Molecular Doping of Graphene: Towards a Low-Field Quantum Hall Standard

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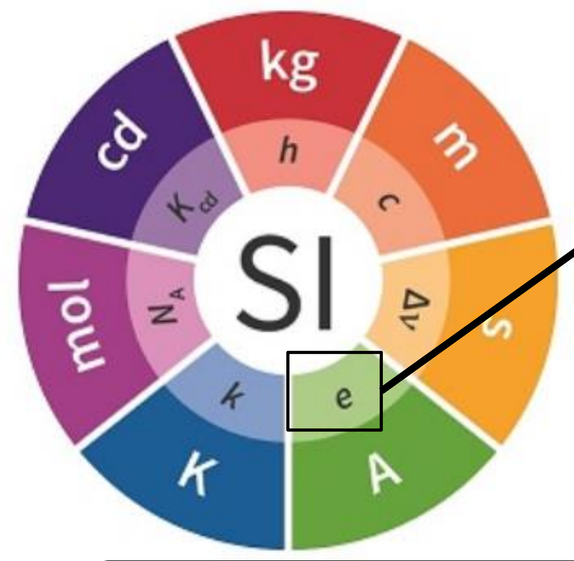
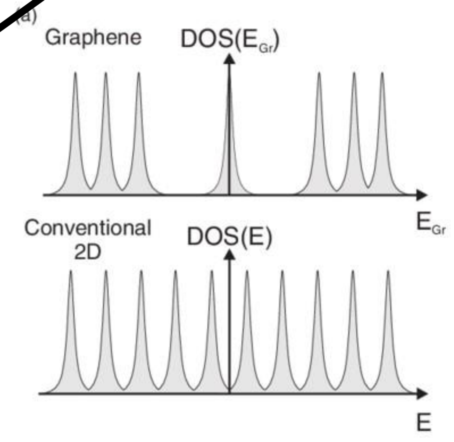
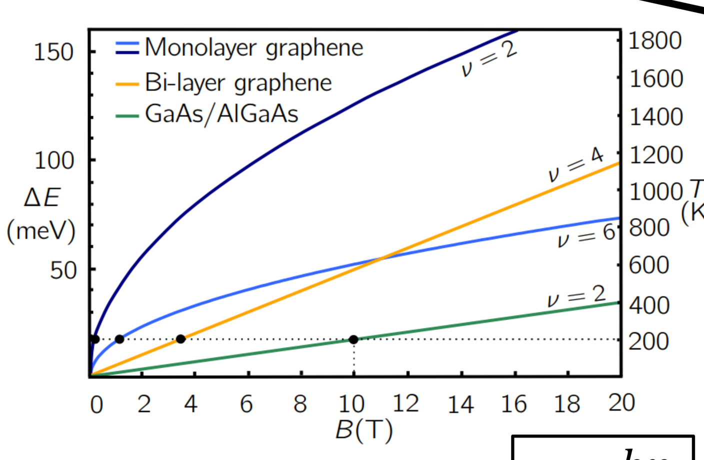
Revised International System of Units SI (2018): based on fundamental constants

