SAND2008-1363C

Electronic Structure and Morphology of Graphene Films on SiC

Taisuke Ohta
(previously)
Advanced Light Source, Lawrence Berkeley Nat. Lab., Berkeley, California
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
(now at)
Sandia National Laboratories, Albuquerque, New Mexico

APS March Meeting
Session L29: Focus Session: Carbon Nanotubes and Related Materials VIII: Electronic Structure of Graphene, 2:30PM - 3:06PM
New Orleans, Louisiana, March 11th, 2008

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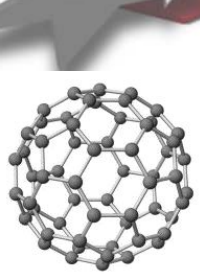
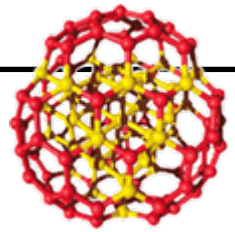
Acknowledgements

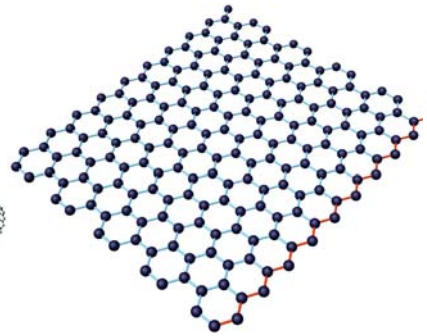
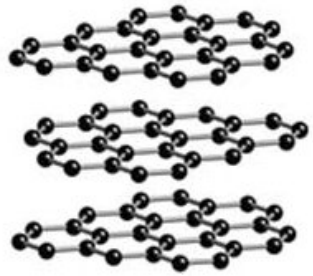
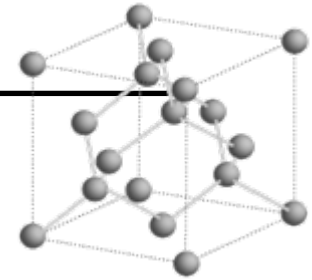
- Collaborators:
  - Aaron Bostwick, Jessica L. McChesney, Farid El Gabaly, Andreas Schmid, Eli Rotenberg
    - Advanced Light Source & National Center For Electron Microscopy Lawrence Berkeley National Laboratory, Berkeley, California
  - Karsten Horn, Johan Carlsson
    - Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
  - Konstantin V. Emtsev, Thomas Seyller
    - Institut für Physik der Kondensierten Materie, Universität Erlangen-Nürnberg, Erlangen, Germany

- Funding:
  - U.S. Department of Energy, Office of Basic Sciences under Contract No. DE-AC02-05CH11231.
  - Max Planck Society
  - European Science Foundation, EUROCORES SONS program

- Supports:
  - Sandia National Laboratories
    - Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Graphene and Allotropes of Carbon

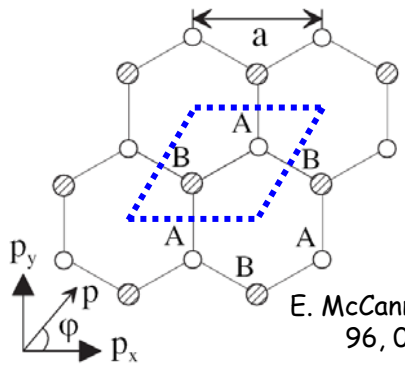



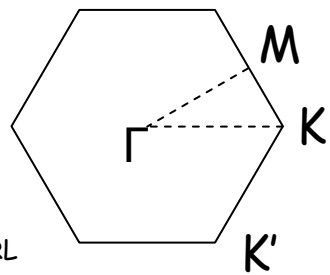
C_{60} (0-D) CNT (1-D) graphite (3-D)

