The Inclusion of Impurities in Graphene Grown on Silicon Carbide

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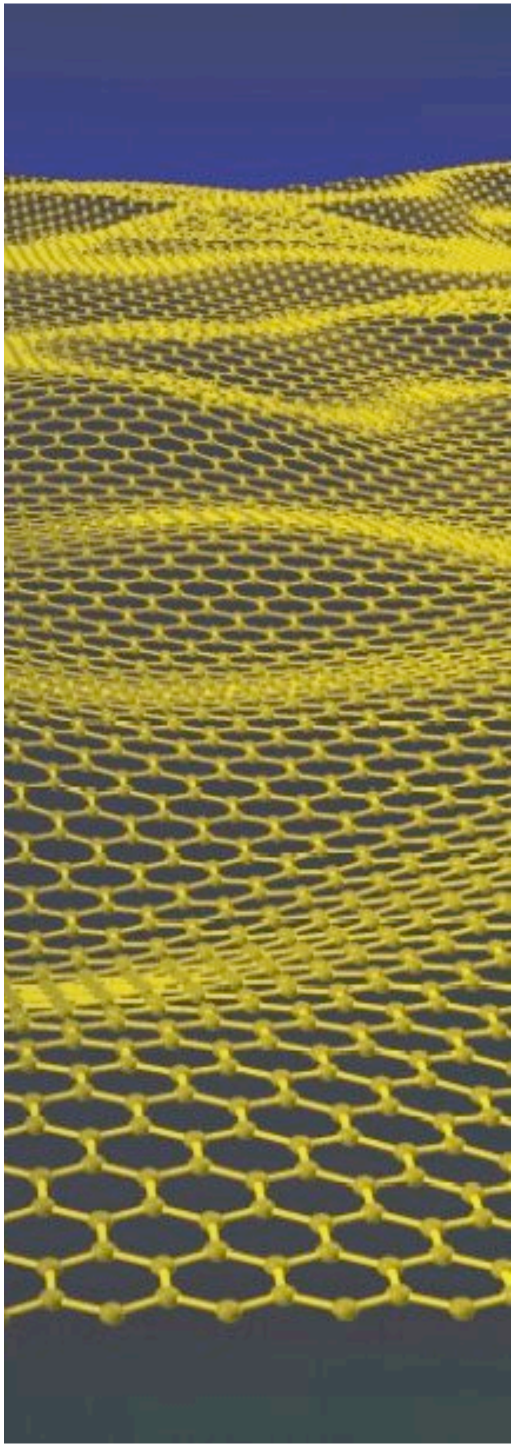
Goal:

Experimentally Fabricate
Doped Graphene



Procedure:

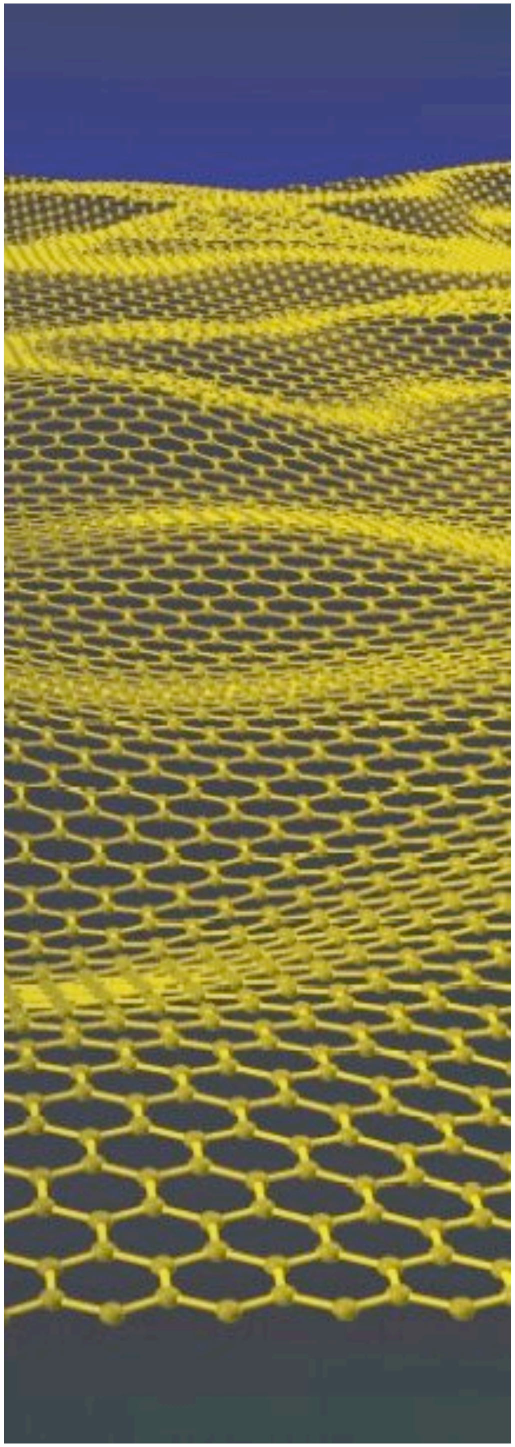
1. Introduce dopant in substrate
   - Implantation
   - NO Process
2. Grow graphene
   - Controlled Silicon Sublimation
3. Analyze graphene for dopant inclusion and quality
   - Raman: graphene quality
   - XPS: dopant concentration, bonding energies,
   - ARPES: band structure,
   - STM: electronic structure, topography,
   - TEM: lattice site

Goal:

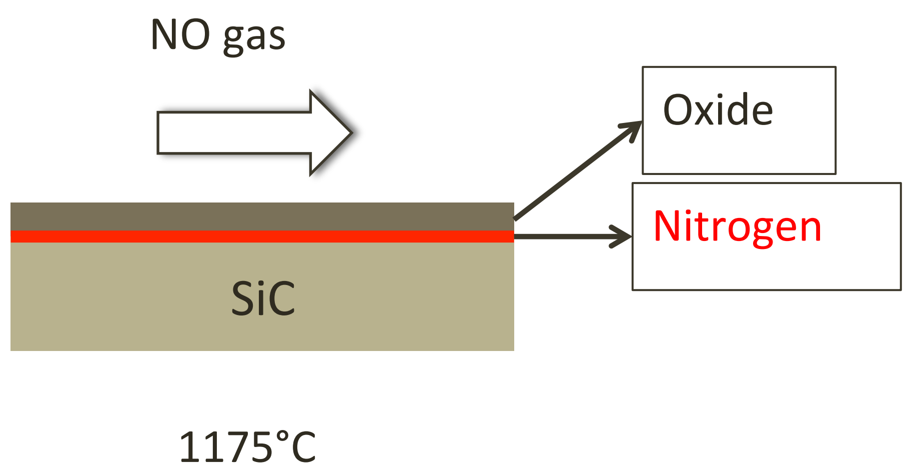
Experimentally Fabricate
Doped Graphene

Conclusions:

- NO Process treated SiC Graphene:
  - NO Graphene is continuous (Raman, STM)
  - Nitrogen is at interface (XPS)
  - NO Graphene has a Bandgap (ARPES)
  - Bandgap changes with thickness (ARPES, XPS)
  - Buckled and strained (STM)



