Wide Bandgap Semiconducting Graphene by Nitrogen Seeding

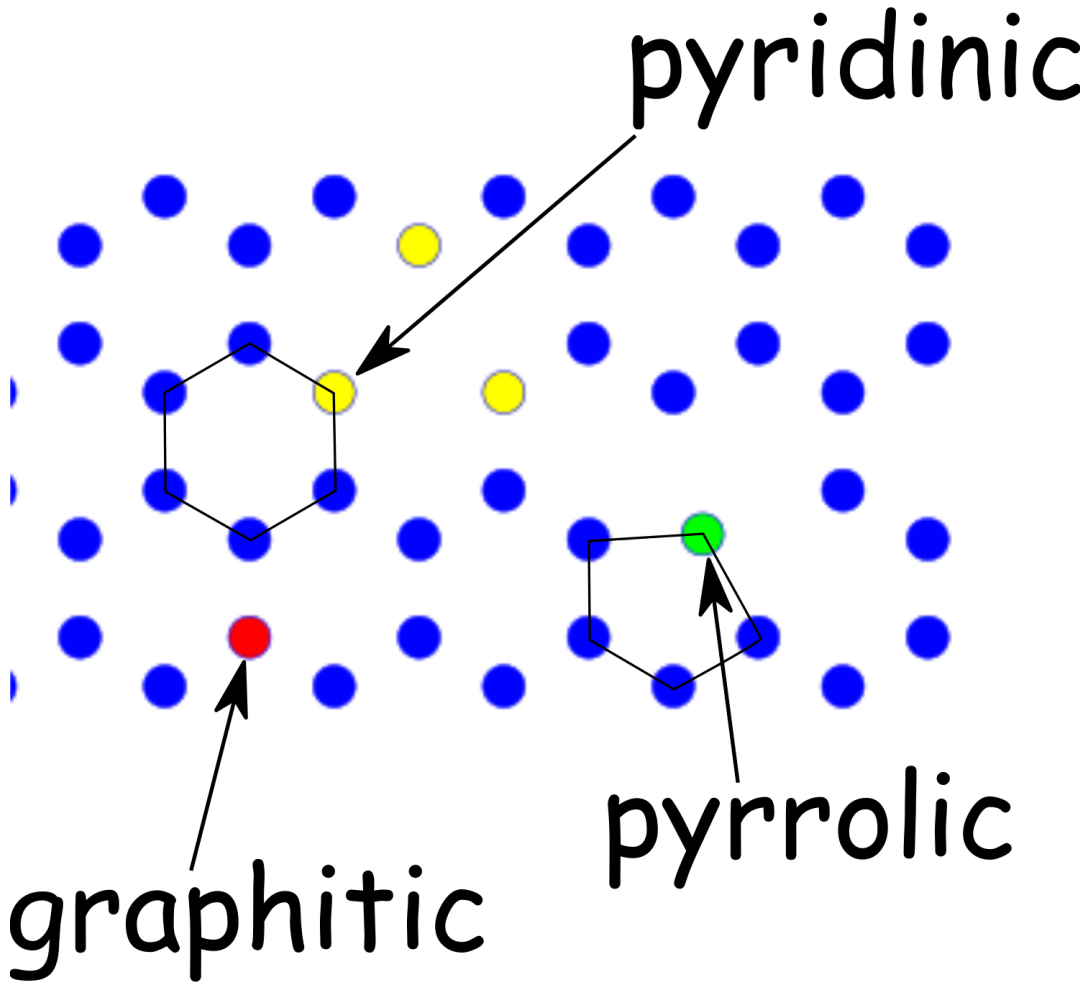
E.H. Conrad and F. Wang
Georgia Institute of Technology

G. Liu and L.C. Feldman
Rutgers University

S. Rothwell and P.I. Cohen
University of Minnesota

Supported in part by the NSF (DMR)