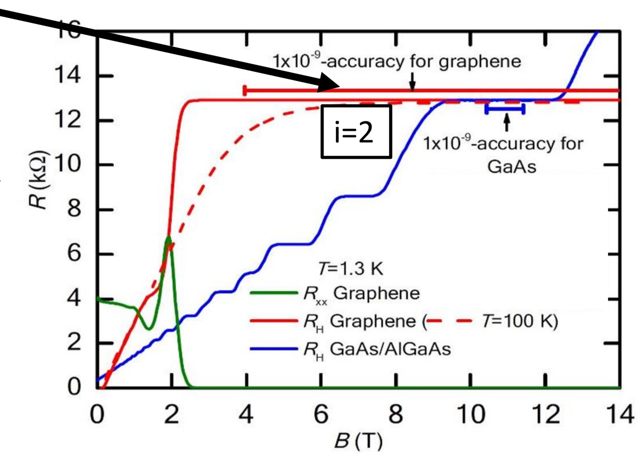


$$R_K = \frac{h}{e^2}$$ $$R_H = \frac{R_K}{i}$$

Quantum Hall resistance Standard : Universality effect







$$\nu = \frac{hn}{eB}$$

R. Ribeiro et al, Nature Nano., 10, 965 (2015)
F. Lafont et al, Nature. Commun., 6, 6805 (2015)

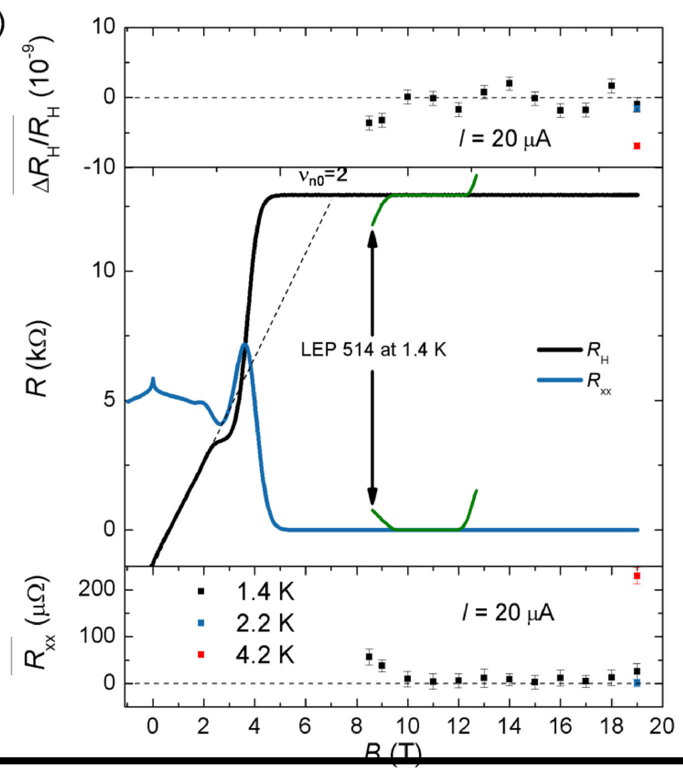
Quantization Criteria for QHE:

- $\frac{\Delta E}{K_b T} \gg 1$
- $\mu B \gg 1$
- Low dissipation ($R_{xx} \leq 100\ \mu\Omega$)
- High Quality Contacts ($R_c < 10\ \Omega$)

Graphene on silicon carbide (SiC) for metrology

	Usual GaAs/AlGaAs	Graphene this work
B	10 T	3.5 T [1.3 K, 10 µA]
T	1.3 K	10 K [8.5 T, 20 µA]
I	50 µA	500 µA [8 T, 1.3 K]

R. Ribeiro et al, Nature Nano., 10, 965 (2015)
F. Lafont et al, Nature. Commun., 6, 6805 (2015)



Compatible with table-top and portable cryomagnetic systems for broader dissemination:

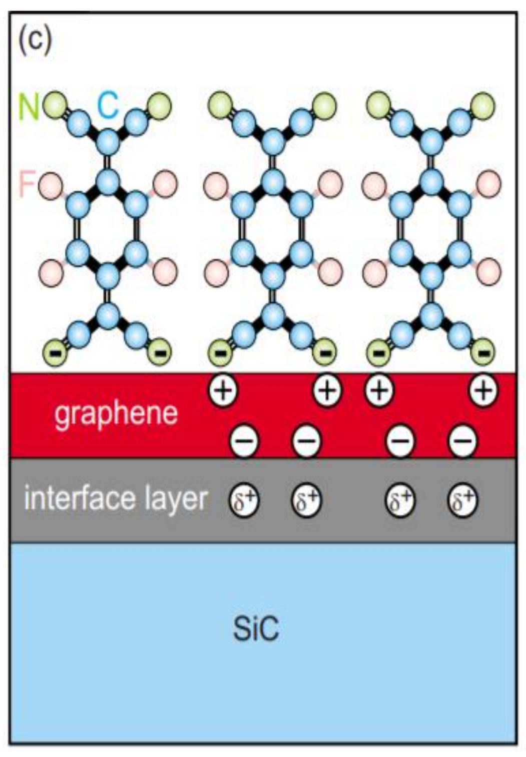
- Lower Magnetic Field ($1-3T$)
- Higher Temperature ($> 4{,}2\ K$)
- Increased Current ($> 100\ \mu A$)

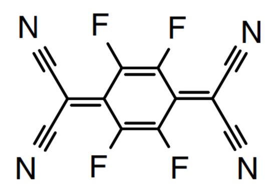
Requirements for relaxed conditions operation:

- High Mobility ($\geq 10\ 000\ cm^2.V.s-^1$)
- Controlled Carrier Density ($0{,}5\ -\ 2\ .10^{11}\ cm^2$)
- Reproducible Growth Methods

