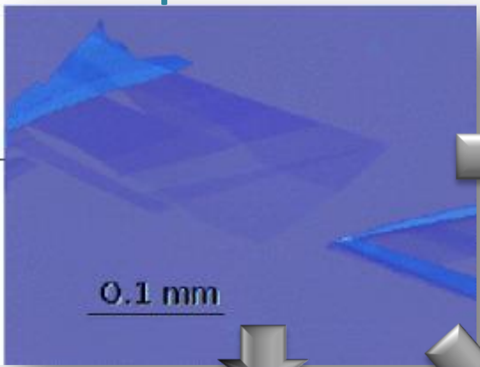

***After transferring on glass***



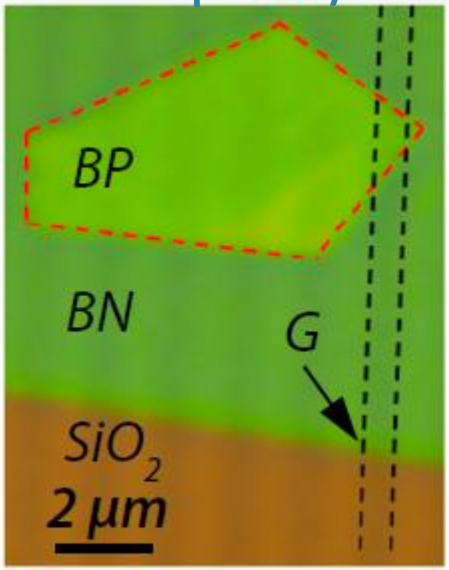
# Rewinding the Story

**Redo challenges and change the story from this point on**

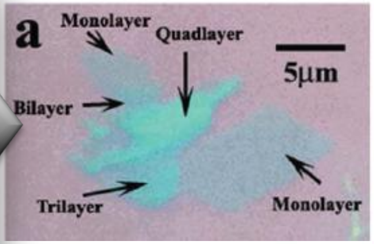
## Graphene Flake

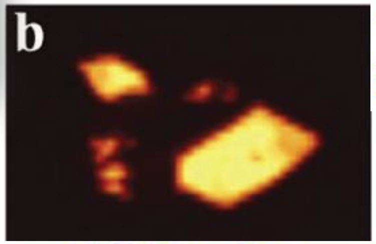


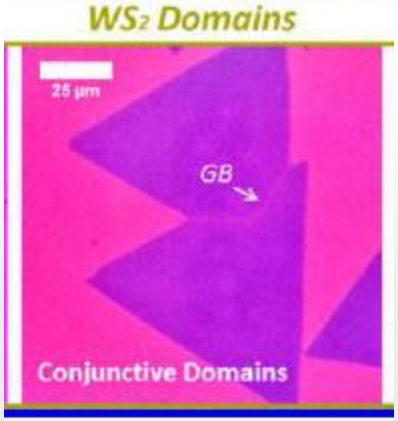

## Black Phosphorus/h-BN




## $WS_2$

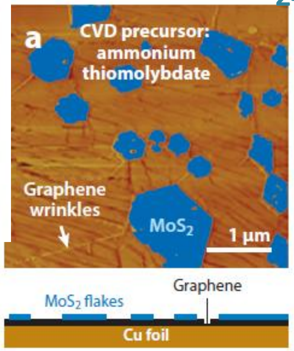


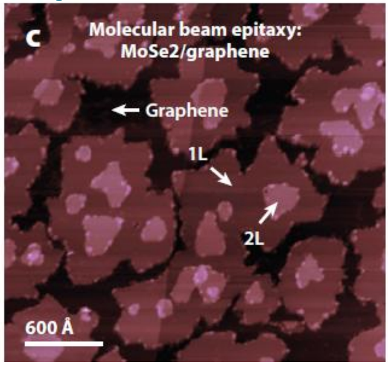




[H. Zeng et al. Chem. Soc. Rev., 2015, 44, 2629]

## $MoS_2$/Graphene

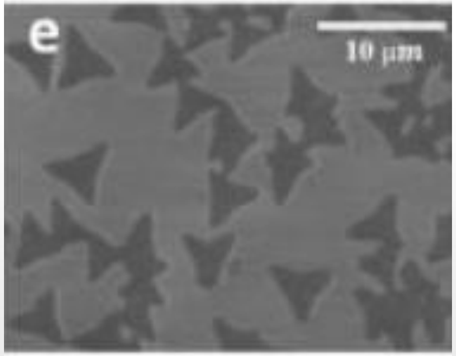



[Chem. Soc. Rev., 2015, 44, 2664]

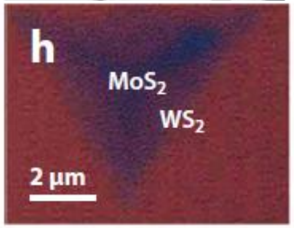
[

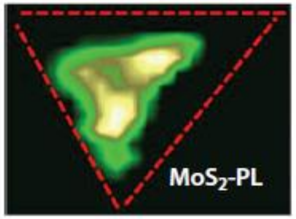
## $MoS_2$/h-BN

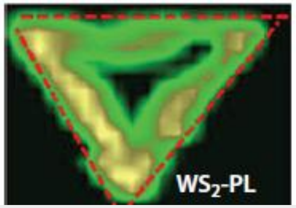



[Wang et al. ACS Nano 9, 5246 (2015)]

## $WS_2$/$MoS_2$

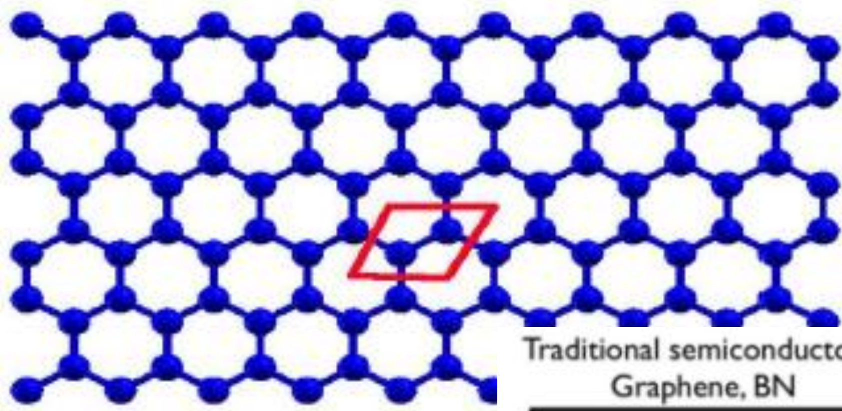



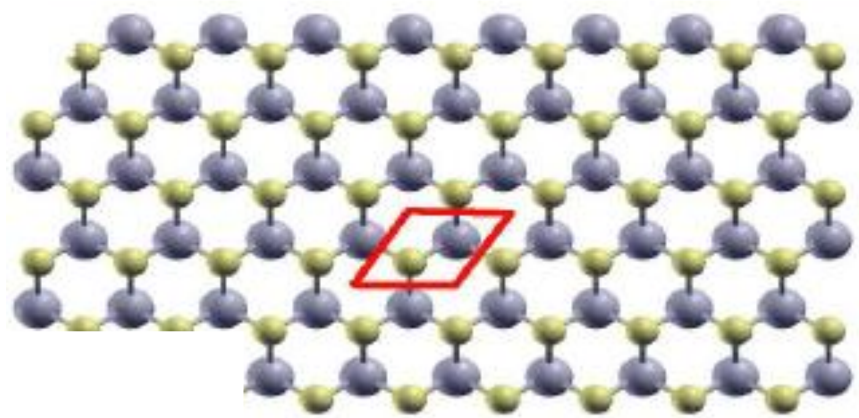



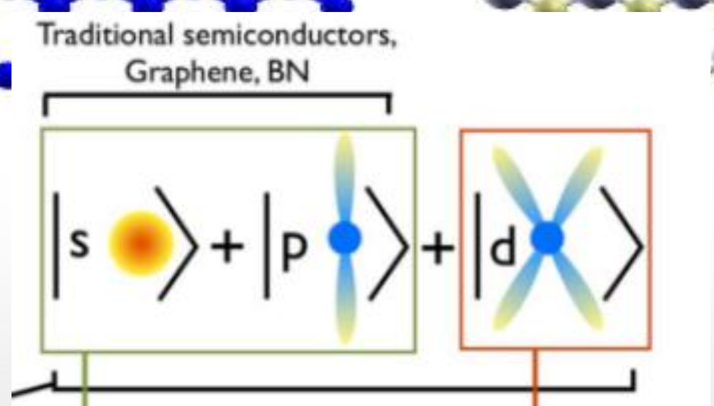

[Chem. Soc. Rev., 2015, 44, 2664]

# From Graphene to TMDs

| graphene | $MoS_2$ |
|---|---|
| Lattice constant, a=2.46 Å<br>Bond length, b=1.42 Å | Lattice constant, a=3.09 Å<br>Bond length, b=2.39 Å |








- *Chemical bonds are made of s, p, and d-orbitals.*
- *No out-of plane bonds → No dangling bonds → Low chance of interface traps.*
- *Interfaces are 'pristine', no strain as in 3D heteroepitaxial materials.*
- *Heterostructures are formed by 'stacking' or 'van-der-Waal' epitaxy.*

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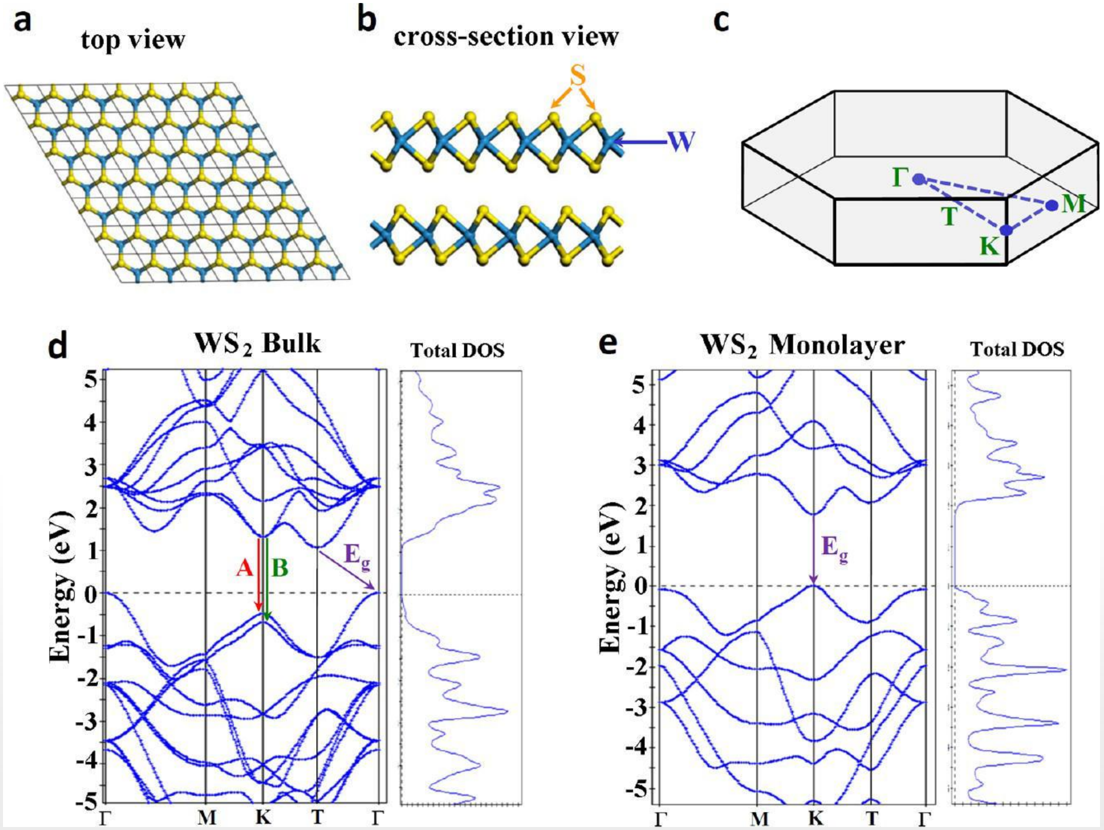
# $WS_2$

The 2H-WS2 polytype crystalline structure has the hexagonal space group P63/mmc with lattice parameters of a = 3.1532 Å and c = 12.323 Å



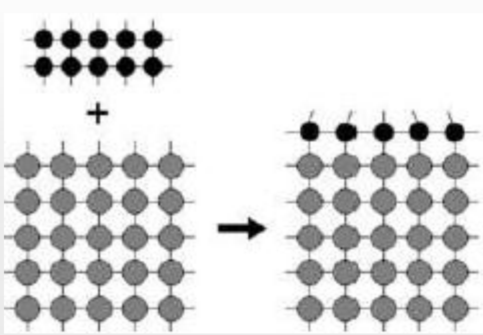

bulk $WS_2$ is an indirect-gap semiconductor; it has a gap of 1.3 eV

# Two Options for Crystal Growth of 2D Materials

**3D Process:** *vs* **2D Process:**

1. Deposition/Growth on a substrate while allowing interaction and/or chemical bonds with substrates
2. Isolation of 2D materials by disconnecting from substrate
3. Transfer to a supporting substrate (only coupled by van der Waals interaction)

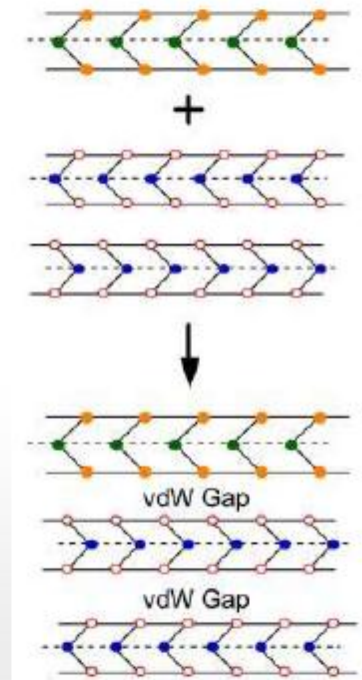
HeteroEpitaxy: deposition of a crystalline layer on a crystalline substrate **(registry between layer and substrate)**



Direct Growth of 2D material on desirable and suitable (flat) substrate **by Van-der Waals Epitaxy**

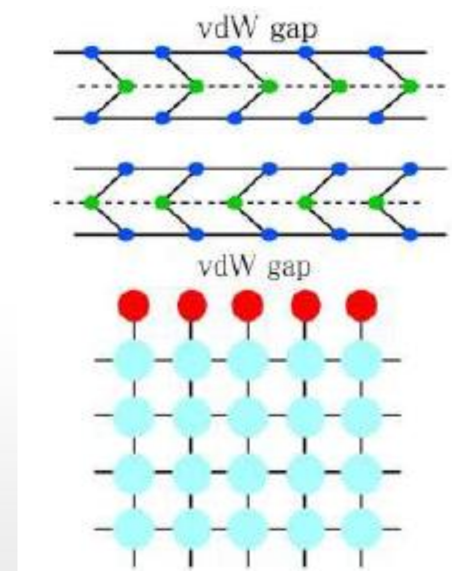
**NO** chemical bonds to any substrate or layer!

**VdW epitaxy on layered material**



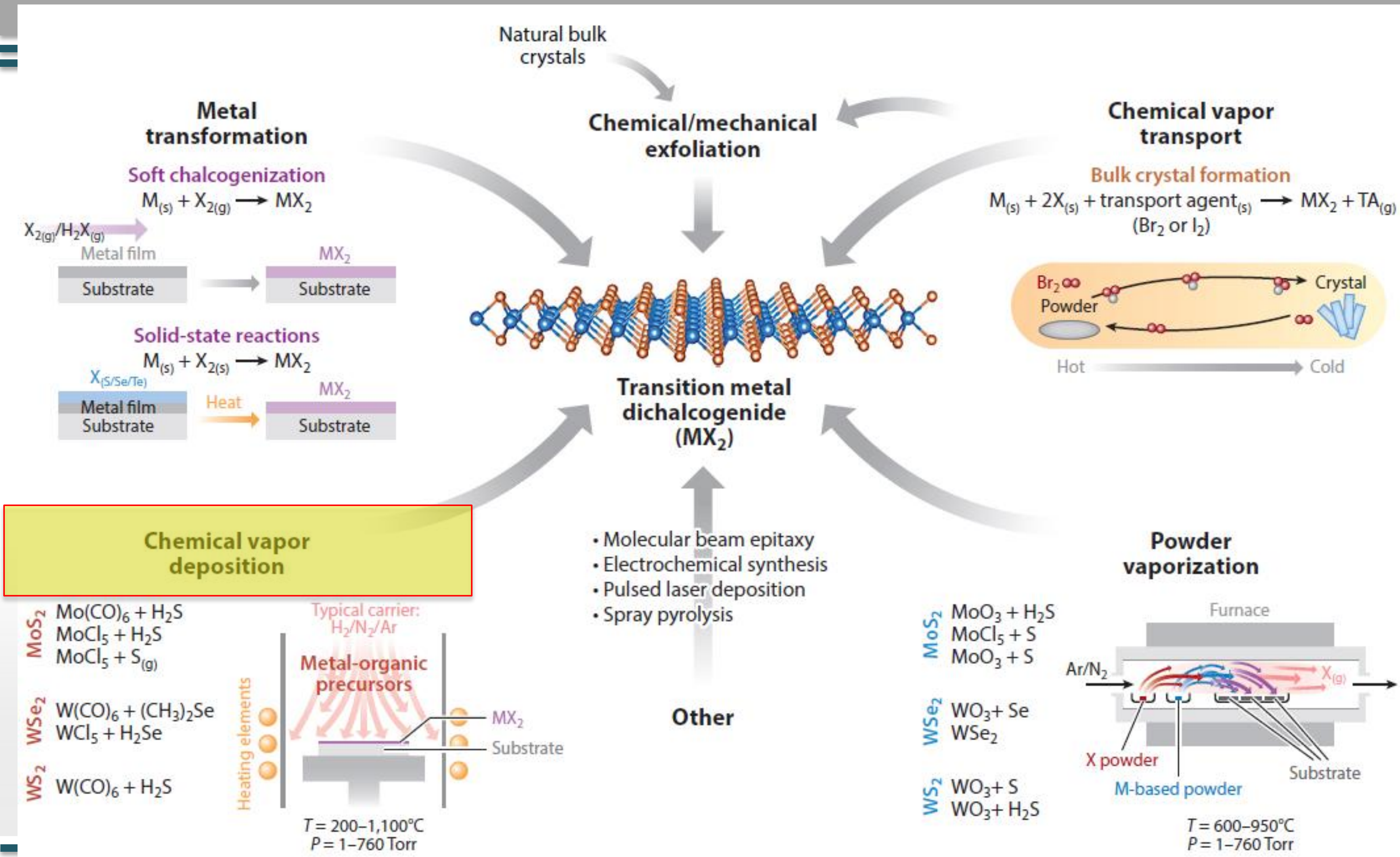

*e.g. graphene, (T)MDC, In2Se3, Bi2Se3, on, hBN, graphene, sapphire …*

**VdW heteroepitaxy**




*e.g. NbSe2, GaSe, InSe, … on H-terminated Si (111)*

# Primary Growth Techniques for 2D-Materials





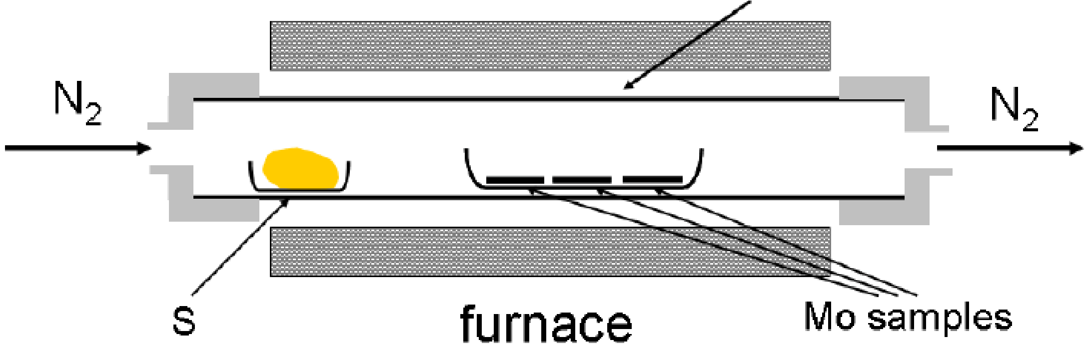

[S. Das et al. Annu. Rev. Mater. Res. 2015.45:1-27]