Previous attempts to incorporate N into graphene

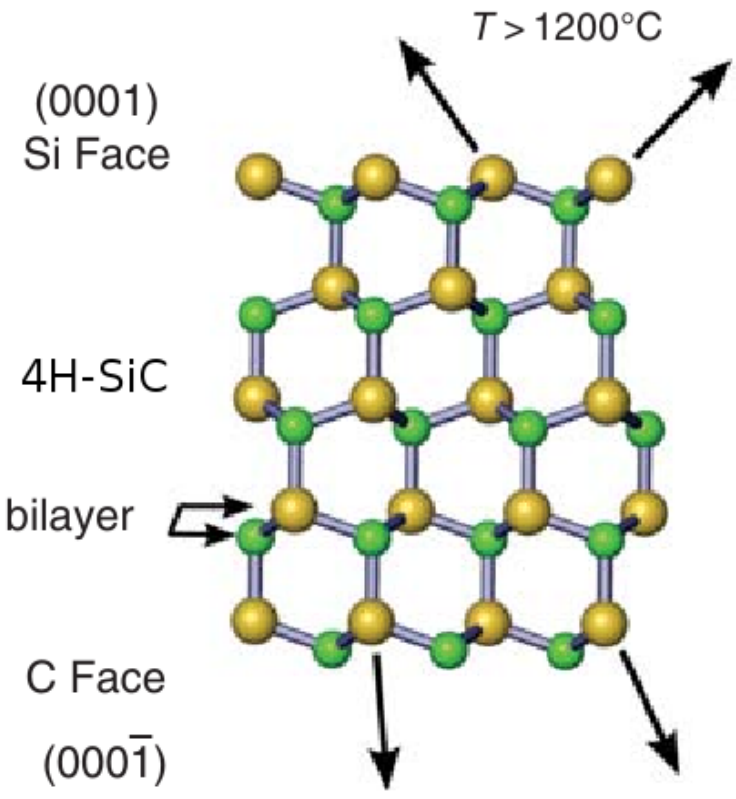


Initial Goals

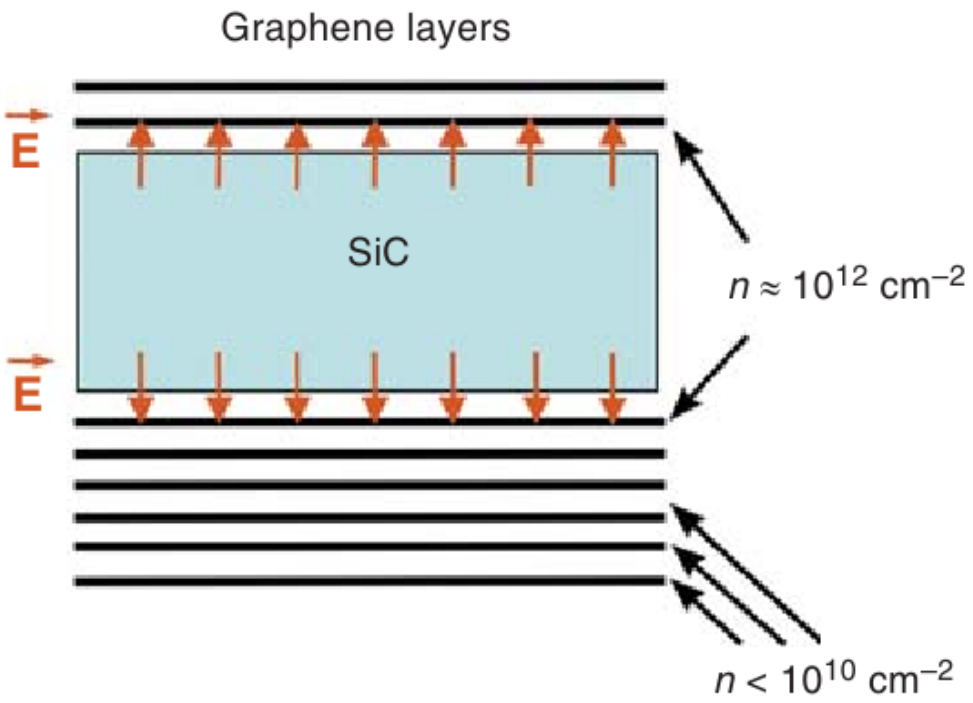
1. Ion implant or otherwise treat SiC to have a high impurity concentration at the surface
2. Grow graphene on SiC
3. Characterize impurity incorporation and their properties in graphene

Main Result: Graphene grown on the carbon face of SiC with a surface coverage of 3 at. % of nitrogen has a bandgap of 0.7 eV.

