GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

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Understanding electronic interactions at the graphene-electrolyte iterface interface

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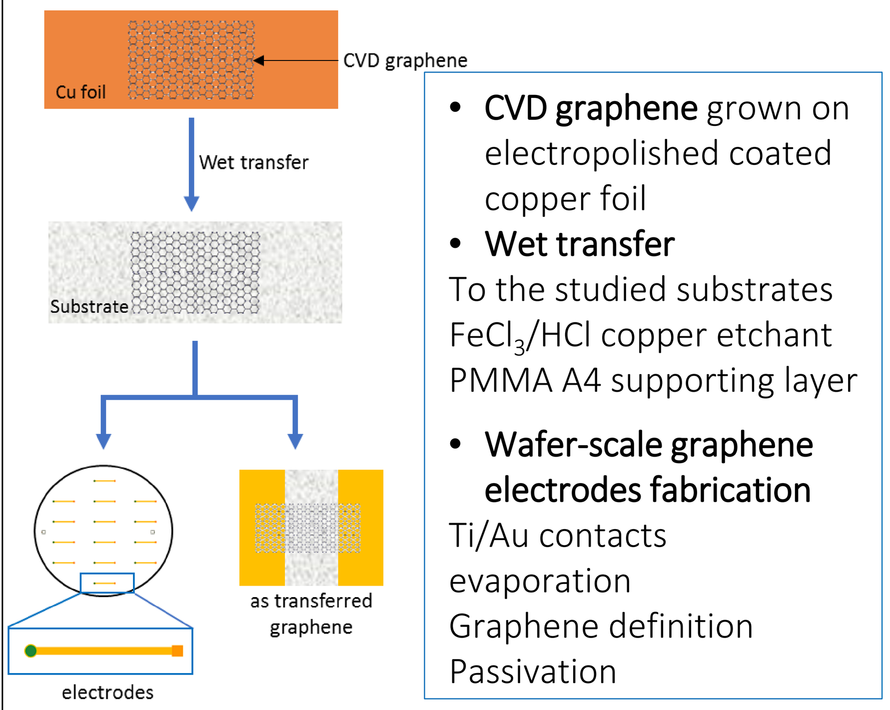
Motivation

Understanding the charge potential landscape at the graphene-electrolyte interface

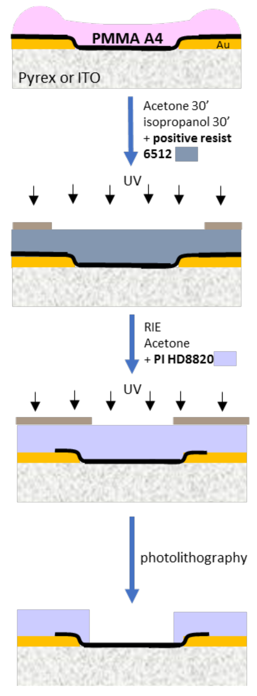
Application of graphene electrodes for biosensing and energy storage

- To evaluate the influence of the wafer-scale fabrication process on the graphene-electrolyte interface
- To analyze the impact on the graphene-electrolyte interface of parameters such as the substrate and the solution pH

Methodology



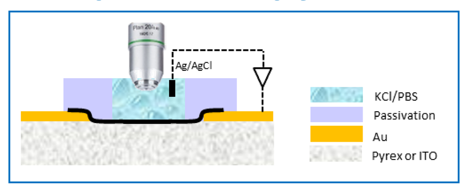
- **CVD graphene** grown on electropolished coated copper foil
- **Wet transfer**
  To the studied substrates
  $FeCl_3$/HCl copper etchant
  PMMA A4 supporting layer
- **Wafer-scale graphene electrodes fabrication**
  Ti/Au contacts evaporation
  Graphene definition
  Passivation



