Microwave Characterization of Graphene Inks

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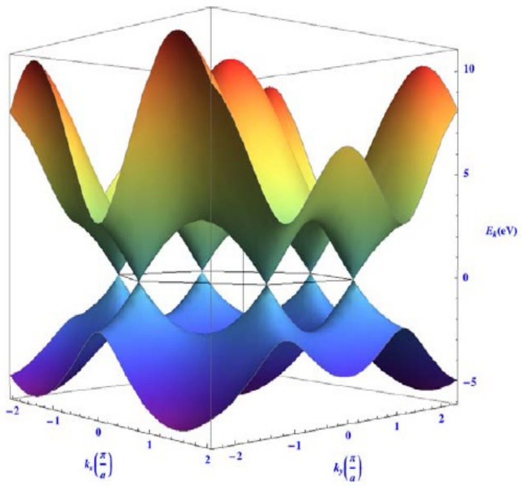
Outline -

- Testing methods for evaluating Graphene properties
- Focus on Non- contact microwave cavity (IEC 6207-6-4) & Quantum Hall Resistance
    - Microwave Resonant Cavity Instrumentation for Graphene conductivity
    - Measurement examples: 1L-Epitaxial Graphene, Graphene Inks

Graphene Definition: <u>Science</u> (ISO/TS 80004-13)

Single-layer of carbon atoms with each atom bound to three neighbors in a honeycomb structure.

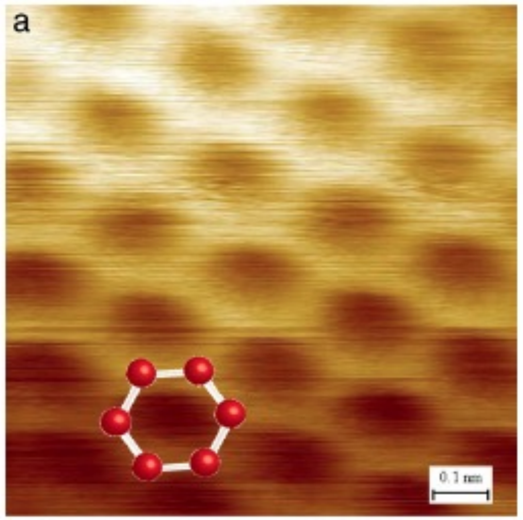
<u>Calculated electronic structure</u>



- surface conductivity **at the Dirac Point**
  $\sigma_{DP} \sim e^2/h \approx 3.8\times10^{-5}\ S_{sq}$
  $(\rho_{DP} \approx 25.7\ k\Omega_{sq})$ $\mu \approx 2 \times 10^5\ cm^2/Vs$

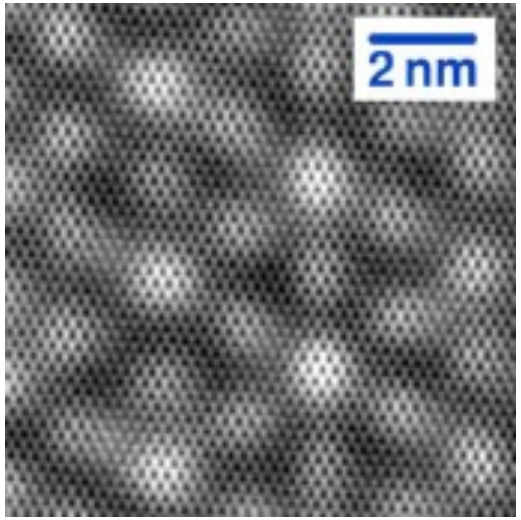
<u>Test methods</u> STM (scale 10^{-9} m)

1 L Graphene (exfoliated)



E. Stolyarowa, PNAS 2007

2 L Graphene, (epitaxial Moiré pattern)

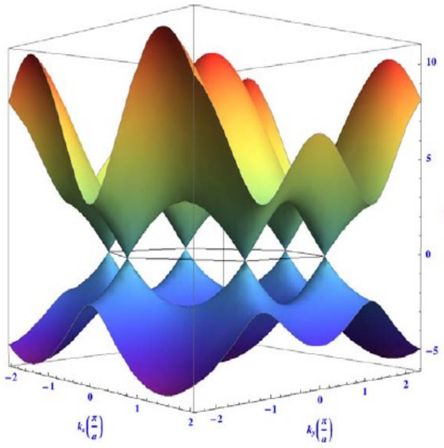


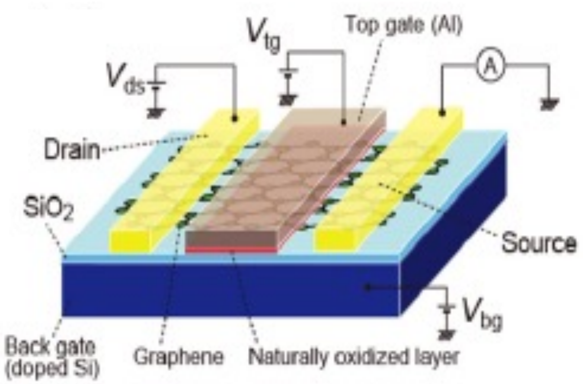
J. Stroscio, PRB (2010)

STM – sub- nanometer resolution for direct imaging Graphene 2D lattice at atomic distances.

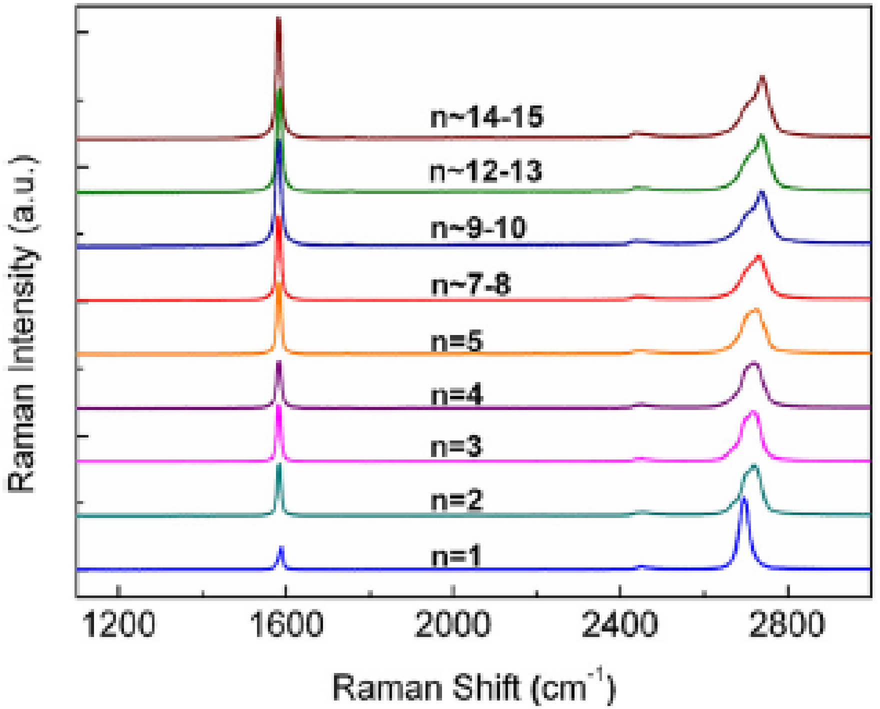
- Very small scale, hard to measure.
- Difficult to establish reliable quality projection, beyond atomic distances.