Few Layer Graphene on carbon face-SiC

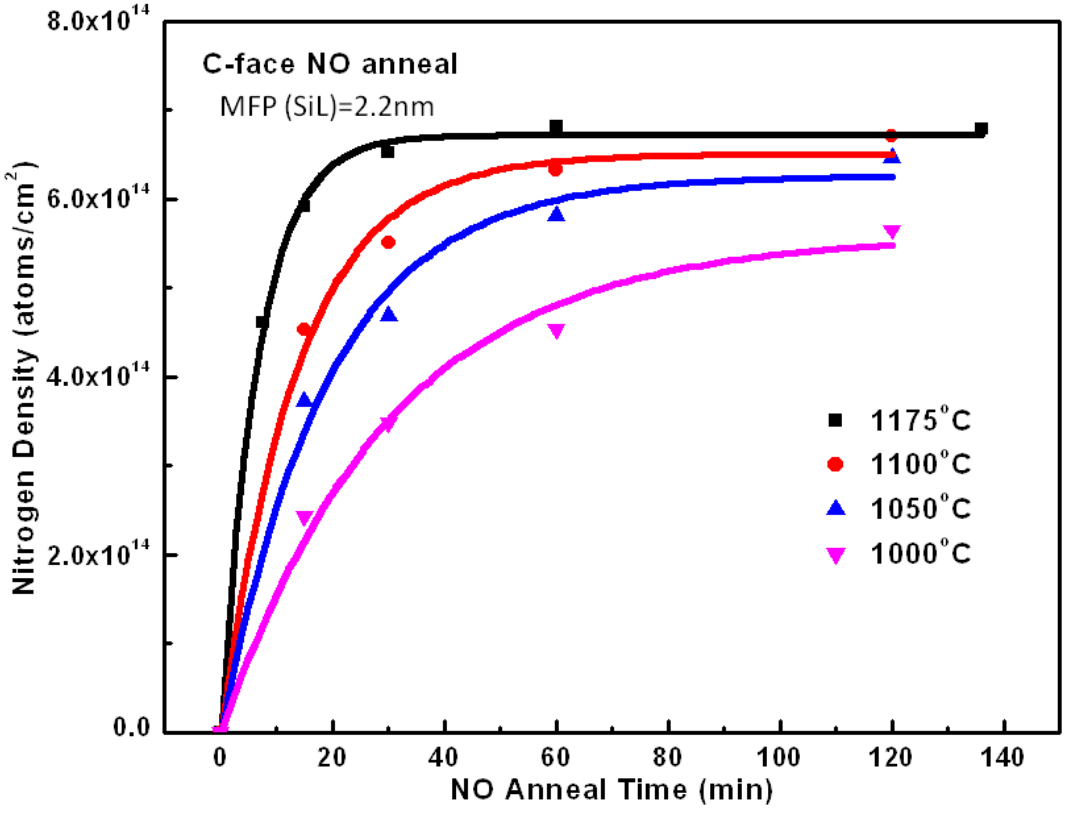


P.N. First et al. MRS Bulletin 35 (2010) 296

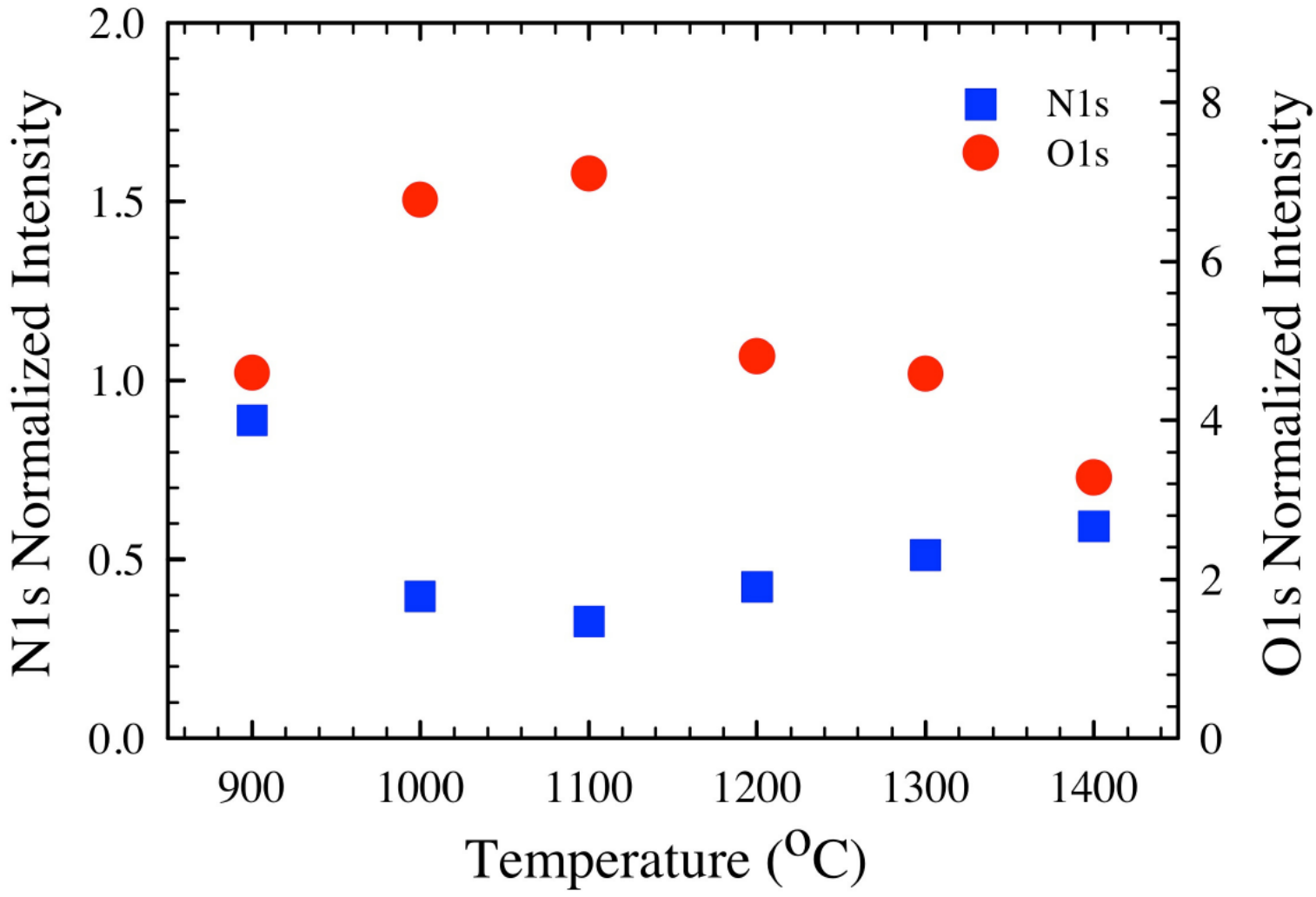


The graphene layers are relatively uncoupled and exhibit the Dirac cone band structure.

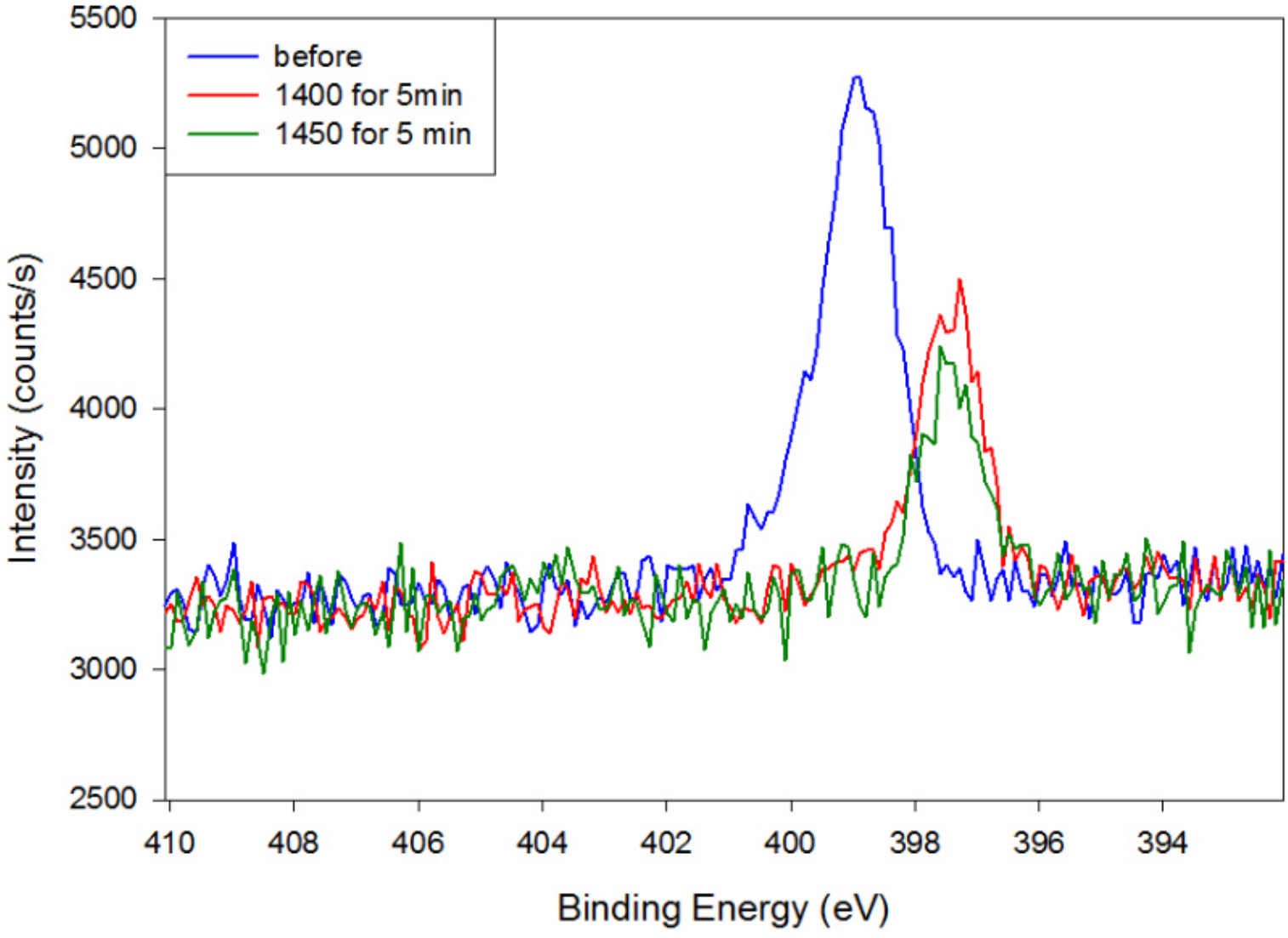
N uptake


C-face NO anneal
MFP (SiL)=2.2nm
Nitrogen Density (atoms/cm^2)
8.0x10^{14}
6.0x10^{14}
4.0x10^{14}
2.0x10^{14}
0.0
0
20
40
60
80
100
120
140
NO Anneal Time (min)
1175°C
1100°C
1050°C
1000°C