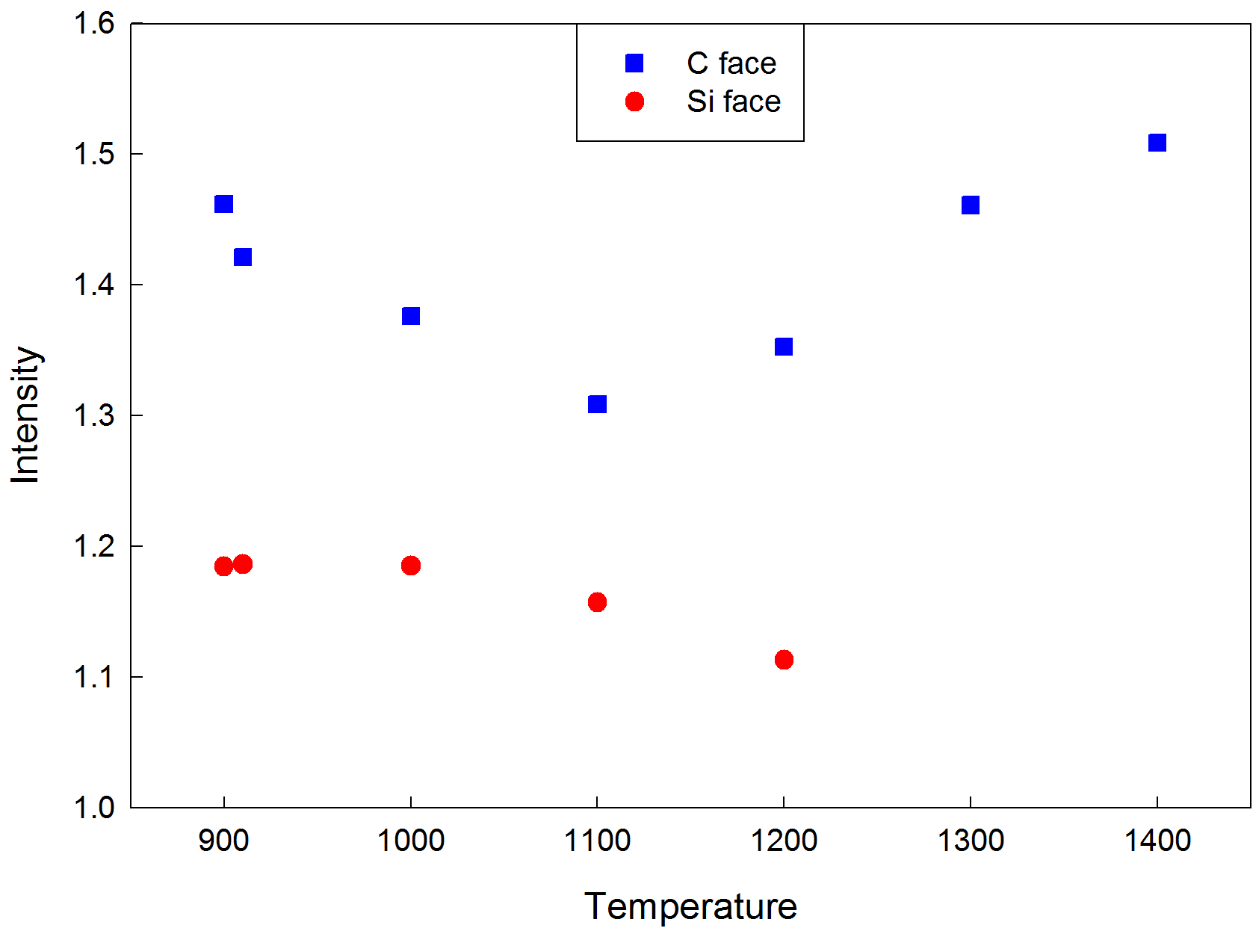
The NO Process



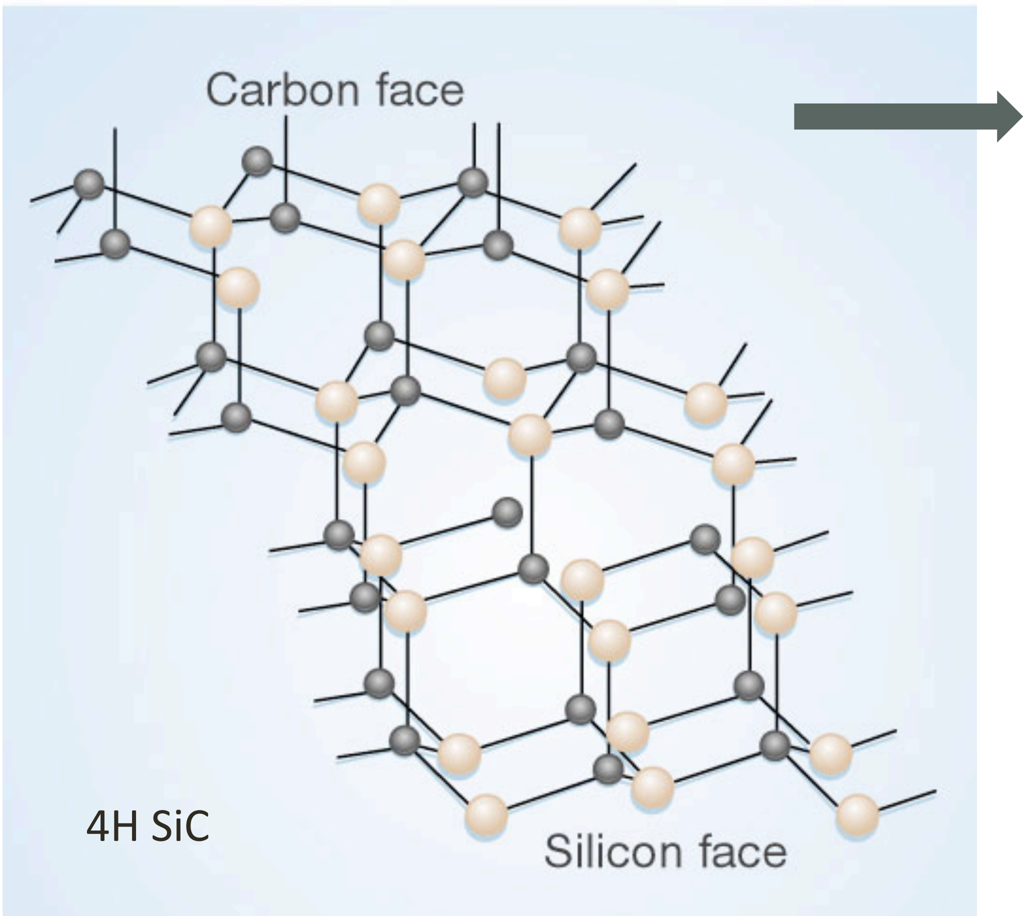
- Process developed at Rutgers University
- Nitrogen coverage measured:
  - ~5*10^{14} atoms/cm^2
  - ~0.5 – 2/3 of a monolayer
  - Nitrogen forms double and single bonds to silicon

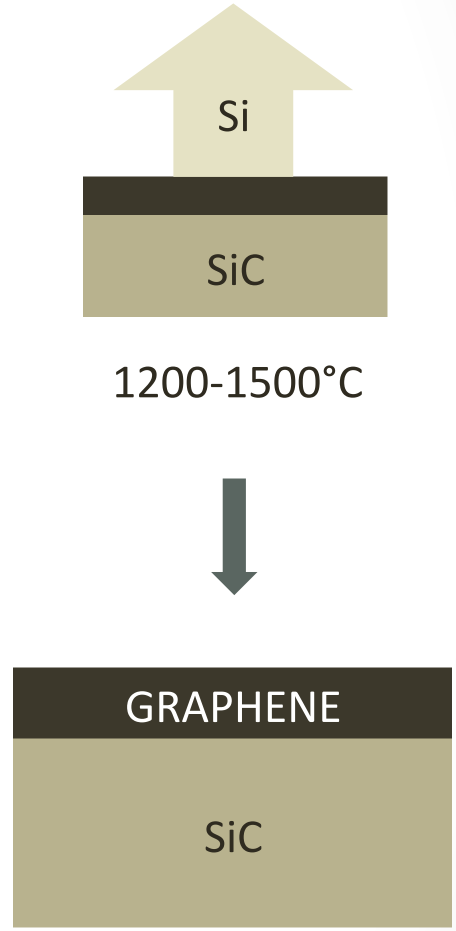
The NO Process

Nitrogen 1s peak intensity from XPS:



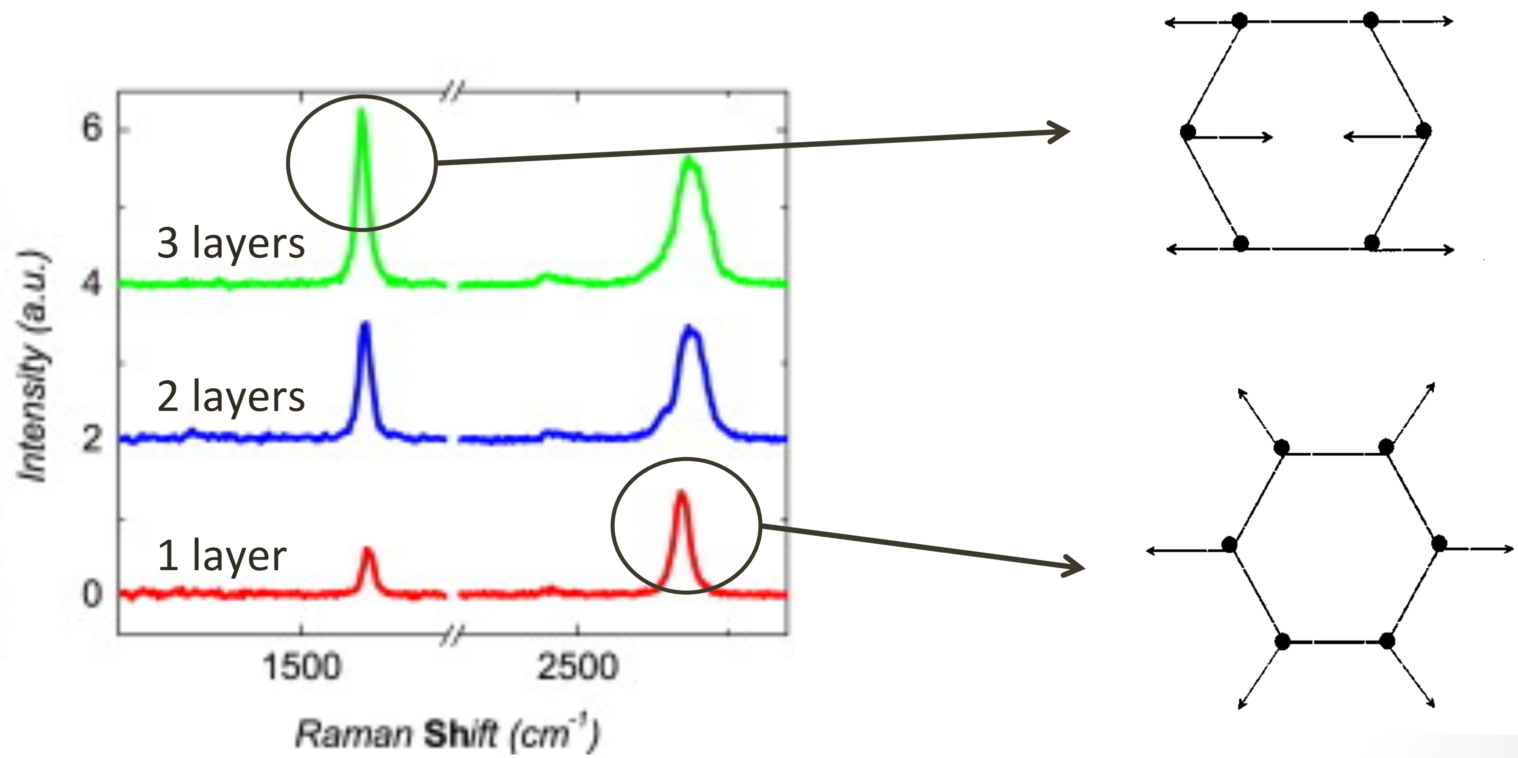
Graphene grown on Silicon Carbide





Raman Spectroscopy

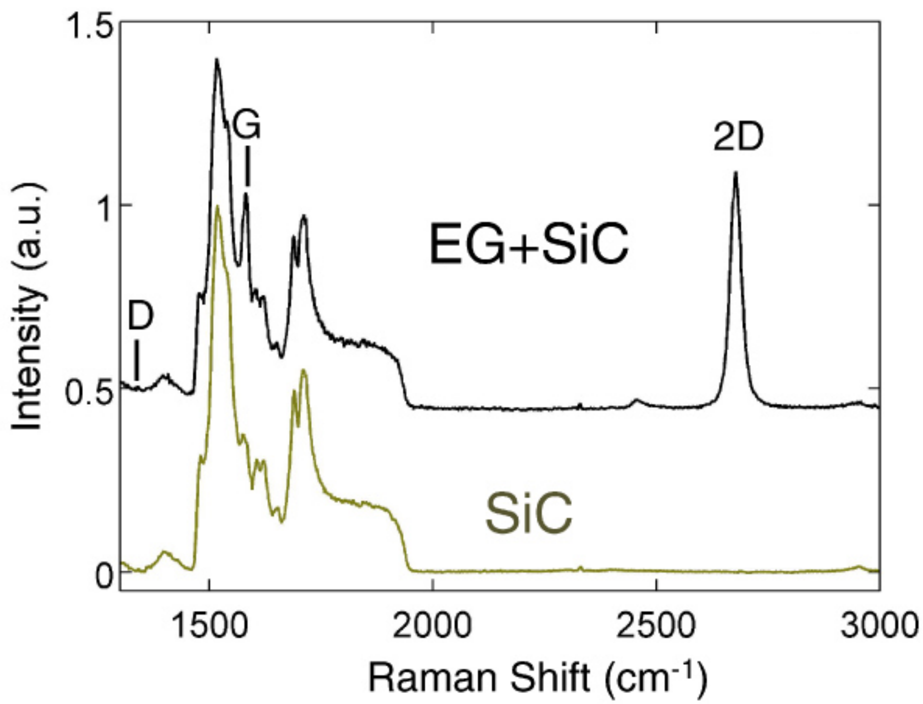
Typical Spectra



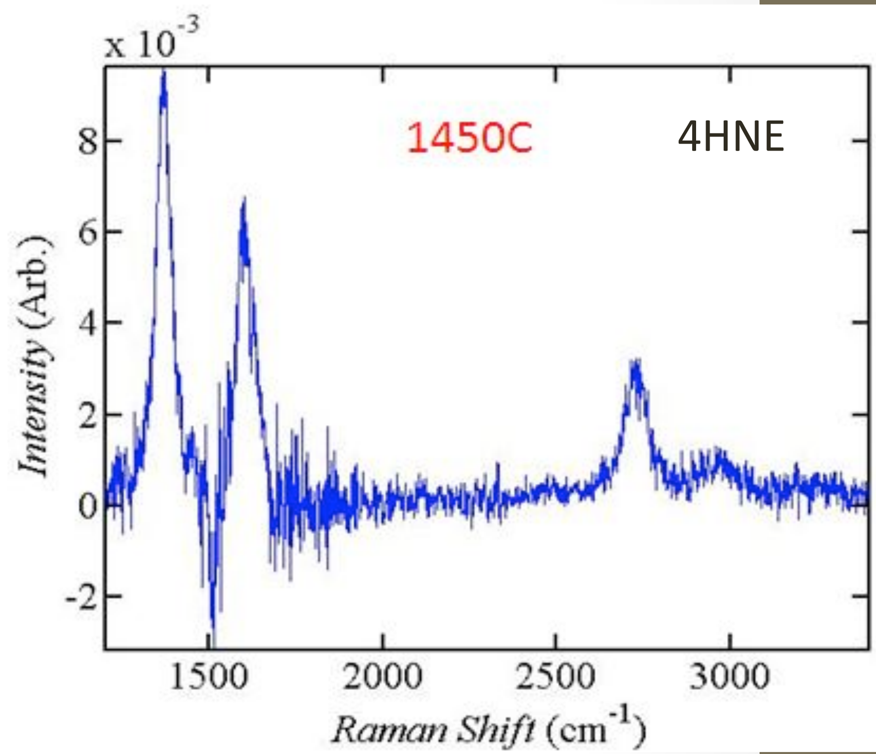
Malard, Phys. Reports 473, 5-6 pp. 51-87 (2009).

Raman Spectroscopy

Graphene on SiC



Graphene grown on NO treated SiC

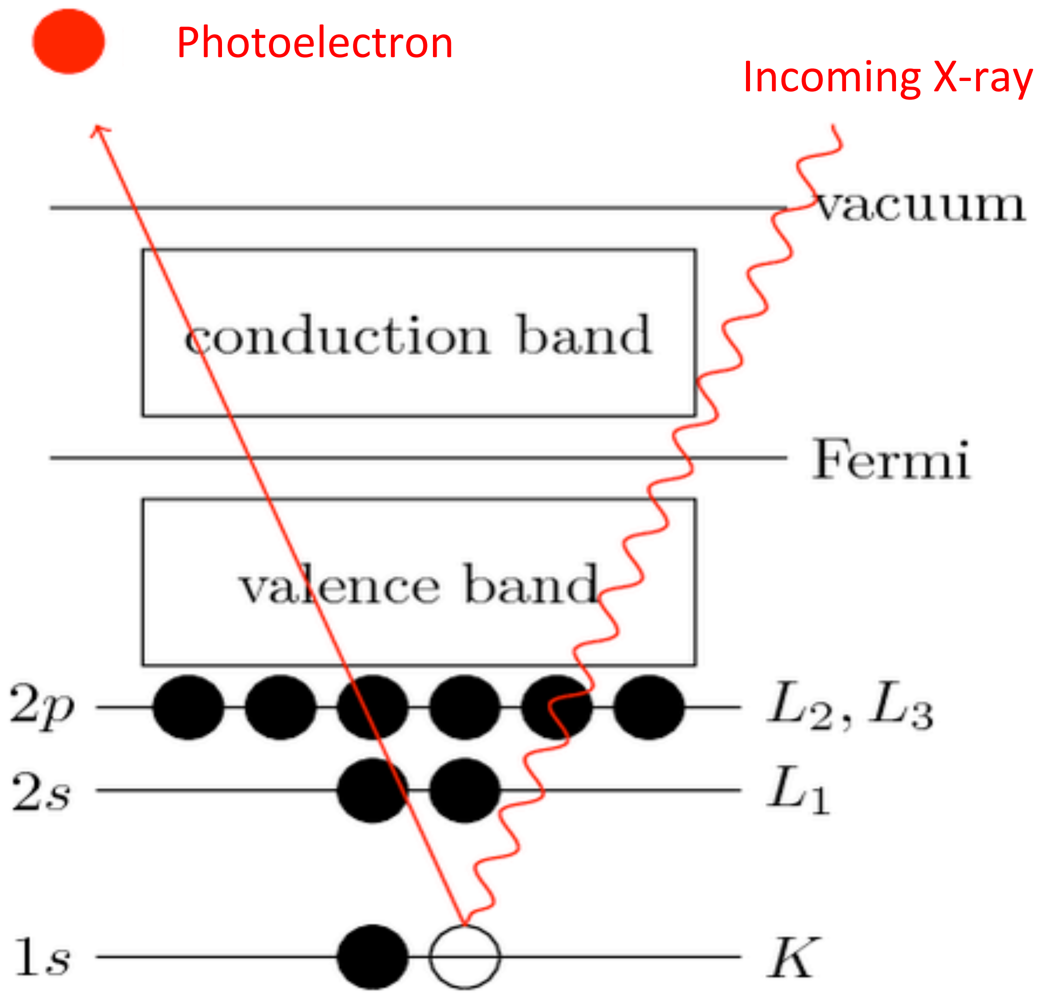


Raman analysis:

- NO Graphene is continuous

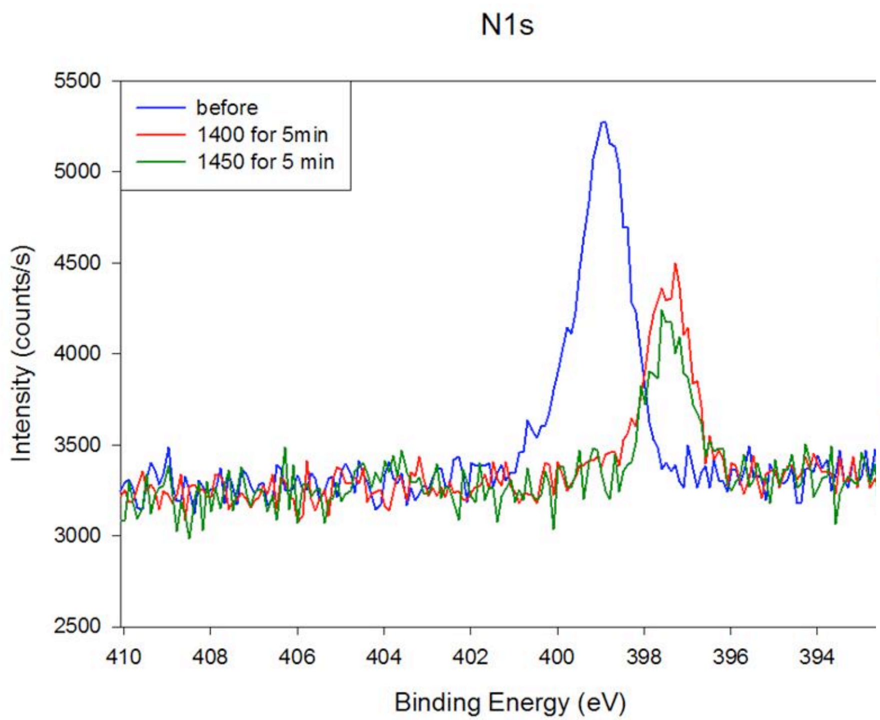
Hu et. al., J. Phys. D: Appl. Phys. 45 154010 (2012).