KCl solutions in PBS (10 mM): 50 to 650 mM; pH 3 to 10; HCl/NaOH

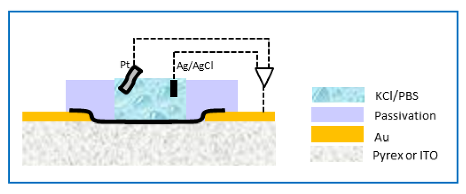
In-situ Raman spectroscopy

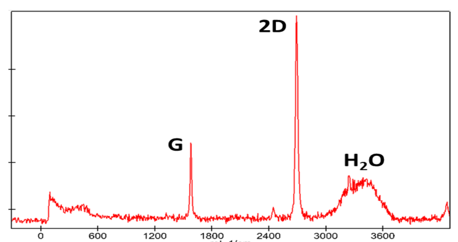
Immersion 63x objective
488 nm laser (power 2 mW)
400 mm² maps (100 spc)
600 g/nm grating

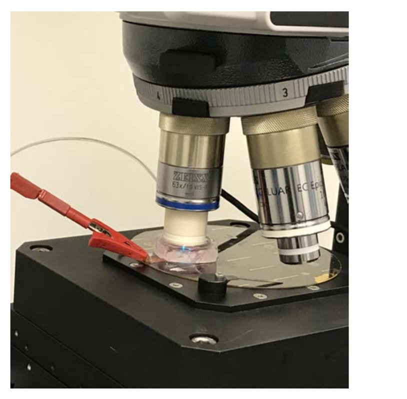


Impedance spectroscopy

20 mV AC
-0.15 to 0.30 V DC
Capacitance at 30 Hz





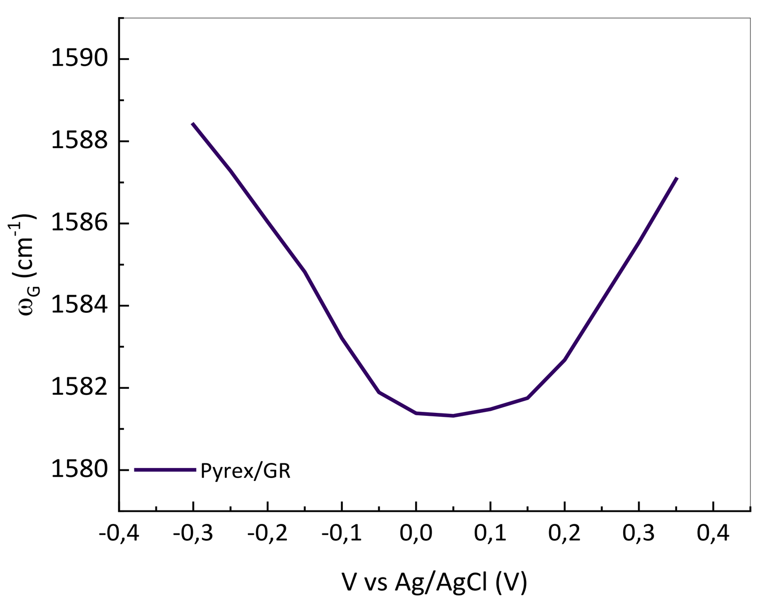


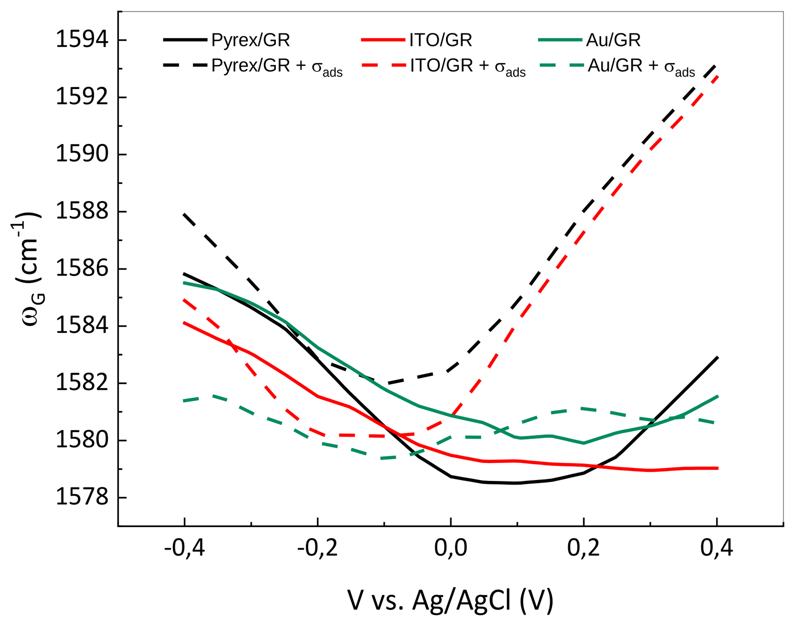