Graphene 1L electronic structure (scale 10^{-4} m)

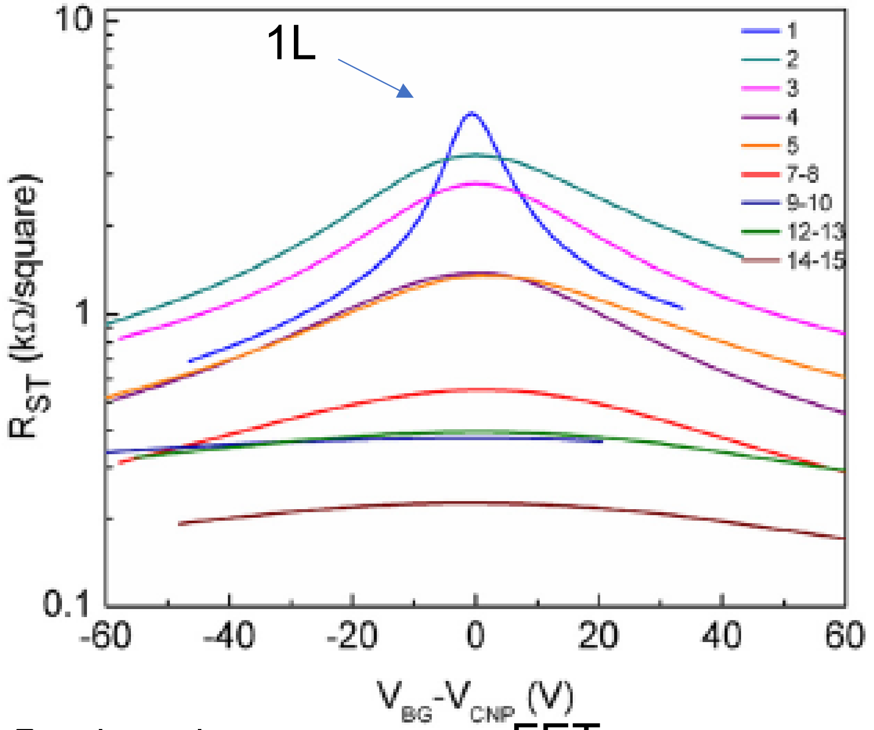




Raman - difference between n*L* is small



FET gated to Dirac Point



n – number of Graphene layers

FET

Resistance, R_{ST}, depends on the device parameters. $R_{ST\_max} \approx 6$ kΩ

1 L Graphene at the Dirac point , $\rho_{DP} \approx 25.7$ kΩ) Multi-layers show lower $R_s \sim n$.

Gated or doped $\sigma_s = en\mu$ (phonon limited) $n \approx 10^{12}$ cm^{-2}, $\boldsymbol{\mu \approx 2 \times 10^5}$ **cm²/Vs**; $\sigma = 0.0322\ S_{sq}$ ($\rho \approx 31\ \Omega_{sq}$)

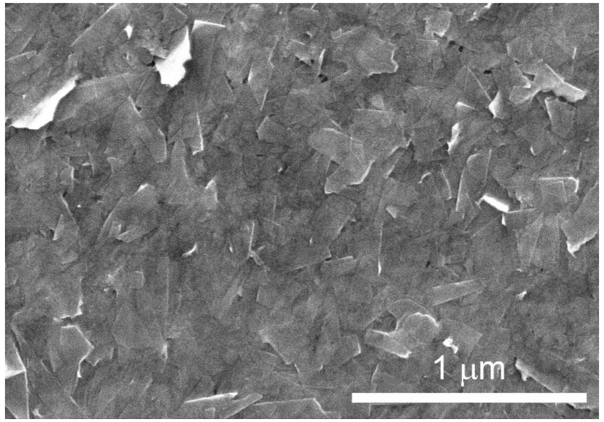
G. Liu et al, Appl Phys Lett **102**, 093111 (2013)

- **Definition of Graphene: <u>Manufacturers & Commerce</u>**
  <u>Graphene-based material</u> grouping of carbon-based 2D materials that include one or more of **1L Graphene**, **bilayer Graphene**, **few-layer Graphene**, **Graphene nanoplate**, and functionalized variations thereof as well as **Graphene oxide** and reduced **Graphene oxide** (ISO/TS 80004-13, IEC/TS 62565-3-1)

<u>Test methods</u>

- Presence od C sp2 hybridization and π-$\pi*$ delocalized carbon bonds
  Raman (IEC 62607-06-11), XPS (IEC 62607-06 21)
- Presence of structural defects, crystallinity:
  Raman (IEC 62607-06-11), XRD (IEC 62607-06-17)
- Number of atomic Layers : AFM, TEM (ISO TS 31356-1)
- Dimensions of graphene flakes in z-axis and shape (Platelets, Spherical Ribbon)
  AFM (ISO TS 21356-1), SEM (ISO TS 21356-1)
- Bulk density (graphene powder): ASTM D7481-18
- Chemical and elemental analysis / Impurities / Oxygen content
  XPS (IEC 62607-06-21, IEC -06-19)
- Graphene layers stacking TEM, XRD (IEC 62607-06-17)

SEM scale 10^{-4} m (sampling)

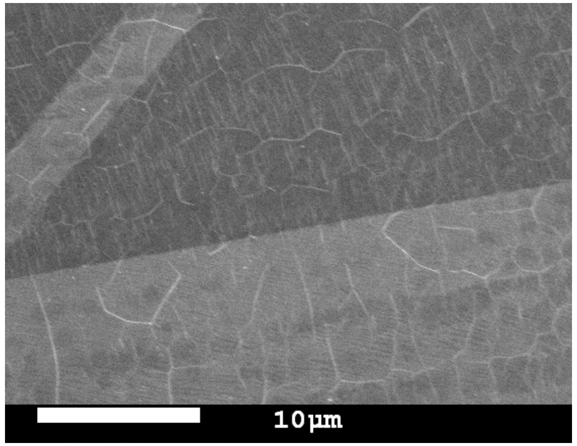


Graphene Powder:
Composites, Printable inks

Commercial Graphene - Optical, SEM, Raman, XPS (non-contact, scale 10^{-2} m)

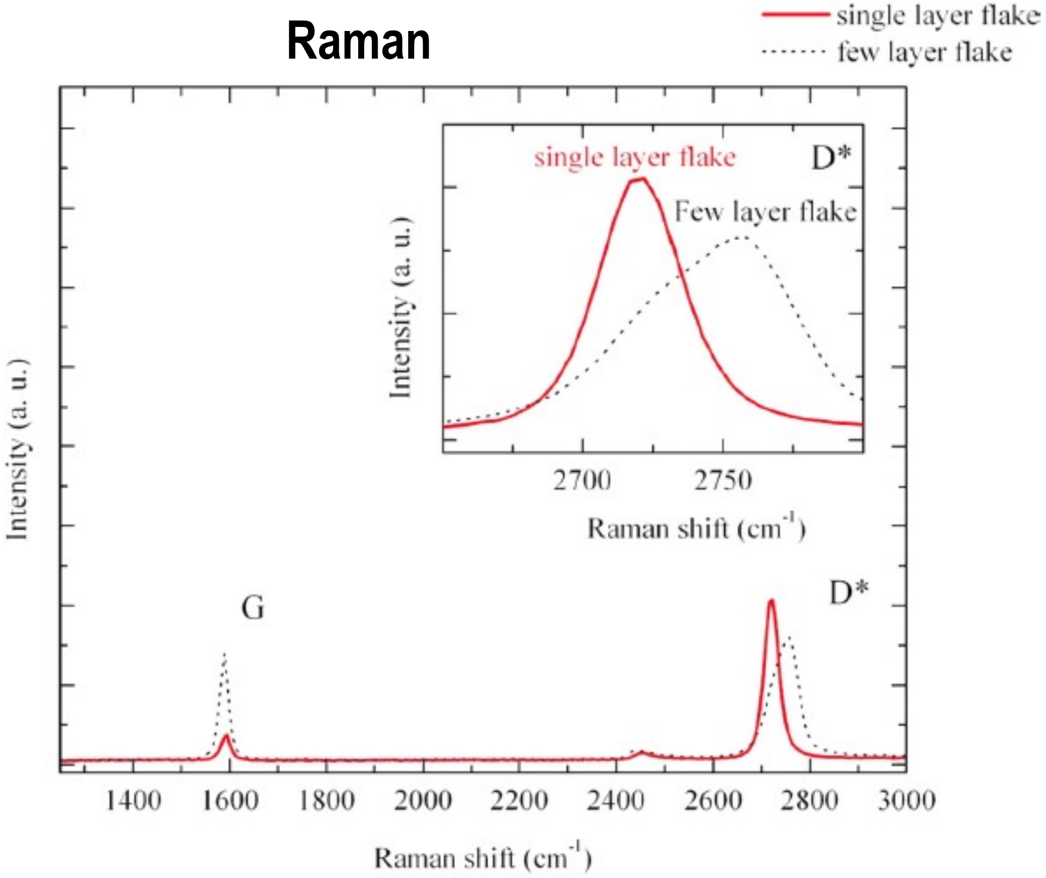
www.graphene-supermarket.com

Optical contrast of 1 Layer Graphene flowers grown by CVD on copper and transferred onto silicon dioxide/silicon wafer   Absorption 2.3 %