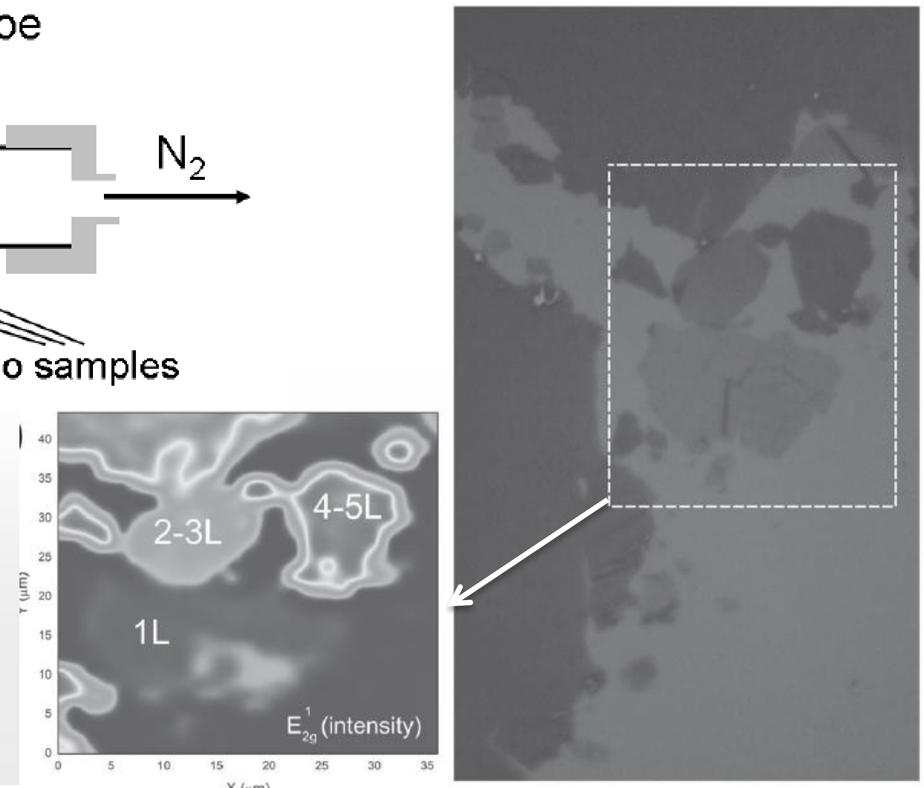
# $MoS_2$ growth: Sputtering + Sulfurization

## Sulfurization on substrate with thin deposited Mo film

A gas carries evaporated sulfur and Mo atoms that are deposited on substrate surface

$$Mo(Target) \xrightarrow{sputtering} Mo(layer) \xrightarrow{S_2} MoS_2$$



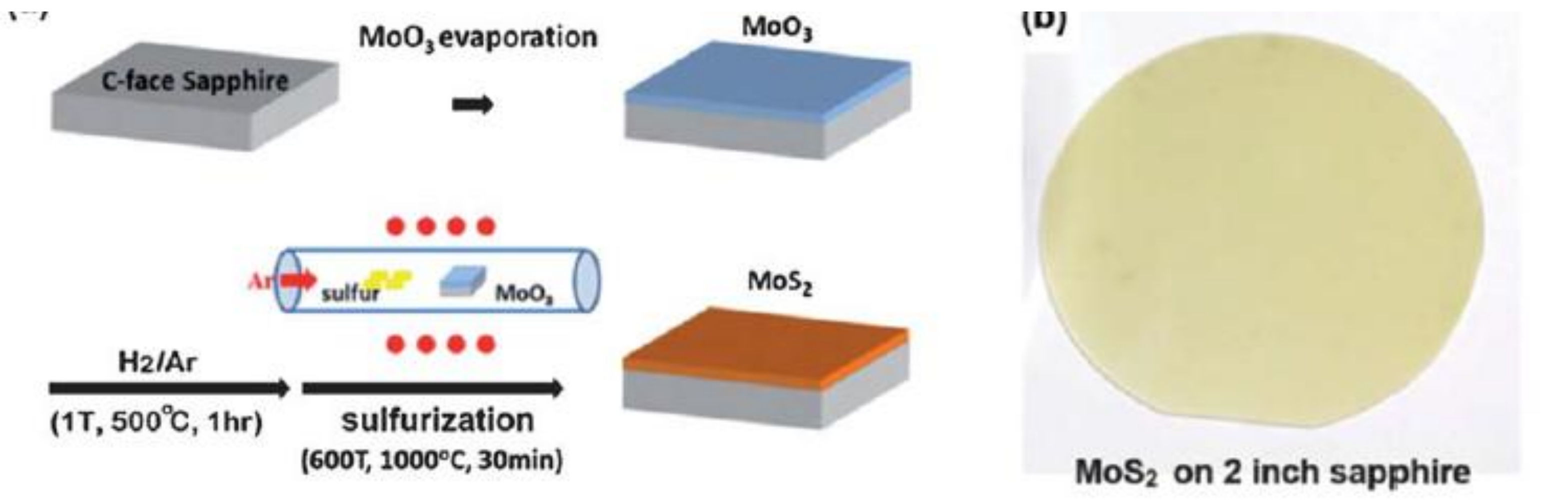



# Wafer-scale $MoS_2$ thin layers prepared by $MoO_3$ sulfurization

the one-step direct sulfurization of MoO3 with sulfur at 1000 C, where the obtained MoS2 films exhibited semiconductor properties, but the electrical carrier mobility was at least one order of magnitude lower than that from the two-step thermal process. The chemical equations for the two-step reaction are proposed in eqn (1) and (2).

$$MoO_{3(s)} + H_{2(g)} \rightarrow MoO_{2(s)} + H_2O_{(g)}$$

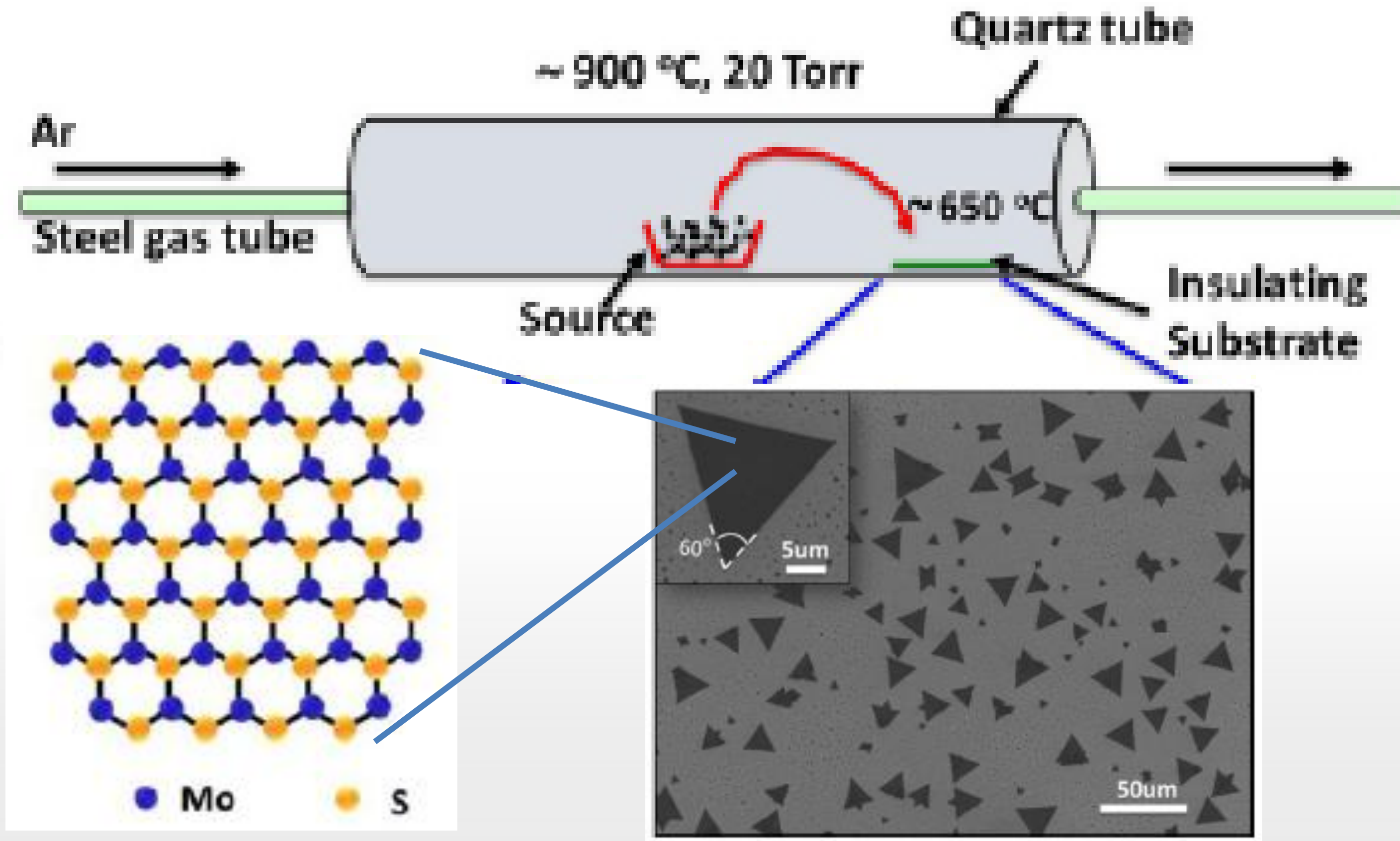
$$MoO_{2(s)} + 2S_{(g)} \rightarrow MoS_{2(s)} + O_{2(g)}$$




Y. C. Lin et al Nanoscale, 2012, 4, 6637

# Powder Vaporisation

$$MoS_2(solid) \xrightarrow{900°C} MoS_{2-x}(gas) + x/2\,S_2(gas) \xrightarrow{650°C} MoS_2(solid)$$




ACS nano, 7 (3) 2768–2772 (2013)

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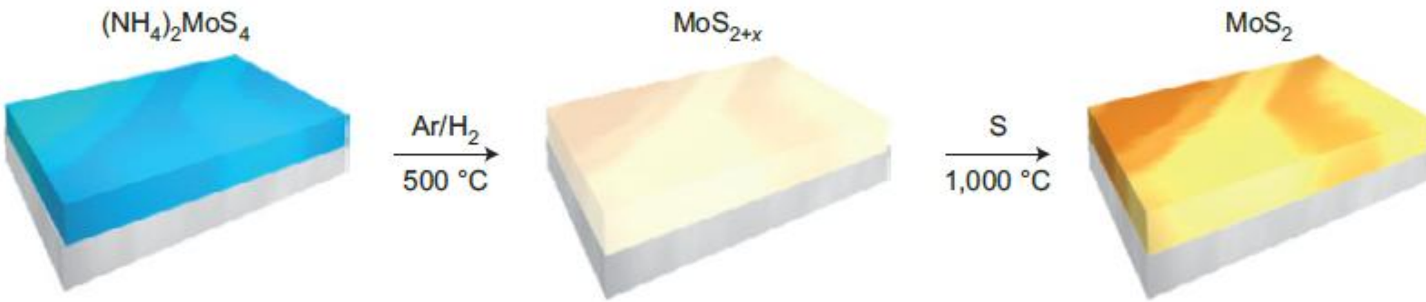
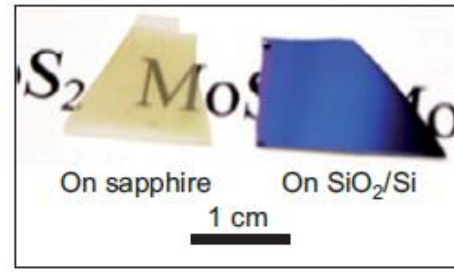
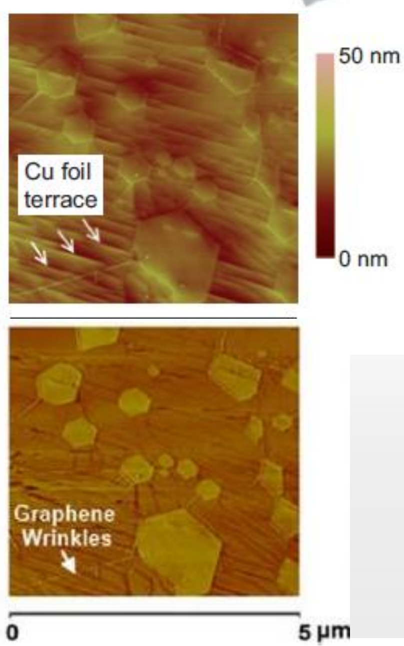
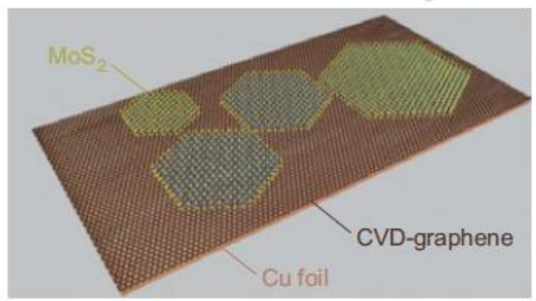
# VdW Epitaxy of $MoS_2$ CVD reactor

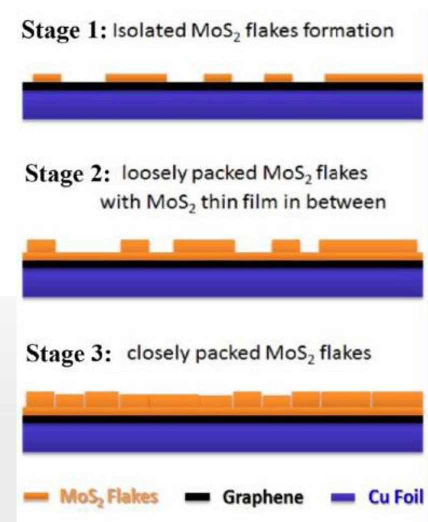
$$(NH_4)_2MoS_4 + H_2 \rightarrow 2NH_3 + 2H_2S + MoS_2$$




Y. Shi et al. Nano Lett. 2012, 12, 2784–2791

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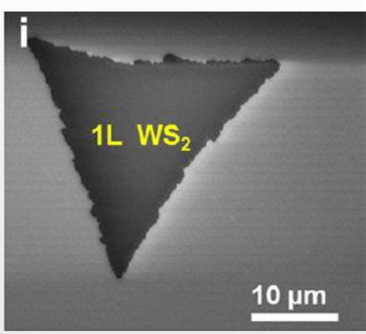
# CVD of dichalcogenides ($MoS_2$, $WS_2$ )

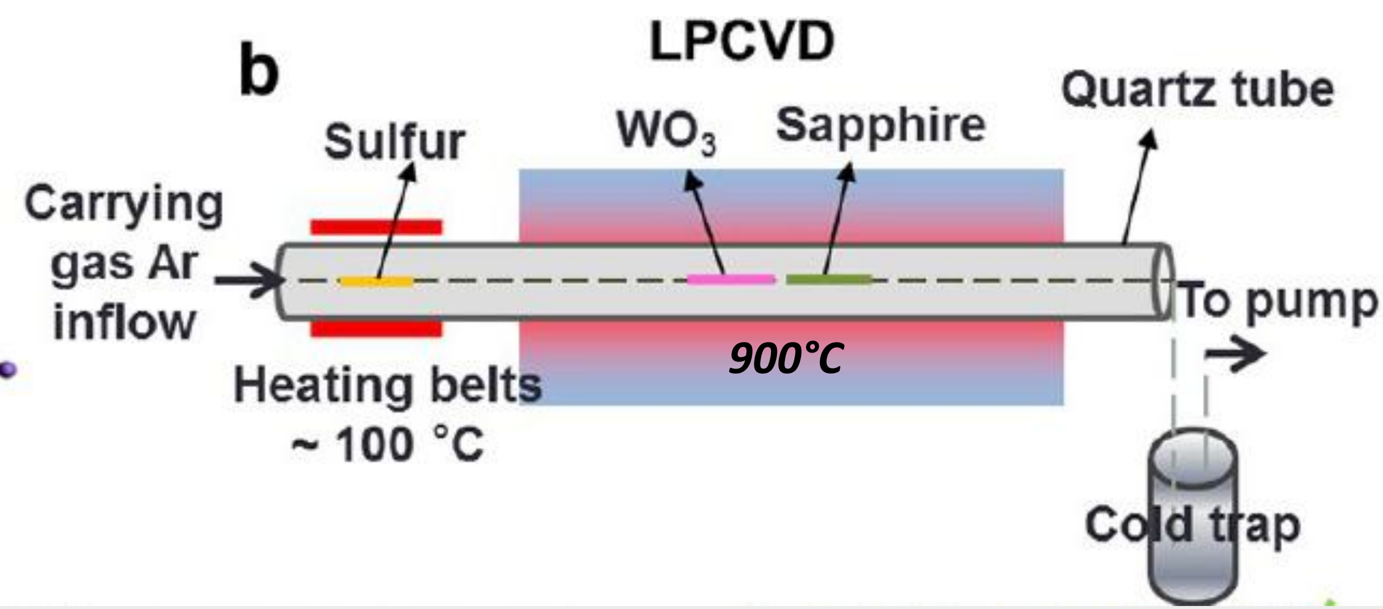
WO3 partially reduced by sulfur vapor to form volatile suboxide species $WO_{3-x}$, which is further sulfurized

