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Growth and Modification of Graphene

An Overview of Graphene (Opto)Electronics R&D at Sandia

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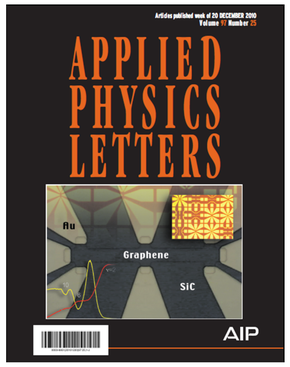
Purpose & Goals

Graphene, a single layer of graphite, is a promising material for many future electronic and optical applications potentially impacting SNL Energy and National Security Missions.

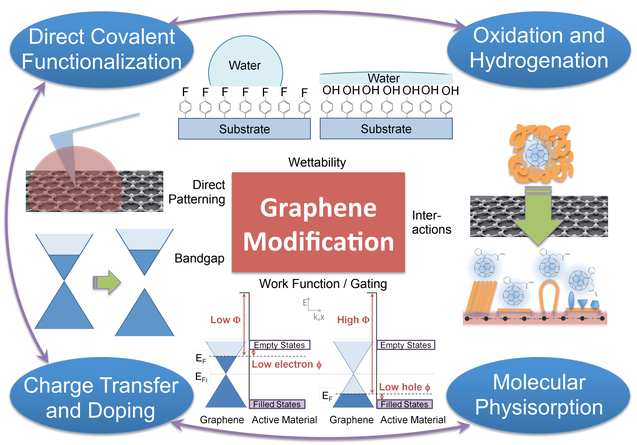
Our work is geared towards:

- Developing a fundamental understanding of graphene growth, properties, and applications using various microscopy techniques.
- Modifying graphene to have tailored electronic, optical, chemical, and physical properties for specific applications.



Graphene

Approach

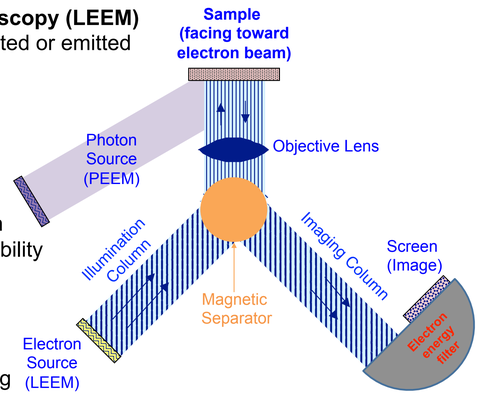


Graphene modification:

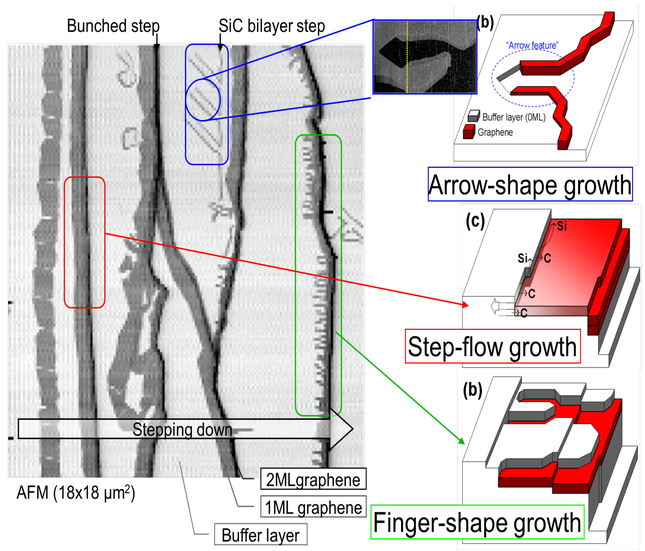
- High quality epitaxial graphene grown on SiC(0001)
- Basal plane functionaliza-tion to understand intrinsic effects.
- Investigate electronic, chemical, surface, and physical properties.