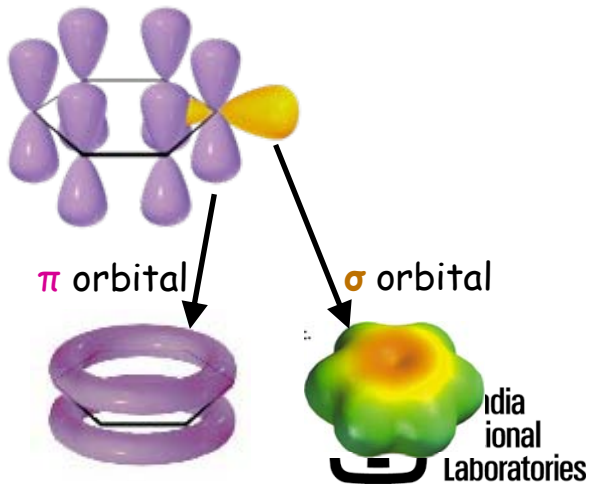
nano diamond (0-D) **graphene (2-D)** diamond (3-D)

- **Graphene**
  - **sp^2 hybridized carbon in honeycomb structure**
    - **Building block for graphite, carbon nanotube, C_{60} etc.**
  - **Delocalized π and σ orbitals**
  - **K and K' points equivalent**
    - **Hexagonal Brillouin zone**

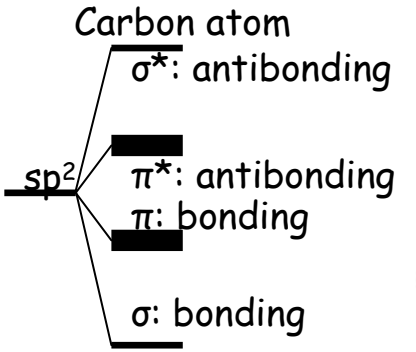


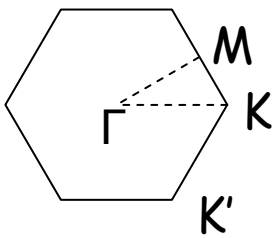
E. McCann and V. Fal'ko, PRL 96, 086805 (2006)