N coverage vs temperature



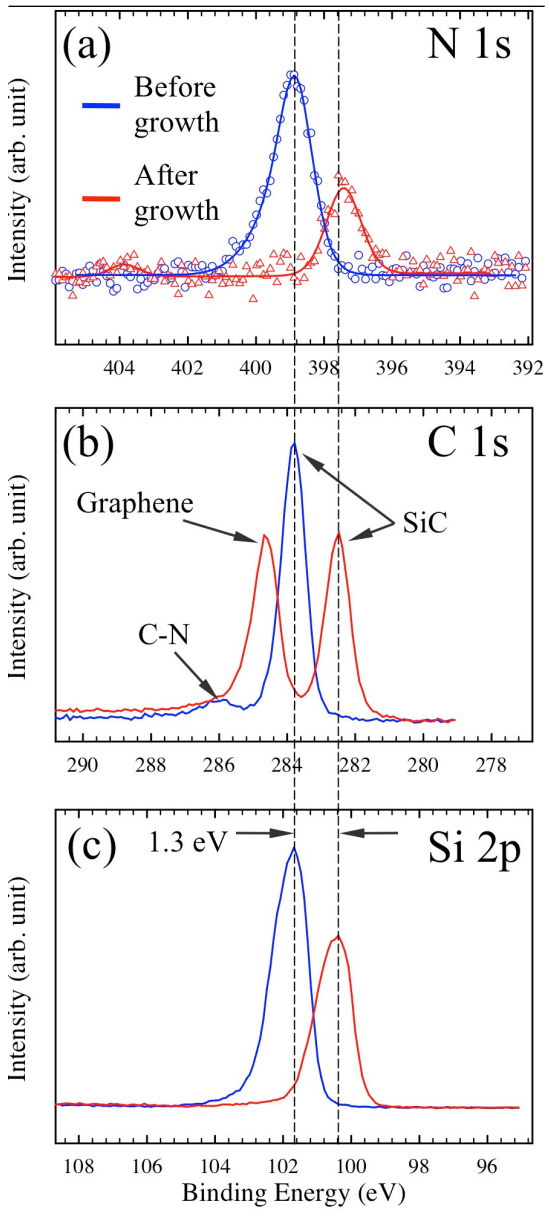
N 1s XPS


before
1400 for 5min
1450 for 5 min
Intensity (counts/s)
5500
5000
4500
4000
3500
3000
2500
410
408
406
404
402
400
398
396
394
Binding Energy (eV)

N incorporation by nitridation

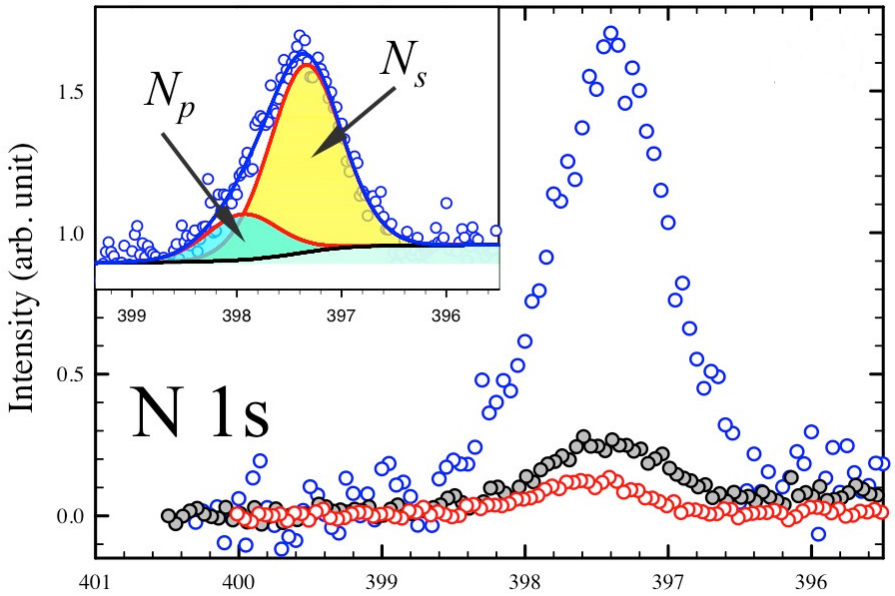
1. NO treatment of SiC for about 1h at 30 Torr
2. HF removal of oxide
3. XPS characterization of remaining SiC shows a very robust 3 at. % of N on either face of SiC
4. Heating to graphene growth temperatures removes the N on the Si face but not on the N face (based on XPS)
5. XPS of graphene grown on C-SiC with 3 at. % of adsorbed N shows that N remains at the SiC/graphene interface
6. Characterize with XPS, Raman, STM, and ARPES
7. Distributed sources of N in the SiC, larger N coverages, other impurities, or incorporation into graphene on the Si-face of SiC have not yet been examined.

