Tailoring the properties of Graphene

Myrsini Lafkioti
Motivation

• 2DEG of graphene lies at the surface

• Lattice Defects
  - Missing atoms, distortions

• Interaction with
  - Substrate
  - Adsorbates

• Edge $\rightarrow$ Yang et al. Adv. Matter. 22, 4014
  Shi et al. DOI: 10.1002/adma.201100633
Graphene on SiO$_2$

- Mobilities on substrate typically ~5000cm$^2$/Vs
- Doping (normally p) depending on the preparation and ambient conditions
- Hysteresis in field effect
- Crystal defects of SiO$_2$
- SiO$_2$ surface is saturated with –OH groups forming polar silanol $\rightarrow$ hydrophilic
Hydrophobic Template

- HMDS (Hexamethyldisilazane)
- 93° contact angle
- Deposited at RT from solution (HMDS:Acetone 1:1)
- Replaces the hydroxyl groups on the surface with trimethylsilane
- Creates a stable hydrophobic surface on the substrate
- Eliminates polar adsorbates
Effects of HMDS

- Hysteresis in the field effect not observable on the treated substrate
- Charge traps contributing to the doping and the hysteresis often observed in the field effect are removed.

Hydrophobization of the surface diminishes adsorbates between substrate and graphene.
Effects of HMDS

- Doping decreases considerably:
  - Graphene on hydrophobic SAM: -5 V to +10 V.
  - Graphene on untreated SiO$_2$: -5 V to +54 V.
  - Mobility rises by a factor of up to 10 for samples on HMDS.

Nanoletters 10(4):1149-53
Effects of HMDS on QHE

- Very clear Shubnikov de Haas oscillations (black curve; hydrophobic substrate).
- Oscillation onset in graphene on untreated substrates at ~1.4 T in comparison to 0.8 T on HMDS (inset).
- Filling factor up to $\nu=62$ visible.
Pulsed field measurement

- e-e interactions should dominate over scattering
  \( \rightarrow \) electron density >> scatterer density

- samples have a mean free path \( l \sim 300\text{nm} \) at \( n > 10^{12}\text{cm}^{-2} \) with \( d_e \sim 10\text{nm} \)

- shallow minimum in \( \sigma_{xx} \) corresponding to the \( 4/3 \) plateau

- \( \mu n > 10^{16}\text{V}^{-1}\text{s}^{-1} \) corresponding to a conductivity >40\( e^2/h \) is similar to samples on which FQHE was observed

Hall resistance (blue) and longitudinal conductivity of sample B (red curve) at \( n = 1.13 \times 10^{12}\text{cm}^{-2} \) at 4.2K.
Benefits of HMDS

• Better visibility of QHE

• 4/3 Plateau on two different samples detected opposed to measurements in high magnetic fields on untreated SiO$_2$.

→ Different disorder
  – Reduced small angle scattering as mobility remains limited

• Polar adsorbates are diminished
  – Low doping, no hysteresis
  – Independent of ambient conditions

• Reproducable Preparation, no additional sample loss
Definition of the graphene edge with anisotropic H$_2$ Plasma etching
The sample edge

• Edge of graphene effects its properties
  – scattering of edge channels in QHE
  – Doping over covalent bonds at the edge

• Definition of edge is of advantage:
  – Structure
  – Chemical doping
Structure definition

- **E-beam lithography**
  - No definition (zigzag or armchair)
    

- **Catalytic nanoparticle cutting**
  - No control of direction
    
    Campos et al. Nano Lett. 9, 2600; 2009

- **Anisotropic etching of graphite with H₂-Plasma**
Anisotropic etching

- H$_2$ Plasma etching:
  Chemical etching over

$$3H^+ + C_x \rightarrow 3CH_3 + C_{x-1}$$

- Etching starts at edges, grain boundaries and defects
- Etch rate depends on
  - Temperature
  - Sample Thickness
Edge after Etching

- Edge vertical to graphene lattice
  - Zigzag edge
  Etch always along more stable zigzag edge

- Edge bonds passivated by hydrogen
Etching patterns

- Defects induced by O\textsubscript{2}-Plasma after EBL mask structuring

- Controlled patterning of Graphene constrictions

- Reduced defect density as defects are etched.

- Inducing of new defects?
Etching rate on thicker Graphene

- Slower etching rates at thicker samples as number of atoms at the edge increases

- Lattice orientation has to be determined prior to etching

- Determined edge roughness <1nm (TEM)
Quality

- Raman spectroscopy:
  - Etched monolayer shows different G to D* ratio → zigzag edge?
  - Shift of D* → doping
  - Bilayer show double peak from the edge.
  - Low D-Peak
Electronic Transport

- Bilayer GNR:
  - No gap
  - FE does not change with Width
  - Resistivity increases
  - Low $I_{\text{min}}/I_{\text{max}}$ ratio: quasimetallic characteristics?
  - Bilayer graphene is known to have a lower $I_{\text{min}}/I_{\text{max}}$ ratio!
FE of „large area bilayer“

- Bilayer graphene on hydrophobic substrates shows a ratio of 2-10.
Summary

- No uncontrolled doping over the edge (e.g. O₂)
- Zigzag edge signature observed in Raman?
- No gap observed in bilayer GNRs
- Resistivity increases by reducing width
- Control over edge orientation and resulting sample form → zigzag edge