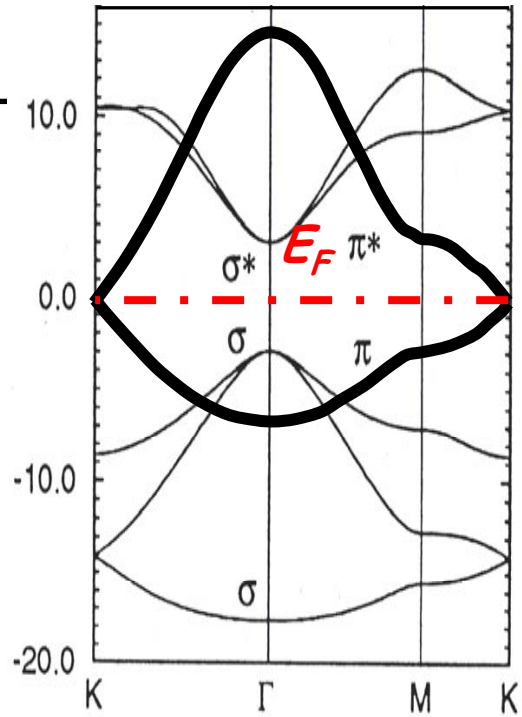




Unique Electronic Structure of Graphene

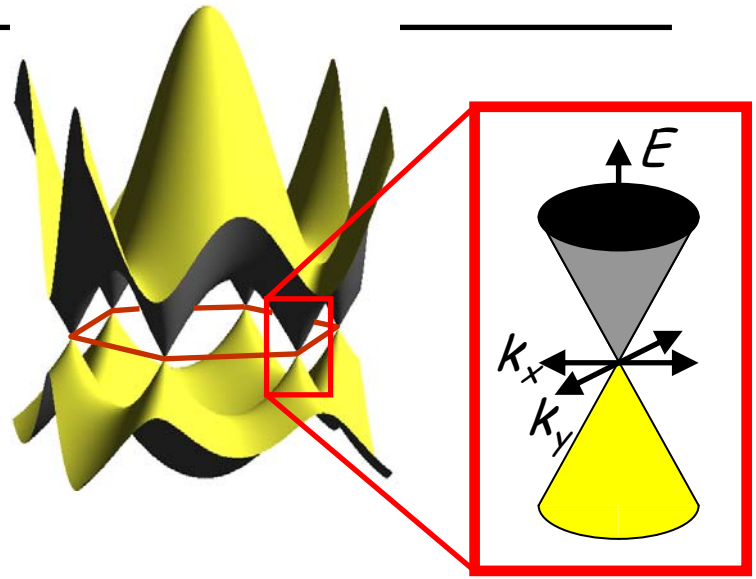






Tight binding calculation

R. Saito et al., *Physical Properties of Carbon Nanotubes* (Imperial College Press, 1998)



$$H = v_F \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} = v_F(\sigma_x p_x + \sigma_y p_y) = v_F \vec{\sigma} \cdot \vec{p}$$

σ_i = Pauli Matrices

- ***E(k)*** **linear around K**
  - **Linear, gapless, conical bands centered at K points**
  - **Formal equivalency with Dirac's equation for massless, relativistic particle**

➡ **"Dirac Fermions"**

  - **Realization of desktop QED experiments (?)**

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Technological Interests toward Graphene

- High electron mobility (25,000 $cm^2/V \cdot sec$)*
- Ballistic transport: long coherent length (> 1μm)*
- High current capacity
- Micro-nano patterning applicable
  - Semiconductor processing technology

➡High-speed electronics

➡Terahertz source

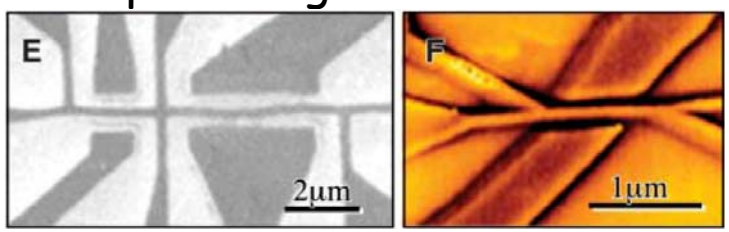
➡Sensitive gas sensors

➡New device principles
  - Klein tunneling, Veselago lensing etc.

- <u>Graphene films produced by scalable synthesis route</u>

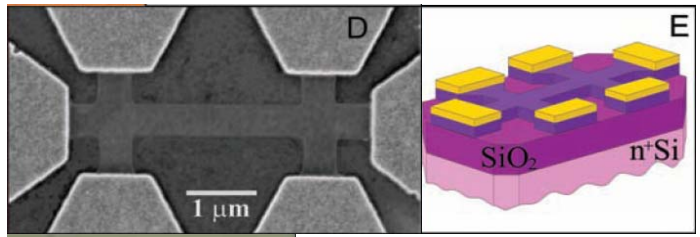
➡ Lead us to study graphene films on SiC

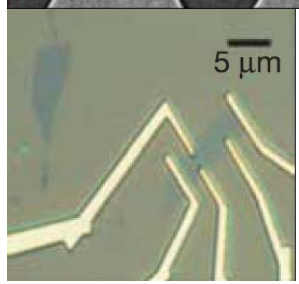
Epitaxial growth on SiC



*C. Berger et al., Science, 312, 1191 (2006)