In-situ Raman-electrical characterization

Results – RAMAN AND IMPEDANCE SPECTROSCOPY

RAMAN SPECTROSCOPY

Energy of the G phonon response to applied voltage





$$\hbar\omega_G - \hbar\omega_G^0 = \lambda\left\{|E_F| + \frac{\hbar\omega_G}{4}\ln\left|\frac{2|E_F| - \hbar\omega_G}{2|E_F| + \hbar\omega_G}\right|\right\}$$

ω_G linear dependence with E_F

Charge balance

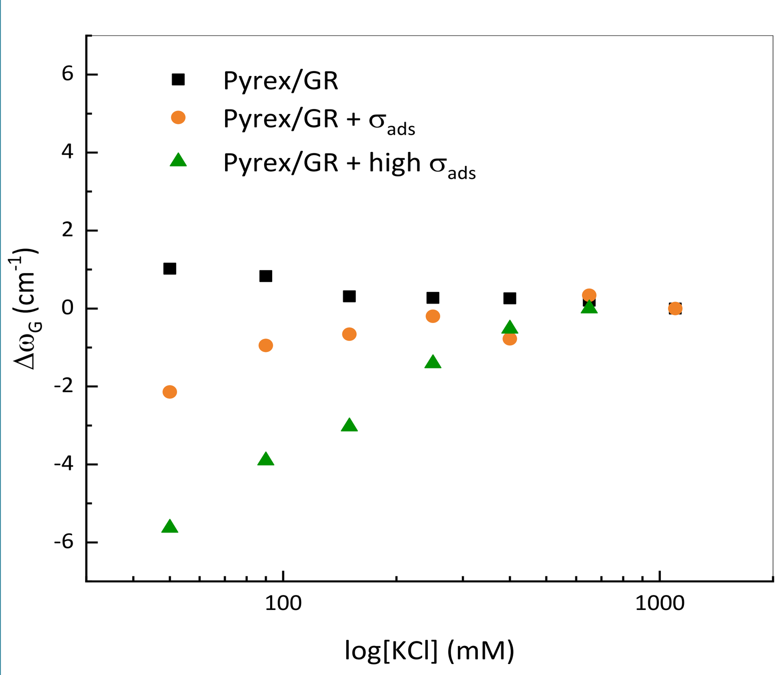
$$\sigma_{subs} + \sigma_{GR} + \sigma_{ads} + \sigma_{diff} = 0$$