Low energy electron microscopy (LEEM)

- Imaging of electrons reflected or emitted from the sample
- Excitations can include:
  - low energy electrons
  - photons
  - thermal
- Surface sensitivity
- Surface electron diffraction
- ***NEW*** Energy filtering capability
  Provides information on:
  - electronic structure
  - chemical structure
  - plasmons
  - 5-10 nm surface mapping
  - live-time changes



Graphene Epitaxial Growth Modes on SiC(0001)



Electrochemically Activated Covalent Functionalization

Functional Group:

- Trifluoromethylphenylene (CF_3Ph) deposited by electrochemistry from an iodonium precursor [bis(4-trifluoro-methylphenyl) iodonium tetrafluoro borate ($CF3Ph)2I^+BF4^-$]
- Self-limiting and sensitive to XPS substrate
- Epitaxial graphene grown on 6H-SiC(0001) in Ar
- High film quality, basal plane functionalization

Electrochemical Solution:

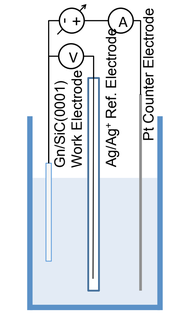
- Anhydrous acetonitrile, 10 mM $(CF_3Ph)_2I^+BF_4^-$ precursor, 100 mM tetra-butyl ammonium tetrafluoroborate (TBATFB) buffer

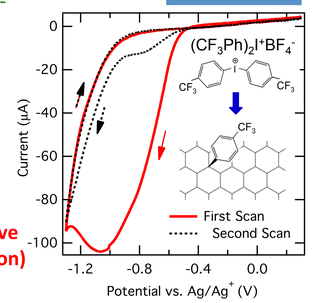
Results from representative cyclic voltammetric deposition at right:

- Scan 1: Reduction peak at –1.05 V
- Scan 2: Reduction peak at –0.75 V

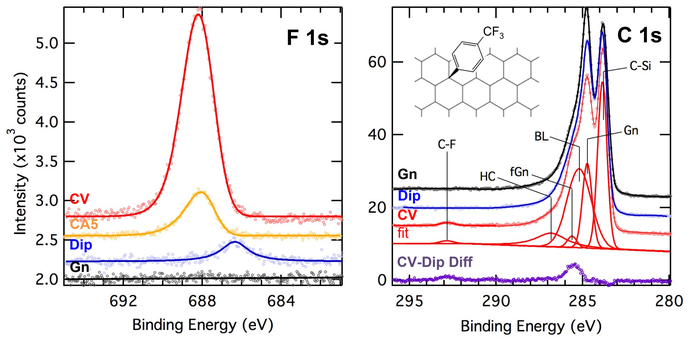
Much lower reactivity

➔ **Formation of electrochemically inactive CF_3Ph monolayer (w/ higher work function)**





Chemical States of CF_3Ph-Graphene from XPS



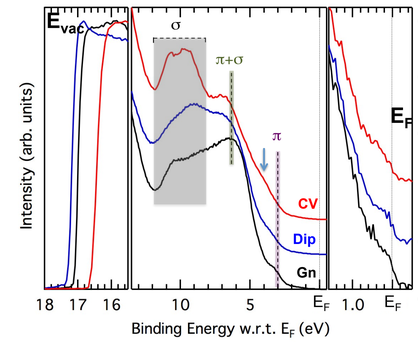
- F intensity increases with more aggressive treatments
- F peak shift indicates decreasing electron concentration due to bonding of CF_3Ph to graphene

➔ **Physisorption vs. chemisorption**

- C-F_3 peak and f-Gn peaks appear from functionalization
- Graphene peak broadening and shift indicate disorder and bonding
- CF_3Ph coverage: 3.2 x 10^{14} cm^{-2}

➔ **Closed-pack monolayer**

Electronics States of CF_3Ph-Graphene from UPS



- Increased σ intensity due to CF_3Ph adsorption on
- Physisorption (dip), broad σ peak indicates disorder
- Chemisorption (CV), sharp σ peak indicates order

➔ **molecules oriented by covalent anchoring**

- Shifting of π states

➔ **sp^2 to sp^3 conversion**

- Work function increases from 4.11 eV to 4.61 eV

Future directions

Characterize the the spatial variation of the electronic structure (valence band and the work function) of epitaxial graphene as a function of

- covalent functionalization
- charge transfer and doping
- contacts with metals and gate dielectrics

Spatial- and momentum-resolved valence-band photoemission spectroscopy and electron energy-loss spectroscopy will be used to address changes in graphene properties that result from these modifications.

U.S. DEPARTMENT OF ENERGY
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