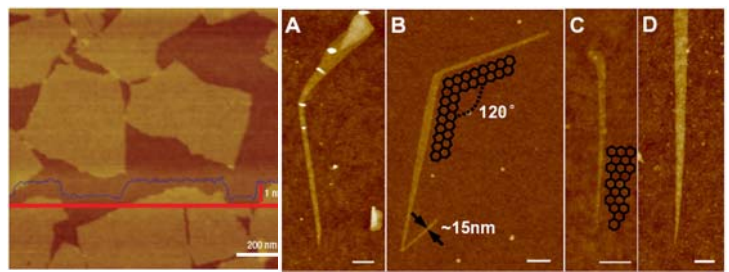
Mechanical exfoliation





Y. Zhang et al., Nature, 438, 201 (2005)
K. S. Novoselov et al., Science, 306, 666 (2004)

Chemical exfoliation



D. Li et al., Nature, published online (2008)
X. Li et al., Science express (2008)

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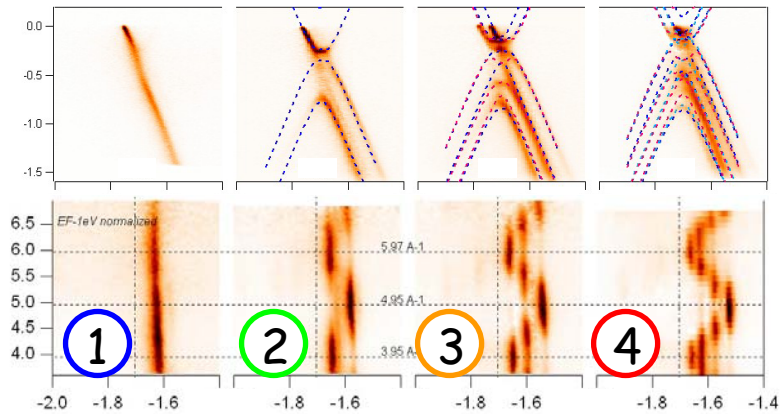
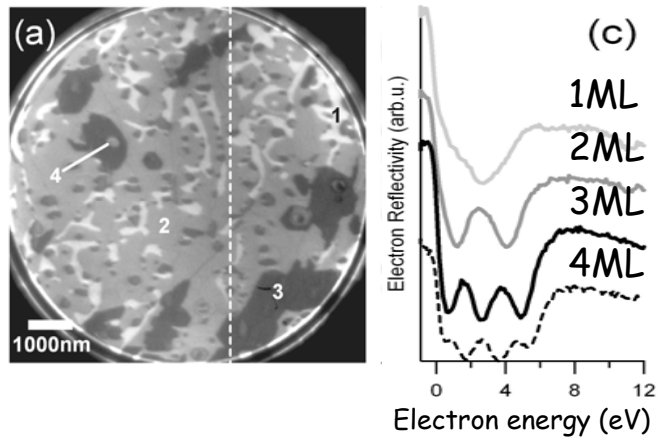
Outline

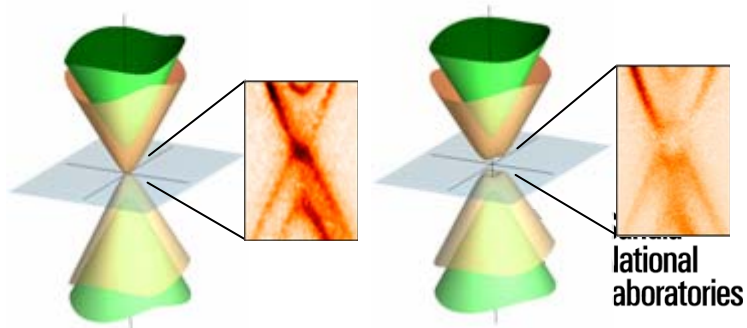
1. Electronic band structure of single and multilayer graphene
   - Transition from 2D (single) to 3D (multilayer)?
   - Potential and carrier concentration profiles in multilayer
     - Interlayer interaction and electron screening

2. Morphology of graphene films on SiC
   - Determining domain size and local thickness
     - Importance of interface-carbon layer on the formation of graphene

3. Controlling the electronic structure in graphene bilayer
   - Gap at E_D dependent on the electron potential of each layer
     - Switching functionality