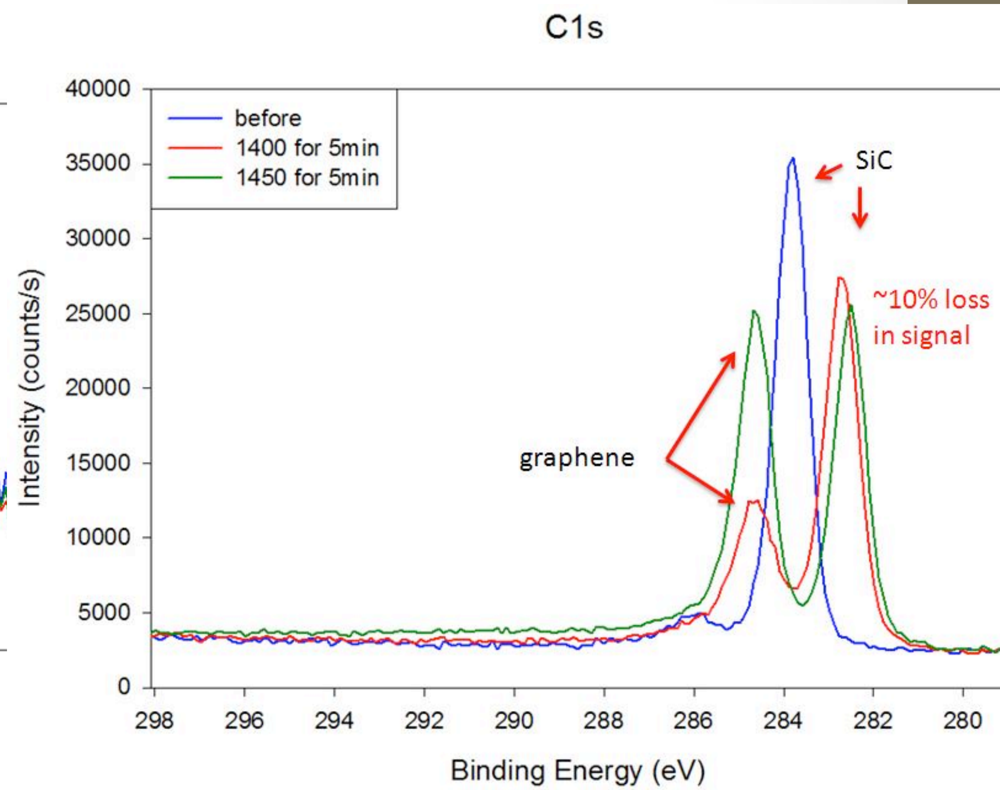
X-ray Photoelectron Spectroscopy



$$E_{photoelectron} = \hbar\omega - (E_{binding} + \Phi_{detector})$$

XPS: NO Graphene



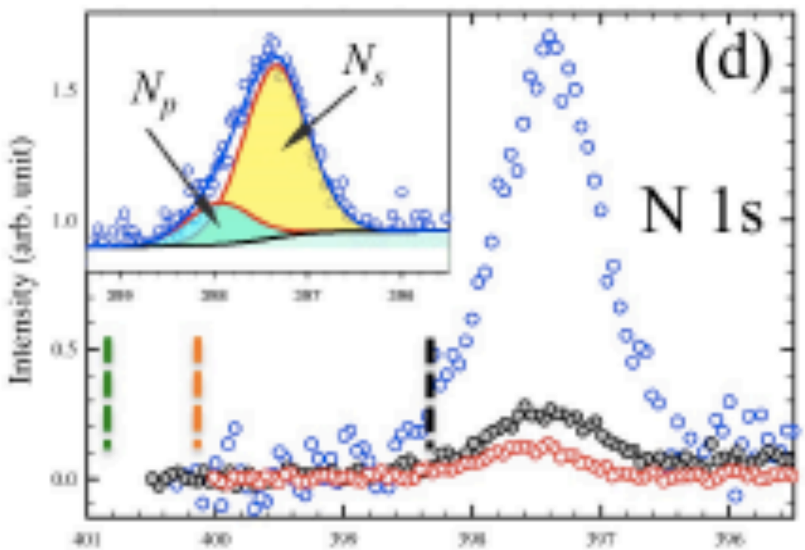


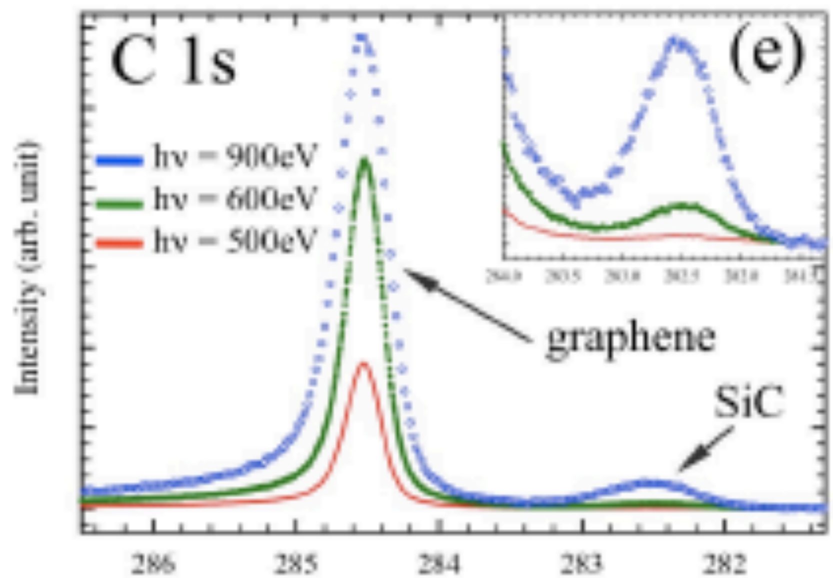
XPS analysis

- Nitrogen still present after graphene growth
- Carbon peak gives film thickness estimate

Variable Energy XPS: NO Graphene

$$E_{escaped\ electron} = h\nu - (E_{binding} + \phi)$$





Variable Energy XPS Analysis:
- Nitrogen is ***not*** in the graphene film
- Nitrogen is at the interface

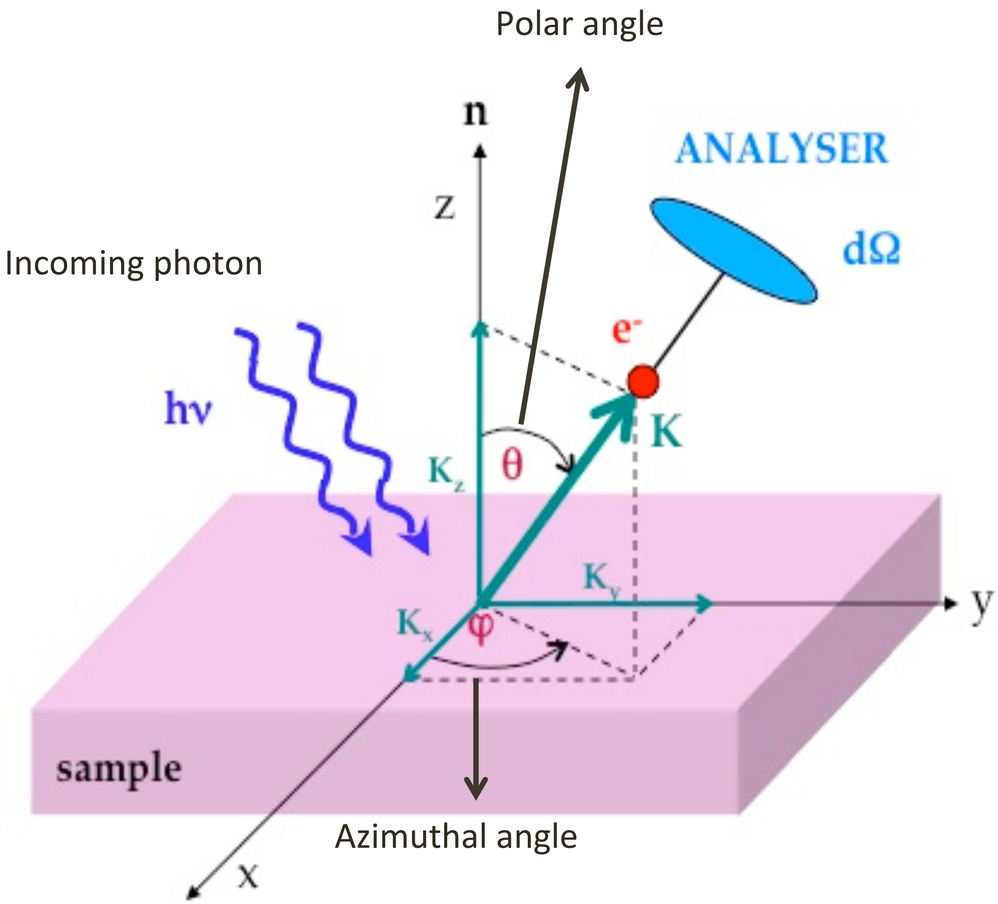
Angular Resolved Photoelectron Spectroscopy