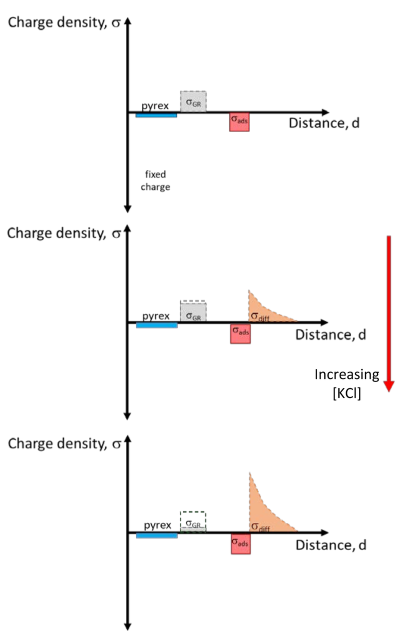
PRESENCE OF ADSORBED CHARGES

CONDUCTIVE/INSULATING SUBSTRATE

Shift of the charge neutrality point (CNP) with σ_{ads}, P doping
W/O σ_{ads} : Strong SUBS/GR interaction, E_F pinning by conductive substrate
WITH σ_{ads} weaker SUBS/GR interaction

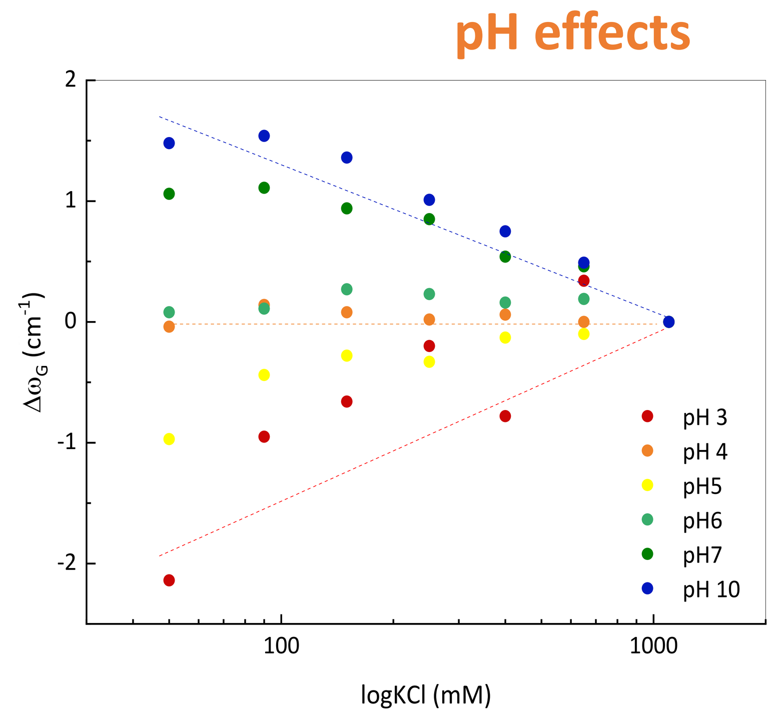
Contamination effects

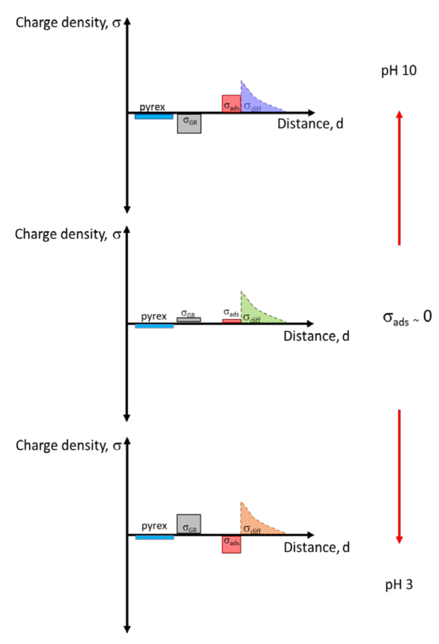




Ions in solution screen σ_{ads} → ω_G shifts towards lower values
No shift of the ω_G for σ_{ads} close to zero