$$7S + 2WO_3 \rightarrow 2WS_2 + 3SO_2$$

$$xS + 2WO_3 \rightarrow xSO_2 + 2WO_{3-x}$$

$$(7-x)S + 2WO_{3-x} \rightarrow (3-x)SO_2 + 2WS_2$$



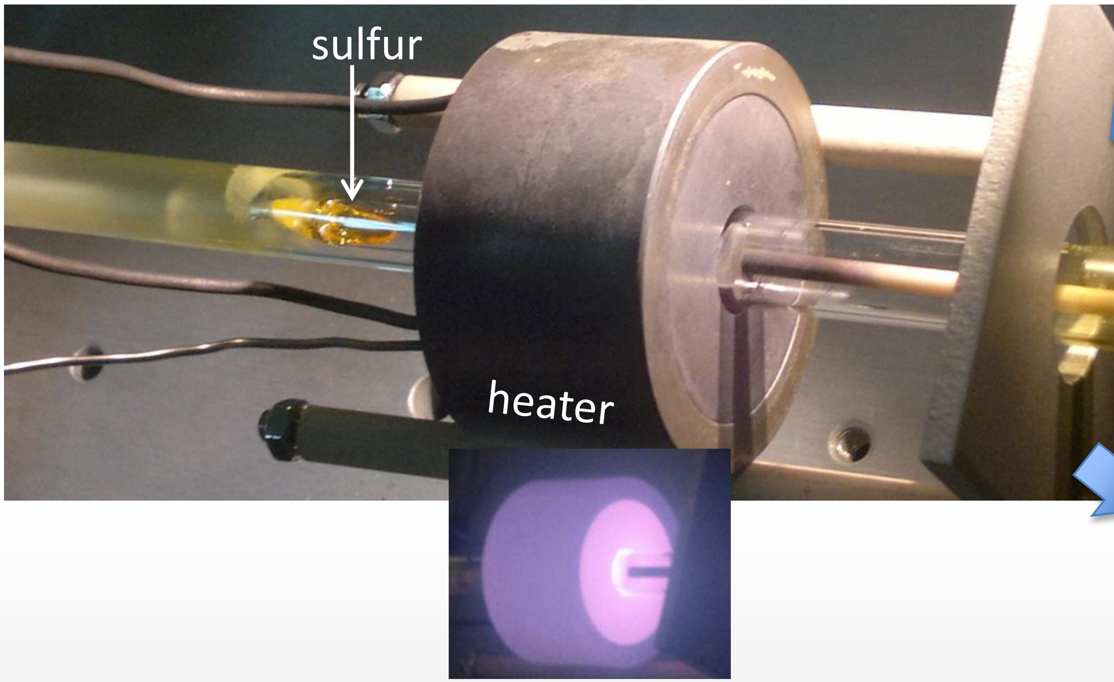



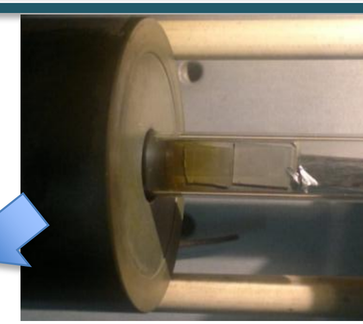

Y. Zhang et al., *Controlled Growth of…..*, ACS Nano **7**(10) 8963 (2013)

# Direct Epitaxial CVD Synthesis of $WS_2$ on Graphene

$$W(CO)_6 \quad + \quad S_2 \quad \rightarrow \quad WS_2 \quad + \quad 6CO$$

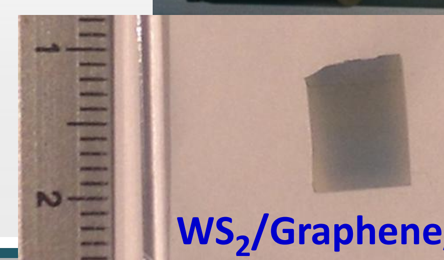
Ar + $W(CO)_6$



Graphene-SiC

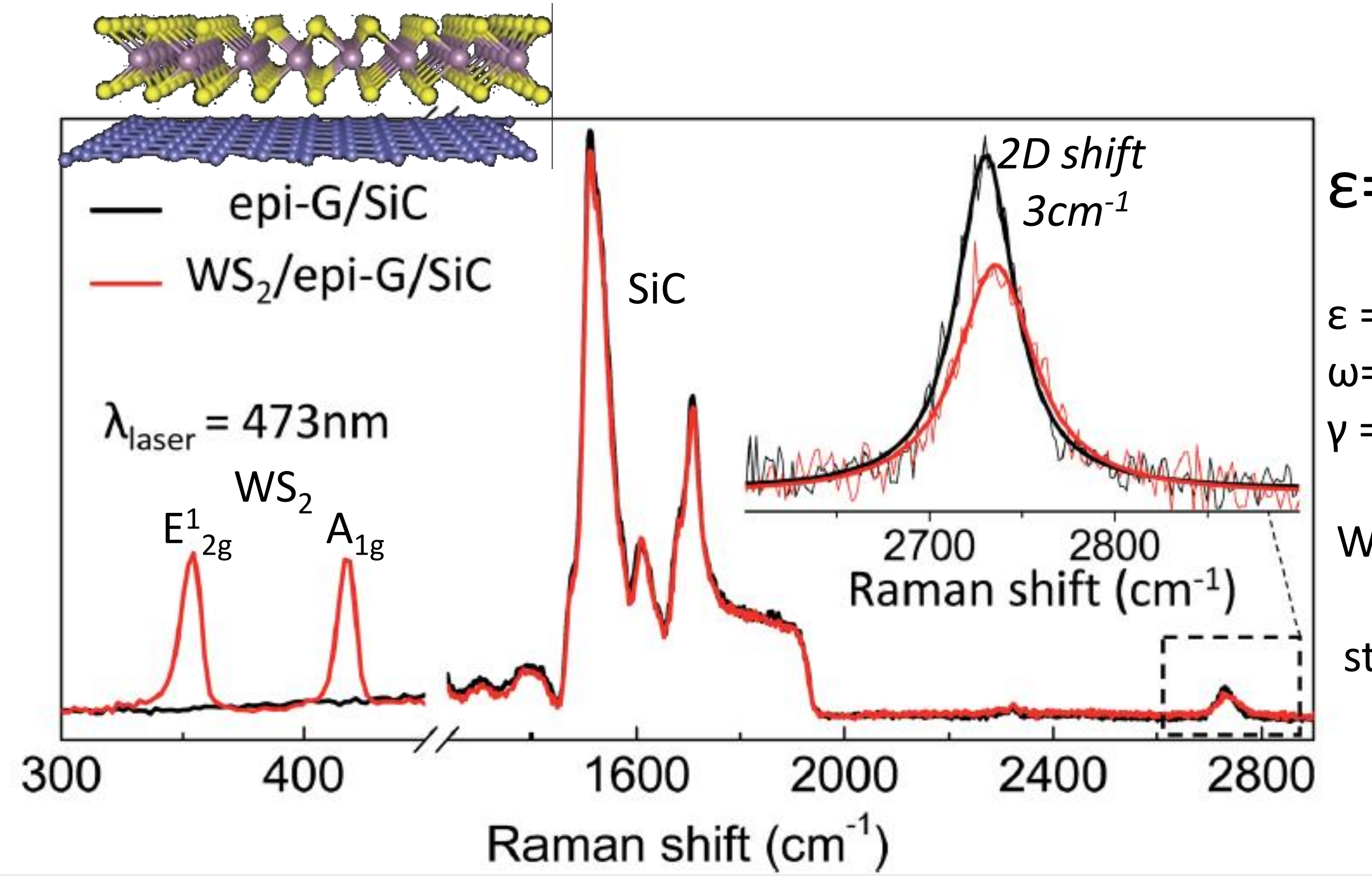
to pump




$WS_2$/Graphene/SiC

[G. V. Bianco et al. RSC Adv., 2015,5, 98700-98708]

# Unstrained $WS_2$/Graphene/SiC




$$\varepsilon=(\omega-\omega_0)/2\gamma\omega_0$$

ε = graphene strain

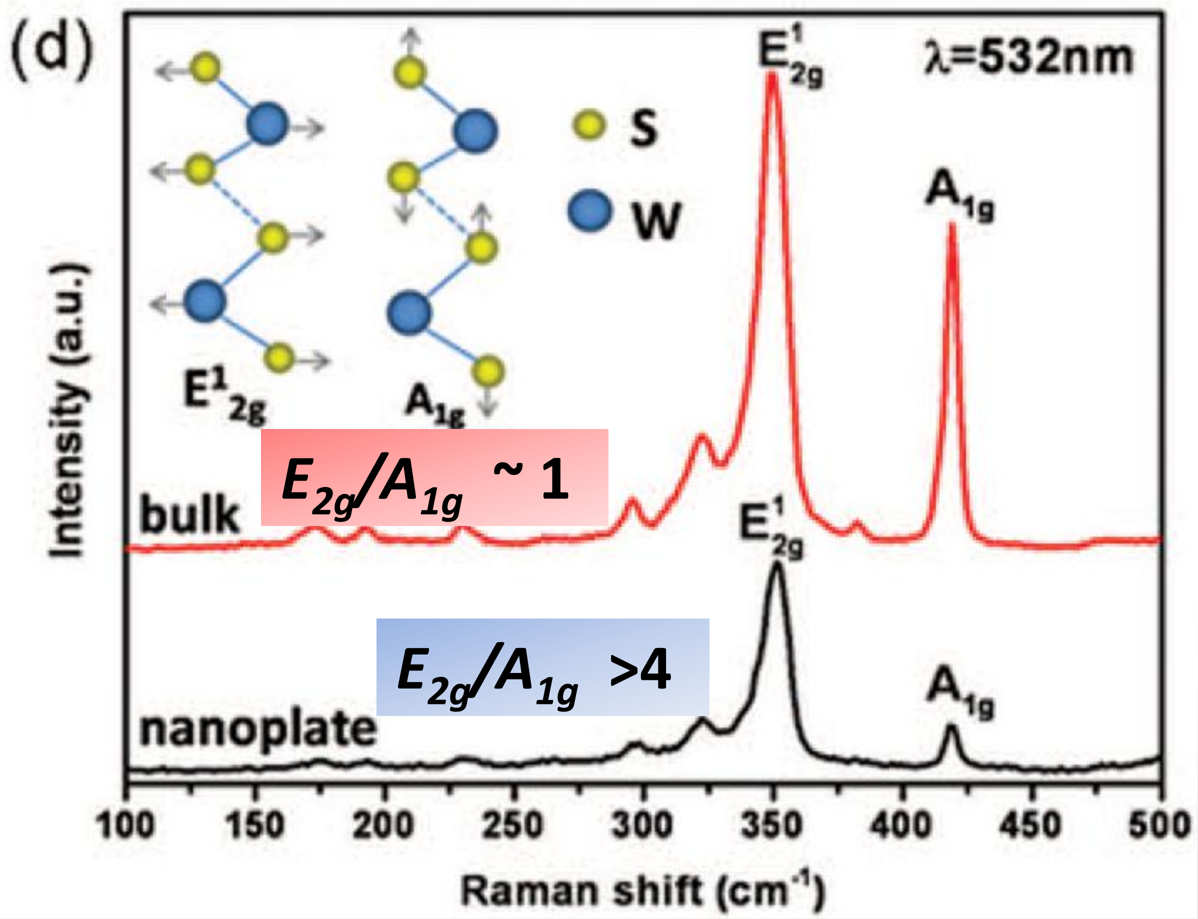
ω= 2D wavenumber

γ = Gruneisen parameter

$WS_2$ deposition induces a neglible compressive strain (ε) on graphene of

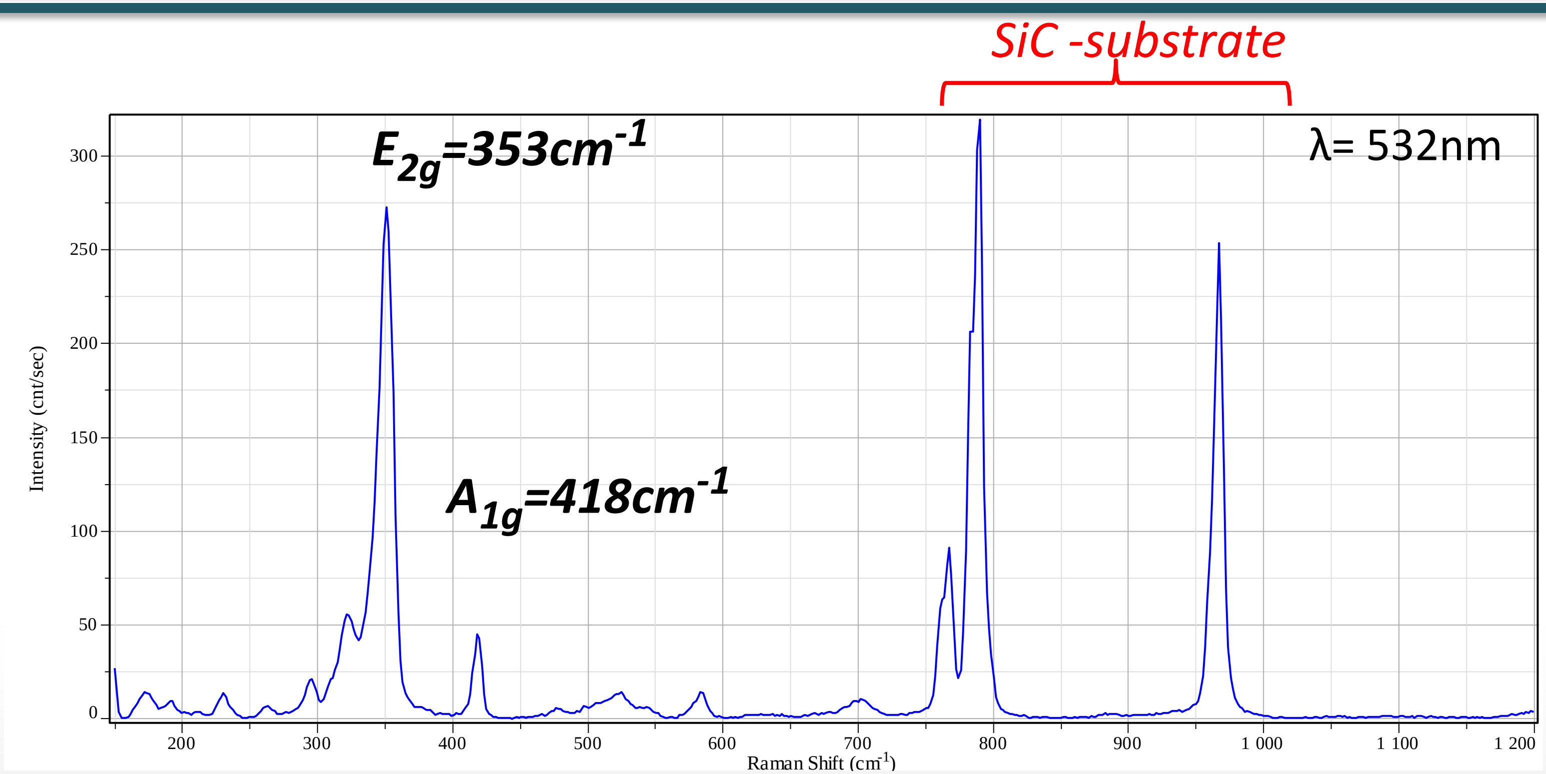
**0.02%**

# Thickness of $WS_2$ by Raman Spectroscopy




The intensity ratio $E_{2g}/A_{1g}$ (also depending on the laser frequency) decreases with the increase of WS2 layers

# $WS_2$ growth on graphene/SiC




The ratio $E_{2g}/A_{1g} > 4$ (with 532 nm laser) is typical for a single layer $WS_2$

Δν = 418-353= 65 nm

*This value is in agreement with the value reported by F. Withers*

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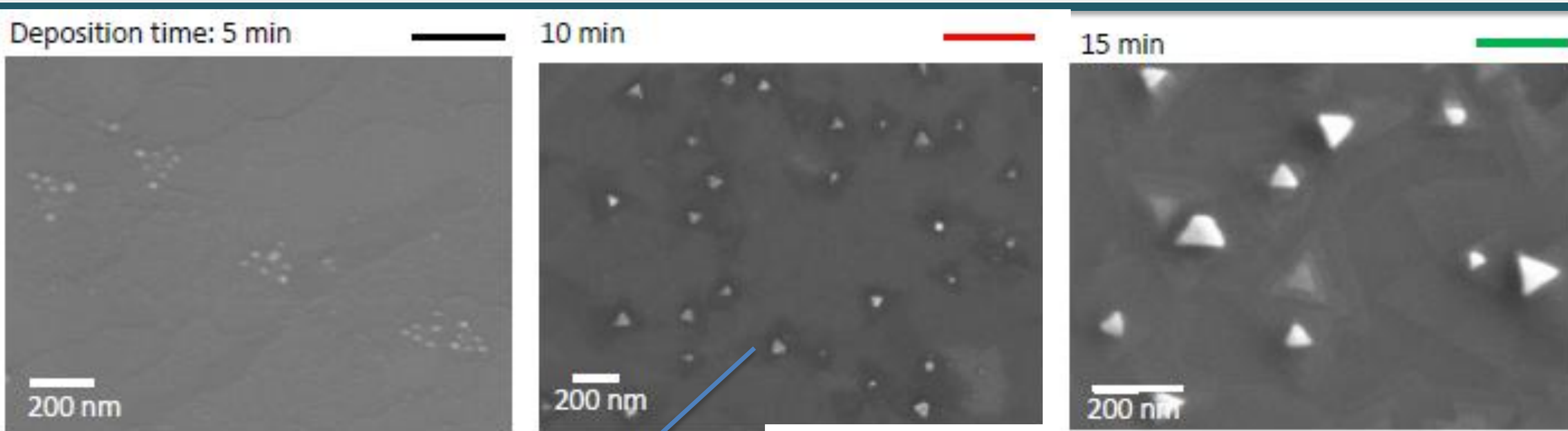
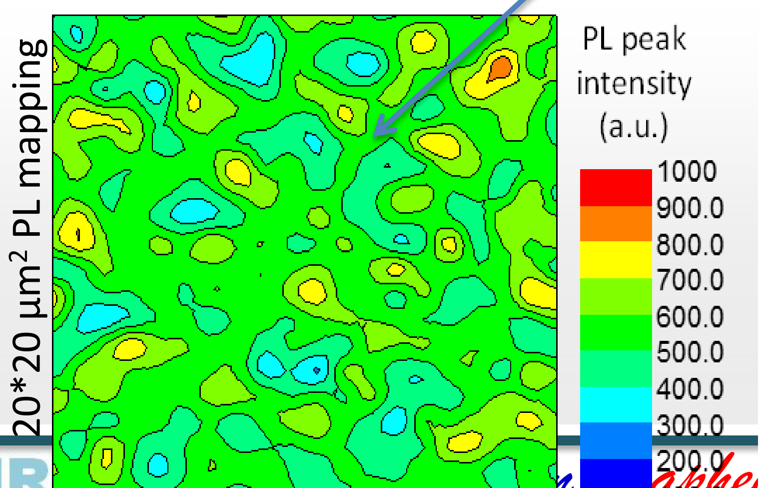
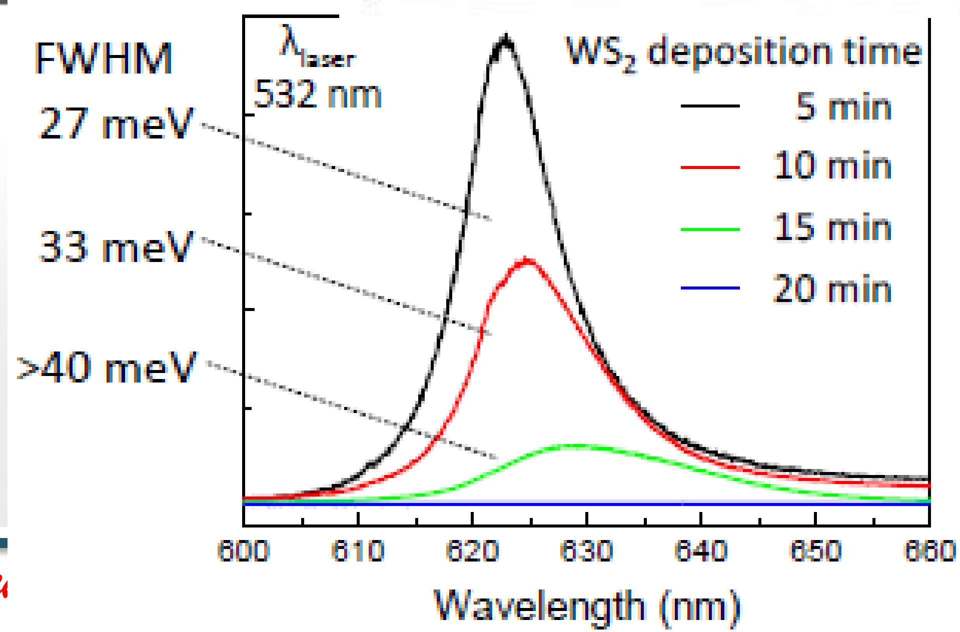
# The Thickness of a 2D Substrate is Crucial in Modulating the Light Emission

## Continuous 1L layer (2-3L) $WS_2$ film

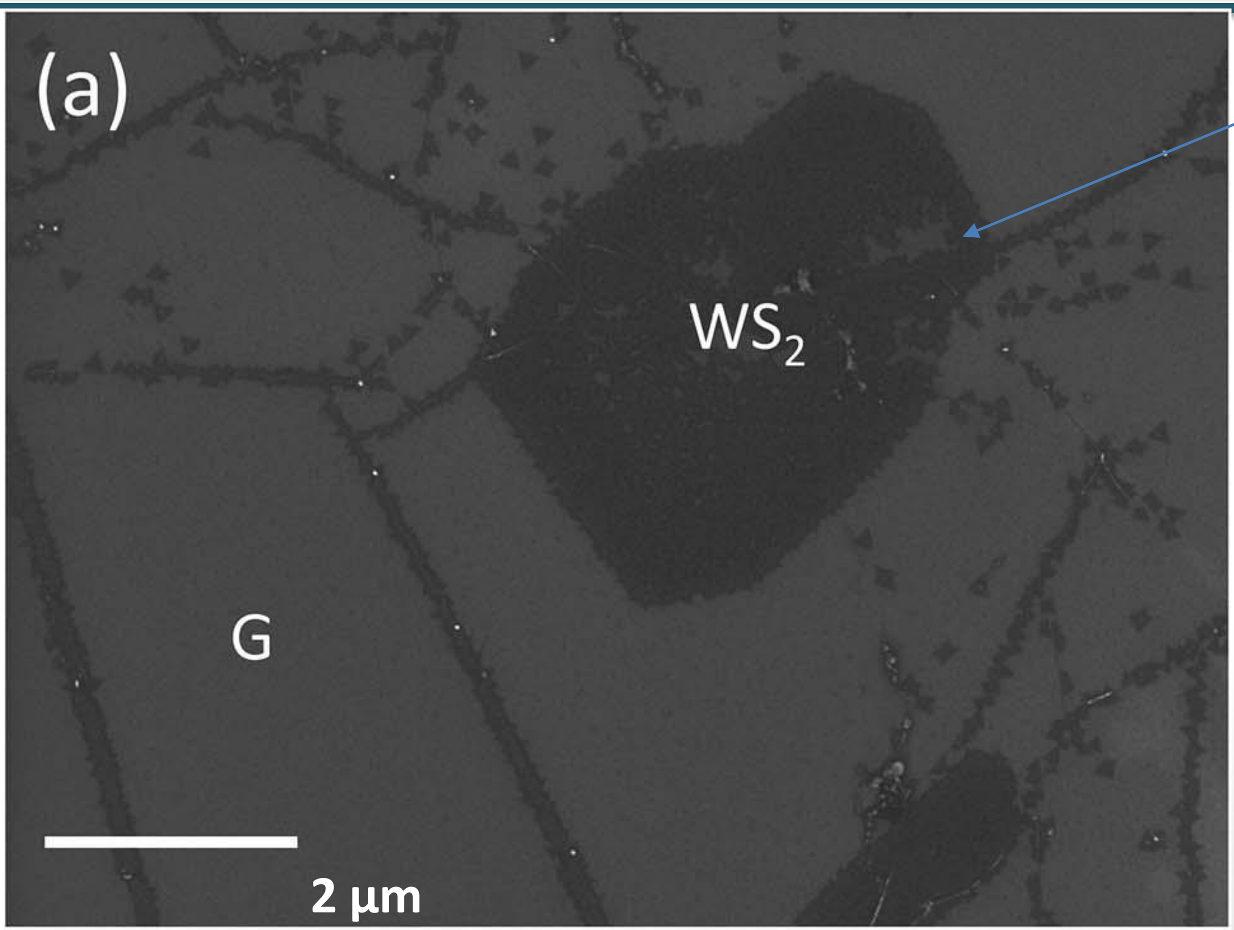



[G. V. Bianco et al. RSC Adv., 2015,5, 98700-98708]