SEM of few Graphene layers Graphene grown on Nickel by CVD

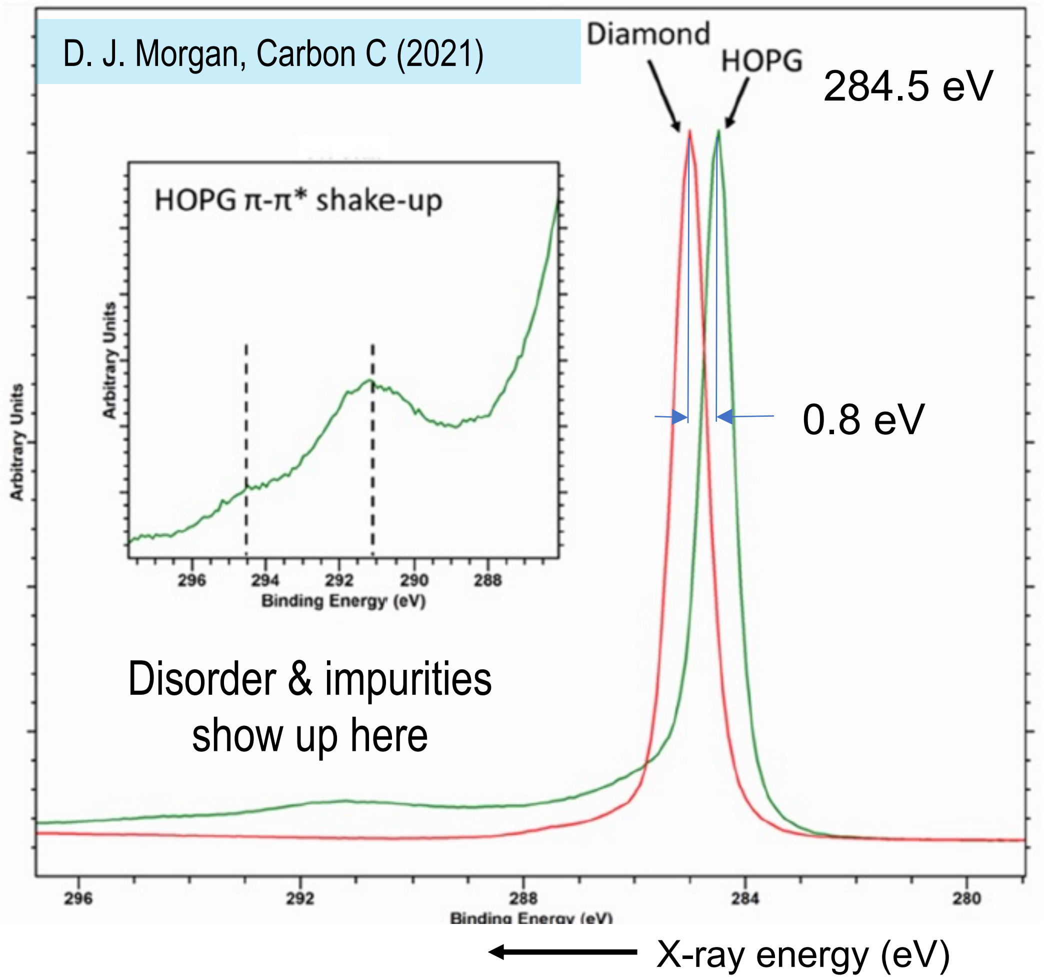
Raman



Non-contact testing is preferred by the industry

Reliable evaluation requires experienced analysis / reference materials

Commercial Graphene – XPS for C-2sp^2 π-π* (non-contact)



XPS limitations :

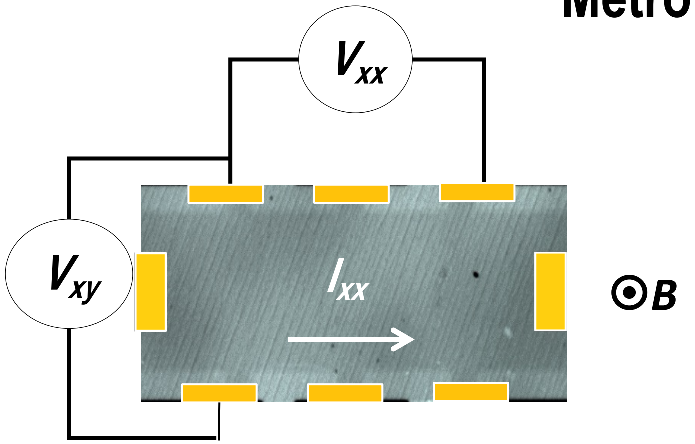
- There is only about 0.8 eV difference between Diamond and HOPG C1s core level– needs specialized instrumentation to distinguish between C-sp^3 (diamond) and C-sp^2 hybridizations (graphite)

- Shake-up Satellites :
  The outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. The core electron energy is reduced and a satellite structure appears a few eV above the core level position.

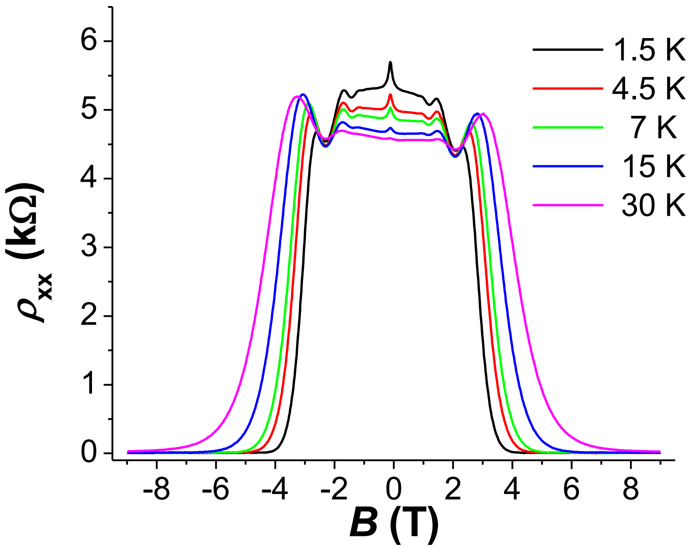
- In Graphene powders the π-π* shake-up structures are often overlapped by oxidized impurities and trapped charges.

XPS testing requires a reference material such as HOPG; typically limited to chemical analysis. Interpretation of XPS beyond elemental analysis is rather complicated and time consuming.

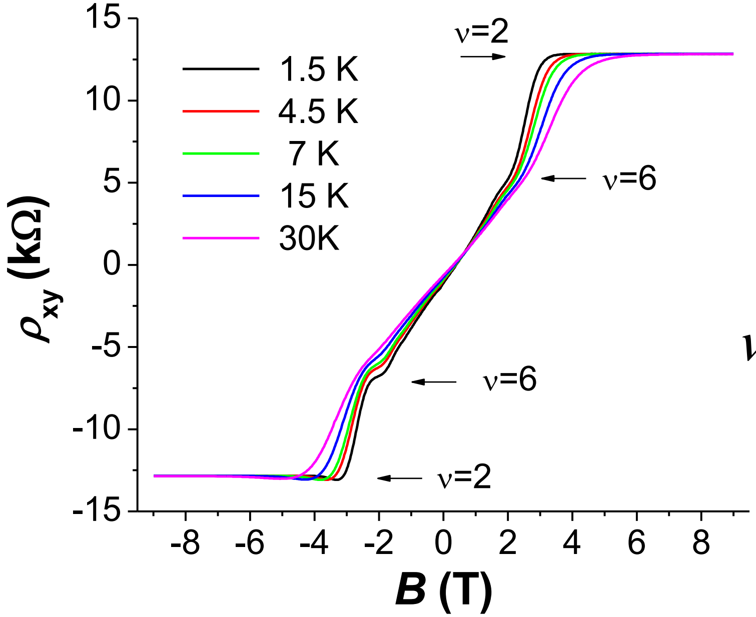
Metrology; 2D Quantized Hall resistance- Epitaxial Graphene (scale 10^{-2} m)