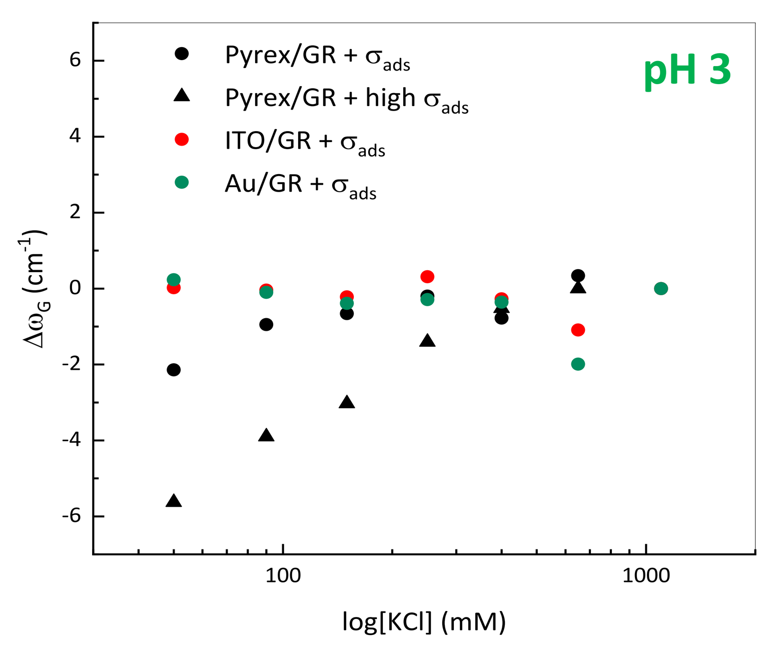
pH effects

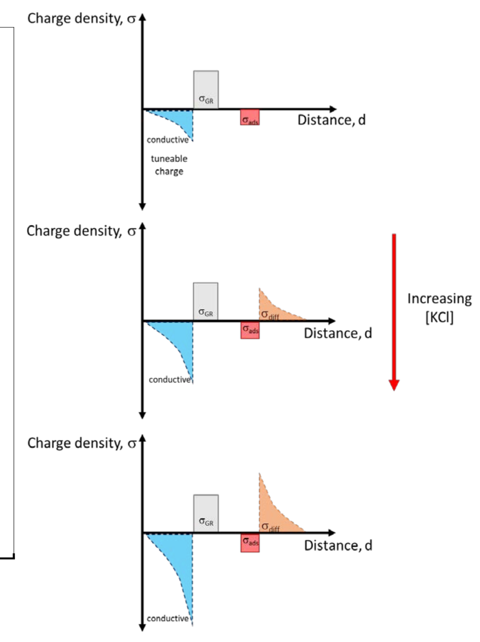




pH modulation of the sign of σ_{ads} → Acidic conditions: ω_G blueshifts; Basic conditions: ω_G redshifts