# $WS_2$ deposited on CVD-G supported on $SiO_2$/Si




Localized $WS_2$ film deposition on Bernal-stacked **bilayer graphene islands**

The favored $WS_2$ nucleation derives from the higher surface energy of multilayer graphene rather than the monolayer one.

| Graphene | 1L | 2L | 3L |
|---|---|---|---|
| γ ($mJ\ m^{-2}$) | 47 | 99 | 103 |

**…possibility of localizing $WS_2$ deposition by tailoring the graphene surface energy**


[G. V. Bianco et al. RSC Adv., 2015,5, 98700-98708]

Our findings highlight the importance of substrate engineering when constructing atomically thin-layered heterostructures

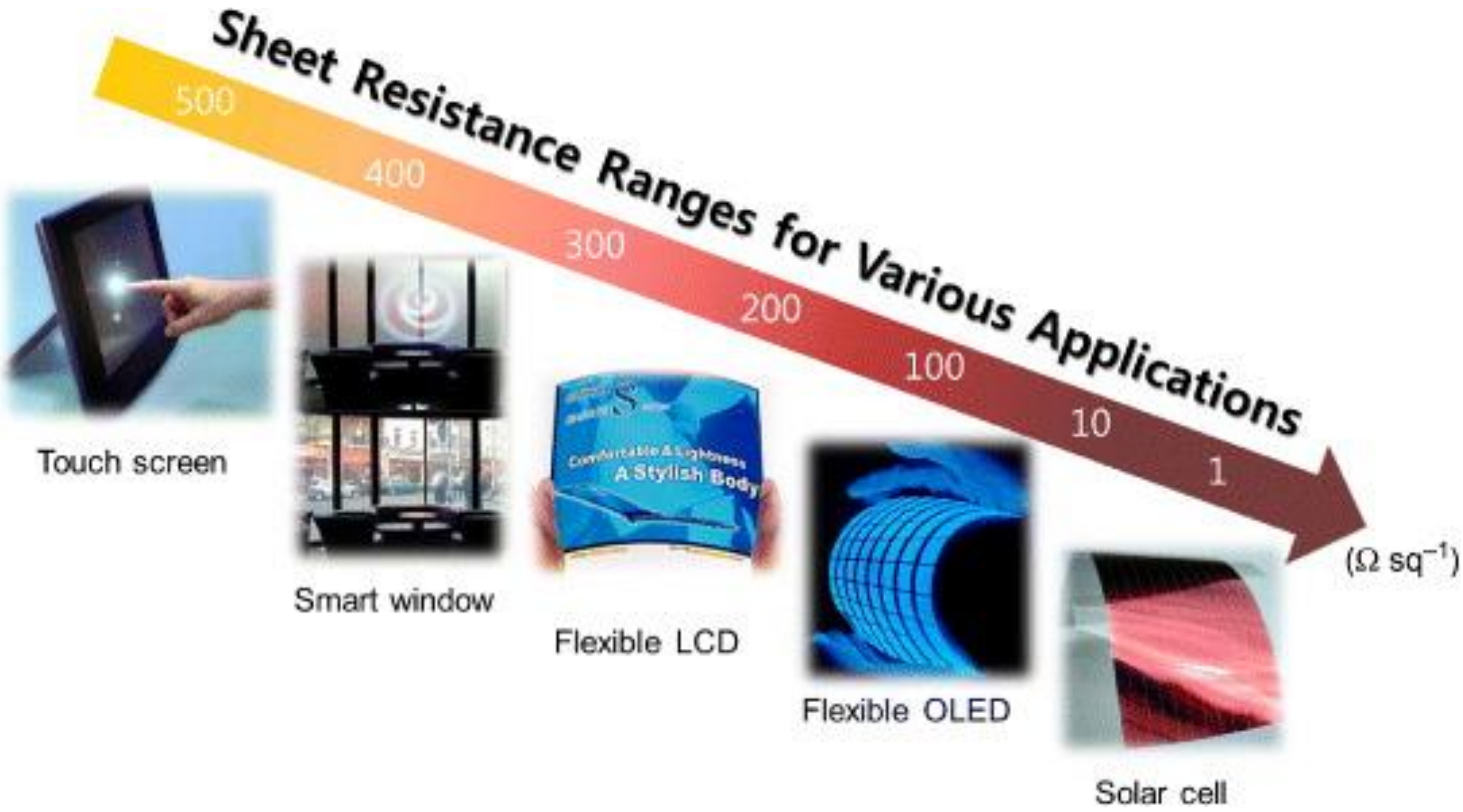
*[quote adapted from J. Milton]*

„Through Love all that is copper will be gold"

"Through Science all that is copper will be graphene"

.. And all that is graphene will be TMDs"

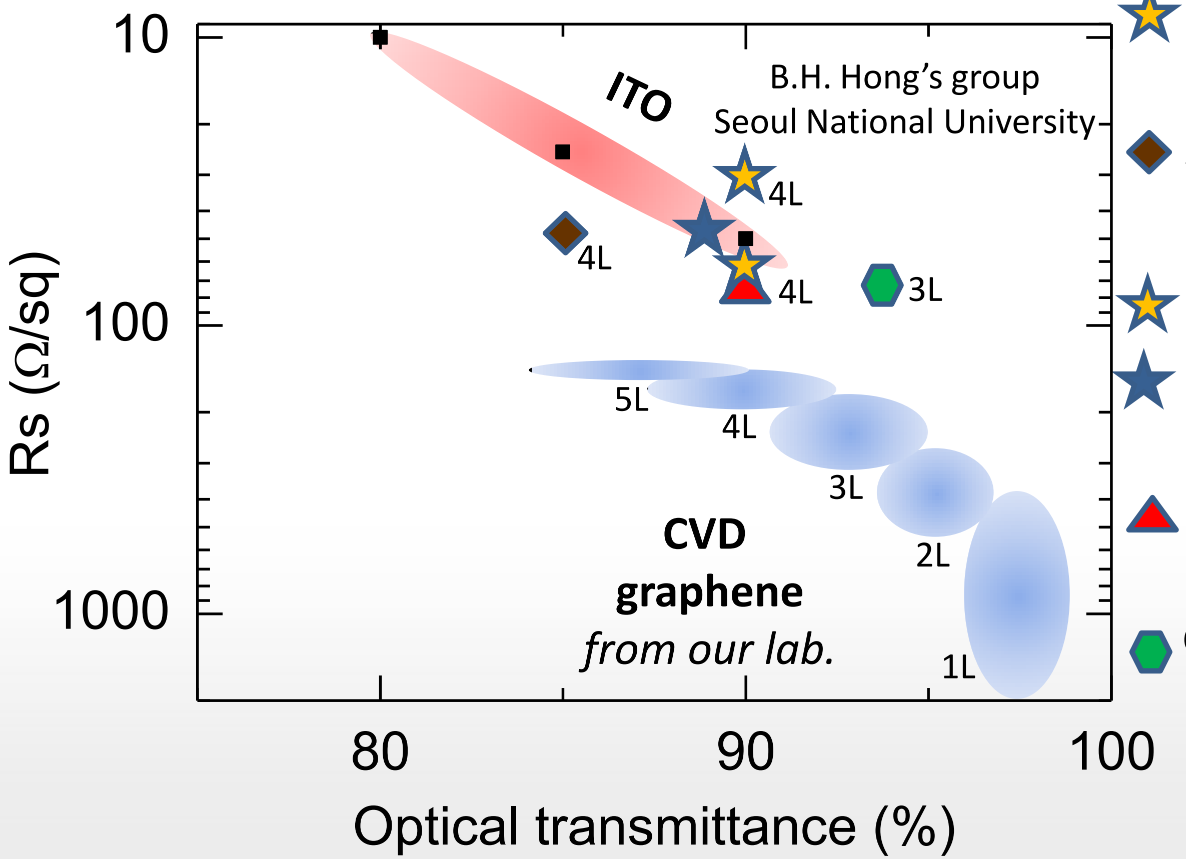
# Doping



Sheet Resistance Ranges for Various Applications
500
400
300
200
100
10
1
(Ω sq⁻¹)
Touch screen
Smart window
Flexible LCD
A Stylish Body
Flexible OLED
Solar cell

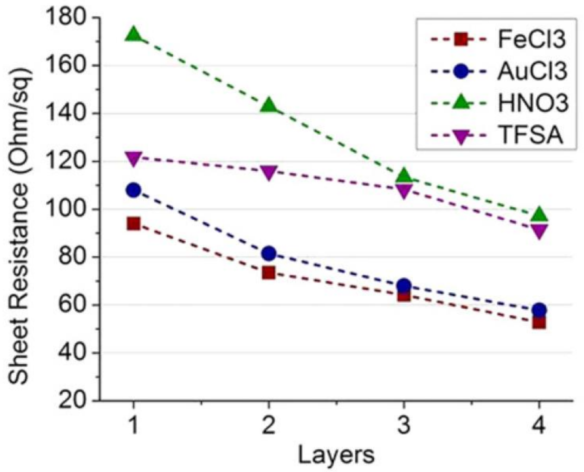
# State-of-the-art:

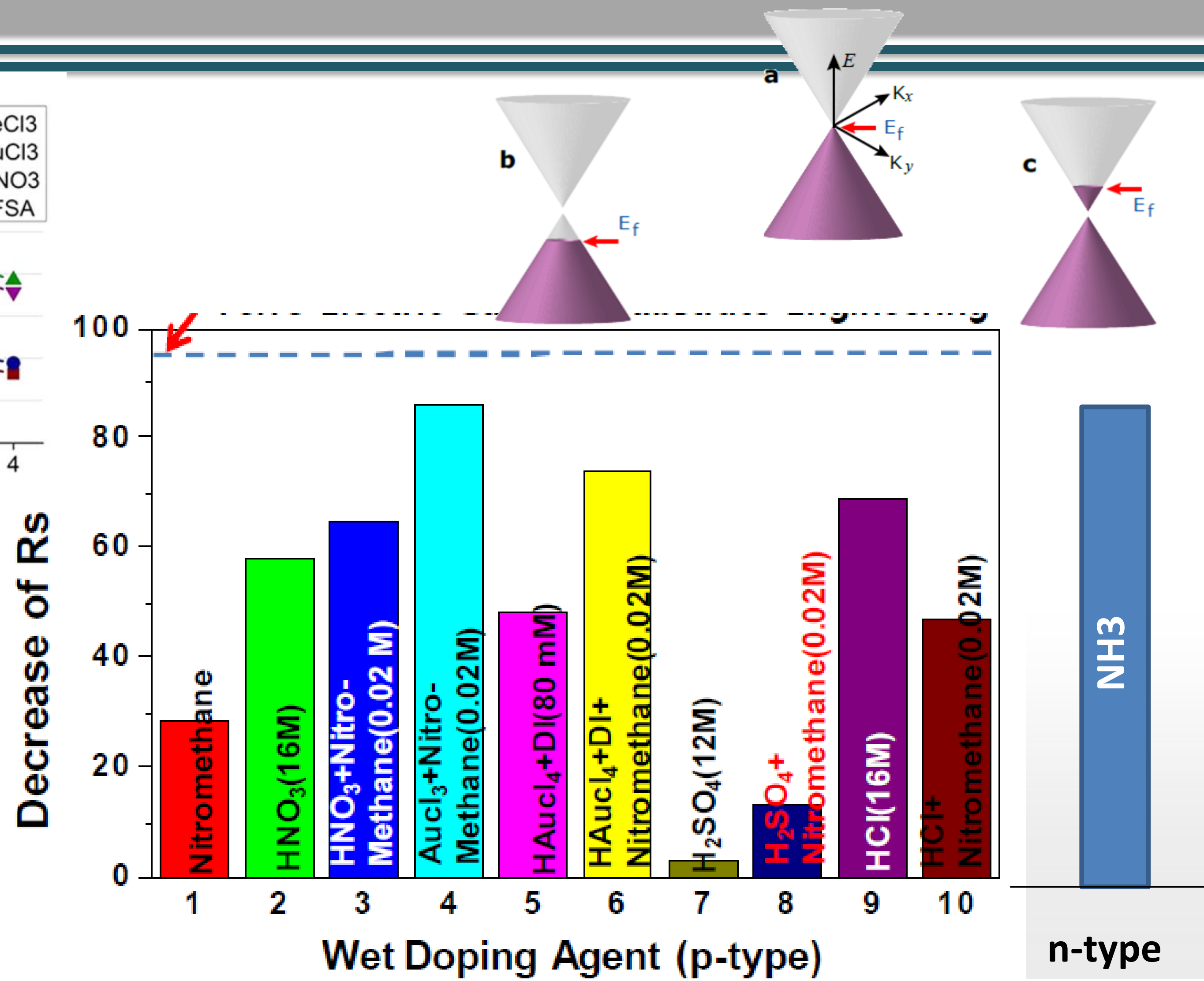
## Lowering the sheet resistance of CVD graphene




- HNO$_3$ doped graphene (30Ω/sq) [Nat. Nanotechnol., **2010**, 5, 574–578]
- AuCl$_3$ doped graphene (54Ω/sq) [ACS Nano, **2010**, 4, 4595]
- HNO$_3$ doped graphene (63Ω/sq)
- AuCl$_3$-CH$_3$NO$_2$ doped graphene (43Ω/sq) [Nano Lett. **2011**, 11, 5154–5158]
- FeCl$_3$ doped graphene (72Ω/sq) [Nanotechnology, **2014**, 25, 395701]
- CL$_2$ doped graphene (70Ω/sq) [Nanoscale, **2014**, 6, 15301–15308]

# Chemical modification: Wet Chemical Doping



# REDOX Graphene Doping

| | | | REDOX POTENTIAL |
|---|---|---|---|
| $Fe^{3+} + e^-$ | $\rightleftharpoons$ | $Fe^{2+}$ | +0.77 |
| $NO_3^-(aq) + 2\,H^+ + e^-$ | $\rightleftharpoons$ | $NO_2(g) + H_2O$ | +0.80 |
| $[AuCl_4]^- + 3\,e^-$ | $\rightleftharpoons$ | $Au(s) + 4\,Cl^-$ | +0.93 |
| Graphene | $\longrightarrow$ | p-Graphene$^+$ + $e^-$ | +0.4 eV |
| $2H_2O + 2\,e^-$ | $\rightleftharpoons$ | $H_2$ + OH- | -0.8277 |

# State-of-the-art: Chemical Treatment forLowering $R_S$ of CVD Graphene: $HNO_3$ p-Doping

$$10HNO_3 + 50C \rightarrow (6HNO_3)2NO_3^- C_{50}^+ + 2NO_2 + 2H_2$$

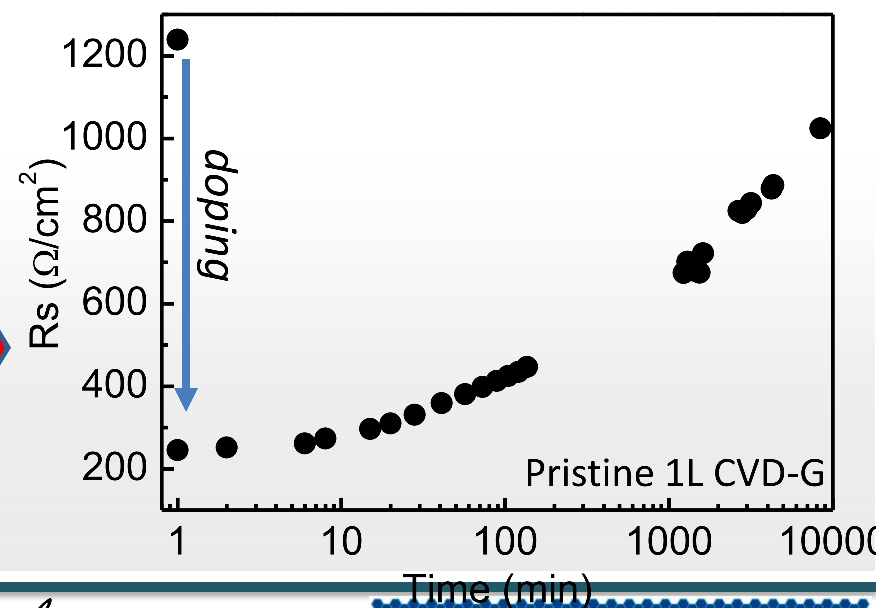
**Redox: C oxidizes and N reduces**


**σ=neμ**

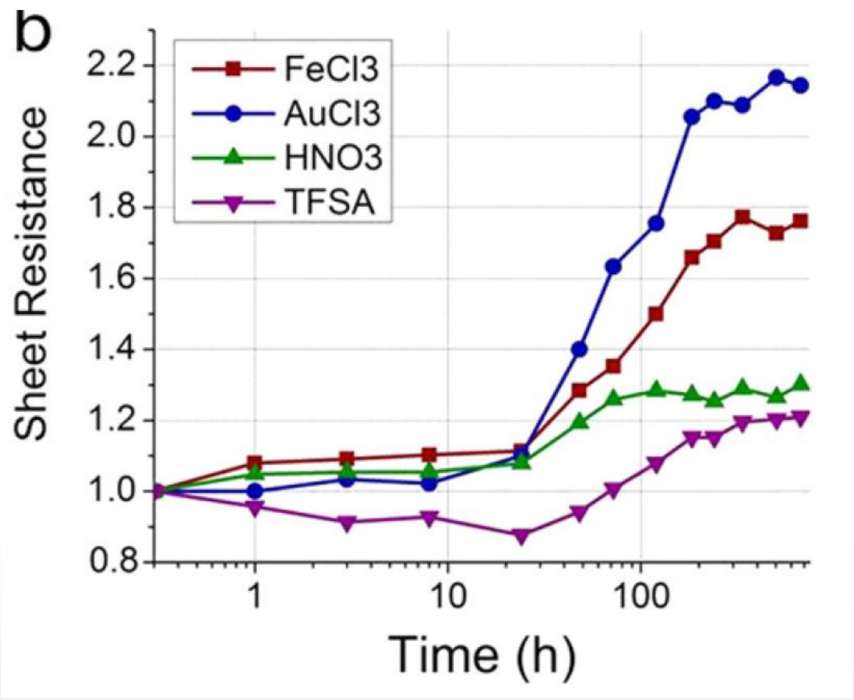
Increasing the graphene carrier density (holes) without introducing charge trapping center (C-sp3)