Epitaxial Graphene on SiC.
Hall test bar (7 x 15 mm)



At magnetic B ≈ 4 T, the longitudinal resistance ρ_{xx} = 0; the transport is quantized



12.91 kΩ

$$\rho_{xy} = \frac{1}{\nu}\frac{h}{e^2}$$

$$\nu = 4(i + 1/2)$$

Quantum Hall resistance plateau $\rho_{xy} = h/2e^2 \approx 12.91$ kΩ at the lowest Landau level (i=0, ν=2); is the evidence of 2D transport implying a mono-layer Graphene

Charge carriers majority – electrons (positive sltingope ρ_{xx} vs B)
Carriers concentration (n) 2.98×10^{11} cm^{-2}
Carriers mobility, (μ) 4500 cm^{2}V^{-1}s^{-1}

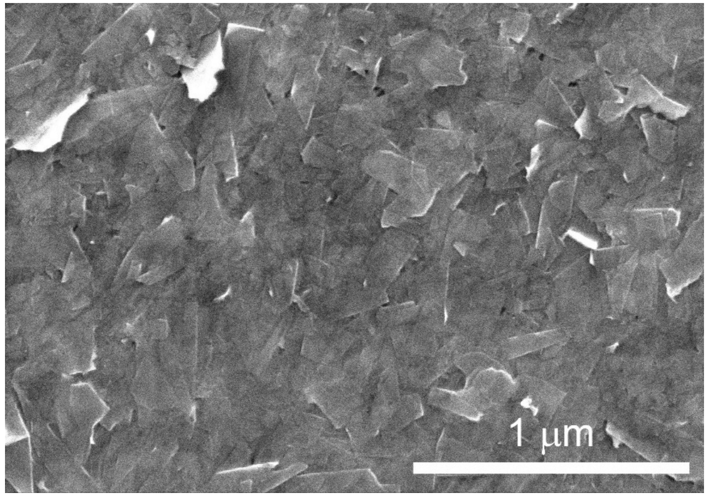
Reliable 2D reference material for electrical testing

Jan Obrzut et al, Measurement (2016)

Non-Contact Microwave Characterization of Graphene Inks (IEC 6207-6-4)

Comparison with Quantum Hall and Epitaxial Graphene

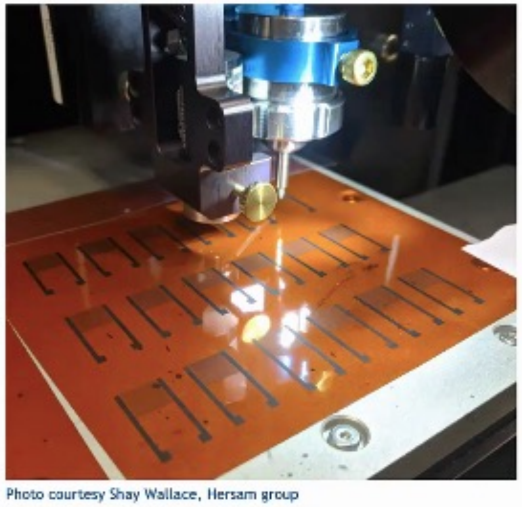
SEM



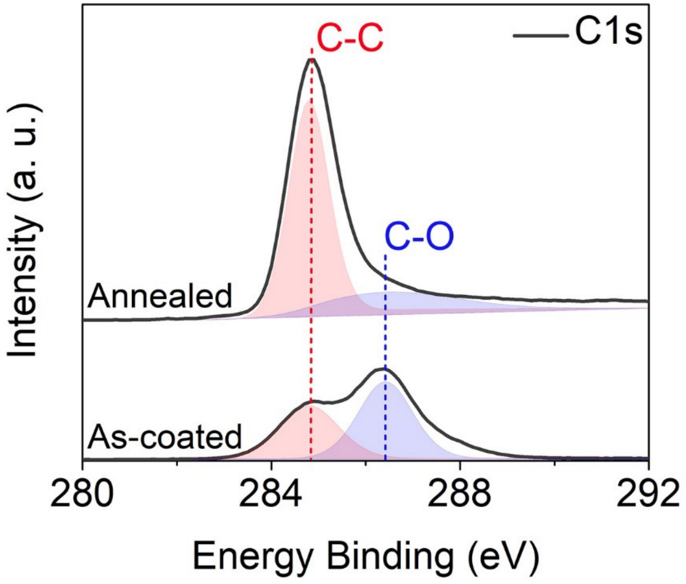
Ink Formulation
ET Cellulose binder

- TGA
- Mass fraction
- Viscosity
- AFM

Ink printing



XPS



Nano plates from liquid exfoliation of graphite flakes

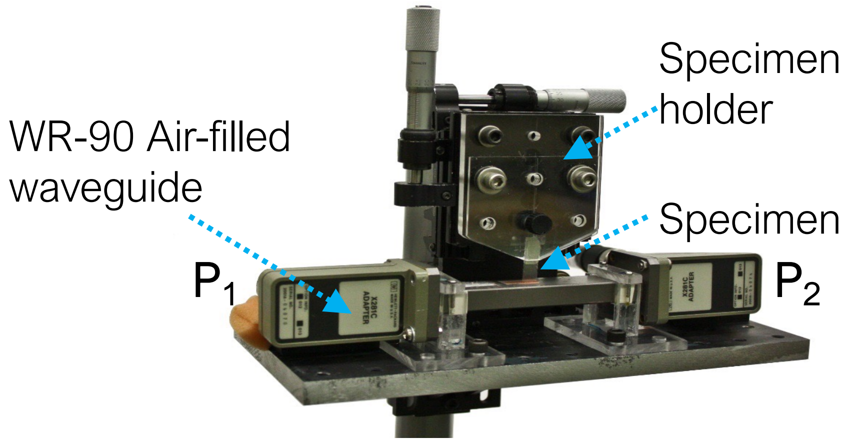
- Sequential process 20 nm each layer up to 500 nm thick coatings on PI substrates
- Annealing at 300 for 30 min in air

Specimen size 7 mm x 15 mm for microwave testing and 7 mm x 7 mm for Hall and DC resistance testing