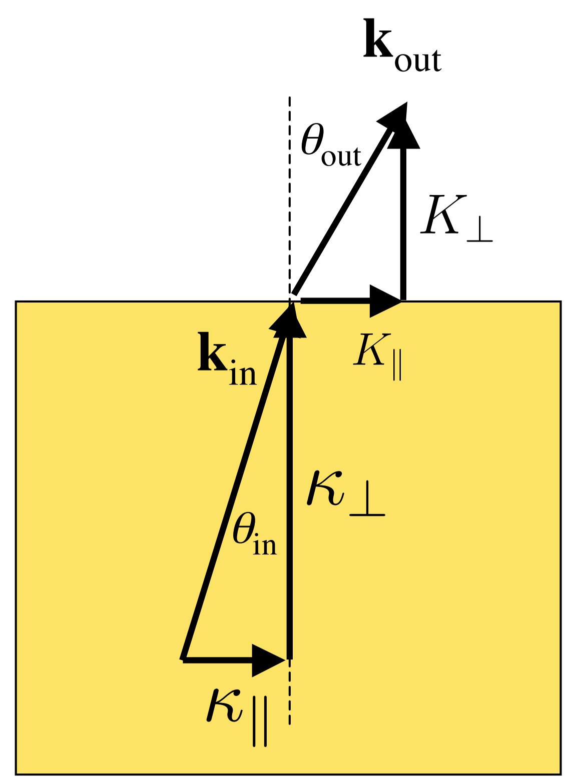
- For ARPES, we record solid angle and energy
- The parallel component of momentum is conserved

$$K_{\parallel} = \kappa_{\parallel}$$

$$E \equiv \frac{\hbar^2}{2m}(K_{\parallel}^2 + K_{\perp}^2)$$

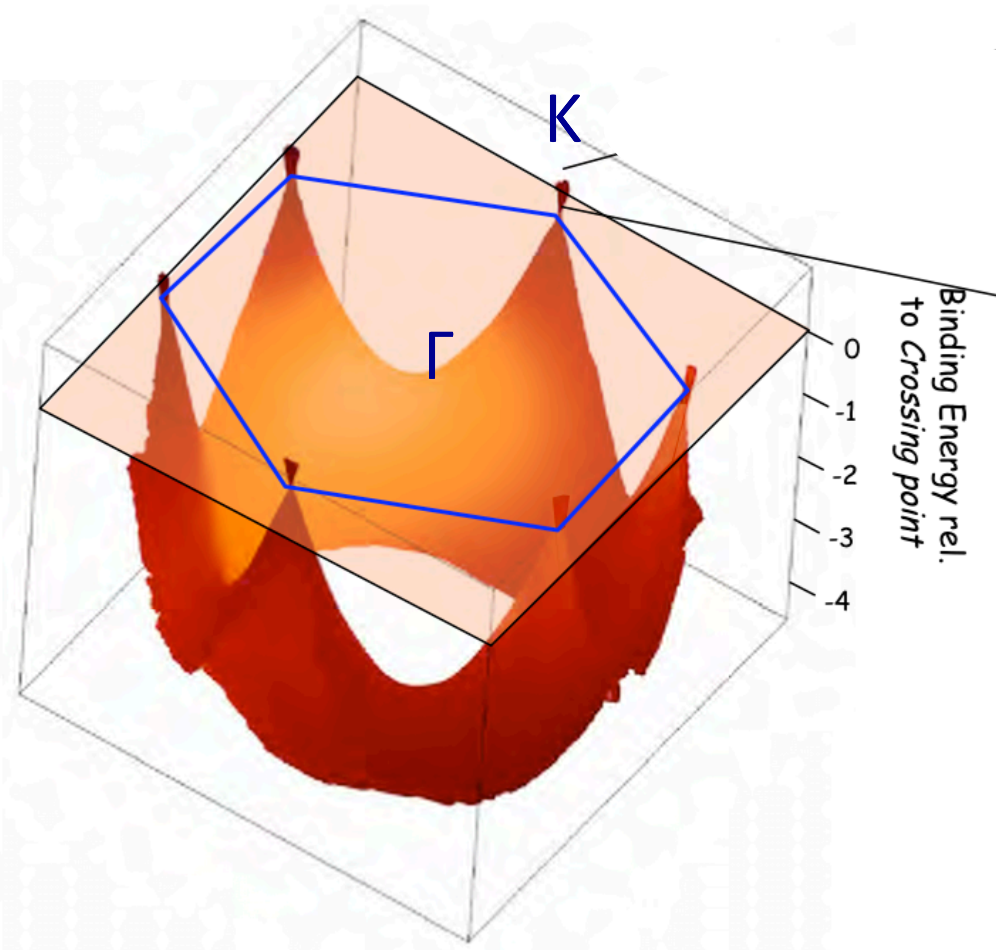
$$\sqrt{\frac{2mE}{\hbar^2}} Sin[\theta] = \kappa_{\parallel}$$





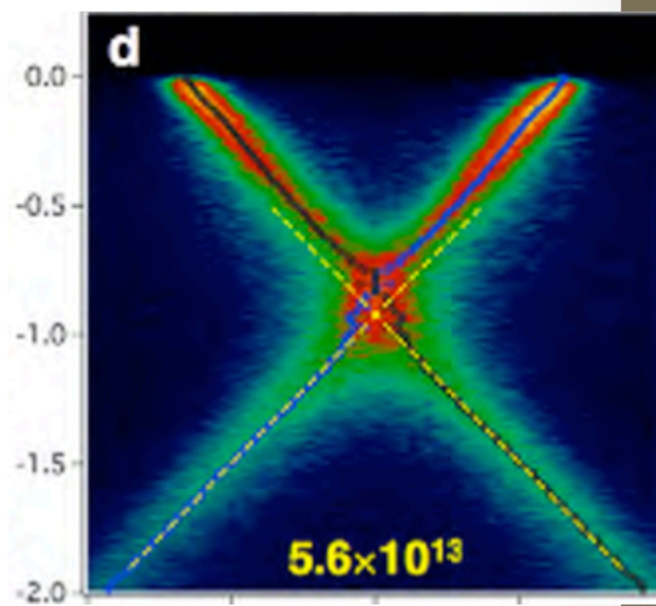
ARPES: Graphene

N-doped graphene



E-k surface for Brillouin zone

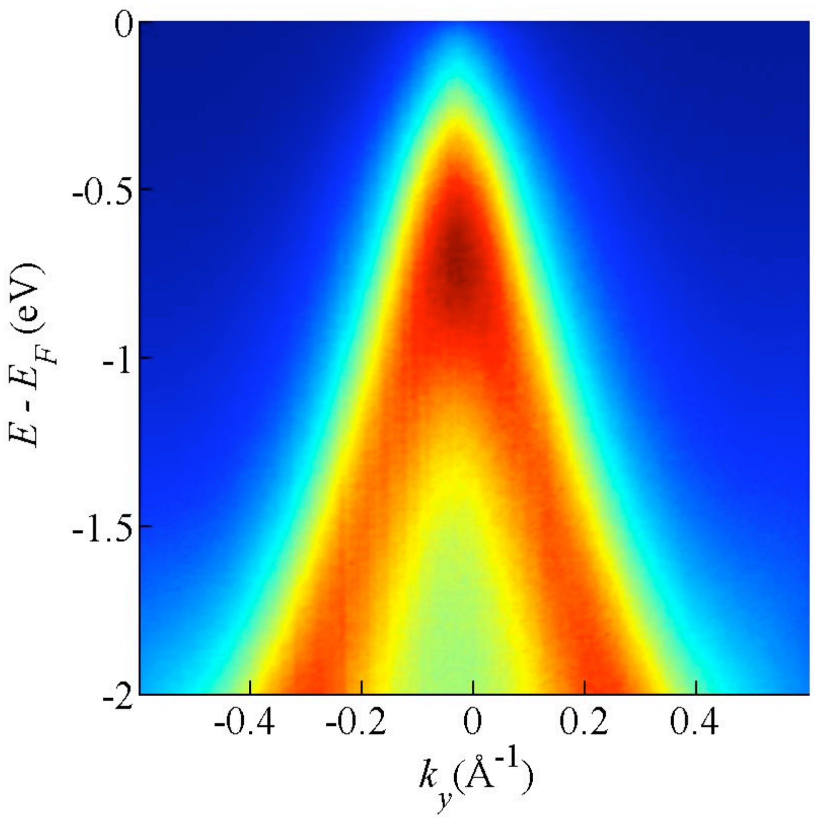
Typical K-point ARPES



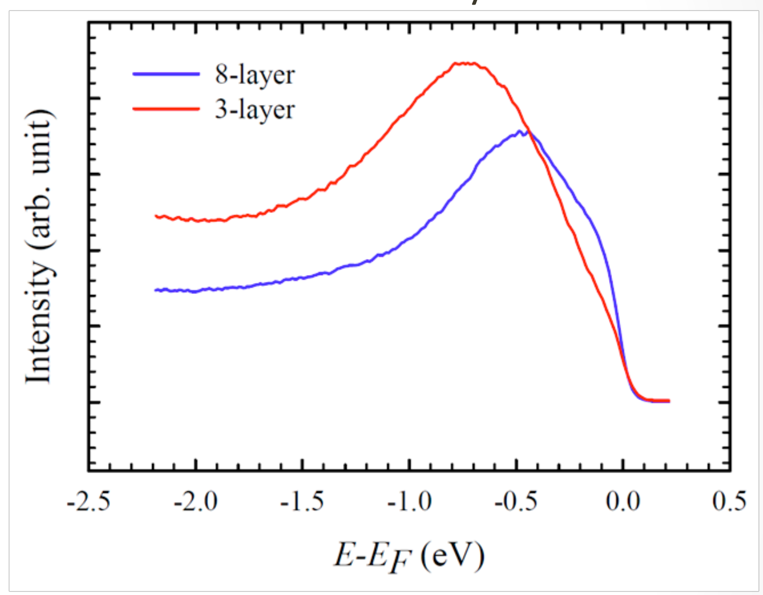
E-k relation for a slice of the BZ

ARPES: NO Graphene

NO Graphene



Cross-section of ARPES at K_y = 0



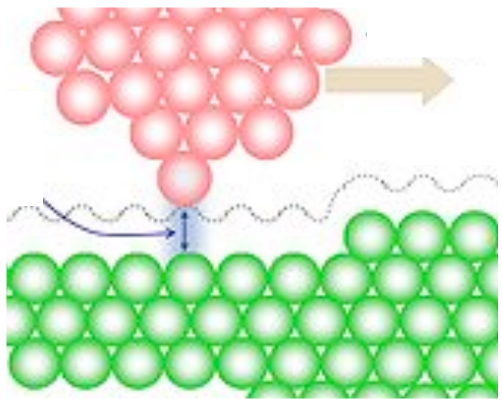
ARPES Analysis:

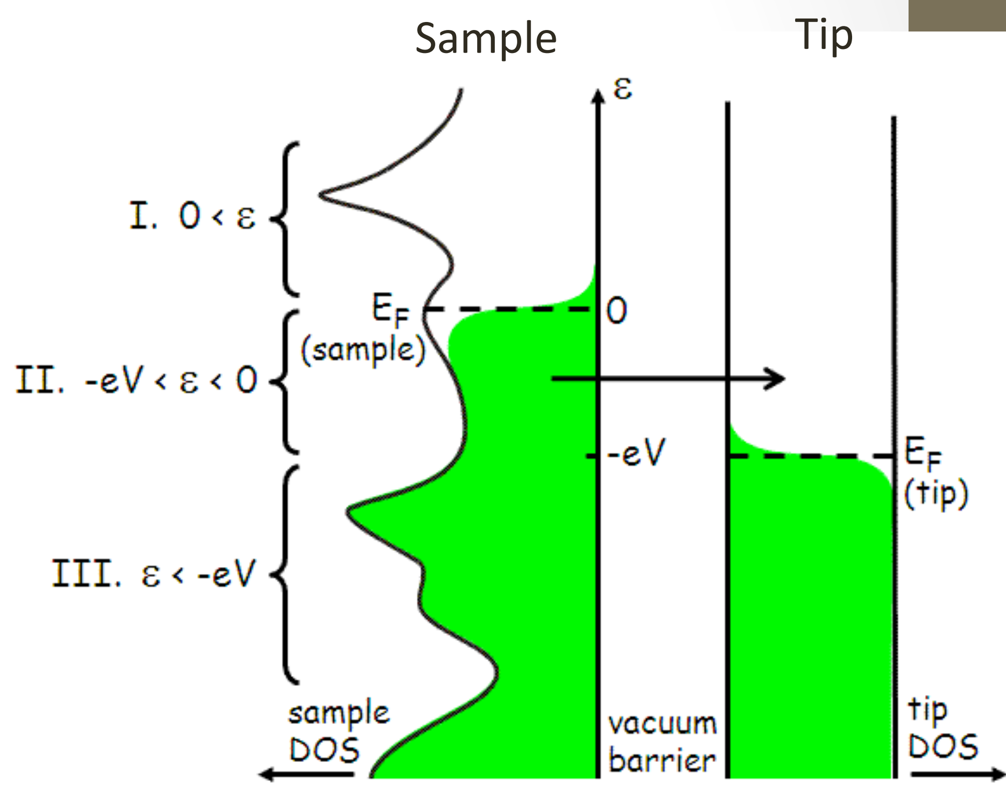
- NO Graphene has a bandgap
- Bandgap changes with thickness

STM: Scanning Tunneling Microscopy

Tip

Sample Surface

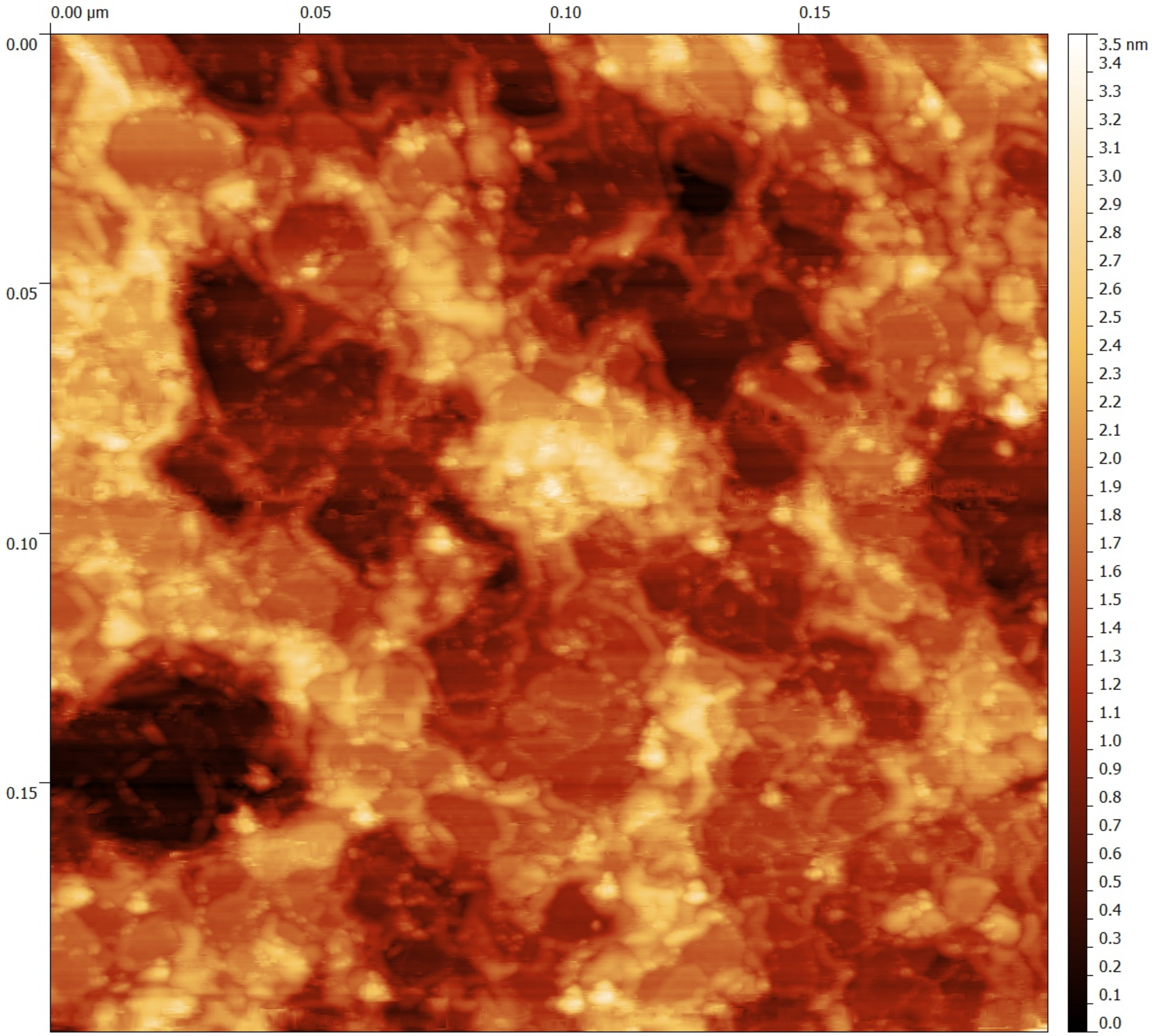




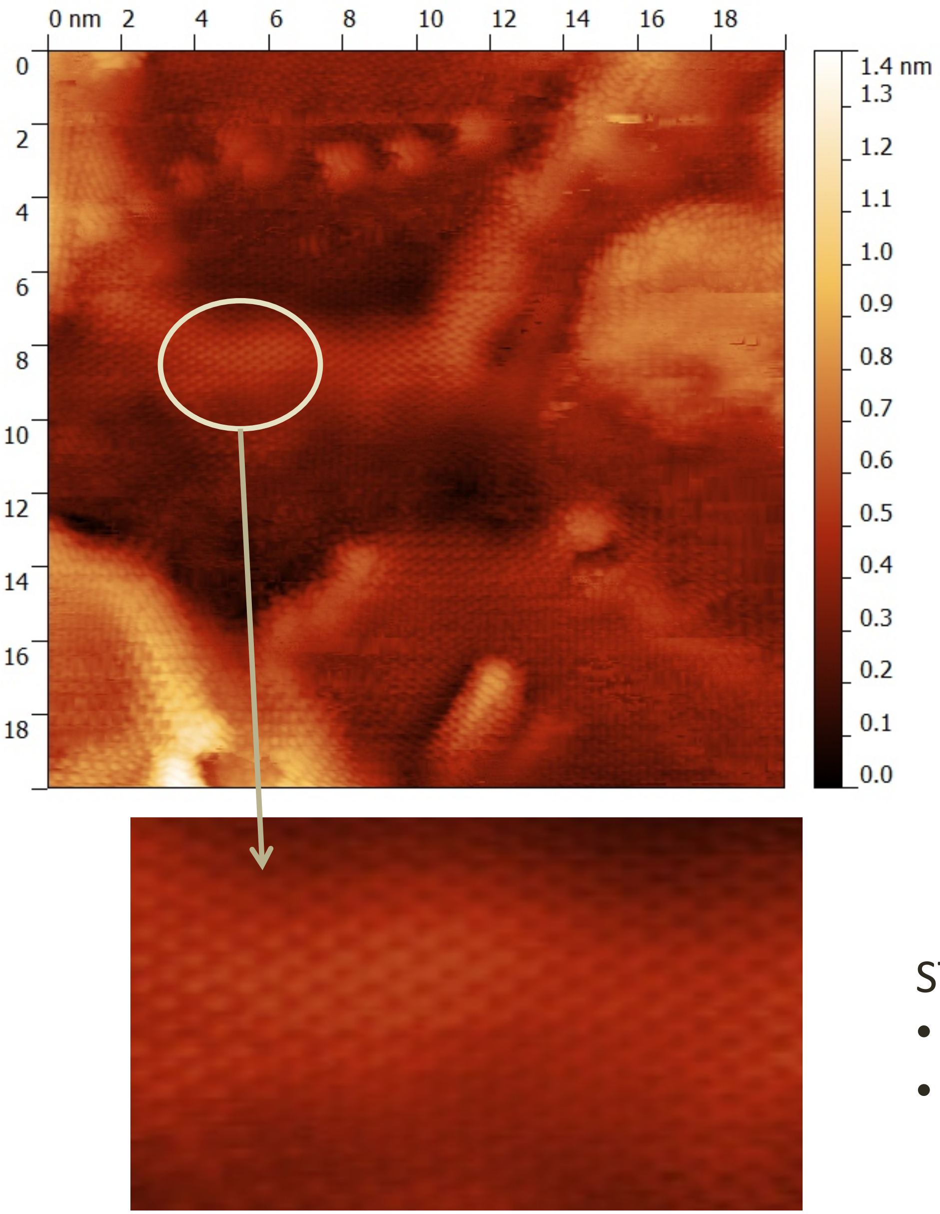
- STM tip and sample form a joint density of states
- Tungsten tip has a step function DOS with thermal fluctuation
- Tunneling current recorded for constant applied voltage