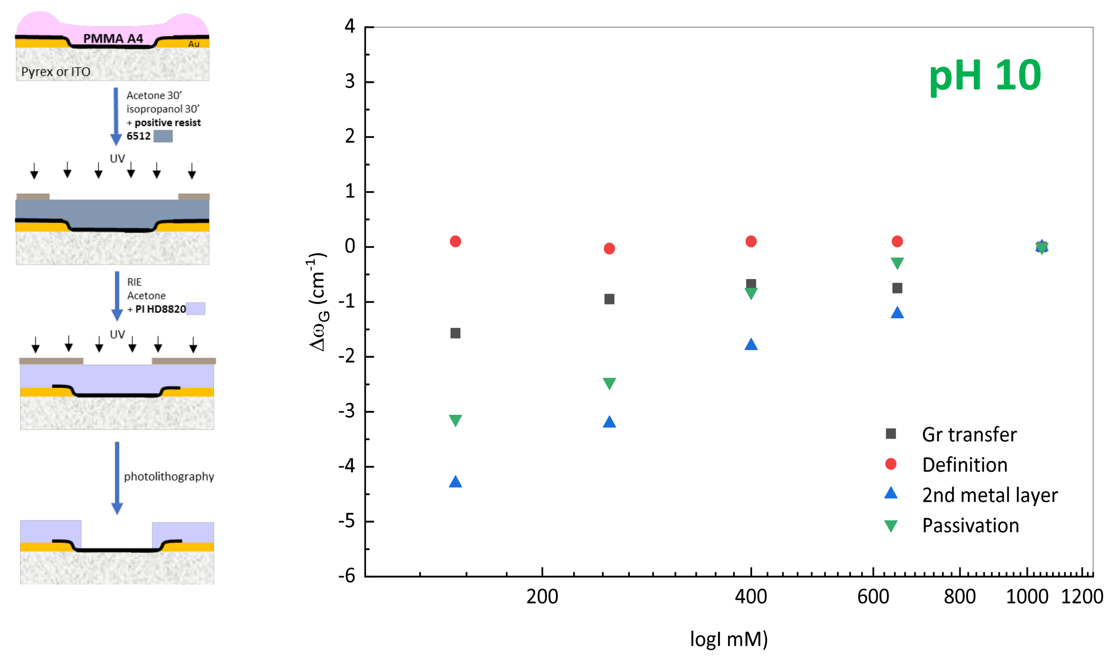
Substrate effects





No ω_G modulation for graphene supported on a conductive substrate

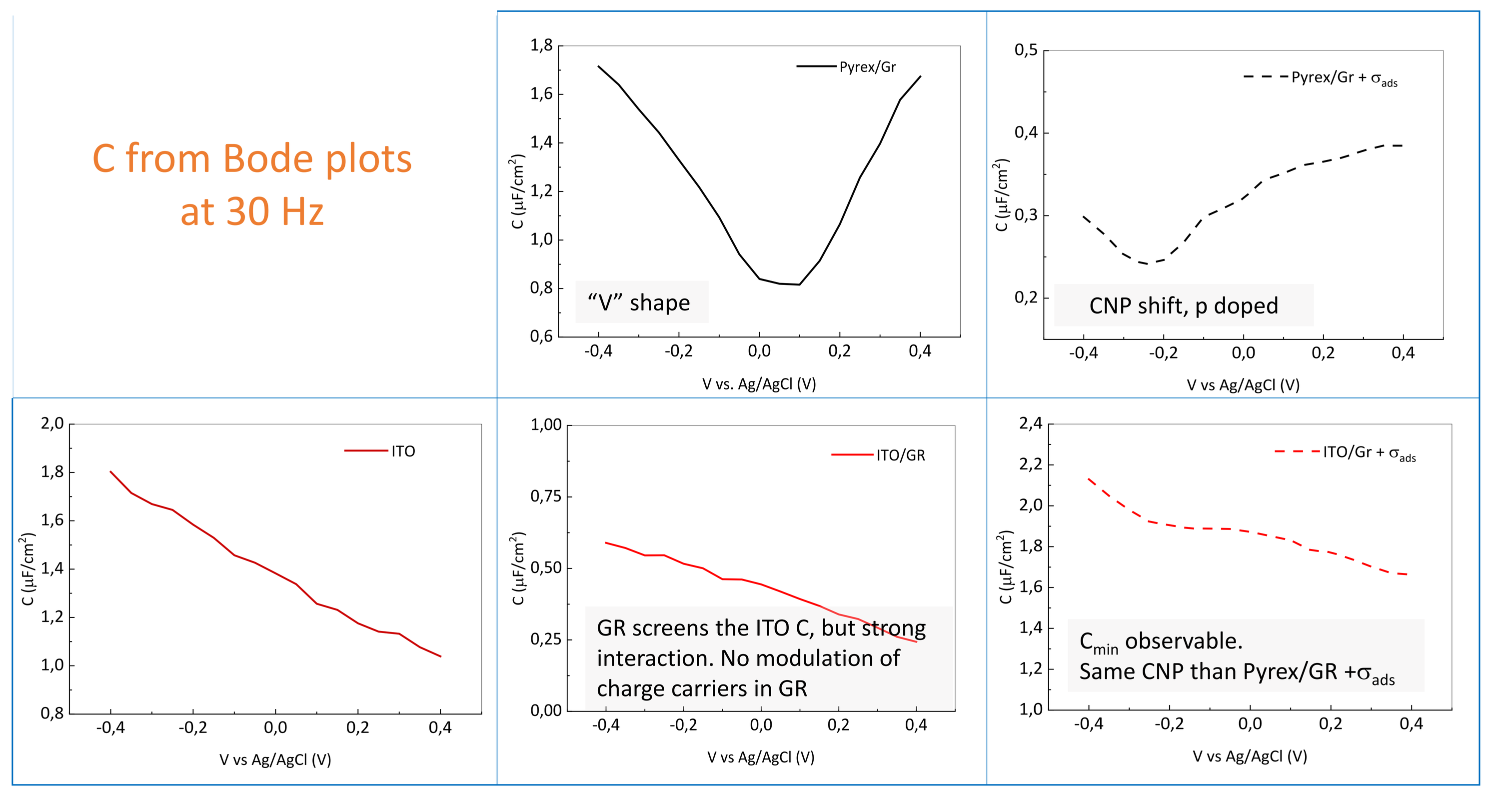
Step-by-step study of the impact of the wafer scale fabrication