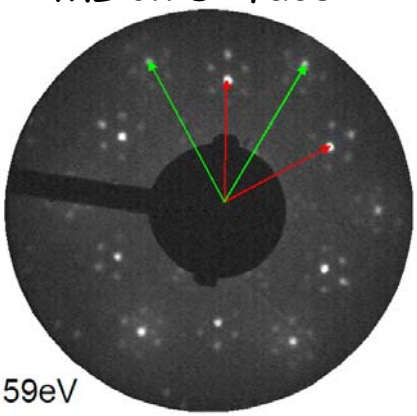


lational aboratories

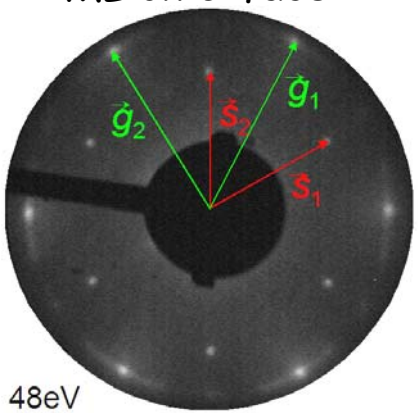
Epitaxial graphene films on SiC

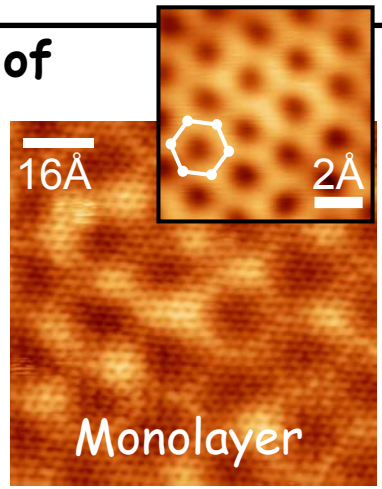
- **Thermal decomposition and Si sublimation of SiC substrate (graphitization)**
- **SiC(0001) (Si-face)**
  - **Azimuthally ordered graphene films**