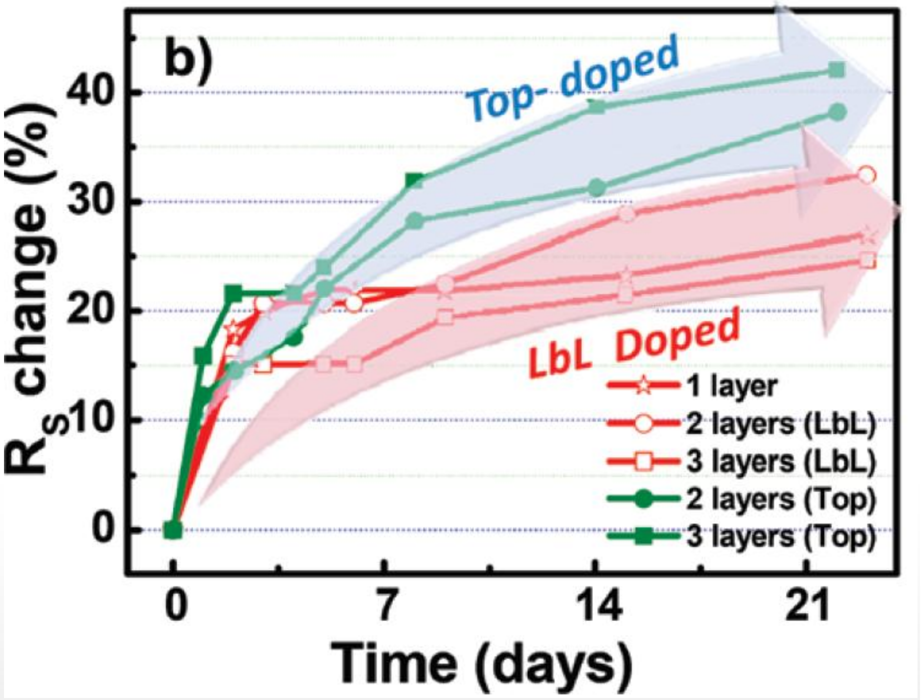
**not stable upon air exposure**

$HNO_3$, $NO_3^-$ and $NO_2$ adsorbed on graphene by non covalent interactions



# Problem/Challenge: Stability of Wet Doping

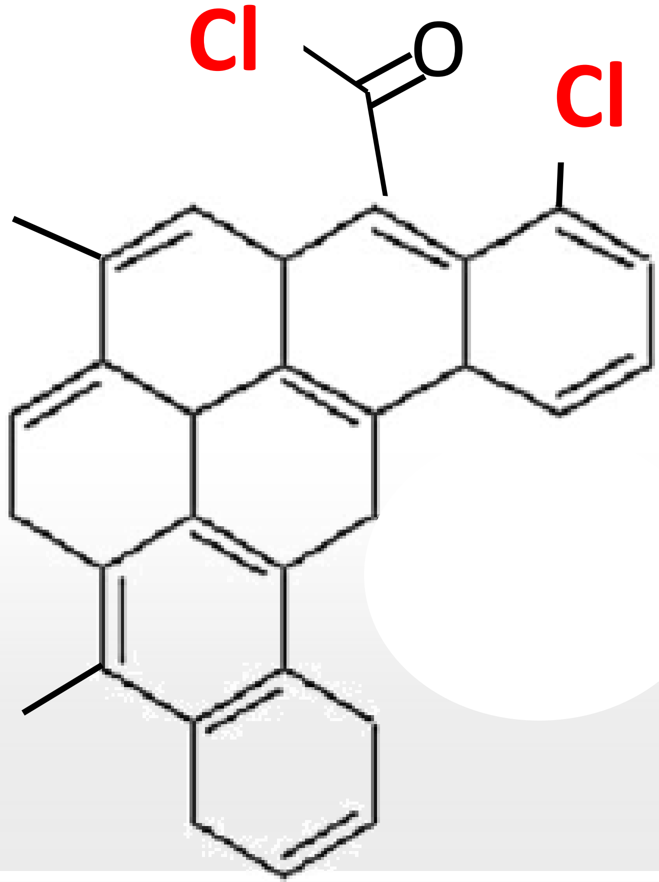


# Our Approach: Graphene doping by thionyl chloride ($SOCl_2$)

**Taking advantage of intrinsic chemical defects in CVD graphene**

Covalent attachment of electron acceptor species (-Cl) without creating new C-sp$^3$ charge scattering center

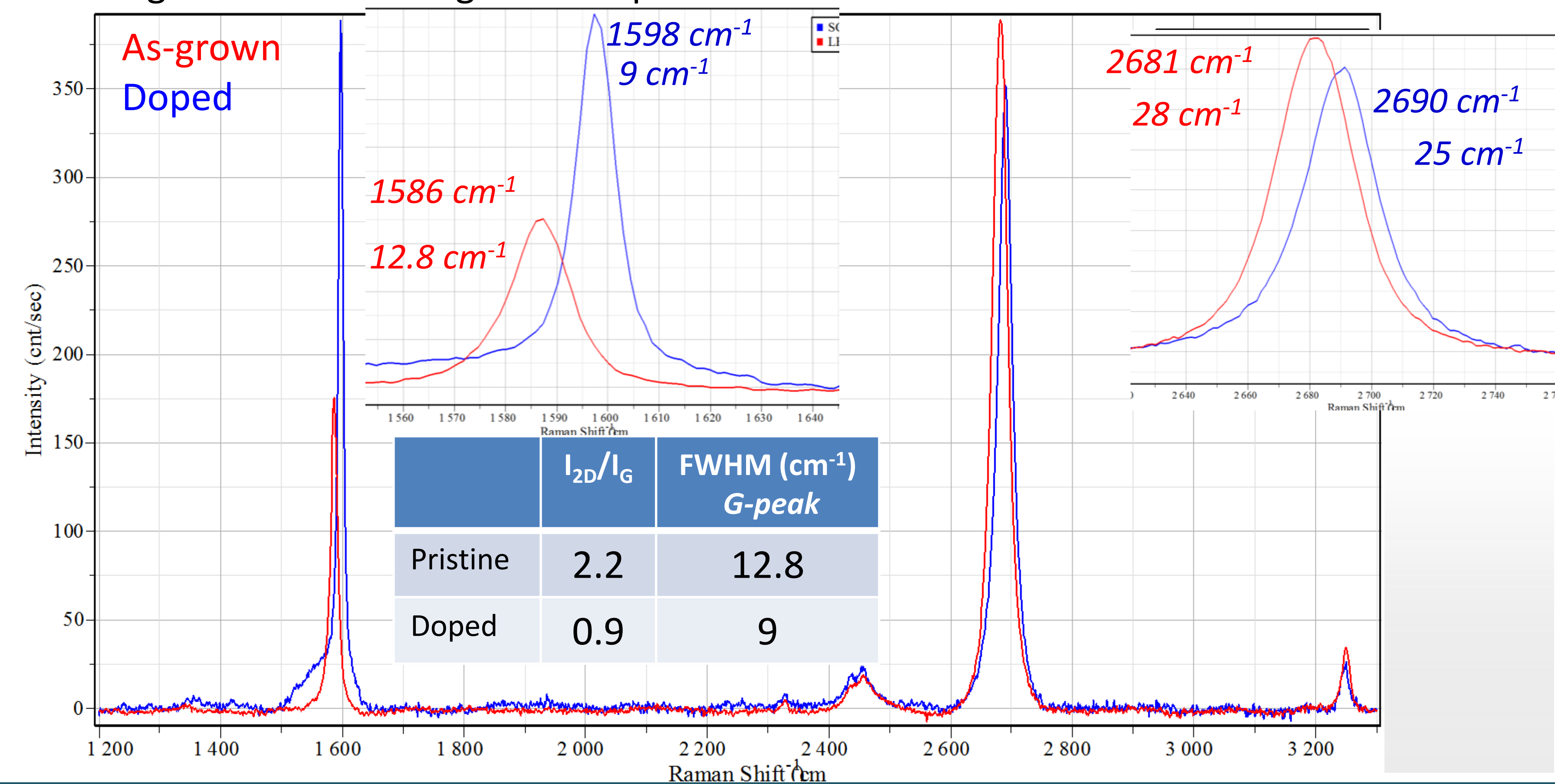



$SO_2$ + HCl

# RAMAN spectra of single layer : pristine *vs* $SOCl_2$-doped-graphene

**Doping without introducing defects**

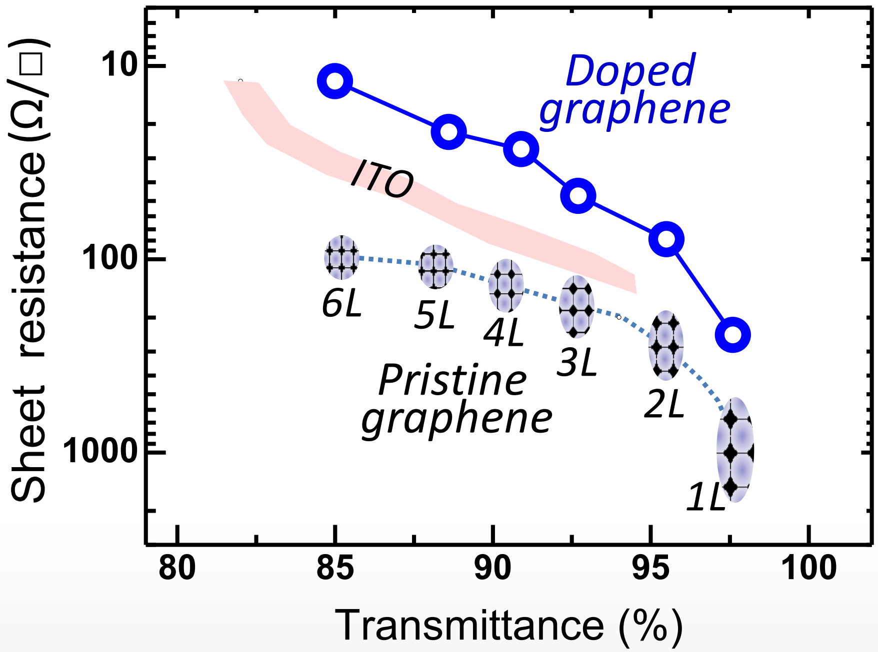
- the $I_{2D}/I_G$ ratio changes from 2.2 to 0.9
- both G and 2D peaks shift to high energy (12 $cm^{-1}$ and 9 $cm^{-1}$)
- there is a significant narrowing of the G peaks from 12.8 $cm^{-1}$ to 9 $cm^{-1}$



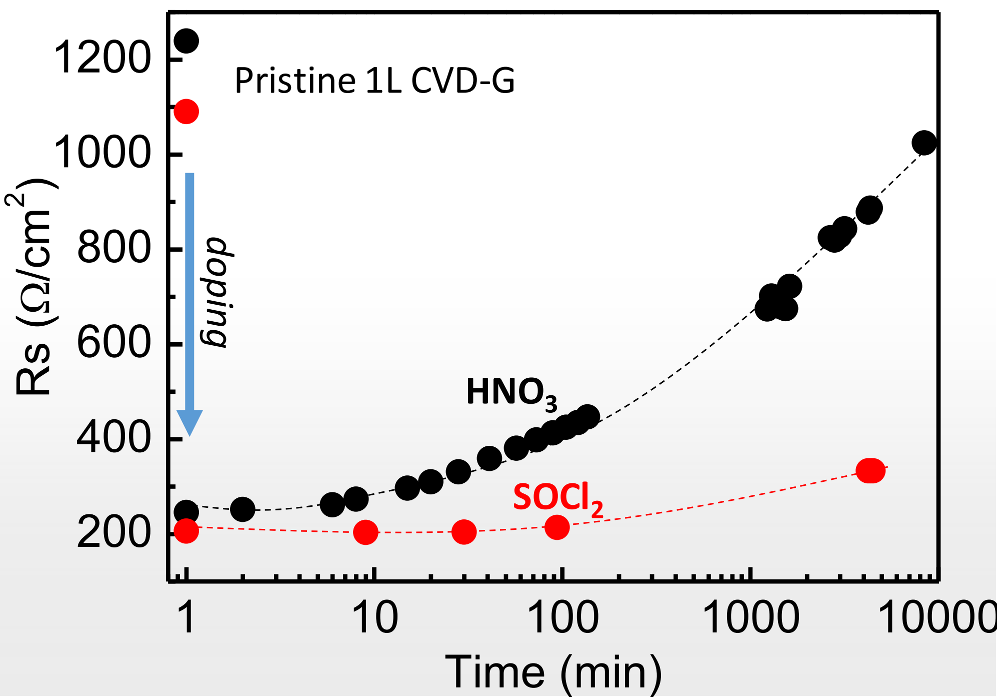

| | $I_{2D}/I_G$ | FWHM ($cm^{-1}$) *G-peak* |
|---|---|---|
| Pristine | 2.2 | 12.8 |
| Doped | 0.9 | 9 |

# Better than ITO!!! *(The impossible made possible)*

## Conductive.........




## ...and stable!!



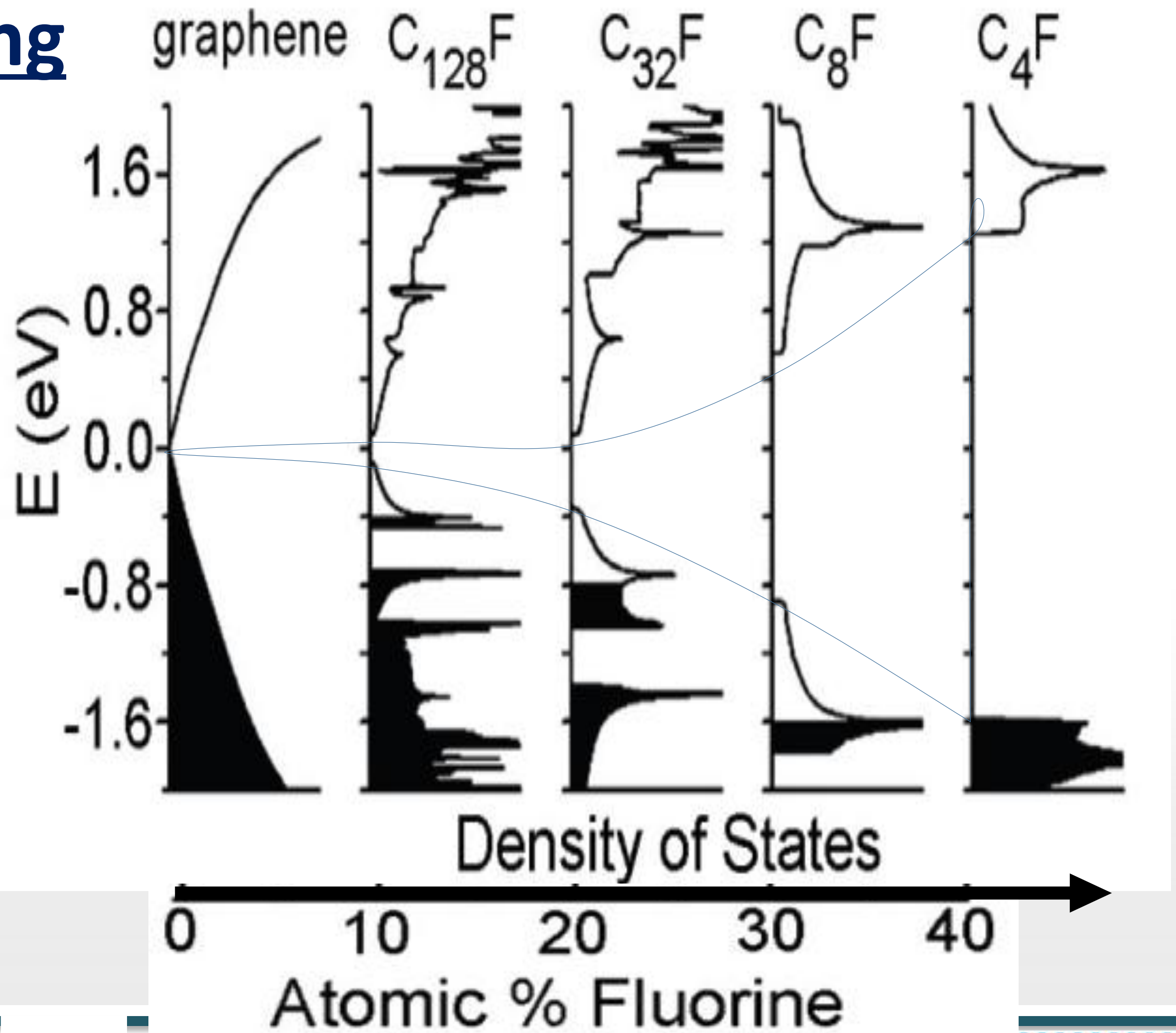
# Functionalization of CVD Graphene

- Fluorination
- Oxidation


Adsorption or chemisorption of e.g. atomic hydrogen, H (or F, OH, NH2,..)

# Graphene Functionalization for…

**Band gap engineering**

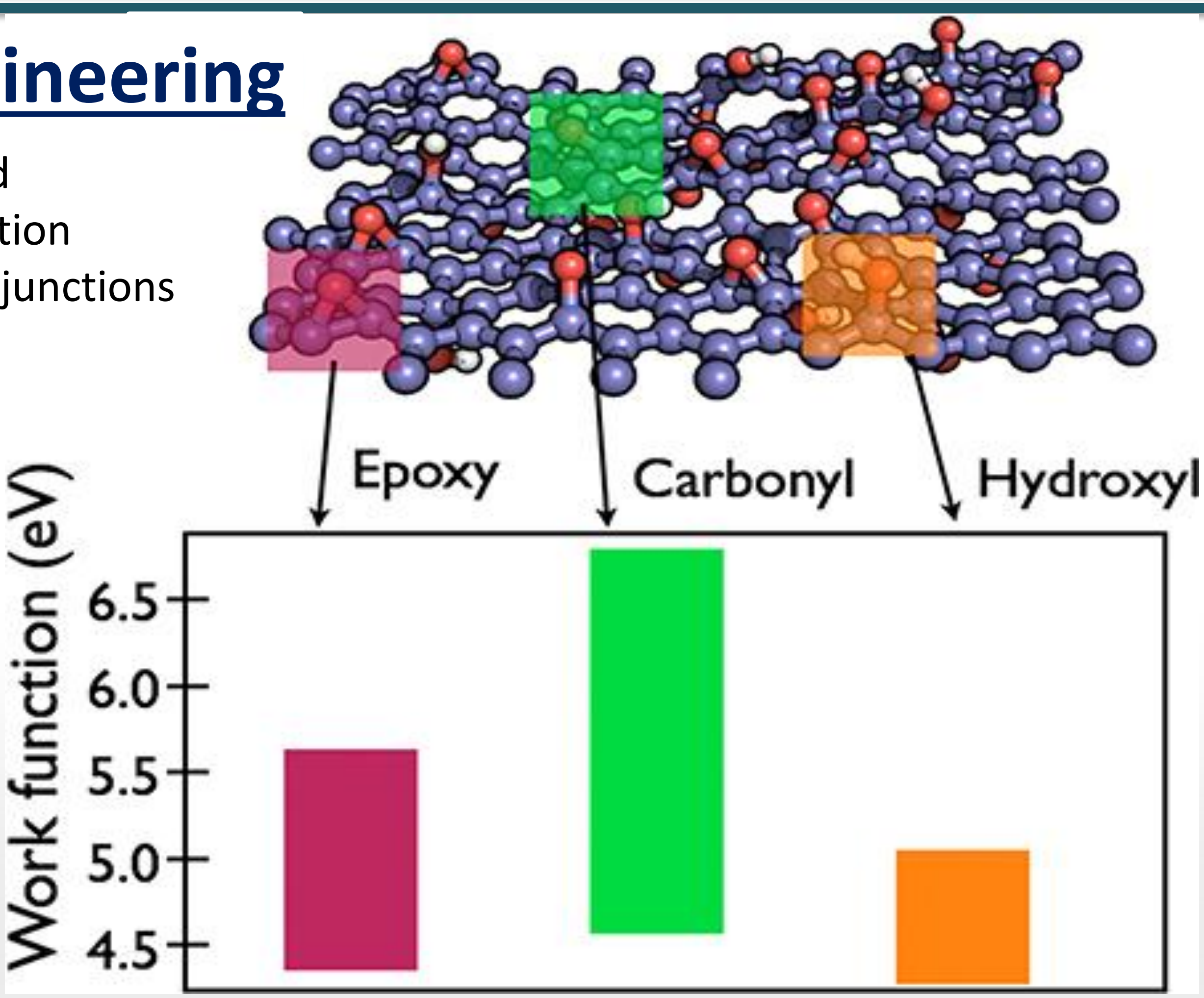



*Nano Lett., 10* (2010) 3001–3005

# Graphene Functionalization for…

## Work function engineering

Graphene doping and
Schottky barrier modulation
in graphene/semiconductors junctions