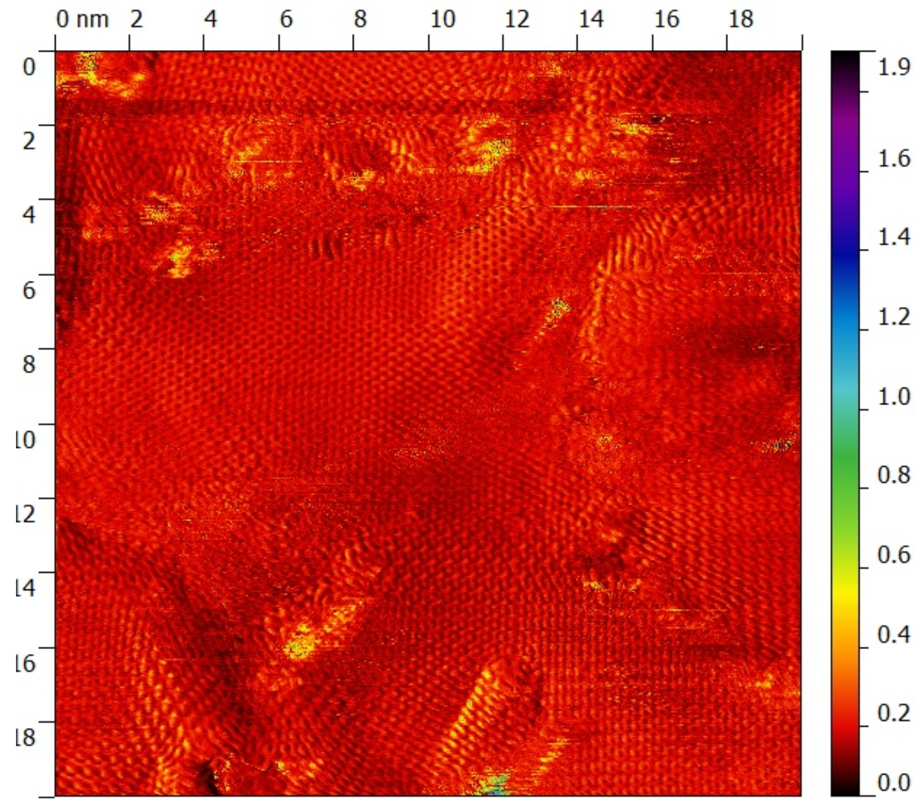
STM is scanning with negative voltage applied

STM: NO Graphene



STM: NO Graphene





STM Analysis:

- Film is continuous
- NO Graphene is buckled and strained

Conclusions

- By treating SiC with the NO process prior to graphene growth, we can grow buckled graphene with a band gap
  - NO nitrogen has been substitutionally accepted into the graphene film
  - The film has a band gap which is a function of film thickness
  - The band gap is a result of either strain from severe buckling, or electron confinement from the severe buckling and disorder

Future Directions

- Study NO graphene and change nitrogen coverage
- Work with implantation, to introduce new dopants
- Grow on insulating substrates to analyze electronic properties
- Exfoliate graphene for analysis in TEM

Raman Spectroscopy

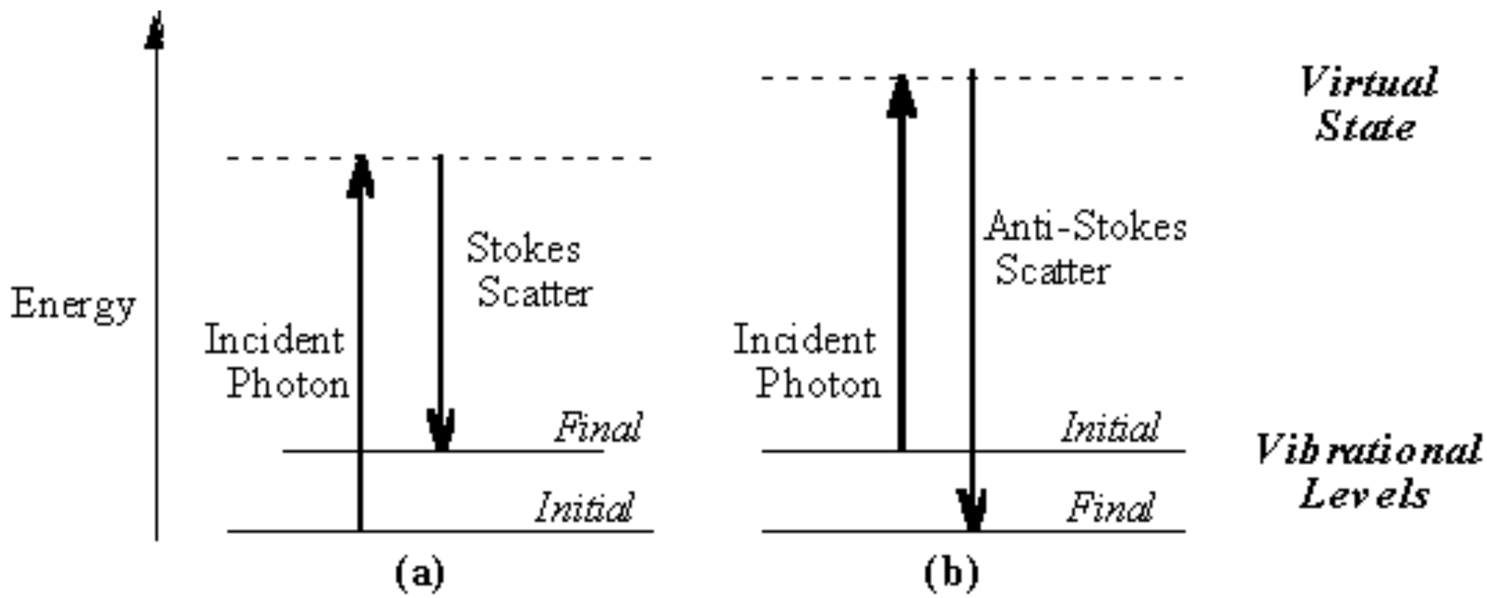
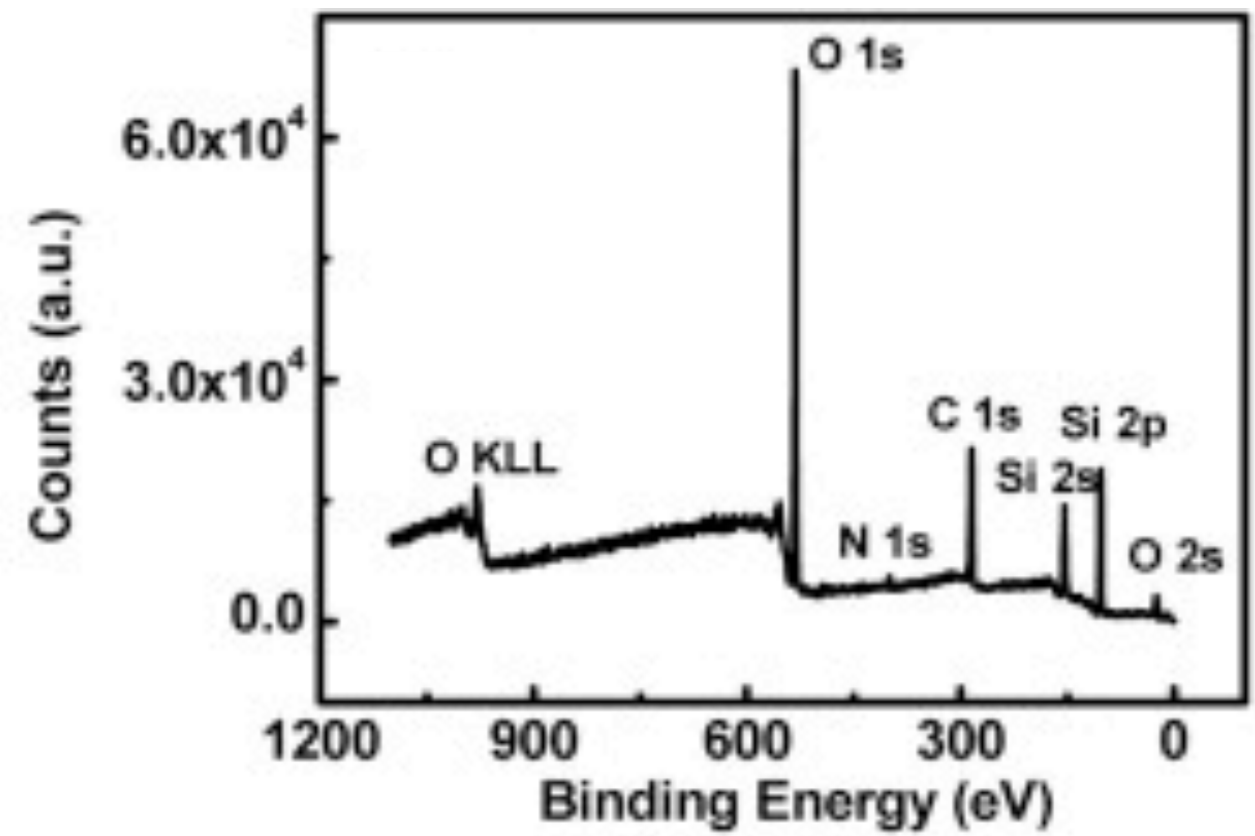