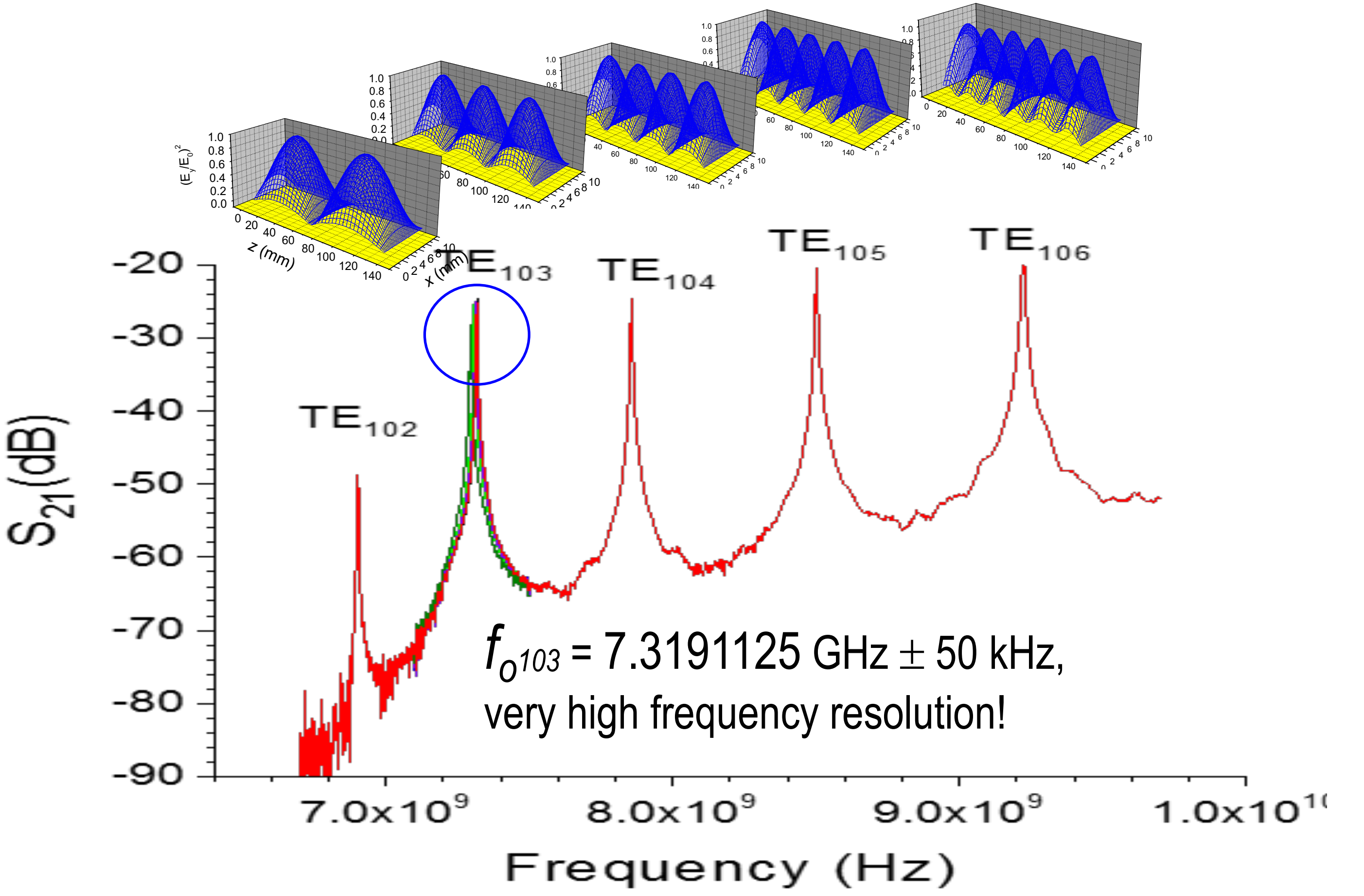
A. C. M. de Moraes et al J. Materials Chem. C, 8, 15086 (2020)

Non contact Microwave Cavity Perturbation Method

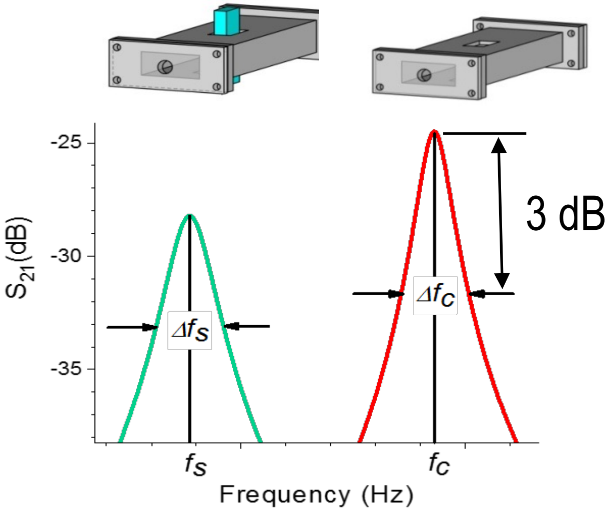
Allowed TE Modes



Specimen insertion shifts resonant modes to lower freq. and decreases Q factor



f_{o103} = 7.3191125 GHz ± 50 kHz, very high frequency resolution!



$$\varepsilon' - 1 \approx \frac{f_c - f_s}{f_c}$$

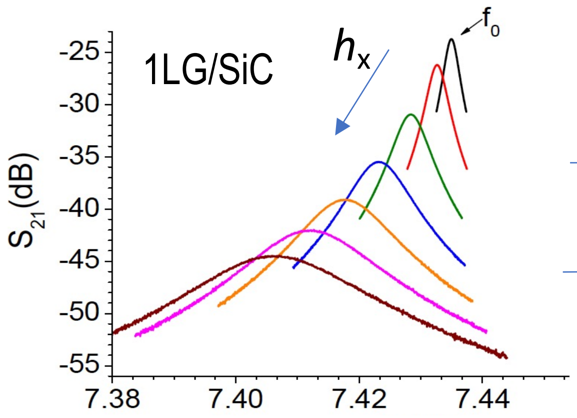
$$Q_s = \frac{f_{peak}}{\Delta f} \approx \sigma_s$$

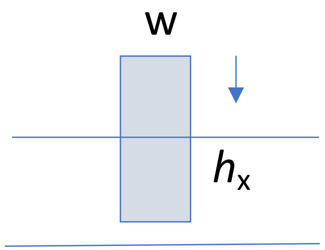
Only frequency is measured

- The quality factor Q decreases in proportion to specimen conductivity Perturbation of odd resonant modes by a 2D specimen can be easily detected
- The relative uncertainty ($\Delta f_s / f_o$) is better than 10^{-6}

Non-contact measurements of Graphene conductivity using microwave cavity

(IEC IEC 62607-06-4)



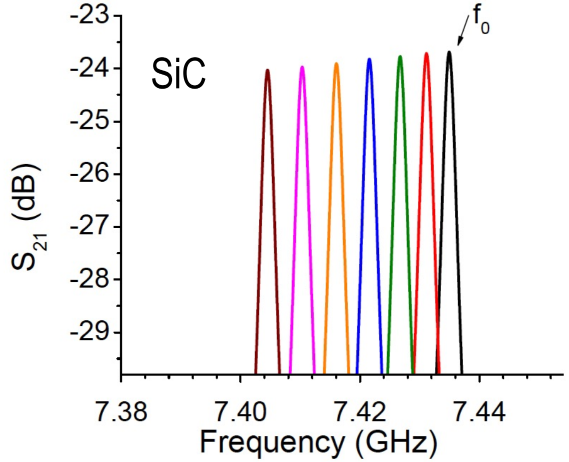


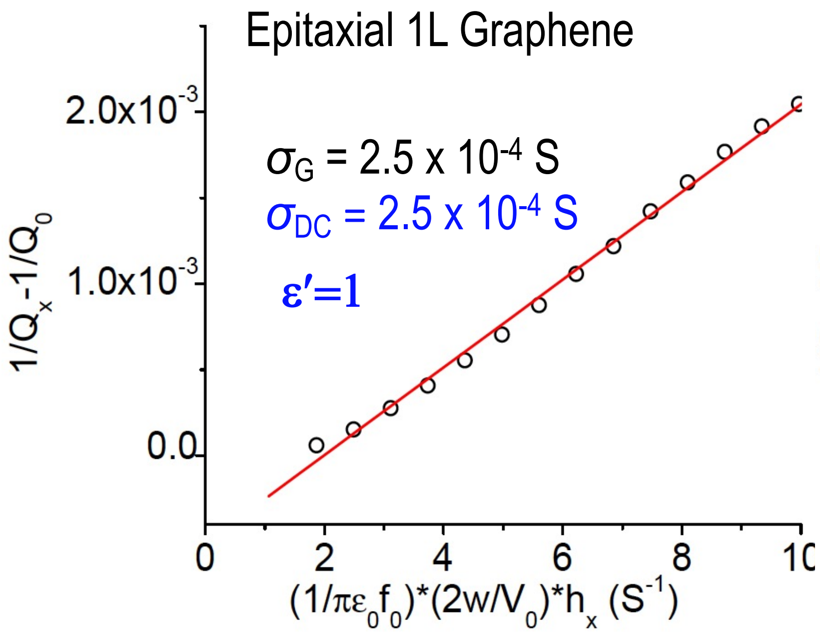
$$\frac{1}{Q_x} - \frac{1}{Q_0} = \sigma_G \left(\frac{1}{\pi \varepsilon_0 f_0} \frac{2w}{V_0} \right) \times h_x - 2b_q \qquad \text{(Eq. 1)}$$