Graphene on SiC limitations:
Electron carrier density ($n \sim 10^{13}\ cm^{-2}$)
mobility ($\mu \sim 1\ 000 - 2000\ cm^2.V^{-1}.s^{-1}$).
Challenge: Density and mobility control at low temperature

Carrier density and mobility control: Molecular Doping

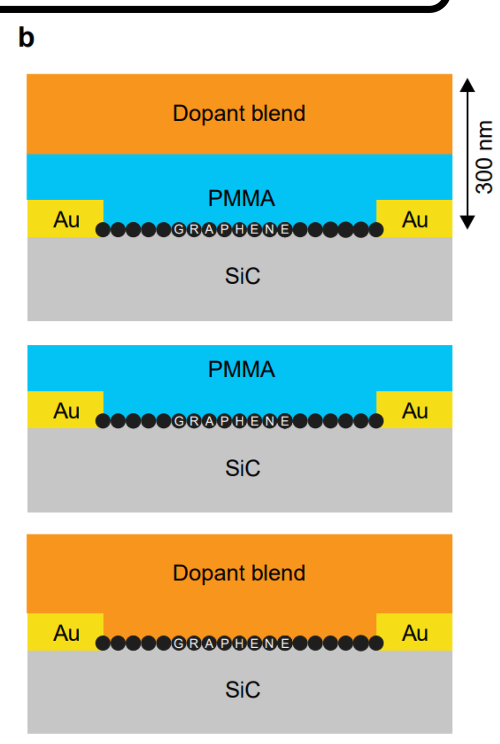


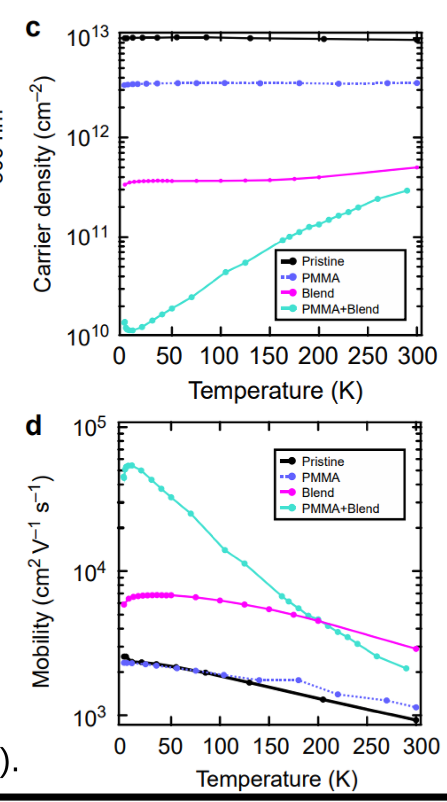


F4-TCNQ functionalization of graphene:

- Stable charge-transfer complex, electrons acceptor
- Durable under ambient and high-temperature conditions.
- **Attractive, feasible addition to technology processes**.

Coletti & al, *Physical Review B* 81, 235401 (2010).



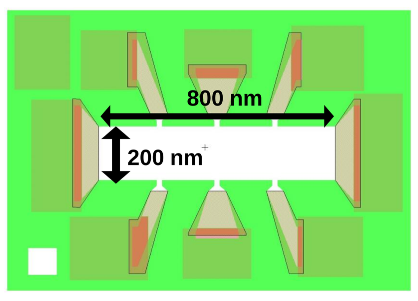


He et al. Nat Commun 9, 3956 (2018).

The crucial role of spacer layer for carrier density and mobility control at low temperatures via spin coating methods

Molecular doping: A promising approach to regulate electronic carrier density and mobility in graphene

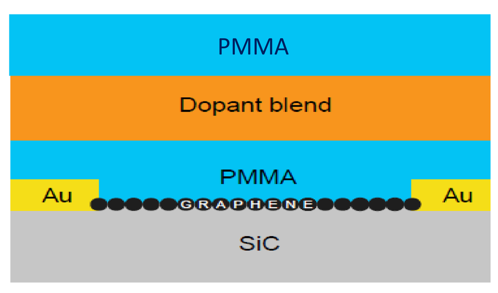
Fabrication and doping process



Epitaxial graphene from CRHEA[3]

Hall bar fabrication (800mm x 200mm):

- Patterning (Electron-beam lithography)
- Graphene etching (reactive ion etching)
- Contacts (metal deposition)