Figure 1. Energy level diagram for Raman scattering; (a) Stokes scattering, (b) anti-Stokes scattering

- Incident photon is absorbed by a vibrational state
- Photon is emitted after relaxation or excitation of vibrational state
- The photon has been inelastically scattered and looses or gains energy

XPS on Graphene



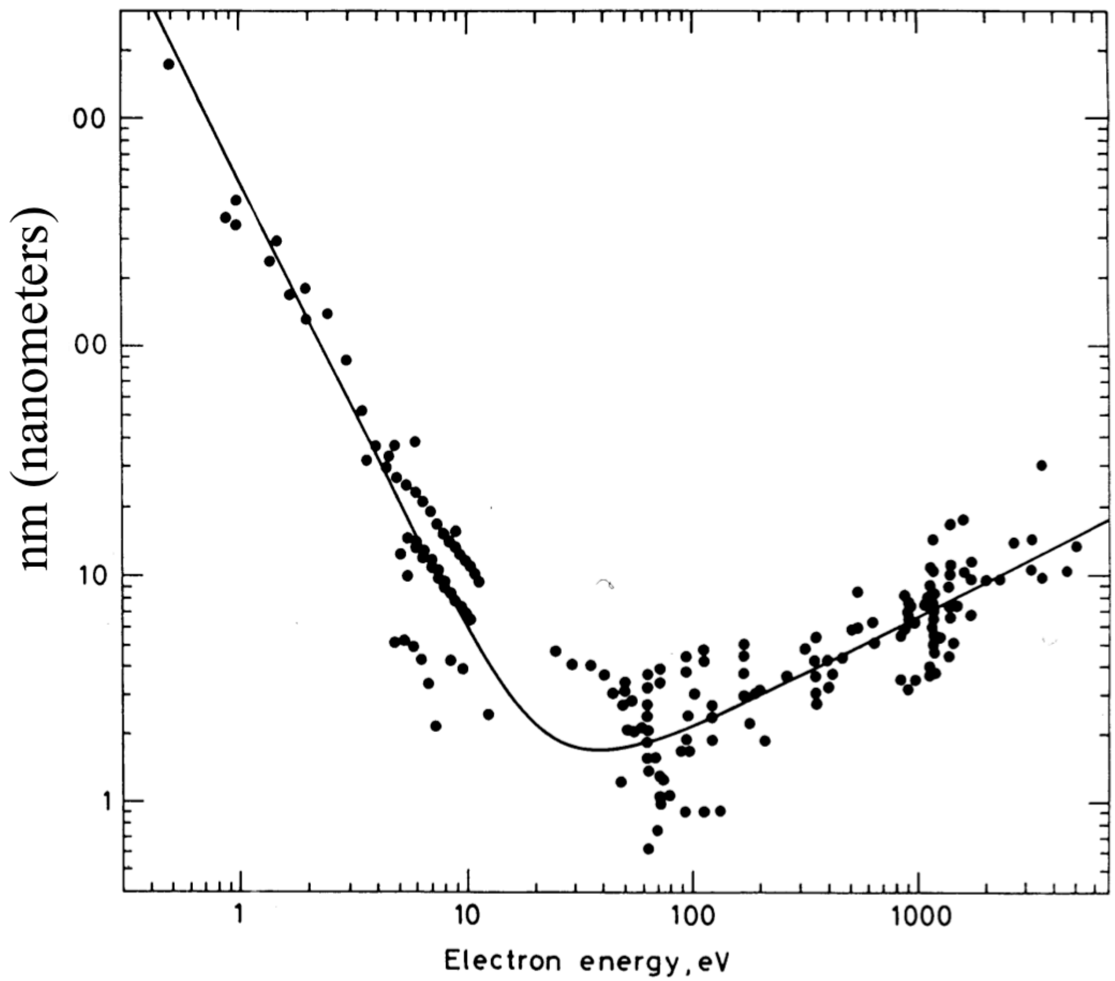
CVD Graphene on Cu foil with ammonia; exfoliated to SiO2

Gao, Carbon 50 12 pp. 4476-4482 (2012).

Variable Energy XPS

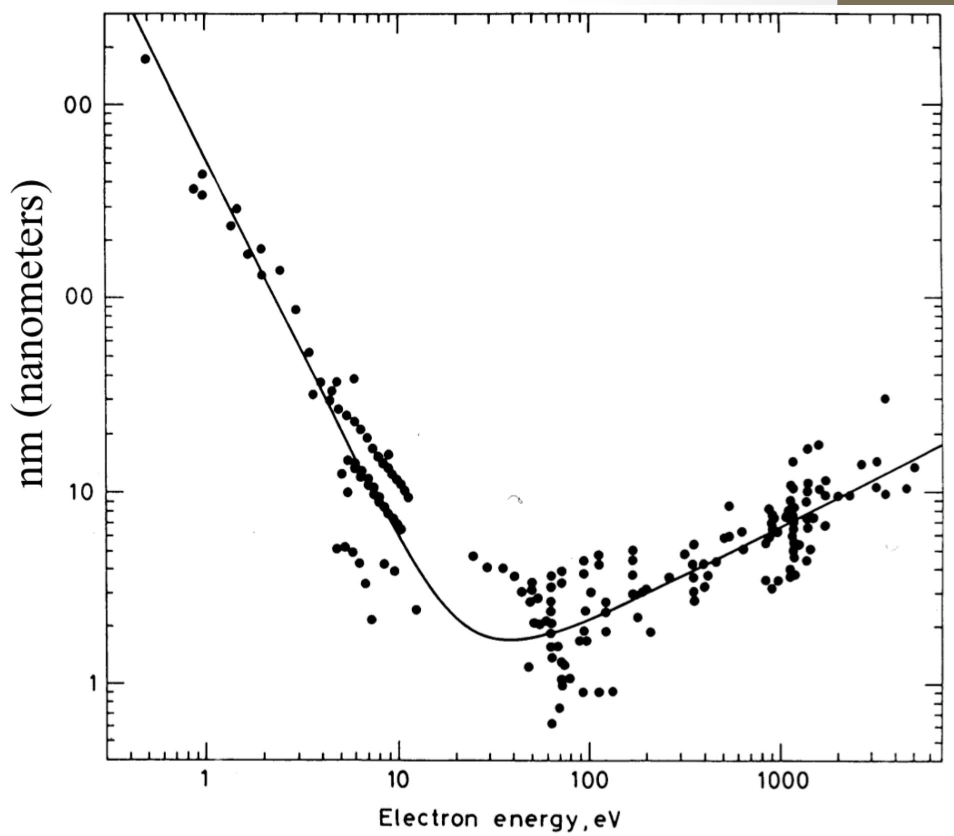
$$E_{photoelectron} = \hbar\omega - (E_{binding} + \Phi_{detector})$$

Inelastic Mean Free Path λ



XPS overview: Electron Escape Length

$$E_{photoelectron} = \hbar\omega - (E_{binding} + \Phi_{detector})$$



As may be noted, when the incident X-ray energy hv is on the order of the binding energy, the energy of the escaping electron is less, which corresponds to a very small IMFP (see graph) so you are probing with much greater surface sensitivity.

Inelastic Mean Free Path (λ, IMFP):

$$1/\lambda = (-\frac{dE}{dx})/(\hbar\omega_p)$$
$$= (-\frac{\omega_p e^2}{\hbar\nu^2}) ln[\frac{2m\nu^2}{\hbar\omega_p}]$$

- The photo-ionization cross-section σ: probability of an electron being ejected by an incident photon
  - To derive:
  - Fermi's golden rule, (using plane wave for free electron, square well wavefunction for bound state to first approximation) gives rate of transition between an initial and final state, and incorporates the DOS available.

$$R = | < \psi_f | H' | \psi_i > |^2 * \frac{2\pi\rho(E)}{\hbar}$$

  - Using parabolic energy, E = hbar^2 k^2/ wm, and DOS = dk/dE * unit of size

$$R = \frac{4e^2\varepsilon^2\hbar}{m}\frac{E_B^{3/2}}{E^{7/2}}$$

The photon flux: $F = \frac{c\varepsilon^2}{2\hbar\omega}$

Ionization cross-section: $\sigma = \frac{R}{F} = \frac{8e^2\hbar}{mc}\frac{E_B^{3/2}}{E^{5/2}}$

:ε^2 Electric field, e, electron charge, E_B, binding energy of square well initial wavefunction.

Other doping goals: include dopants via Implantation
Implantation TRIM modelling overview