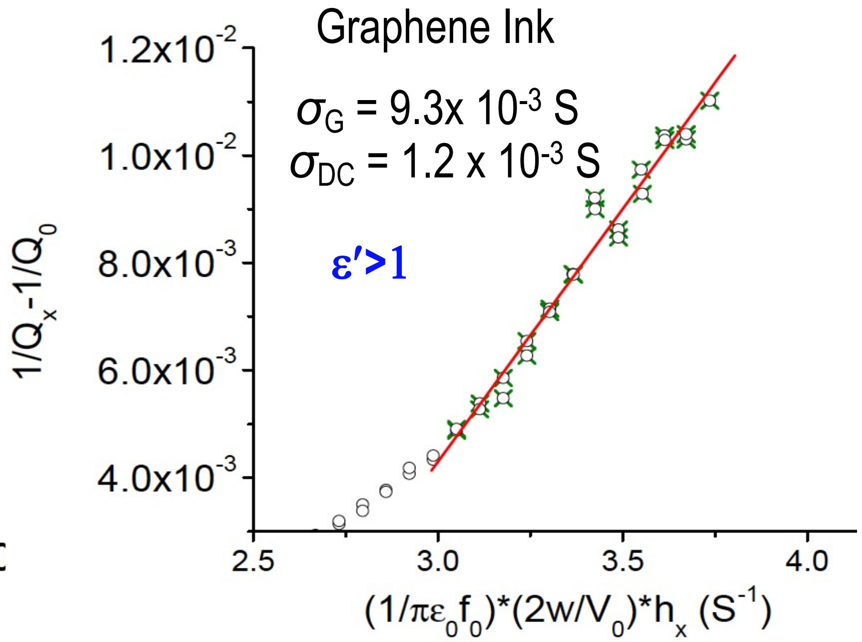
During measurements the specimen is partially inserted into cavity in steps h_x

Conductivity, σ_G is the slope of $1/Q_x$ - $1/Q_0$ vs h_x plot (Eq. 1).

The results do not depend on the specimen thickness.



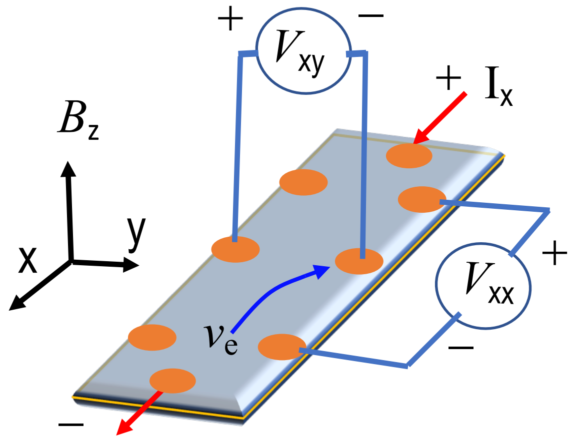




The peaks of epitaxial Graphene (G/SiC) and silicone carbide (SiC) are well aligned: Evidence of monolayer Graphene: $\varepsilon'=1$

J. Obrzut et al, Measurement **81**, 146-151 (2016)

Hall test method: comparison Epitaxial Graphene with Graphene Ink

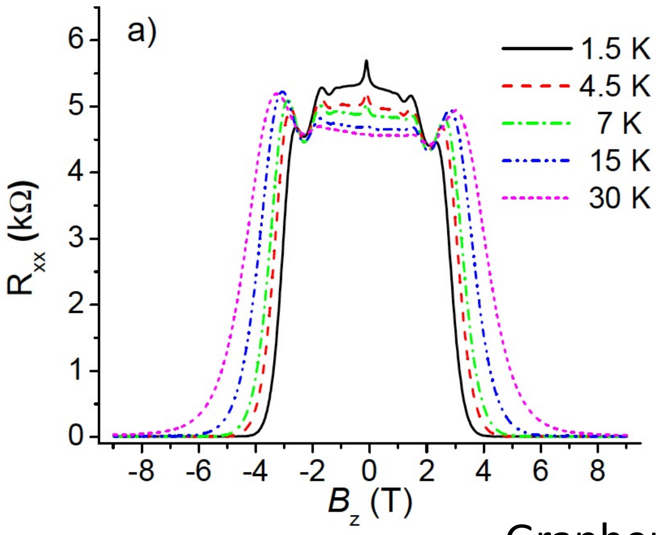


$\mu = d(V_{xy}/B_z)\ 1/(I_x\ R_{xx})$ (1)

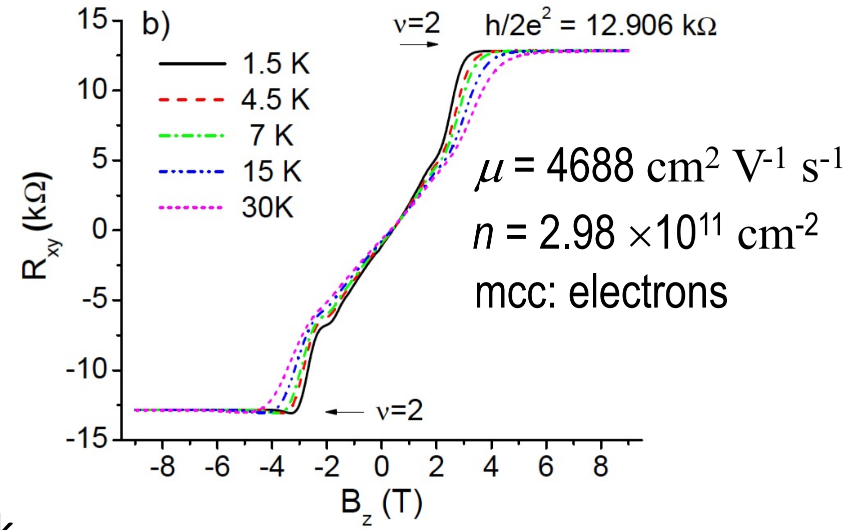
$n = d(V_{xy}/B_z)\ (I_x/q)$ (2)