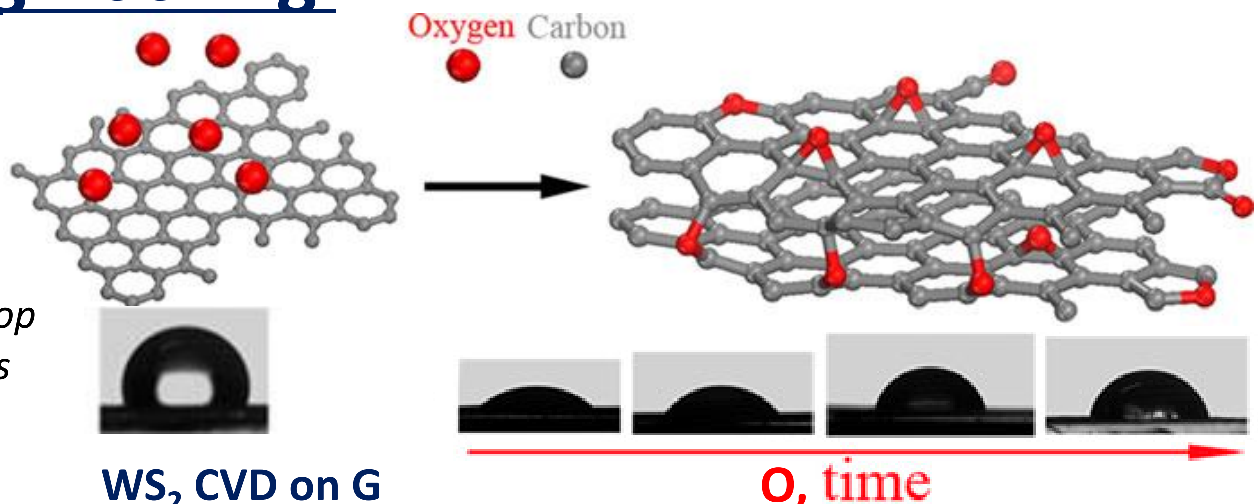

*ACS Nano*, **2013**, *7* (2), pp 1638–1645

# Graphene Functionalization for…

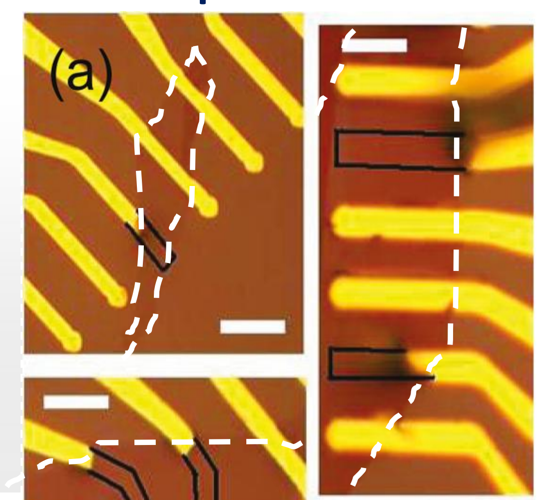
## Surface energy engineering

The low surface energy of graphene (47 mJ/m$^2$) limits its integration with other materials in technological devices

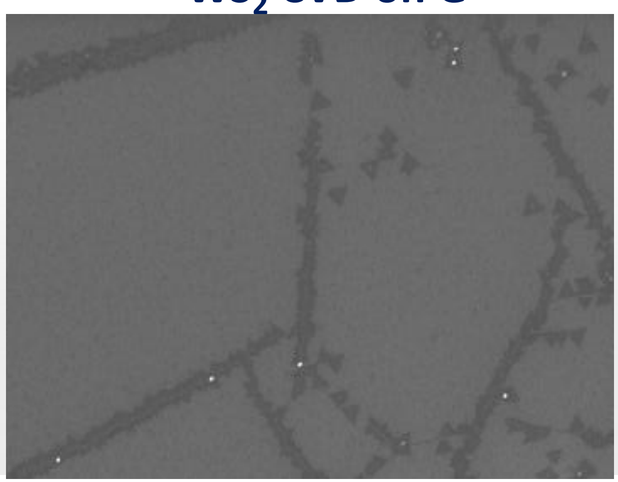
*e.g., in metal contact deposition on top of graphene the process is not always successful (dewetting of the metal)*




**Au evaporation on G**




**$WS_2$ CVD on G**



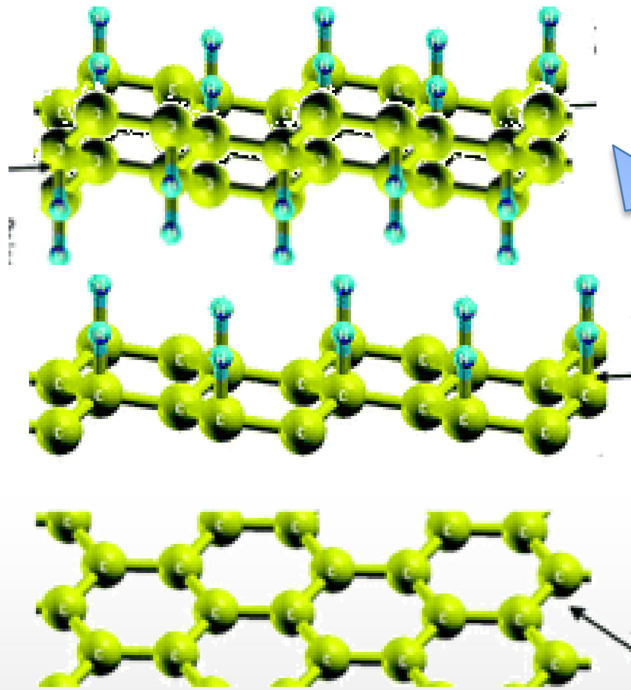
# Chemical modification by Hydrogen (H-atoms)

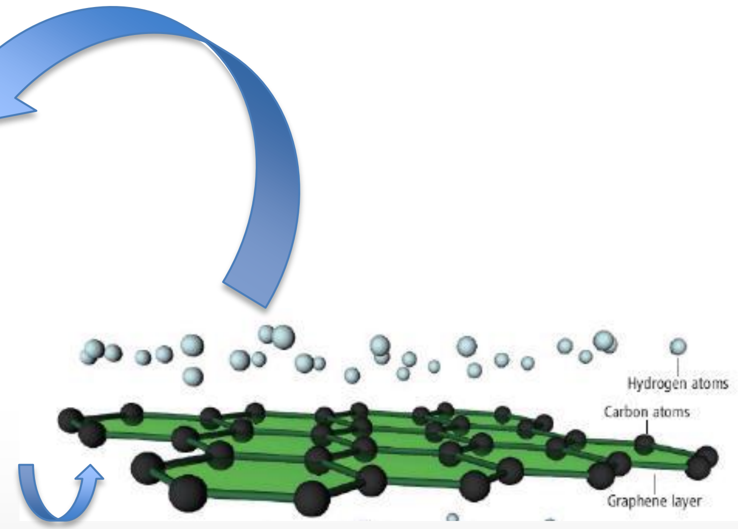
H-increase

**graphane**
(fully hydrogenated)
Bandgap of 4.5 eV

**graphone**
(semi-hydrogenation)
Bandgap of 0.46eV
**ferromagnetic**

**graphene**
Bandgap of 0 eV

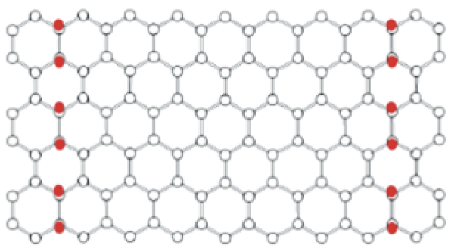




# Hydrogen induced band gap opening
# Hydrogen induced confinement

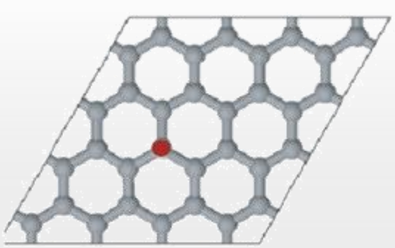
Can atomic hydrogen be arranged in ordered structures on graphene and thereby facilitate gand gap engineering?

a) Hydrogen atoms arranged in lines

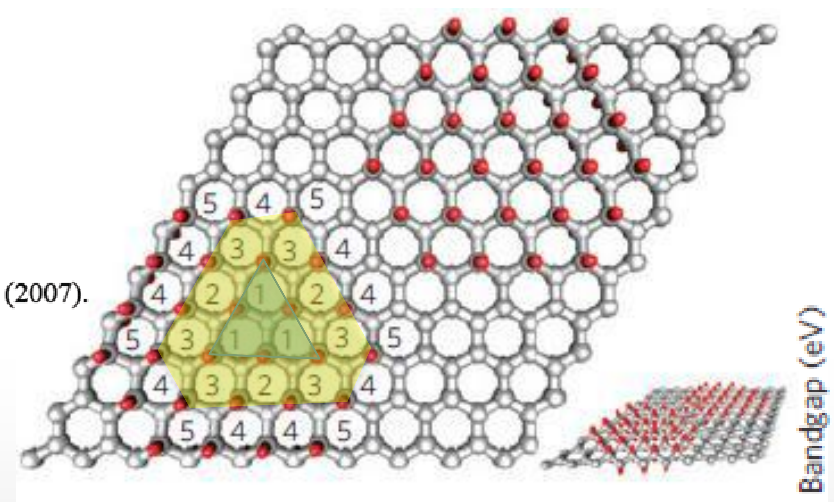


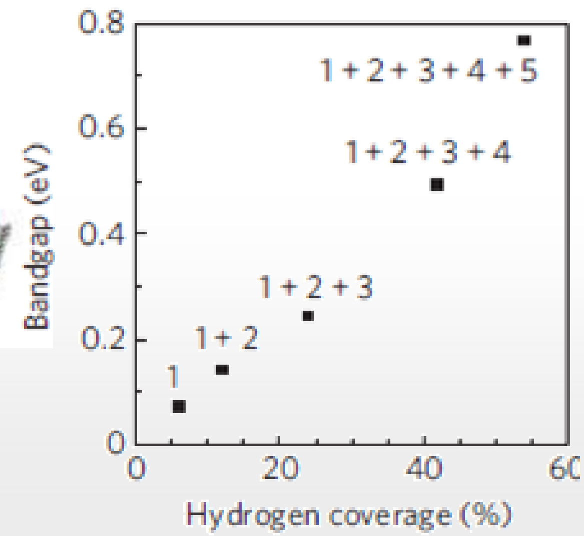
Chernozatonskiĭ et al., *Jetp Lett,* **85** (1), 77-81 (2007).

b) periodic arrangement



Duplock, E.J.et al. *Phys Rev Lett*, **92**, 225502 (2004).



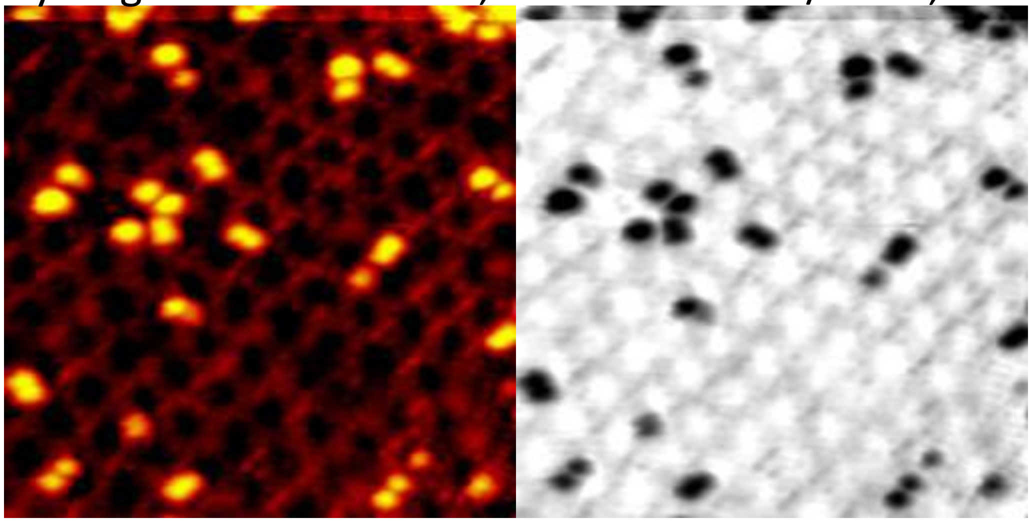

Balog et al., Nat. Mat. 9, 315 (2010)

# H on graphene/SiC

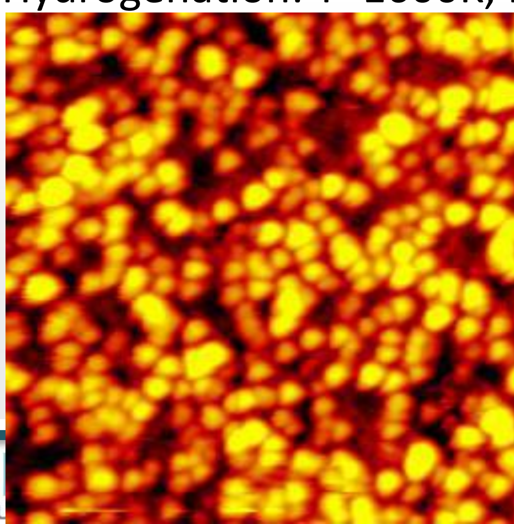
**Real situation from literature: Disorder**

Hydrogen dose at 1600K, F=3x10$^{12}$ atoms/cm$^2$ s, **t=5s**

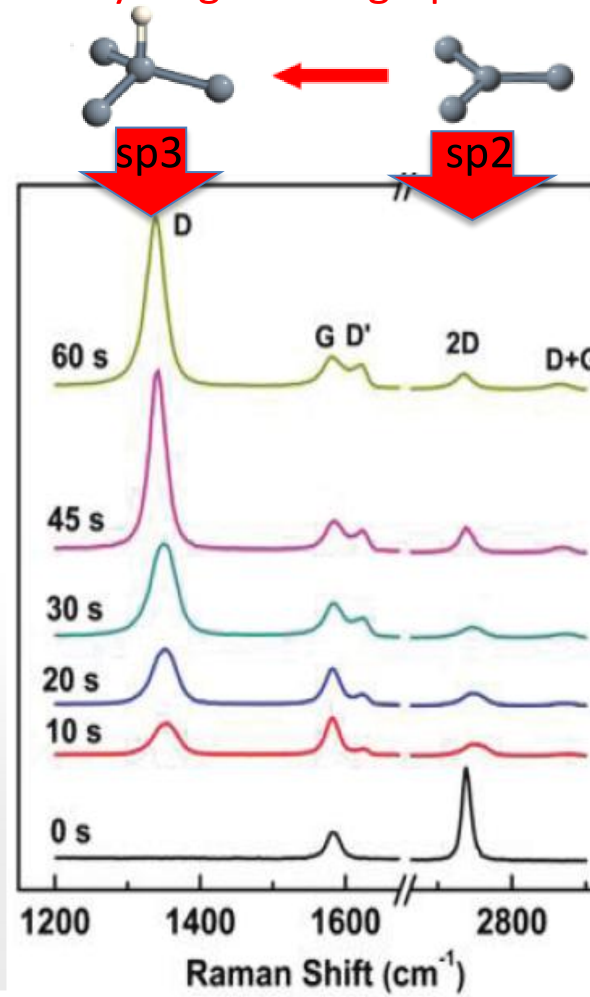
200x200Å



Hydrogenation: T=1600K, F=3x10$^{12}$ atoms/cm$^2$ s, **t=90s**



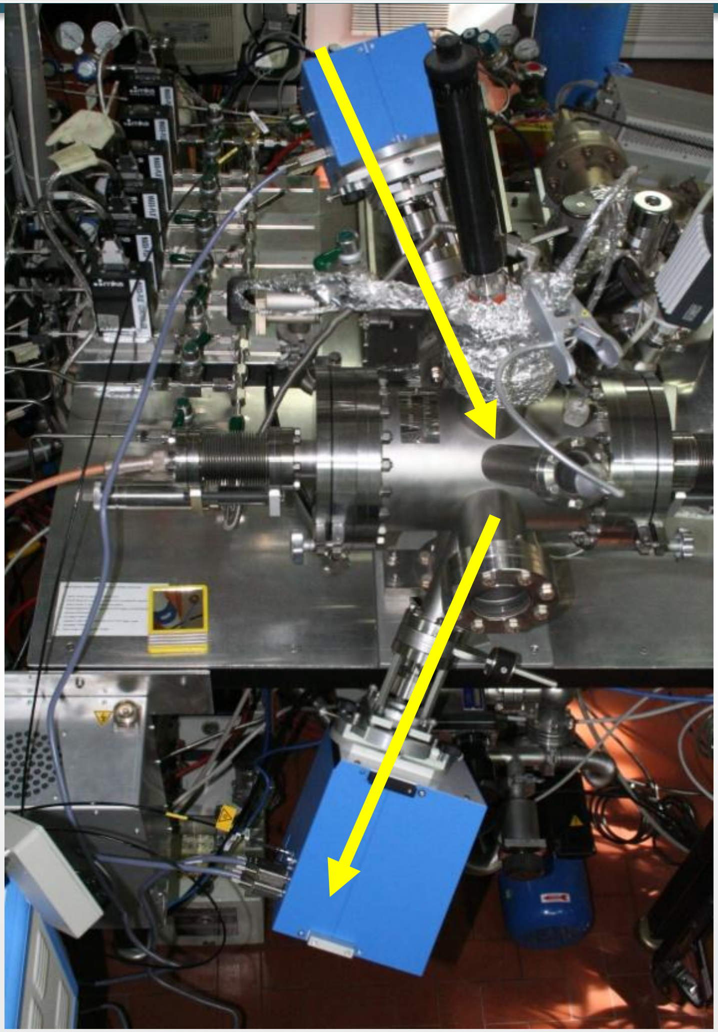
Hydrogenated graphene

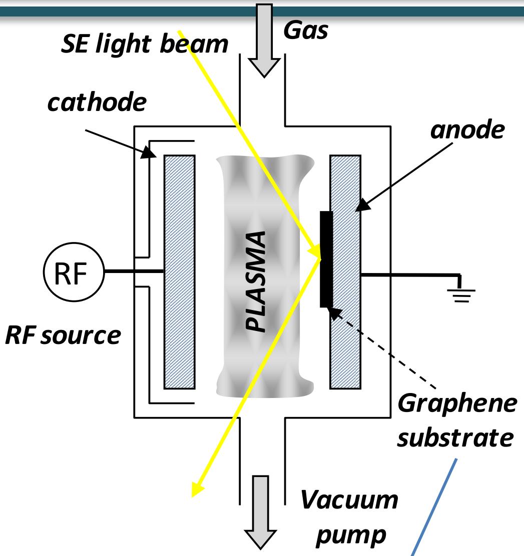


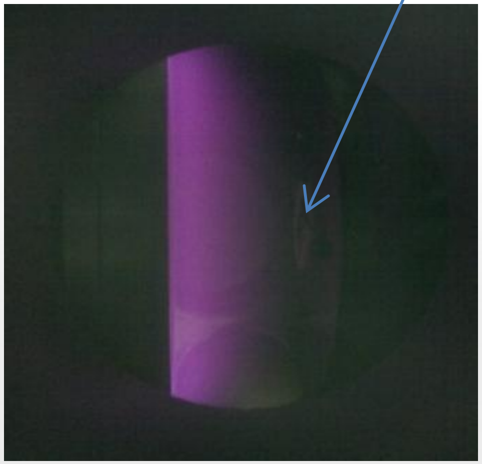

Balog et al. JACS 131, 8741 (2009)