Evidence for a new N site



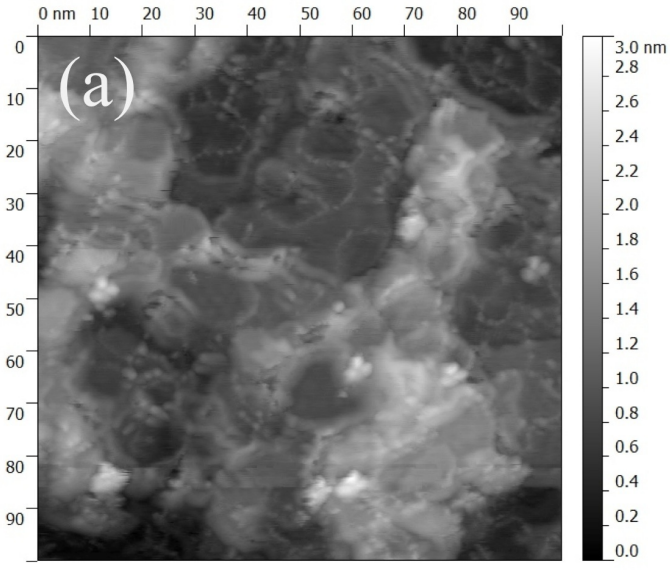
- A work function shift for all peaks occurs after graphene growth
- The N 1s peak at 397.5 has not been observed in other attempts to incorporate N
- N 1s peak in this energy range is usually associated with sp^3 bonds

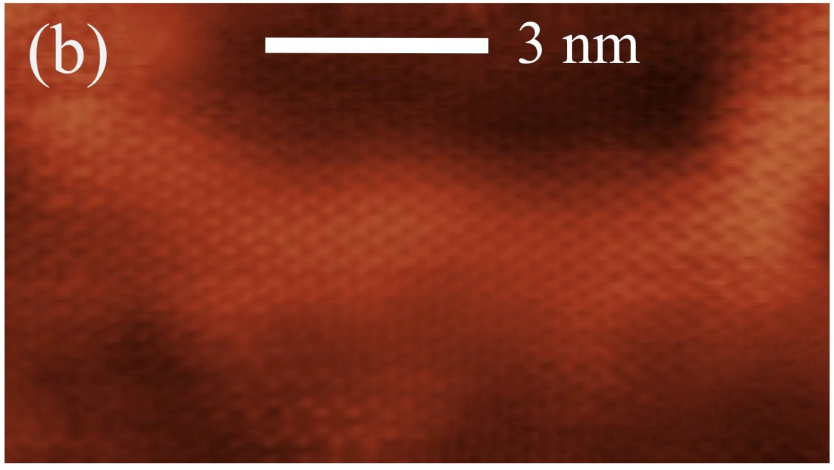
Nitrogen bonding in 3 layer graphene



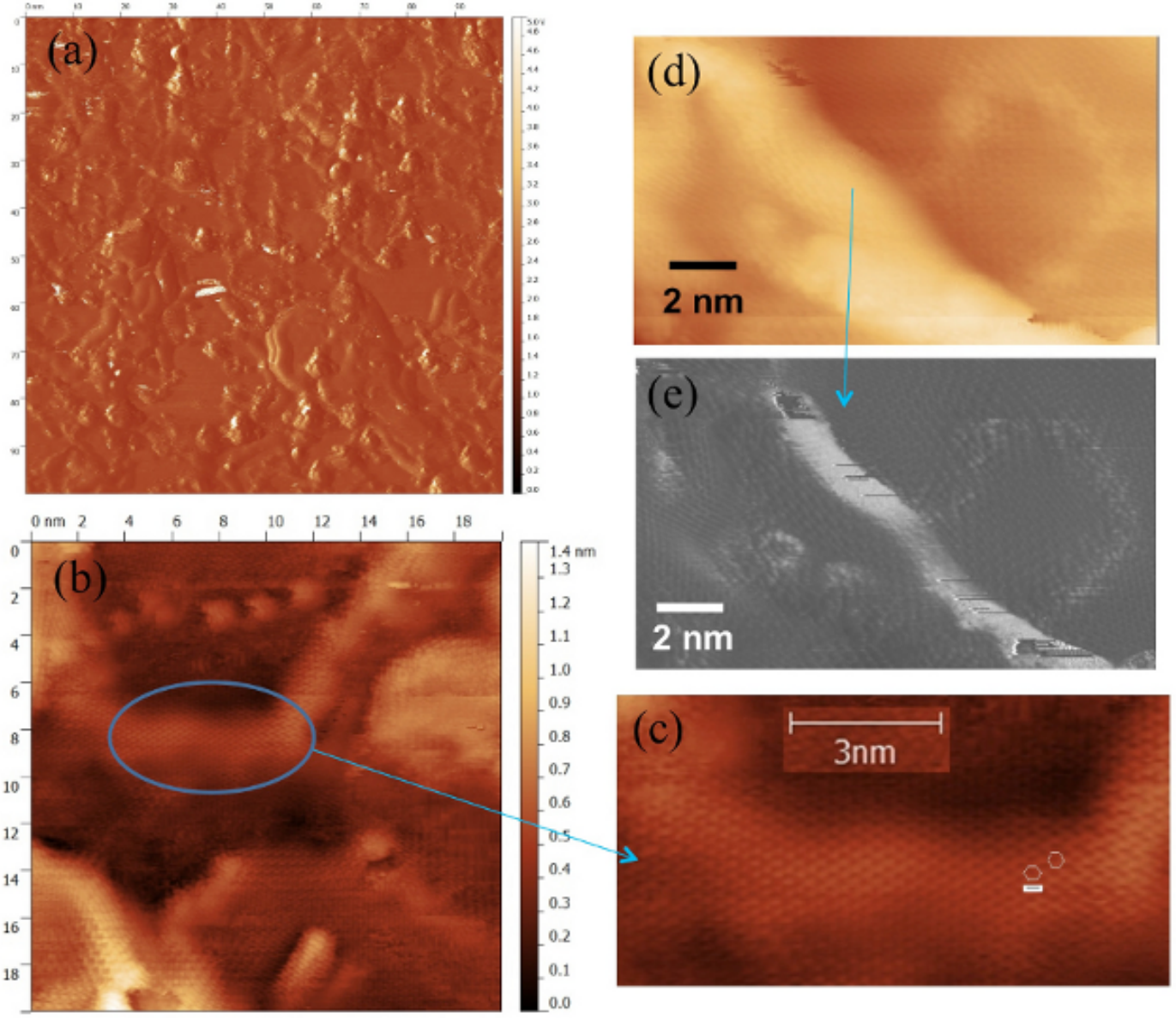
- The N peak in the inset at 398 eV is associated with N–SiC bonds
- The main figure shows N spectra taken at 3 different photon energies. The most surface sensitive (low photon energies) show low coverage of N
- Taken together we associate the N peak with N at the SiC/graphene interface