$d(V_{xy}/B_z)$ =slope of the V_{xy} vs B_z

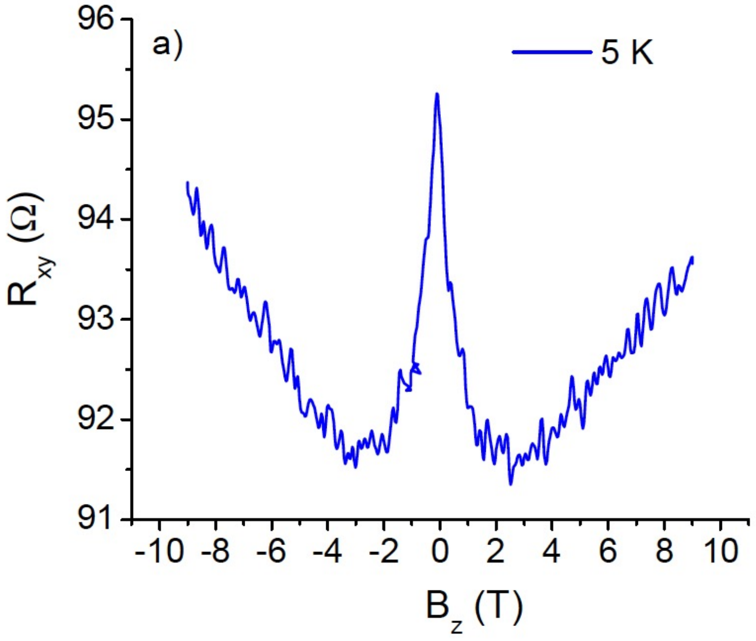
Epitaxial Graphene

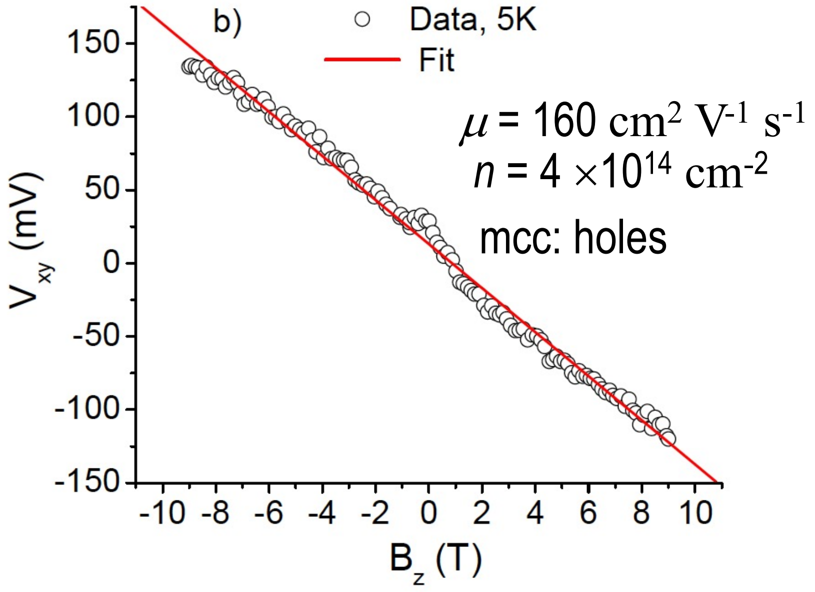


Quantized Hall Resistance

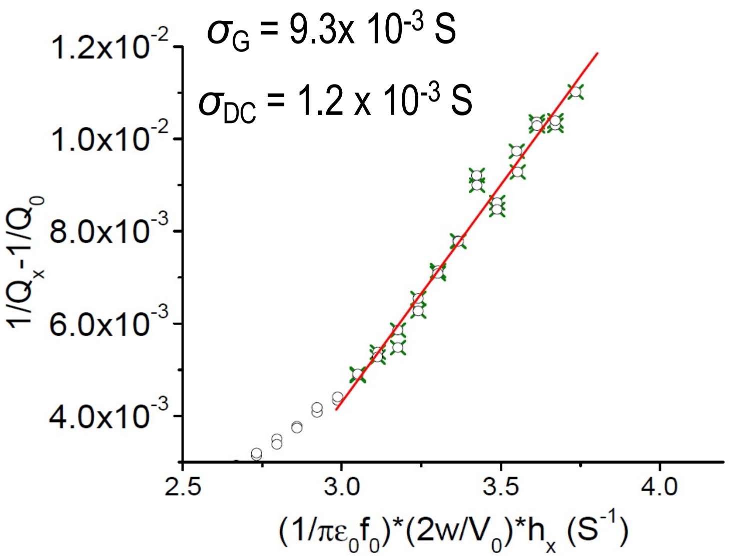


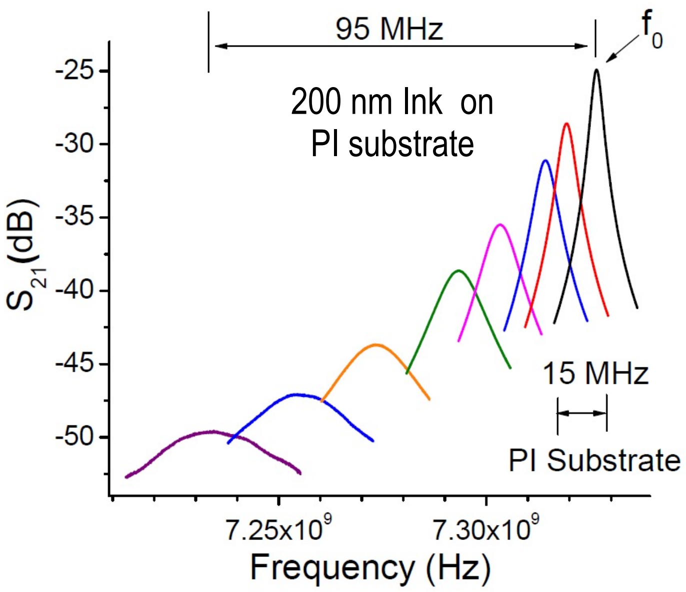
Graphene Ink

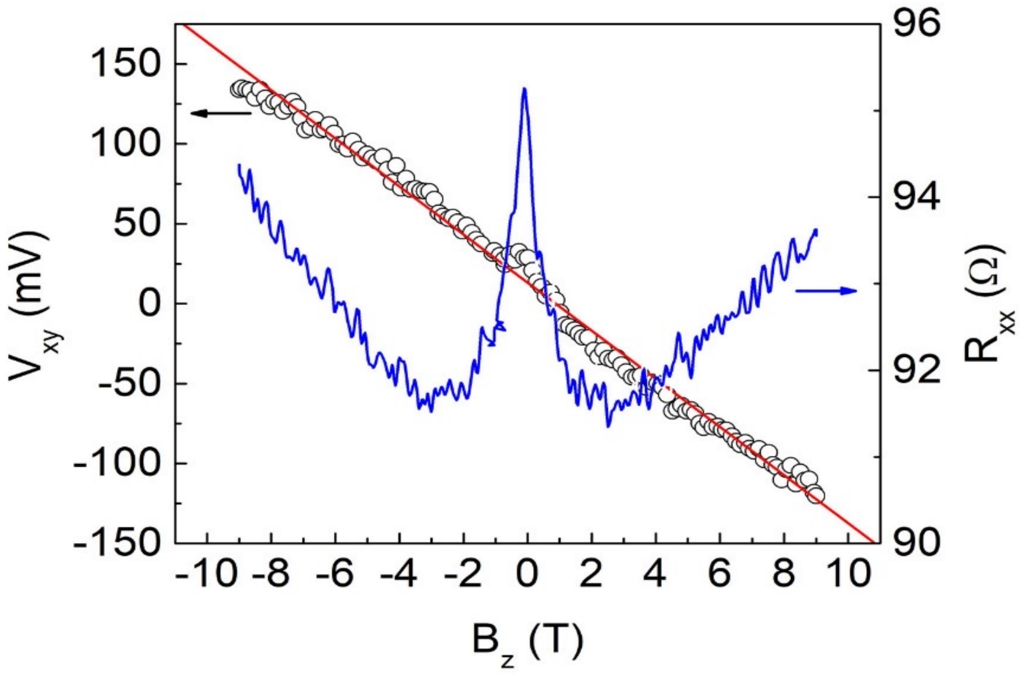




Indicators of disorder in Graphene Inks as compared to Epitaxial Graphene





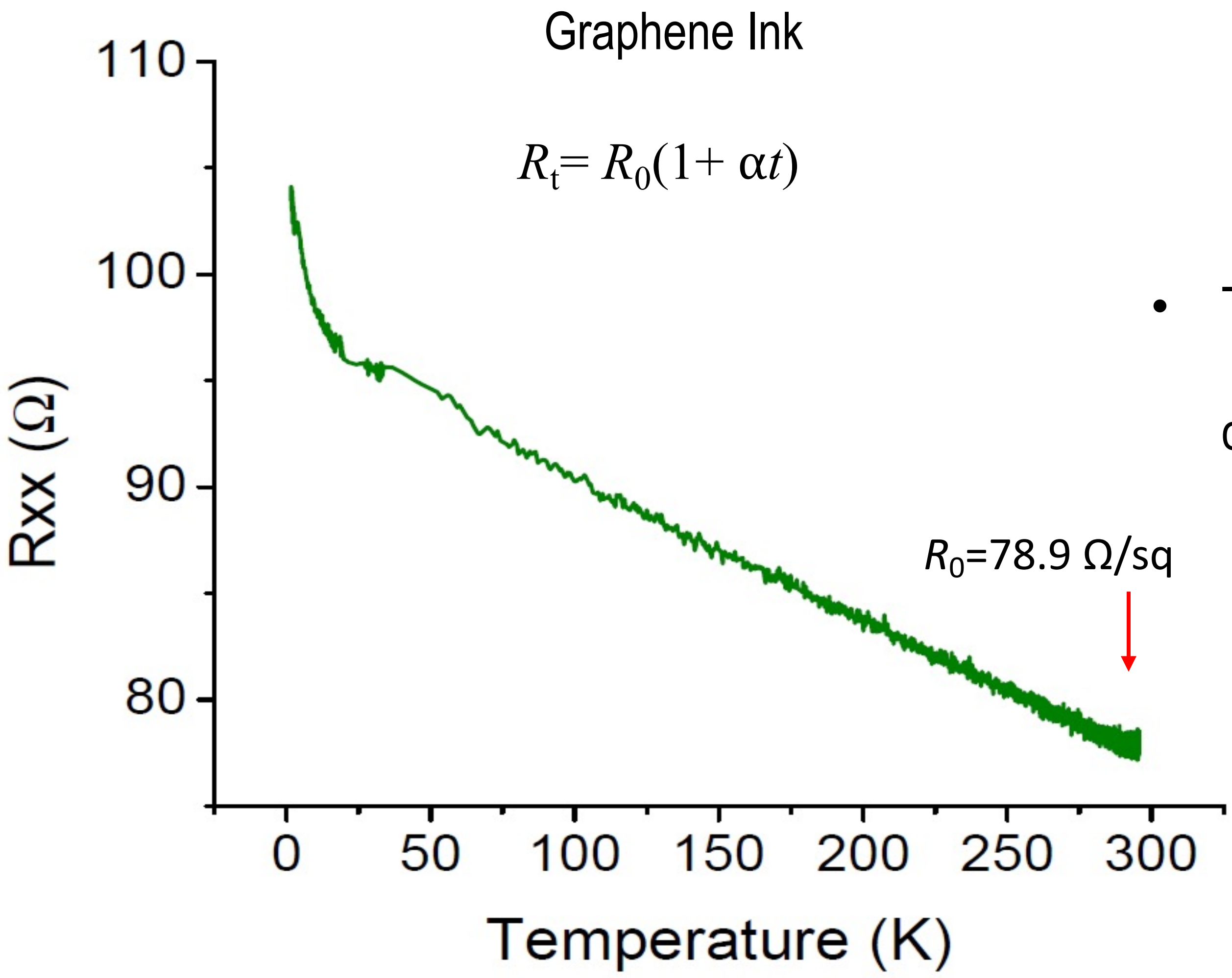


- ✓ High mobility up to microwave frequencies (0.13 ns)
- ○ $\sigma_{DC} < \sigma_{AC}$ due to dielectric polarization from charge traps

- ○ The frequency shift larger than that that of PI substrate results from tcharge polarization at domain boundaries in multi-layer structure ($\varepsilon' > 1$)
- ○ e

- ✓ A peak on the Rxx vs Bz (blue plot) is consistent with 2D mixed metallic-semiconducting charge transport
- ○ The negative slope of $\mathbf{V}_{xy}$ vs B_z (red line) indicates that the majority of charge carriers are positive holes

Thermal coefficient of resistance TCR) - distinguishes metallic from semiconducting charge transport

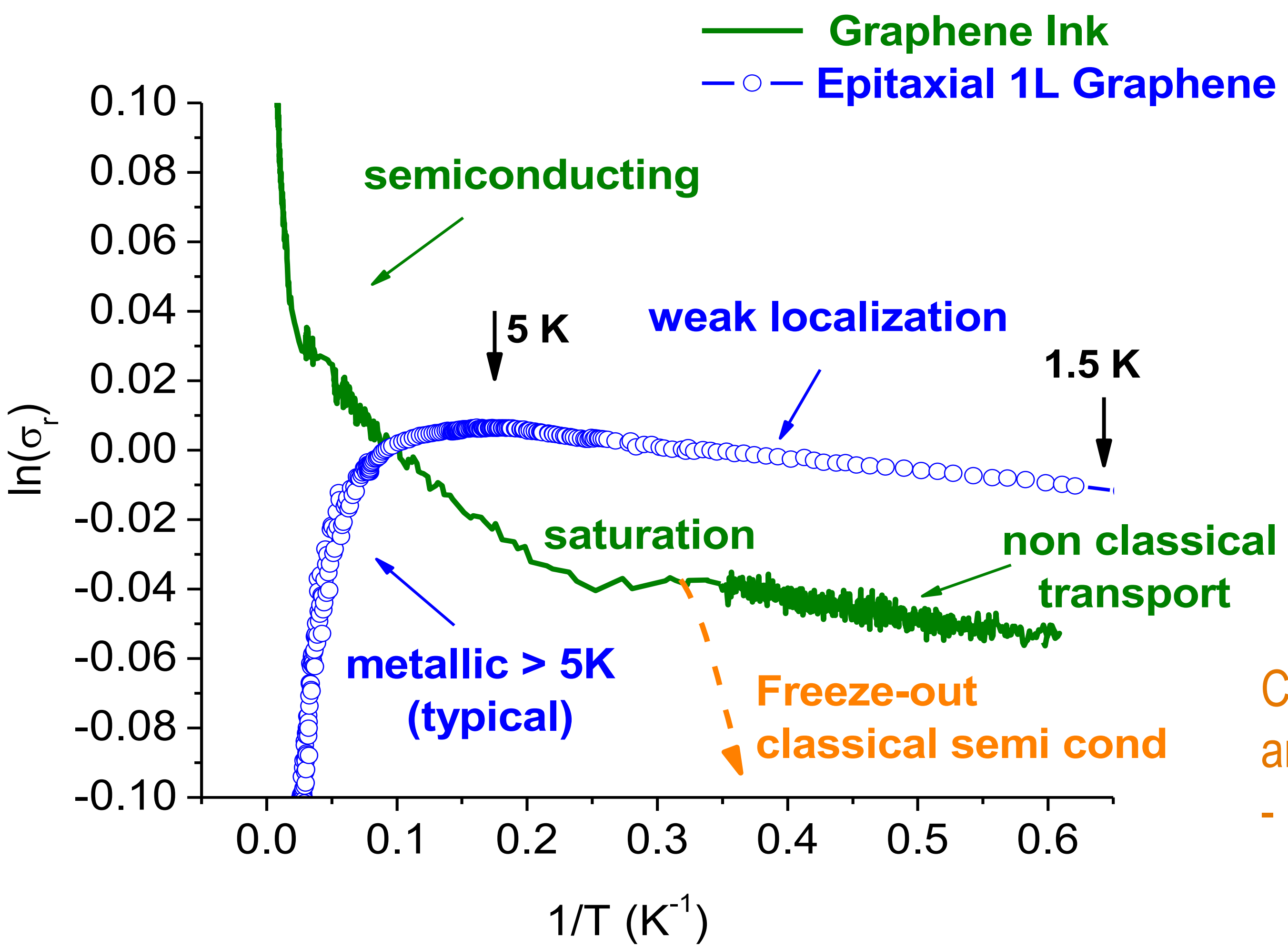


$\alpha = -8.3 \times 10^{-4}$ (K^{-1}) (negative)

- The linear coefficient of thermal resistance $\alpha = -8.3 \times 10^{-4}$ K^{-1} referenced to R_0 = 78.9 Ω at 273 K is comparable to that in crystalline graphitic microstructures

- Thermally activated charge transport with narrow band gap

Evidence of non-classical charge transport in Graphene Inks Comparison with 1L Epitaxial Graphene



←New

Classical: Below freeze-out all charges are within valence band - $\sigma_r \longrightarrow 0$
- no conductivity

Comparison of temperature dependent conductivity of Graphene inks (green line) with epitaxial Graphene having carrier density about 2×10^{11} cm^{-2} (blue line) referenced for clarity to R_{xx} at 5 K.

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SUMMARY

- There is a gap between the available standard test methods to asses quality of raw commercial graphene materials and performance characteristics required by the end users (powders vs Inks).
- Several recommended standards (AFM, Raman, XPS, XRD) are either non-practical at industrial scale or have limited capability for statistical quality projection.
- Graphene standard reference materials are needed to facilitate classification of any form of graphene regardless of production method.

✓ A noncontact nondestructive microwave cavity test method IEC 6206-6-4) is shown capable to reliably determine surface conductance of graphene Inks formulated from graphene powders.

✓ The method allows to evaluate effect of disorder in graphene inks from charge polarization at domain boundaries referenced to epitaxial graphene (Ink $\varepsilon' > 1$, 1LG/SiC $\varepsilon' = 1$)

✓ Complementary Hall measurement of in graphene Inks at cryogenic temperatures evidences charge localization – a characteristic signature of 2D charge transport.

Thank you !