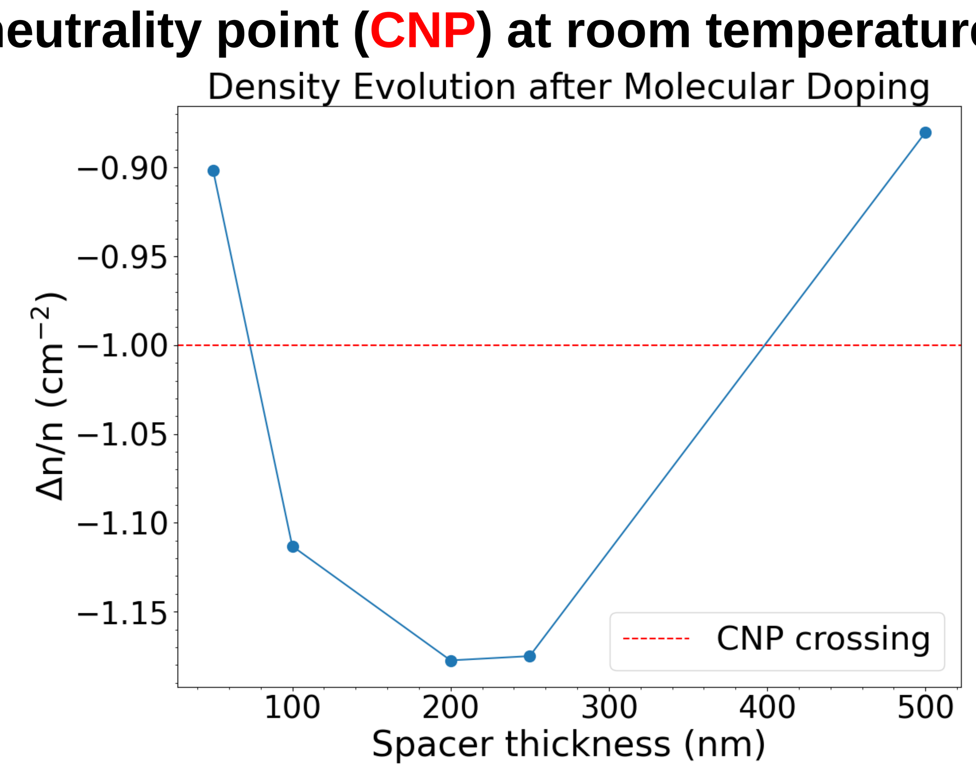


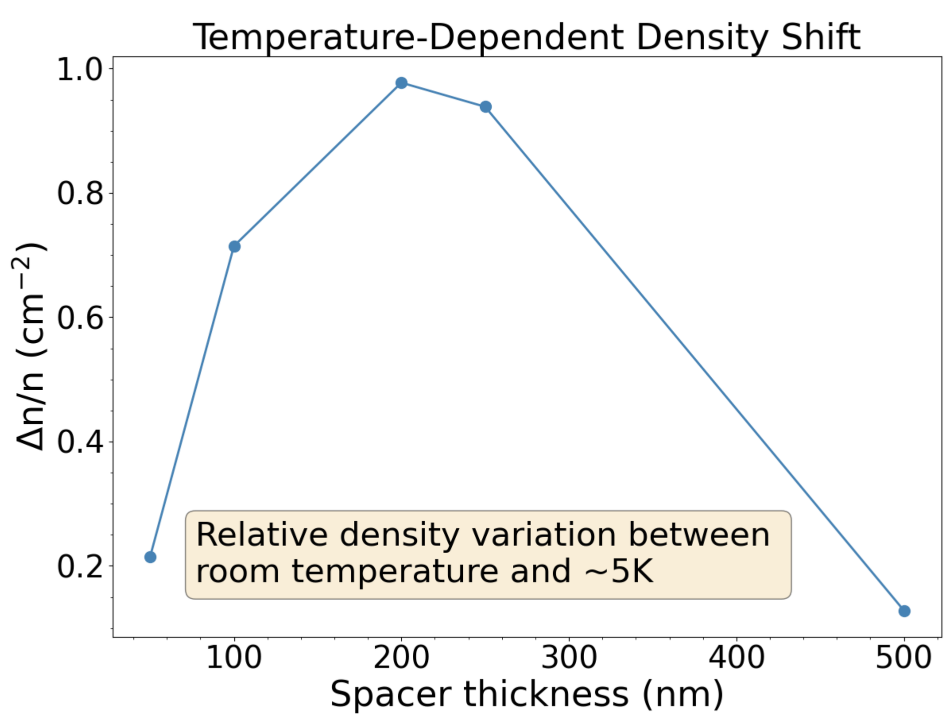
Probing molecular doping via a 3-layer process with different spacer thickness, each layer thermally annealed at 160°C for 5 minutes:

- **Polymethyl methacrylate (PMMA) spacer (50-500nm)**
- **Dopant blend (F4TCNQ dissolved in anisole + PMMA)** (150nm)
- **PMMA encapsulation** (200nm)

Electrical characterizations

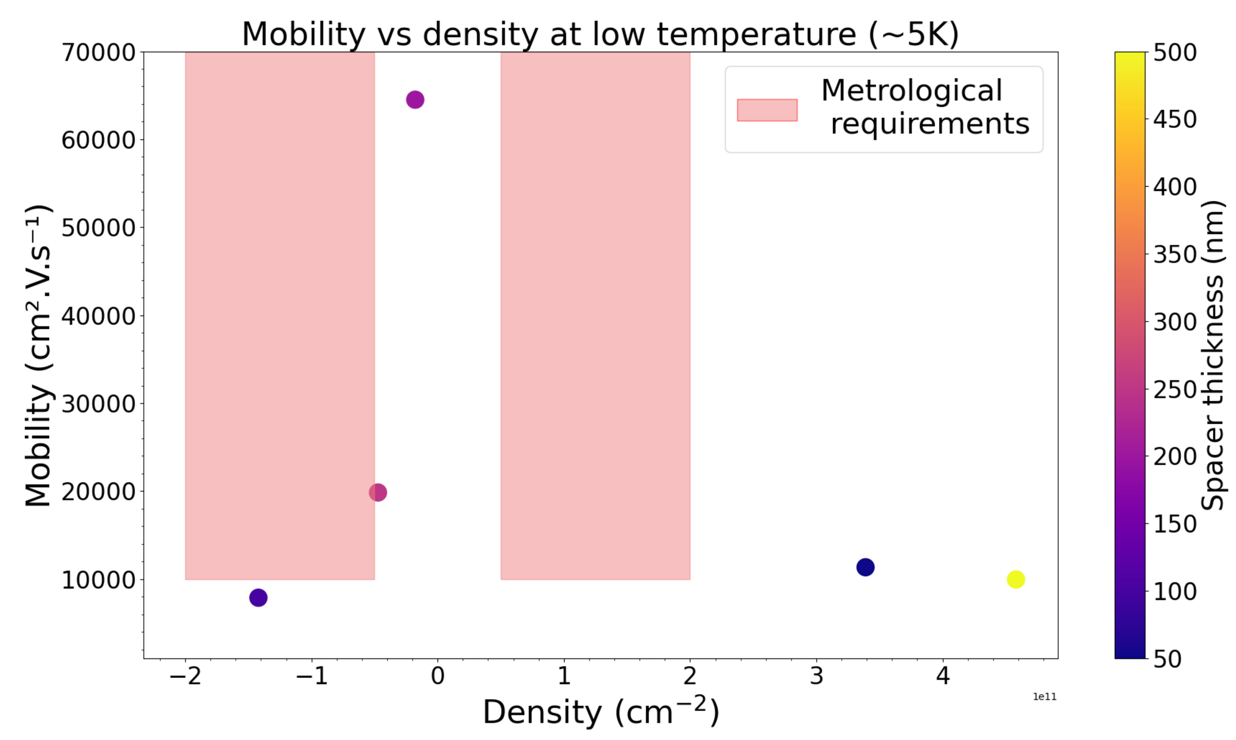
Spacer layer thickness control to cross charge neutrality point (CNP) at room temperature





Spacer layer thickness impact relative density variation with temperature (from 13% to 98%).

Nearing metrological standards requirements through spacer layer thickness control



Conclusion and perspectives

Achieved densities down to $1{,}78.10^{13}\ cm^{-2}$ and mobilities up to $64\ 497\ cm^2.V^{-1}.s^{-1}$ from epitaxial graphene (original density $4{,}4.10^{12}\ cm^{-2}$, mobility $1187\ cm^2.V^{-1}.s^{-1}$) underscore the potential of spacer thickness as a key control parameter for metrological requirements under relaxed conditions.

Ongoing:
- Reproductibility and long-term stability testing of the doping
- Understanding of microscopic effects of molecules as dopant
- Metrological Testing of the Quantization of the Hall resistance