STM


0 nm 10 20 30 40 50 60 70 80 90
0 10 20 30 40 50 60 70 80 90
(a)
3.0 nm
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0


(b)
3 nm

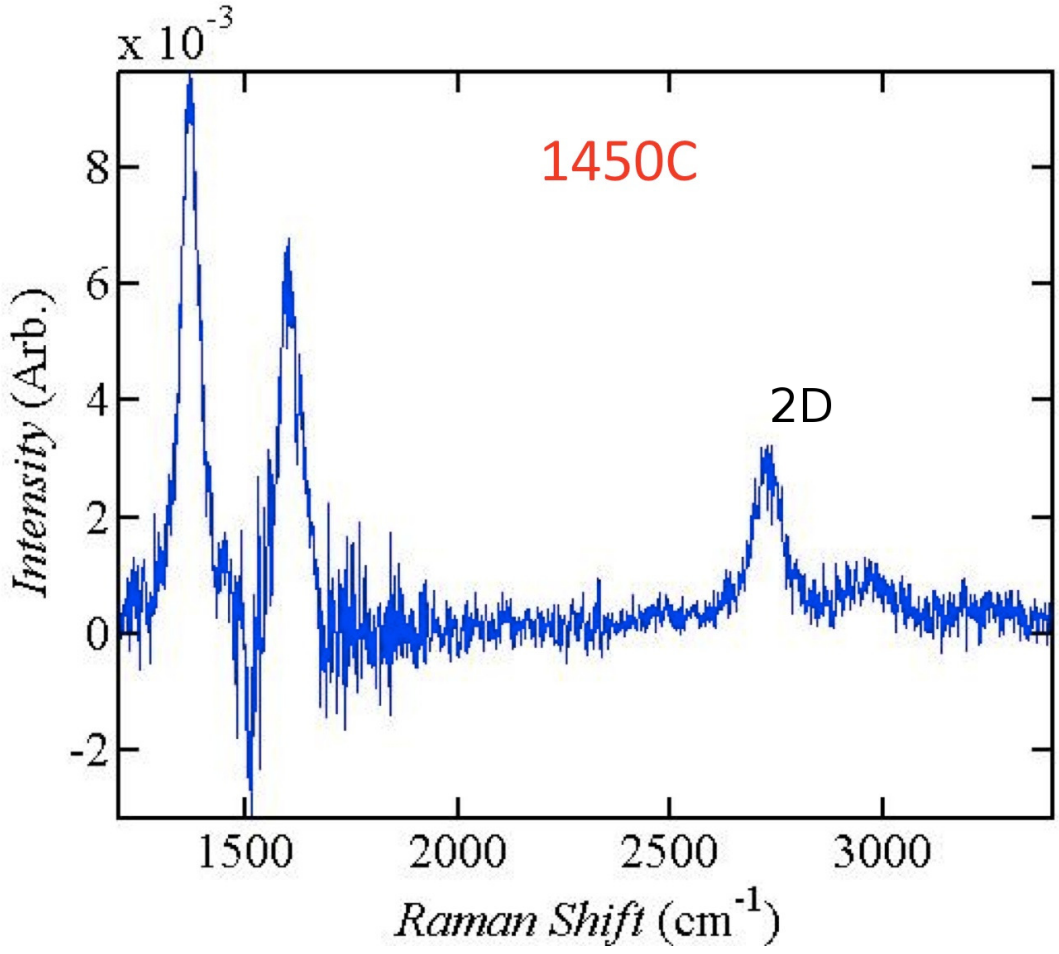
STM results


(a)
(b)
(c)
(d)
(e)
2 nm
2 nm
3nm
0 nm 2 4 6 8 10 12 14 16 18
1.4 nm
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

STM confirms finite size effects

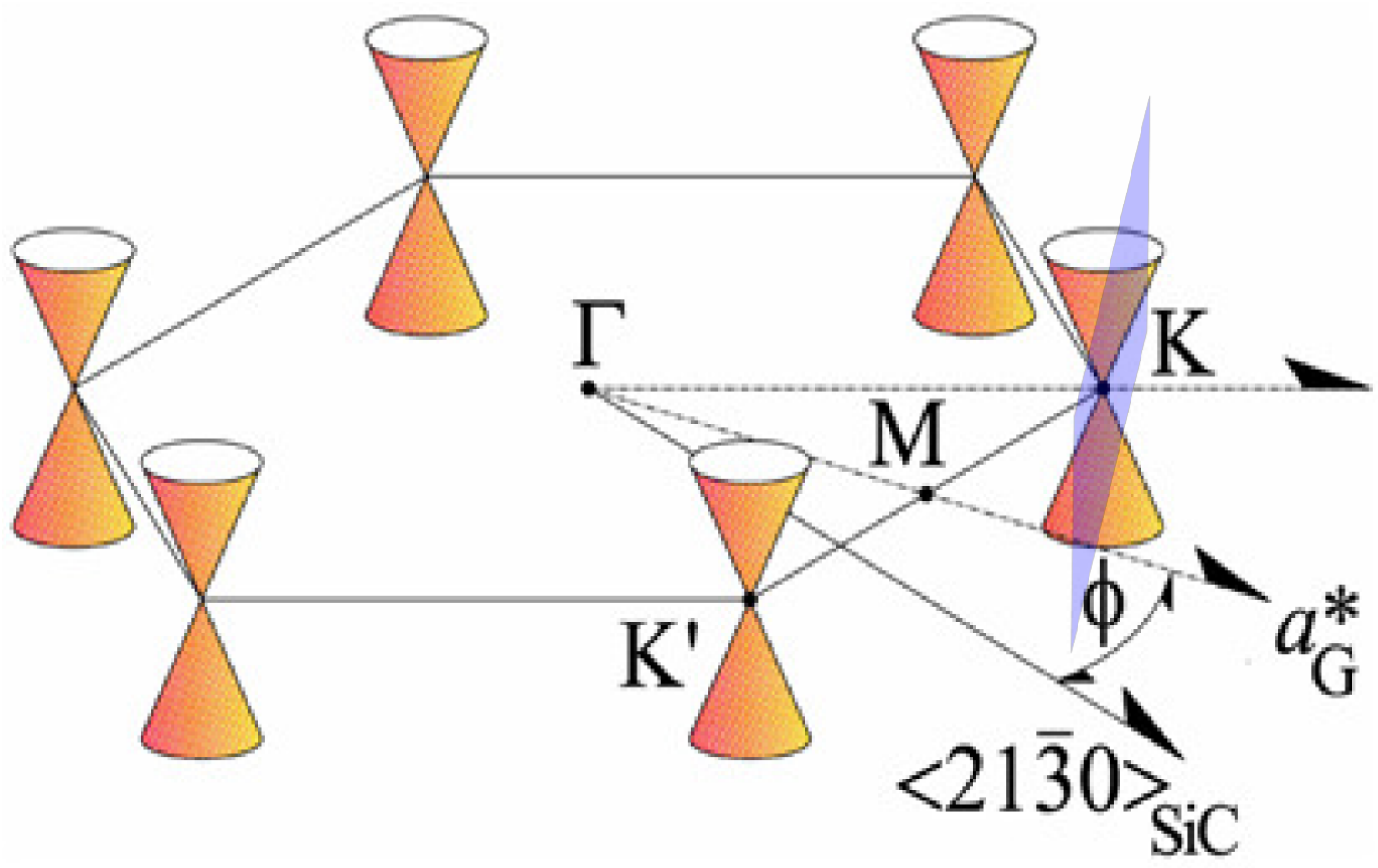
1. The STM results (next slide) do not show evidence of N substitutional impurities in atomic resolution images (unlike CVD results)
2. Overall film shows many folds with an STM height greater than 3 ML of graphene
3. The graphene lattice bends smoothly over these folds
4. The mean separation of the folds corresponds to the measured bandgap