# Alternative Technology: Plasma Modulation

## In situ monitoring by spectroscopic ellipsometry

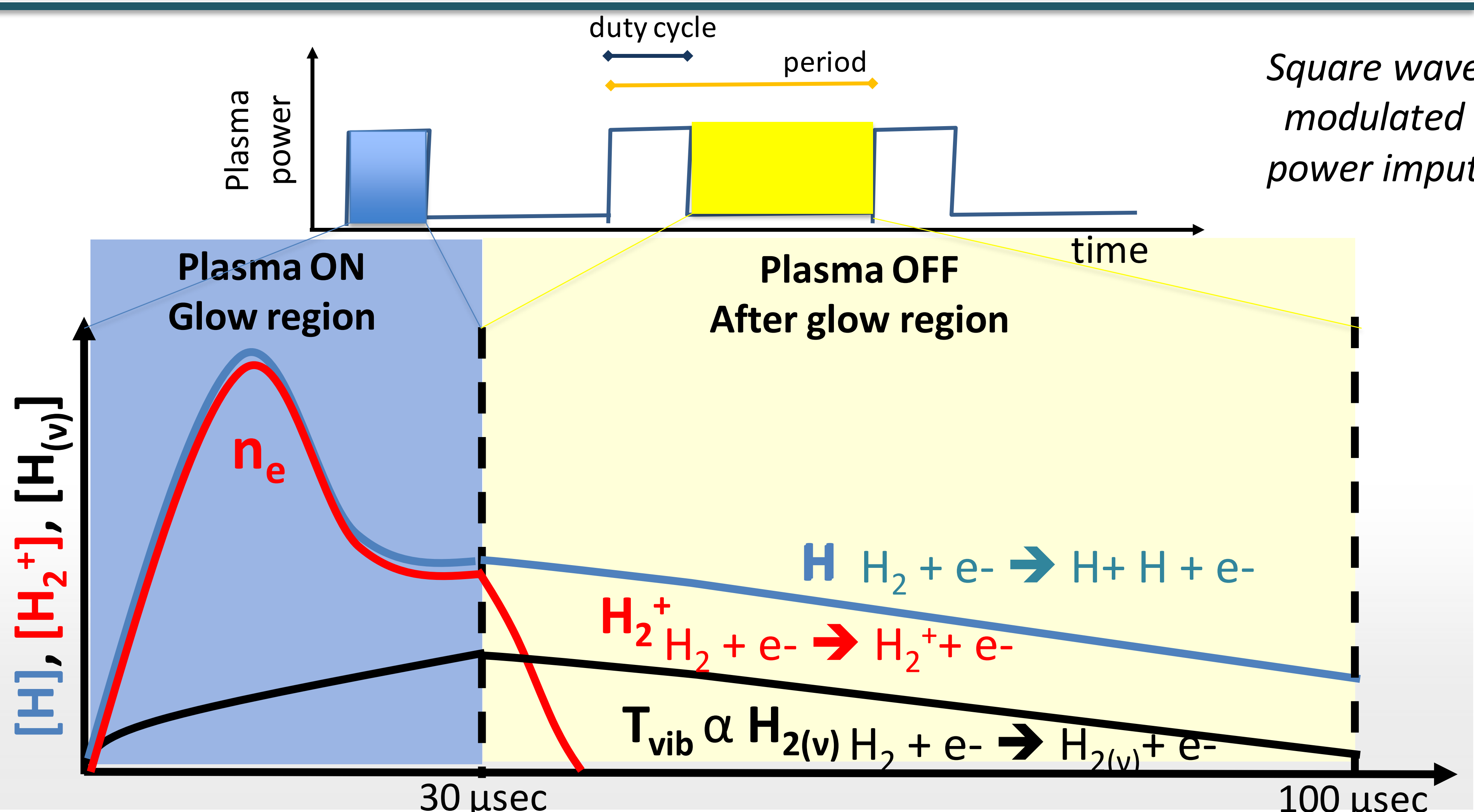




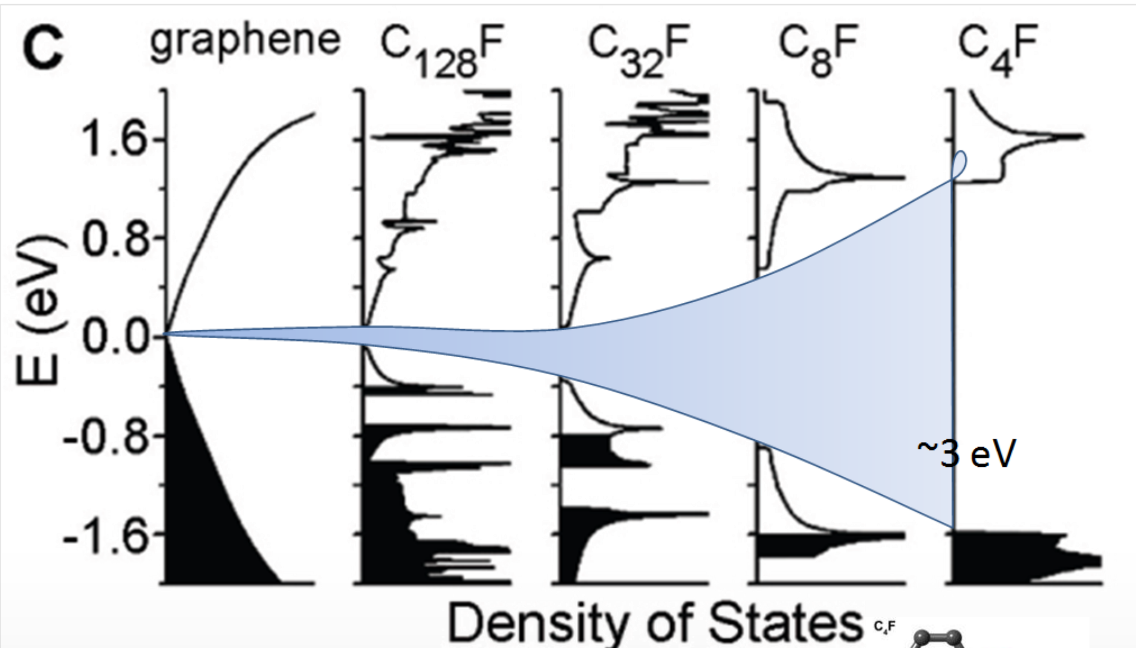
# Graphene Processing by Modulated Plasmas

**Ion and electron bombardment as well as radiative damage is avoided!**



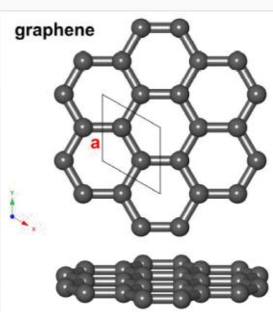
# Covalent Functionalization: Gap Opening by Fluorination

Calculated total density of states of single-side fluorinated graphene for several fluorine coverages




**J. T. Robinson**Nano Lett. 2010, 10,

..............................

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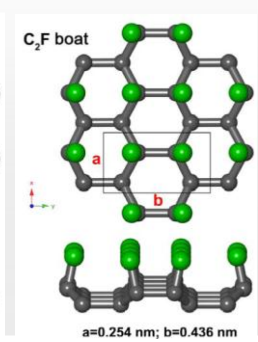
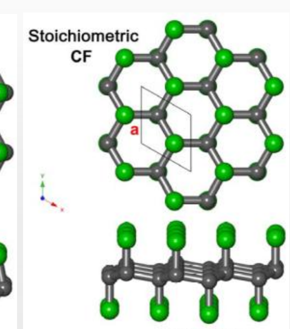
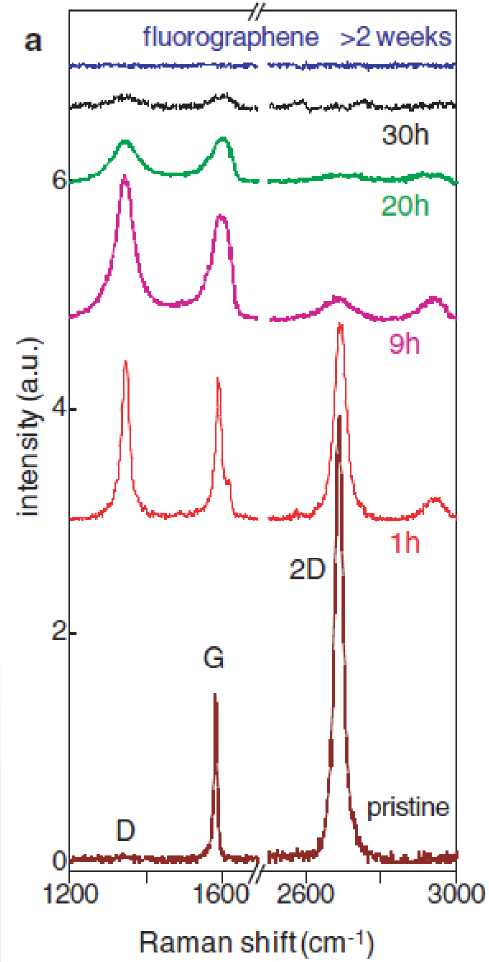
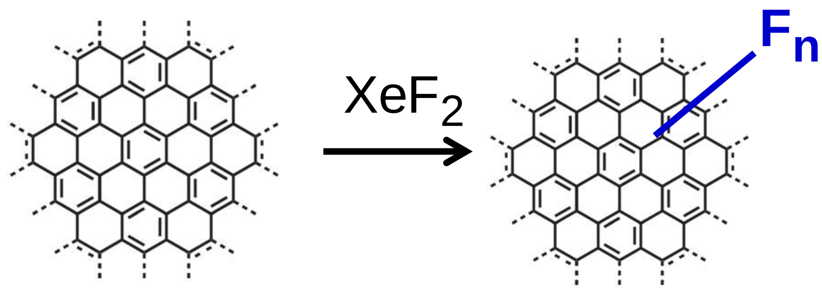


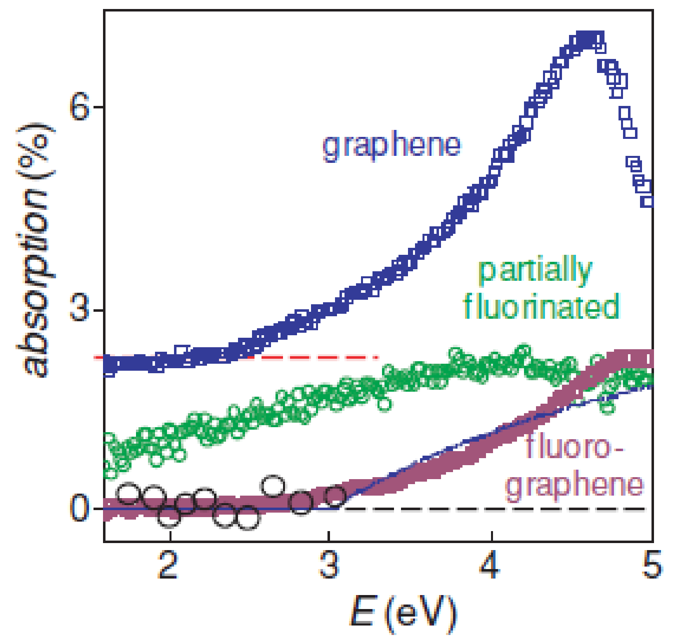




R. J. Kashtiban et al. NATURE COMMUNICATIONS | 5:4902

# State-of-the-Art of Fluorination of Graphene



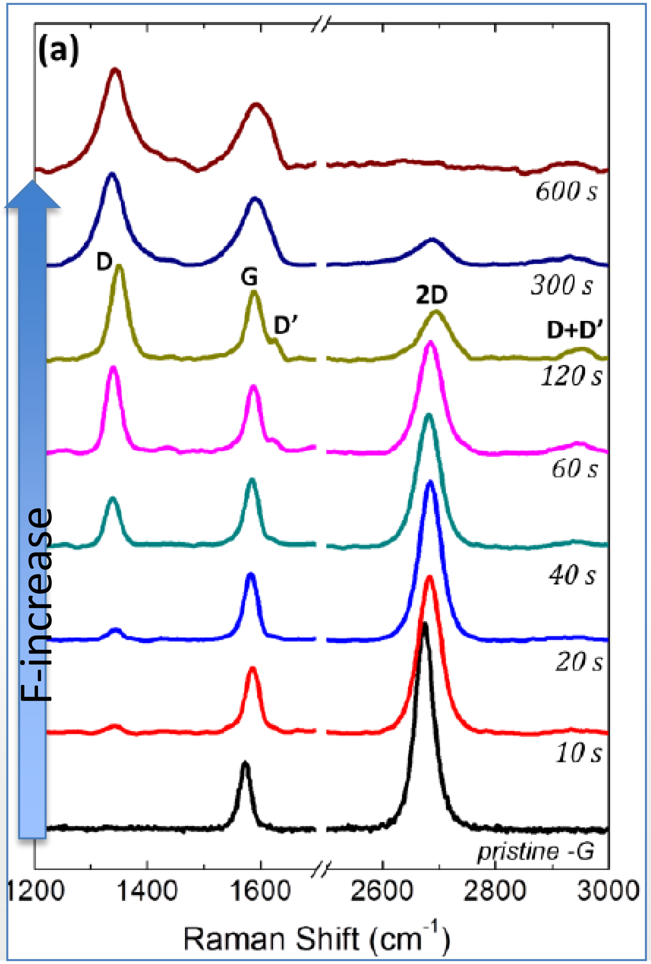



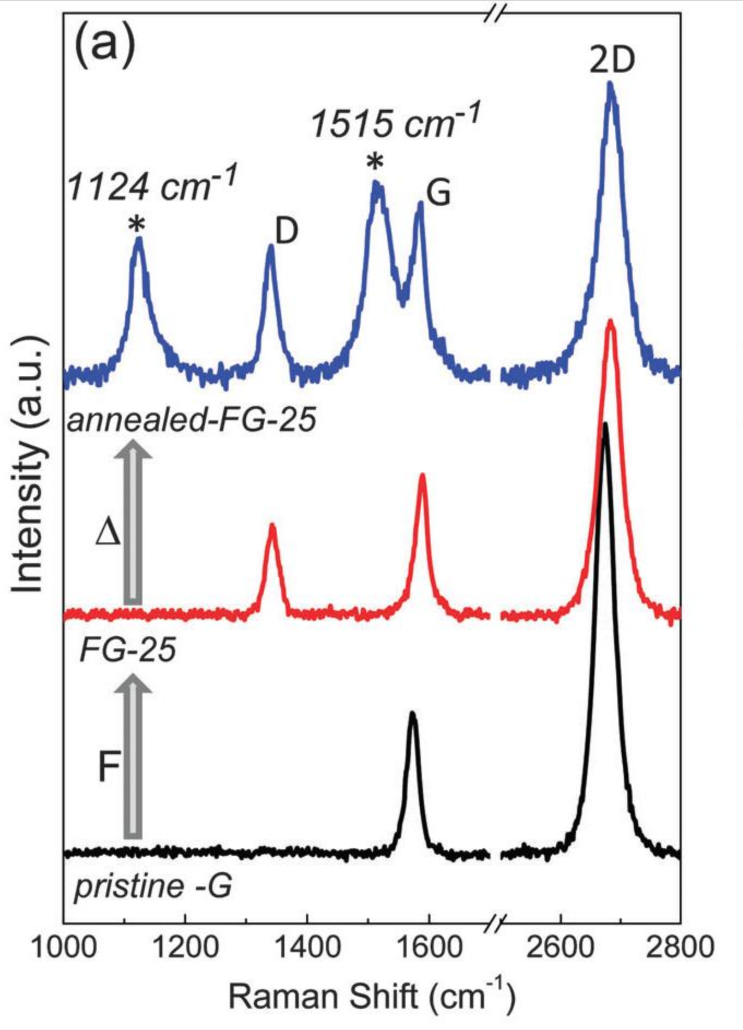

*optical transparency of graphene due to fluorination*

Nair RR "*Fluorographene: A Two-Dimensional Counterpart of Teflon* Small" *2010, 6, No. 24, 2877–2884*

# Plasma modulated Fluorination by $SF_6$

### Control of damage (sp2→sp3)

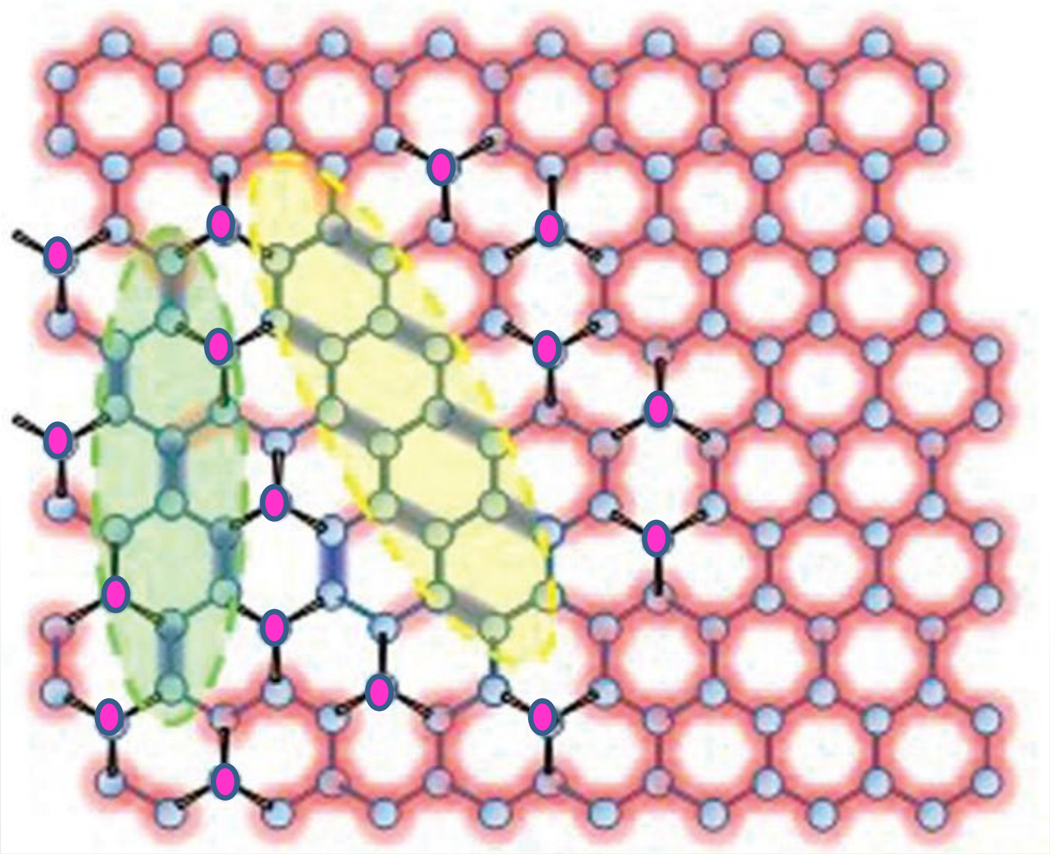


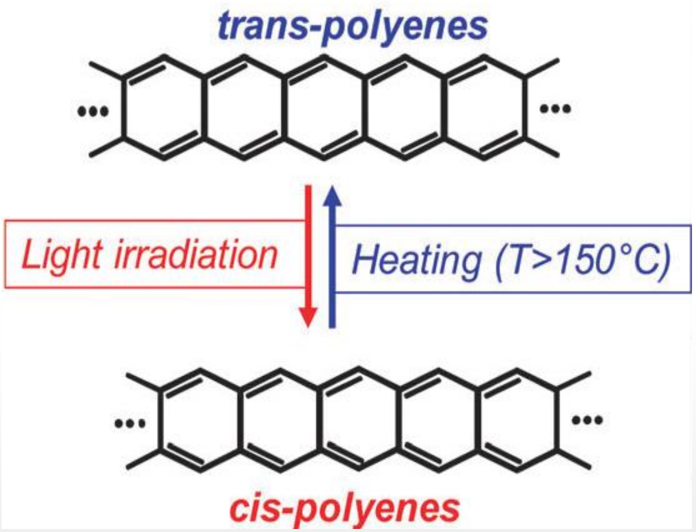



# Plasma modulated Fluorination by $SF_6$:

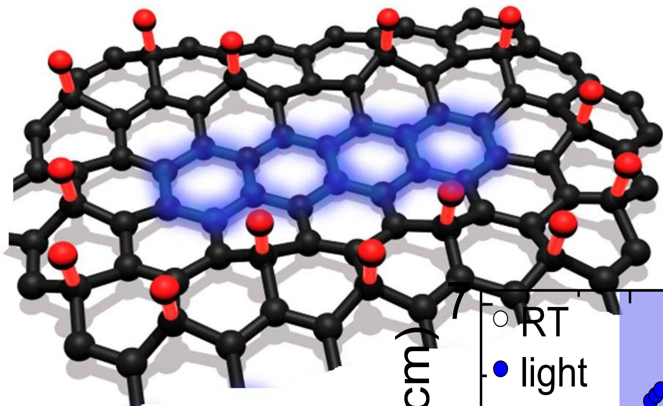
(F/C < 0.25)