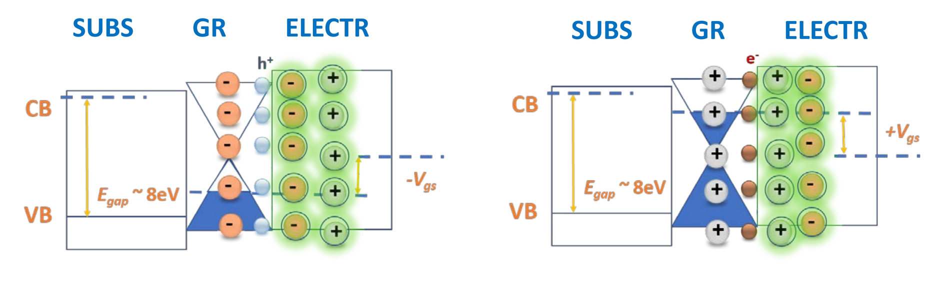


Each fabrication step induces different type of σ_{ads} → variations on ω_G modulation

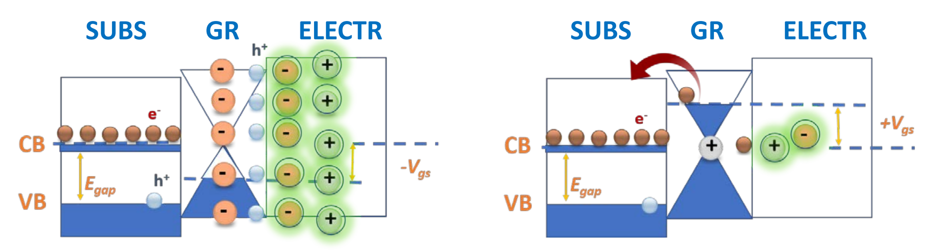
IMPEDANCE SPECTROSCOPY

C from Bode plots at 30 Hz





Modulation for graphene supported on a non-conductive substrate



High amount of states at the ITO conduction band:
- Accumulation of holes
- Non-accumulation of e⁻

Conclusions

The combination of Raman and EIS provides valuable information of the SUBS/GR/electrolyte interface
Both techniques shows the strong interaction between GR and conductive substrates which is weaken by the appearance of adsorbed charges on the graphene surface
The adsorbed charge is screening by the ions in the electrolyte when graphene is supported either on an insulating or conducting substrate. σ_{ads} is quantified with this methodology
pH modulates the sign of the adsorbed charges tuning the sensitivity of graphene to the ionic strength

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