Bottom-up Graphene Nanoribbon Field-Effect Transistors.

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Why Bottom Up Nannoribbons

• Promising material for use in high performance, nano-electronic, spintronic samples.

• Properties dependent on precise geometry of the GNR and are degraded by rough edges.

• Bottom-up chemical synthesis produces GNRs that possess uniform width and precise edge structure.

• Short length and the metallic growth substrate has thus far prevented standard electronic device fabrication and transport measurements.
Fabrication

• Molecular precursor, 10,10’-dibromo-9,9’-bianthryl (DBBA) is thermally sublimed in UHV onto Au(111) and converted into a polymer chain.

• Thermal cleavage of C–Br bonds induces polymerization to polymeric GNR precursors.

• Annealing \(\rightarrow\) cyclization/dehydrogenation sequence \(\rightarrow\) fully conjugated GNRs with atomically defined armchair edges.

• GNRs synthesized with DBBA are exactly 7 carbon atoms across \((n=7, w=7.4\ \text{Å})\) with a band gap on Au(111) of approximately 2.5 eV.

Fabrication

- Synthesis takes place on the crystalline terraces of clean epitaxial Au films predeposited on cleaved mica substrates.

- RT STM image of n=7 armchair GNRs on Au growth substrate. (Inset: T = 7 K).

- PMMA is spun-cast onto the GNRs
- Concentrated HF and Au etchant to remove Mica and Au layer.
- Rinse again and drawn onto 50 nm SiO2
- Annealing to remove residual water and stripping of PMMA with acetone
Characterization

- Raman Spectroscopy performed on samples pre- and post-transfer verifies ribbon integrity is maintained.

- Preservation of the radial breathing like mode (398 cm$^{-1}$), characteristic for n=7 GNRs.

- Observed increase in the D peak intensity (1343 cm$^{-1}$) and slight overall linewidth broadening may be the result of reduced substrate screening effects or defects induced during transfer.
The Device

- Average GNR length 10-15nm→contacts with nanoscale gaps and 100nm width defined using EBL.

- Devices with source-drain gaps greater than 30nm do not show any conductance → inter-ribbon charge transfer negligible/ no single GNRs between the contacts.

- Several devices (20-30nm) show gate-modulated conductance. On-currents from tens of pA to a few nA at 1V $V_{SD}$.

- Ribbon orientation and position is random→actual channel length and number of ribbons is uncertain.
The Device

- 0-2 GNRs long enough to potentially contact source and drain; GNR density is approximately $2 \times 10^4/\mu m^2$ with less than 4% of ribbons longer than 30nm.

- Device yield is expected to increase significantly by further scaling the source-drain gap and/or

- increasing ribbon length during synthesis.
Transport

- GNRs contacted with Pd exhibit p-type conduction in air. Transistors exhibit large random conductance variations and variable hysteresis (adsorbed O₂, H₂O, and residual PMMA).
- Annealed: n-type conduction, caused by reduction of the contact metal work function due to molecular desorption.
- Hysteresis is greatly reduced by desorption from the channel.
Transport

- About half of devices still display hysteretic ambipolar behavior after vacuum annealing or re-exposure to ambient conditions.
- Further passivation with a hydrophobic monolayer, hexamethyldisilazane (HMDS) nearly eliminates hysteresis and switches device polarity.
- Residual hysteresis effects from trapped charges within the back-gate dielectric and not from molecular adsorbates on the contact or channel.
Transport

- Transport is largely dominated by the Schottky junction contacts.

- Polarity switching through small shifts in contact work function, relative to the GNR’s ∼2.5eV band-gap → band alignment of the Pd Fermi level falls close to mid-band-gap, a conclusion in agreement with simulations of n=7 GNR/Pd interfaces.

- Chiral Pd contacted GNR transistors 2-20nm wide, derived from CNTs show small Schottky barriers at the metal-GNR interface.

- Here much larger Schottky barriers up to 1.25 eV, due to the increased band-gap of the much narrower (7.4 Å) GNRs.
Backgate dependence

- 26nm source-drain gap.
- Resistance presumed to limit on-current due to short contact overlap length.
- Contact is no more than a few to perhaps 10 nm long depending on GNR length and alignment.
- Conventional graphene and CNT transistors show large resistance increases as $L_c$ is decreased past the electron mean free path ($\lambda \sim 200\text{nm}$) $\rightarrow$ low transmission probabilities in short contacts.

- Large measurement limited on-off ratio of $3.6 \times 10^3$ at $V_{SD} = 1\text{V}$, $\rightarrow$ semiconducting transport.
Backgate and Bias Dependence

• Behavior typical of a short channel Schottky barrier device.
• Offstate: leakage caused by holes tunneling through the drain barrier, $T$ independent but strongly $V_{SD}$ dependent.
• Larger $V_{SD}$ narrows the width of the Schottky barrier. Threshold voltage for turn-on ($V_T$) also $V_{SD}$ dependent, becoming negative for $V_{SD}>1V$.
• Strong coupling of the channel to the drain $\rightarrow$ gate has to counteract for the device to remain off.
$V_{SD}$ dependence

- Large electric field between source and drain by gated or aggressively biased devices sufficient to induce tunneling through the barriers $\rightarrow$ field emission becomes the dominant current source.

- Unsaturated, nearly exponentially increasing on-current (inset), even at large $V_{SD}$, as the barrier continues to narrow and tunneling increases.
Outlook

• Resistance of the GNR channel is much lower than the Schottky barrier series resistance → intrinsic GNR transport properties cannot be observed before extrinsic factors become weaker.

• Lowering of the contact work function would reduce the source conduction band barrier height, increasing the drain valence band barrier would improve on- and off-state performance.

• Use of wider GNRs (e.g. 1.4nm width and ~1.4eV band-gap) → smaller Schottky barriers and smaller band-gap. Longer GNRs would reduce contact resistance by increasing $L_C$.

• GNRs studied here appear more sensitive to their environment compared to graphene, CNTs, or significantly wider GNRs due to higher edge to surface ratio.

• Novel sensors through edge modification.

• Optimization of electronic behavior through local environment modification and precursor selection during synthesis.
Thank you for your attention