Raman results

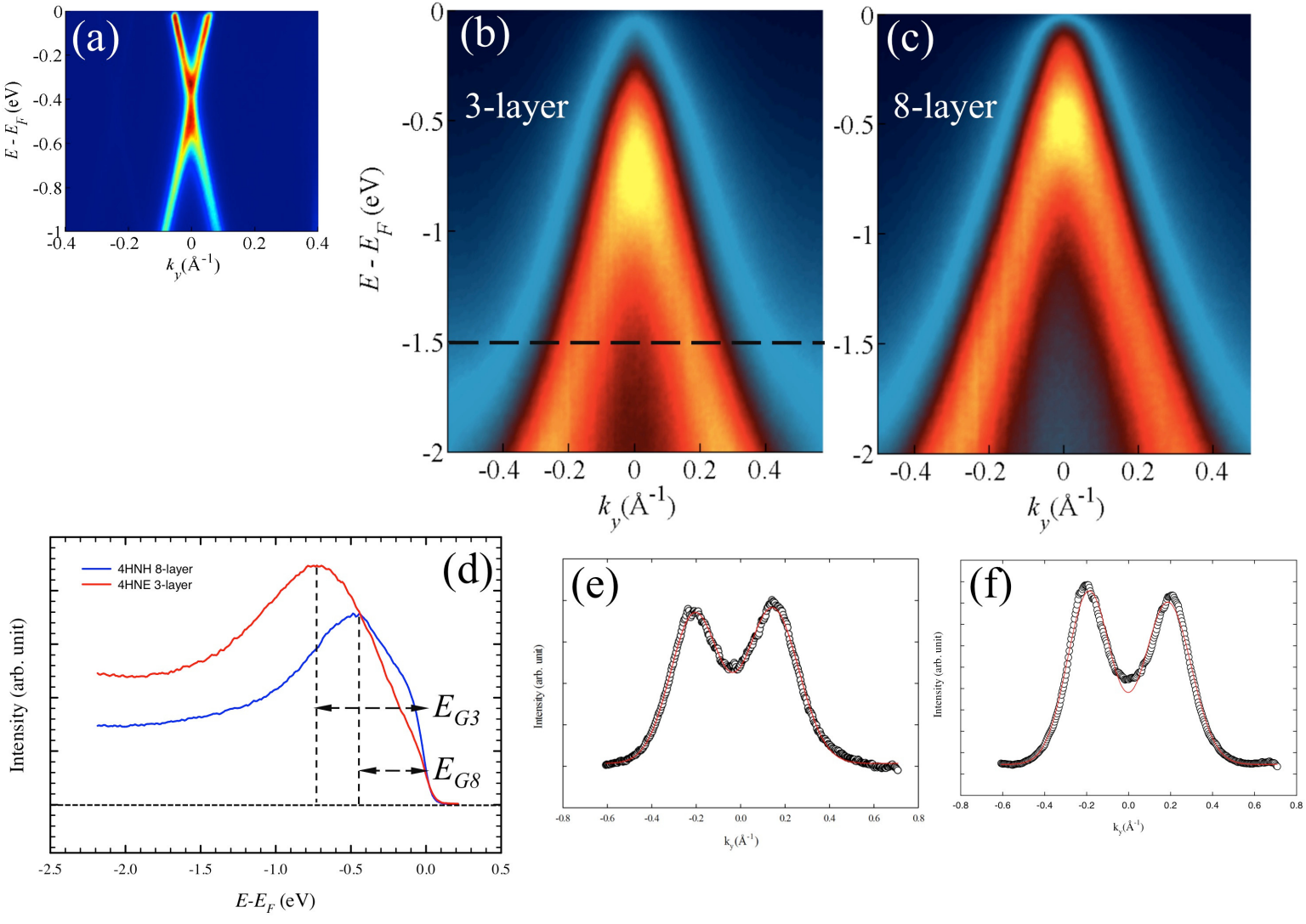


Good quality graphene is obtained as evidenced by the 2D peak – even in the presence of nitrogen at the interface.