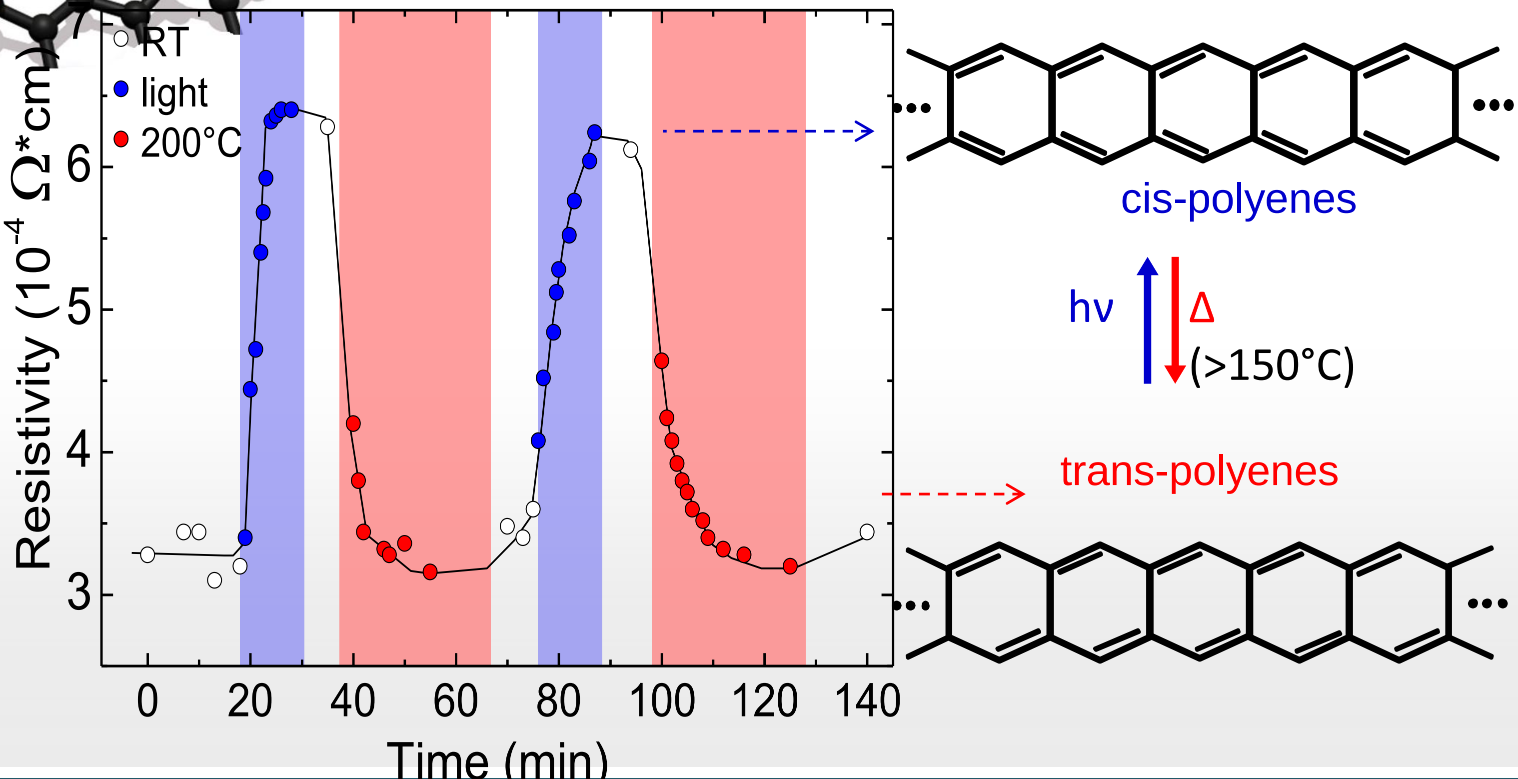
Raman spectroscopy reveals the formation of polyenes in plasma-fluorinated graphene (low fluorine coverage)





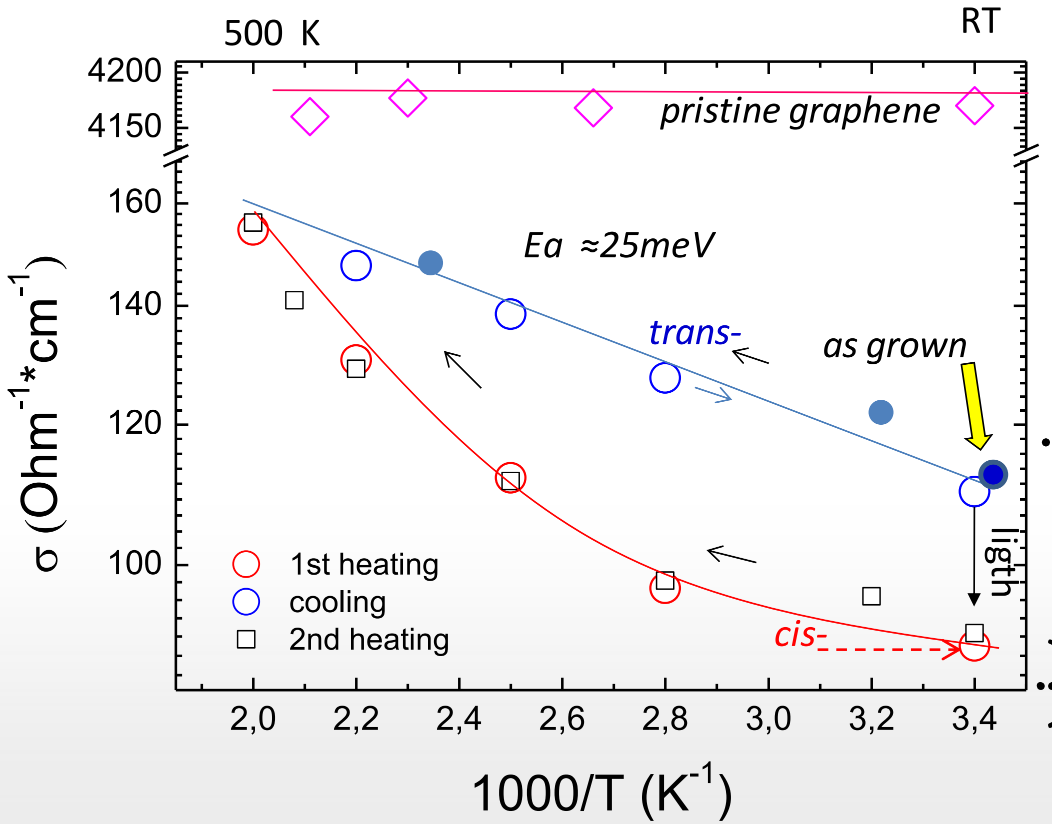
# Polyenes in Graphene

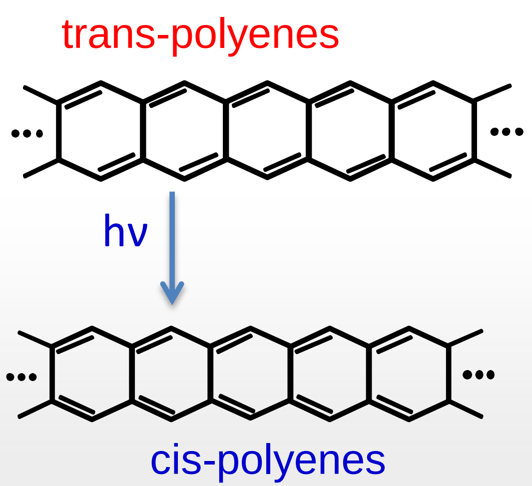




# In SF6 Plasma Modulated Graphene: opening a transport gap of 25 meV

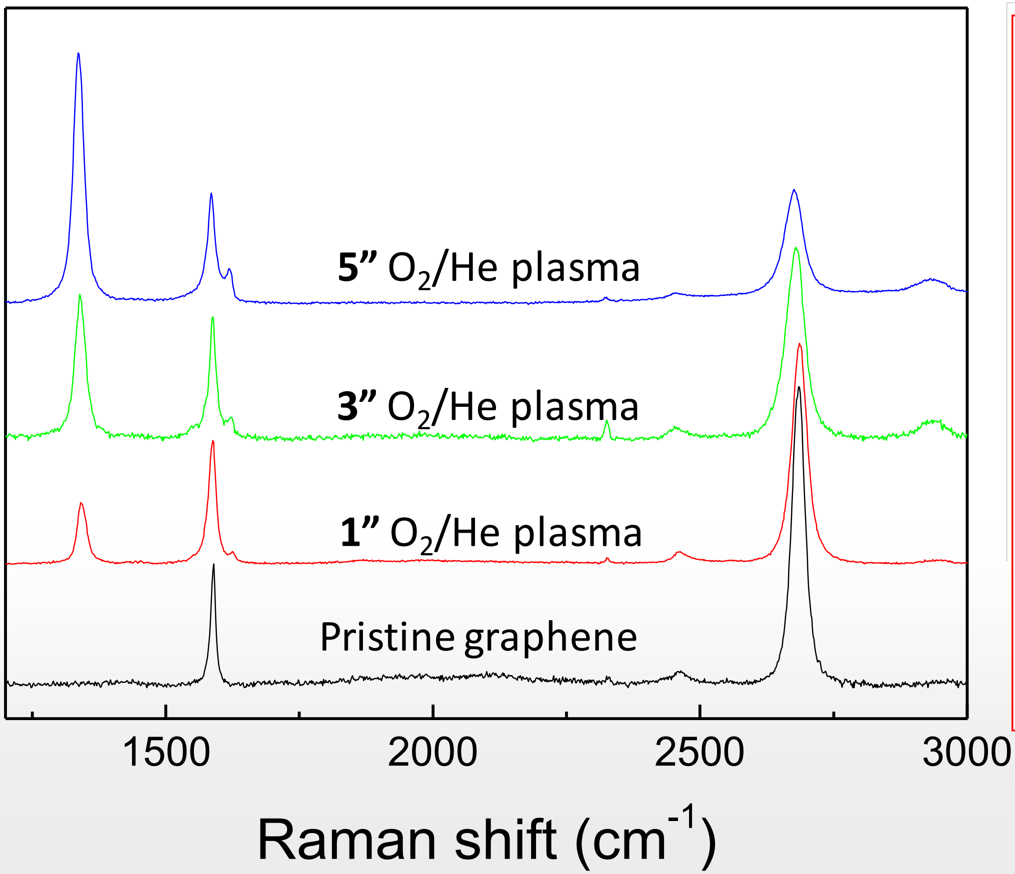
Arrhenius equation $\sigma = \sigma_o \exp(-Ea/k_B T)$



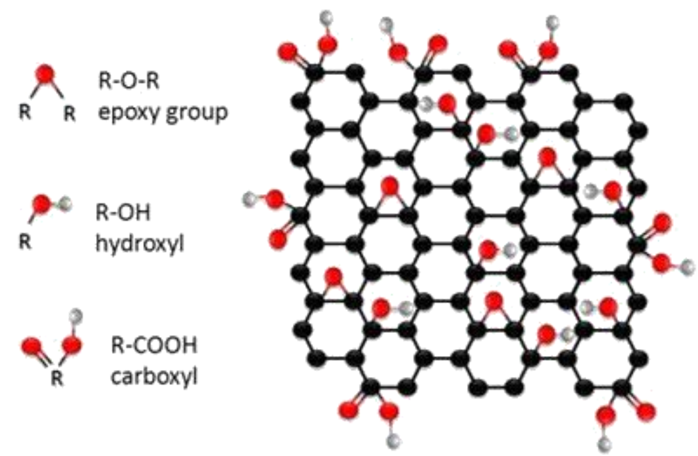




The hybrid graphene-trans polyenes behaves as a semiconductor

# Plasma Oxidation of Graphene

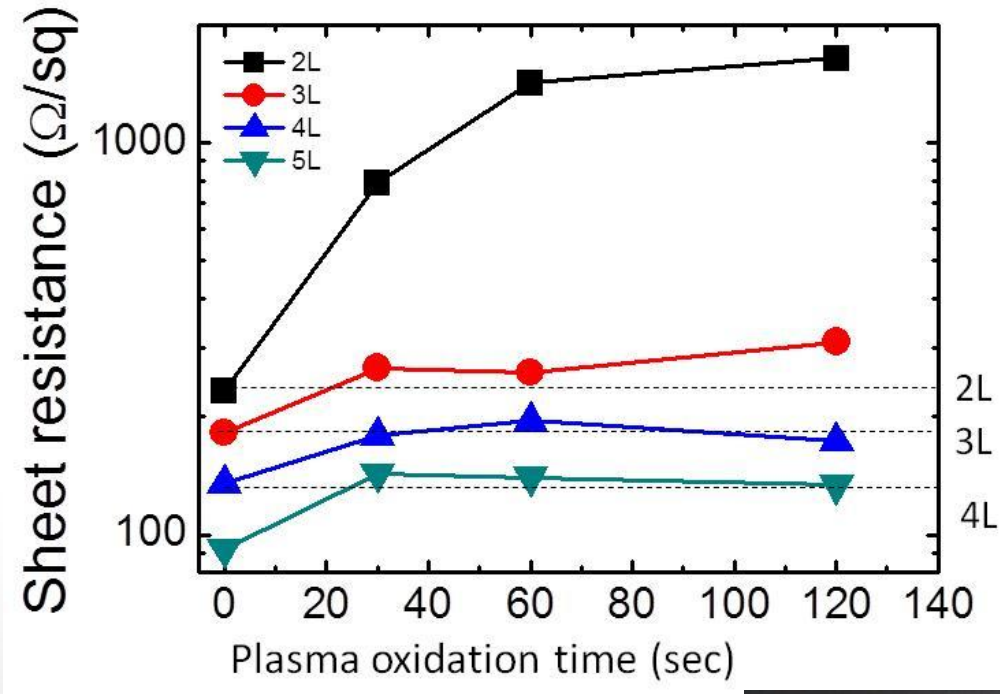


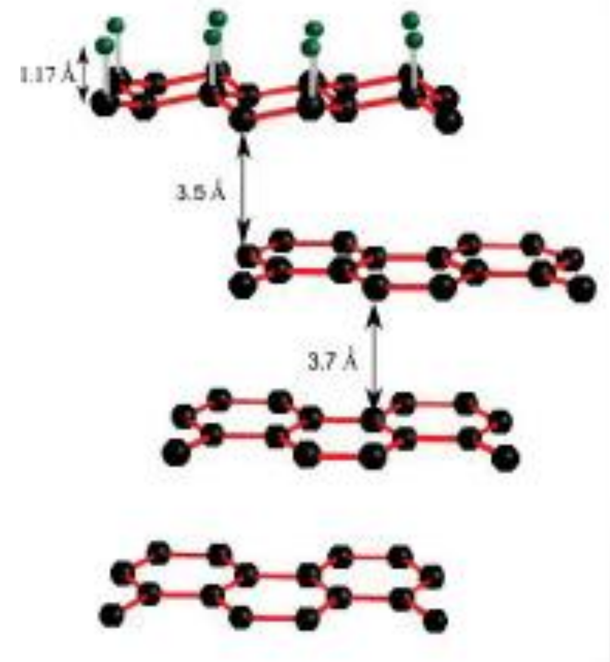

*There in not an univocal correlation between the surface densities of C-sp$^3$ and oxygen functional groups*

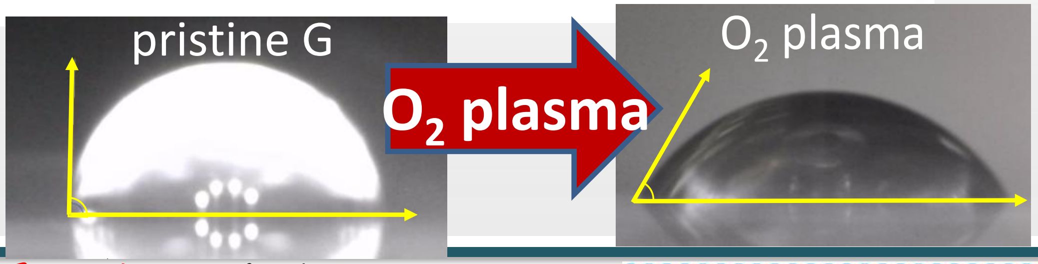


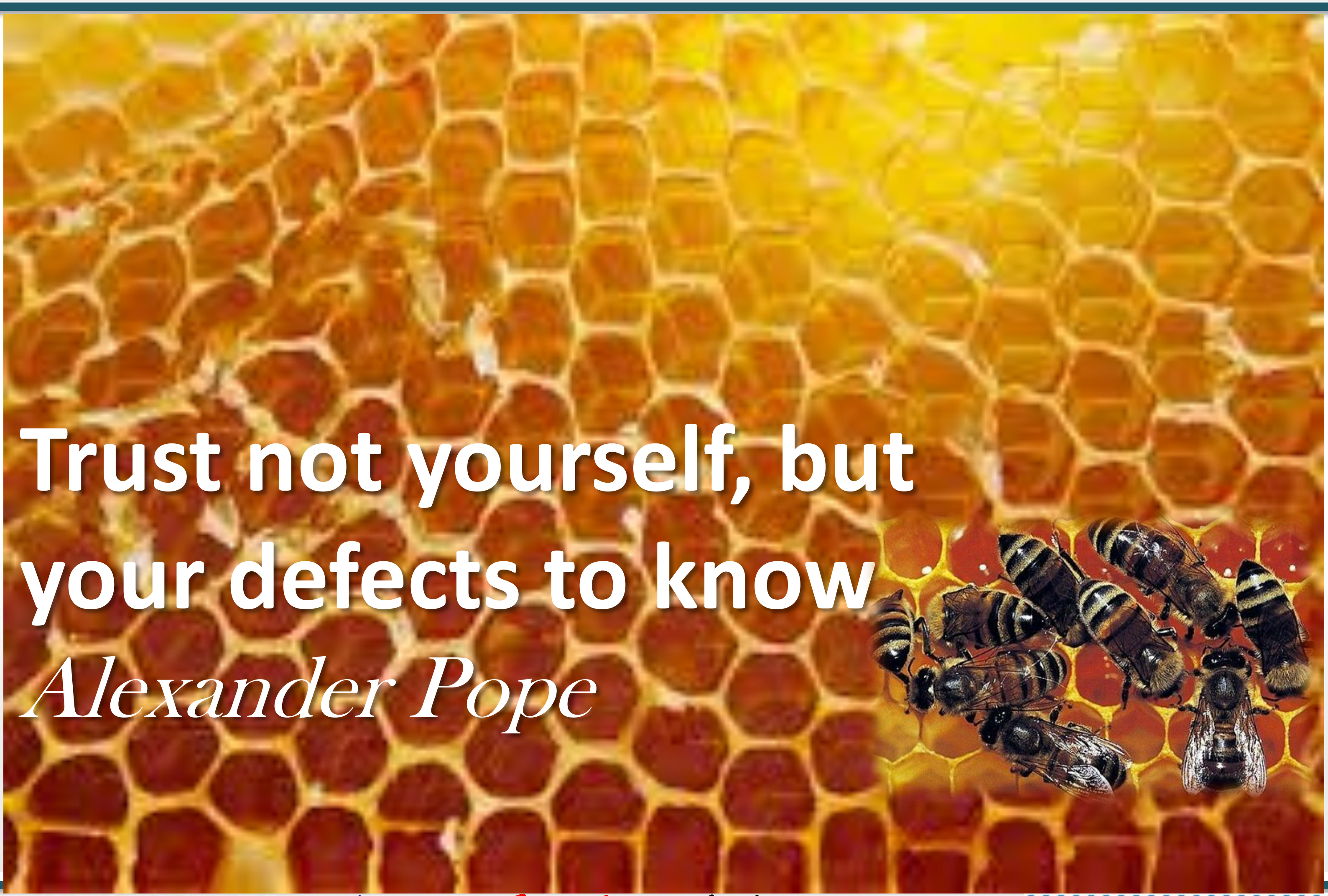
# Plasma Modulated Oxidation

**TUNING OF THE SURFACE CHEMISTRY WITHOUT DRASTIC EFFECT ON THE TRANSPORT PROPERTIES**




Trust not yourself, but
your defects to know
Alexander Pope