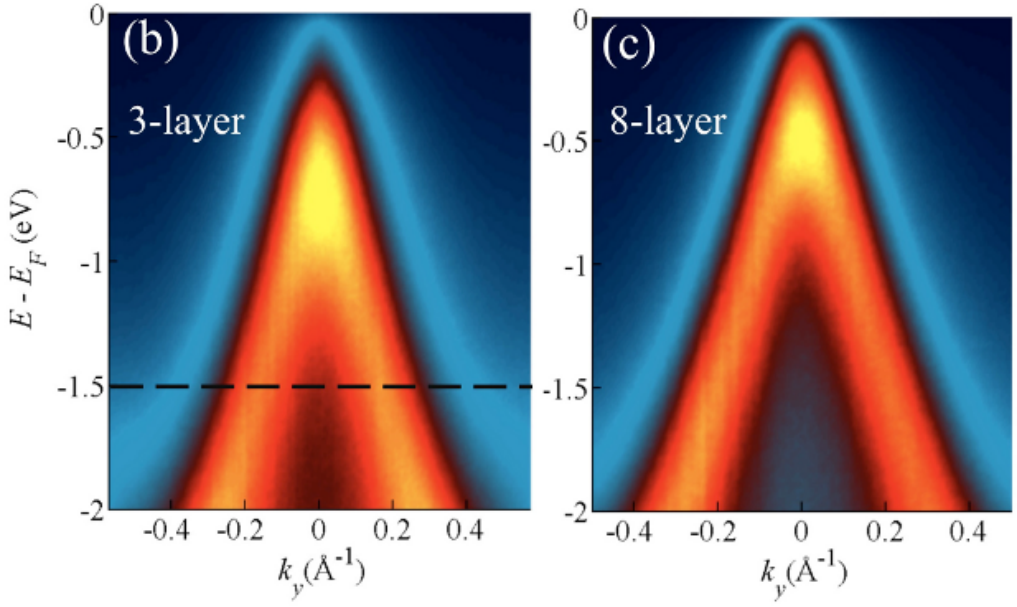
Ideal Graphene Band Structure



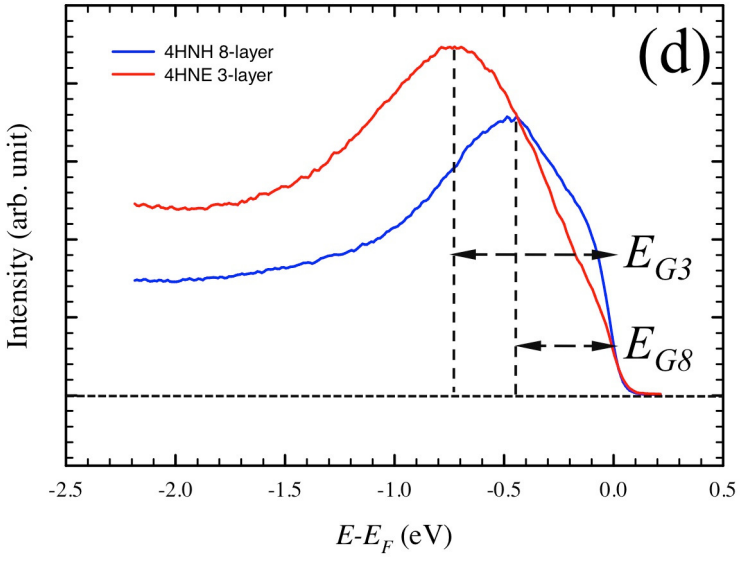
Photoemission measurements



Photoemission Measurements of E_g

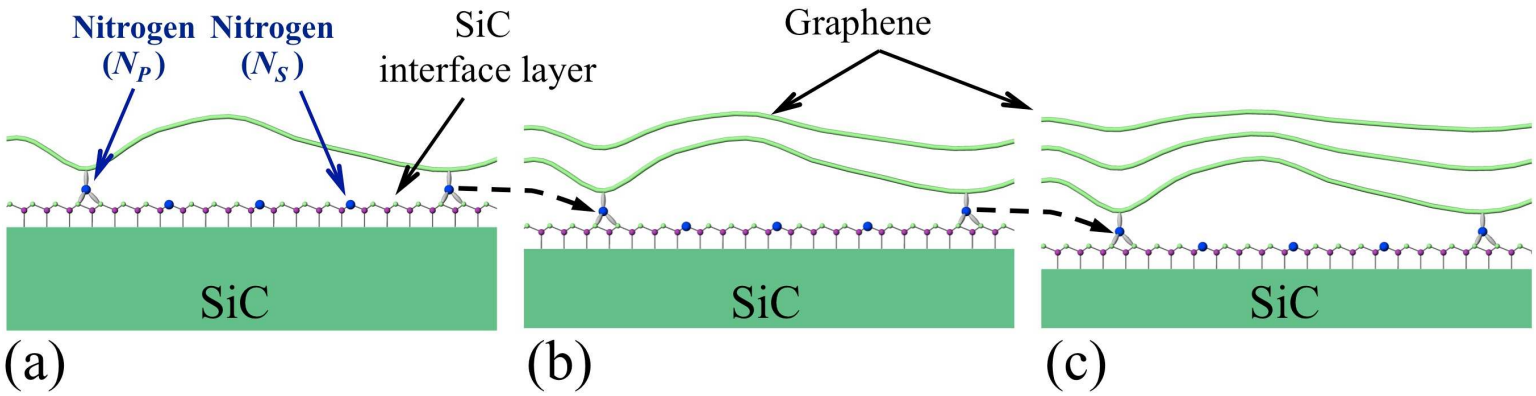


ARPES measurement of Dirac cones from 3-layer and 8-layer graphene.



The peak in the intensity becomes more negative, indicating a bandgap, corresponding to 0.7 eV.

Model


Nitrogen (N_P)
Nitrogen (N_S)
SiC interface layer
Graphene
SiC
SiC
SiC
(a)
(b)
(c)

Mechanism?

- N interfacial bonding affects the $\pi-$ bonding
- Finite size localization of electrons
- Strain induced scalar potential and pseudo-magnetic field (Guinea et al., Nat. Phys. 6 (2010) 30, Low et al., PRB 83 (2011) 195436)

Summary

1. N adsorbed on the C-face of SiC by nitridation is remarkably robust up to about 1450°C
2. XPS measurements show that the N remains at the interface during graphene growth
3. The nitrogen induces finite size features into the graphene film without likely reducing electron mobility
4. The graphene structure causes a 0.7 eV bandgap to form
5. Other impurities, concentrations, and SiC faces have yet to be examined

A bandgap can be induced in graphene. New possibilities include the formation of graphene superlattices by growth on patterned N adsorbates. Switching devices should become practicable.

Collaborations

N. Guisinger, Argonne National Laboratory
M. Nevius, Georgia Institute of Technology
A. Tejeda, CNRS-Univ. de Nancy and Synchrotron SOLEIL
A. Taleb-Ibrahimi, CNRS/Synchrotron SOLEIL