1ML on Si-face

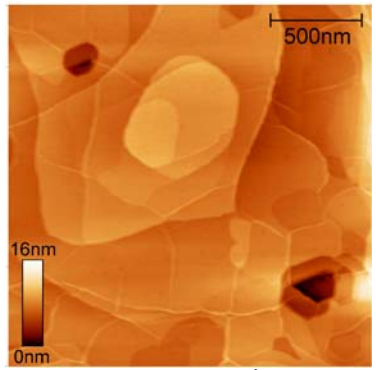


1ML on C-face

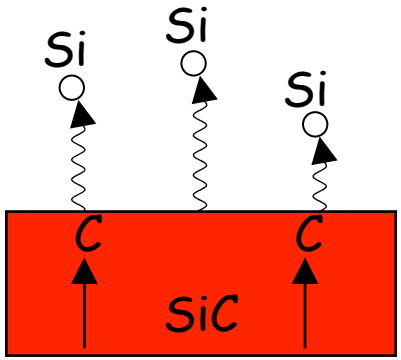




STM on graphene
V. W. Brar et al.,
Appl. Phys. Lett., 91,
122102, 2007



AFM on graphene layers
Th. Seyller et al.,
unpublished



Interface carbon layer
SiC
~1000 C

Interface layer formation

1st graphene sheet
Interface carbon layer
SiC
~1200 C

1st graphene sheet formation

2nd graphene sheet
1st graphene sheet
Interface carbon layer
~1300 C

2nd graphene sheet formation

Higher temp/longer anneal

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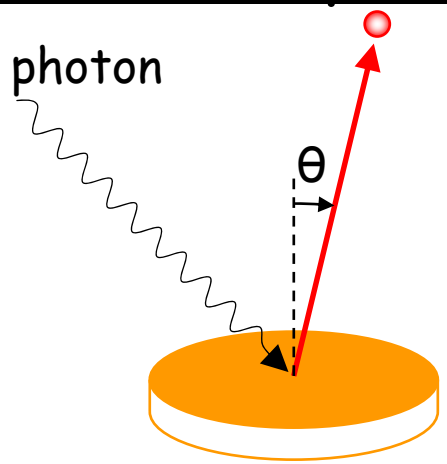
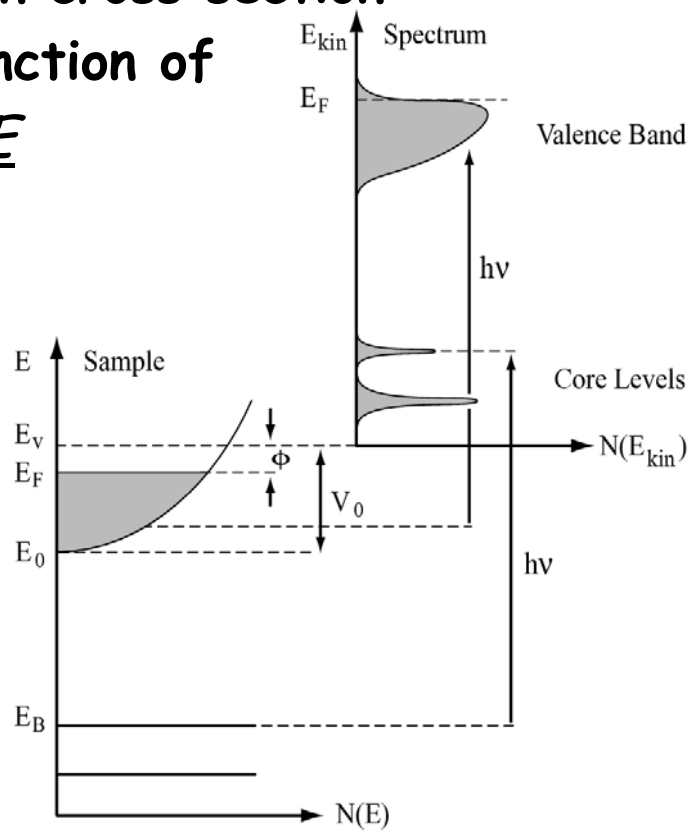
Photoemission spectroscopy

- **Directly tool to measure electronic band structure**
  - **Detect photoelectron**
  - **Photoemission intensity**
    = density of states (number of electrons) × photoemission cross section
  - **Spectra as a function of** electron energy *E*
  - **Spectra as a function of momentum *k***
- **Momentum conserved in translational symmetry**

$$k_{\parallel} = \sin\theta_{out}\sqrt{\frac{2m}{\hbar^2}E_{kin}}$$

Photoemission process





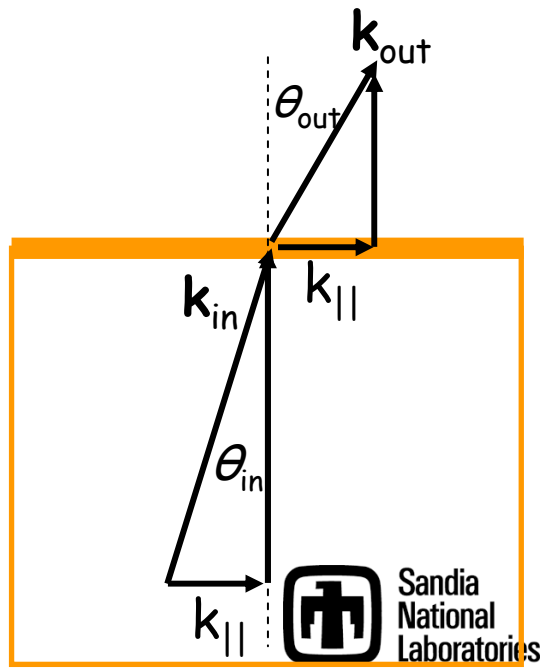
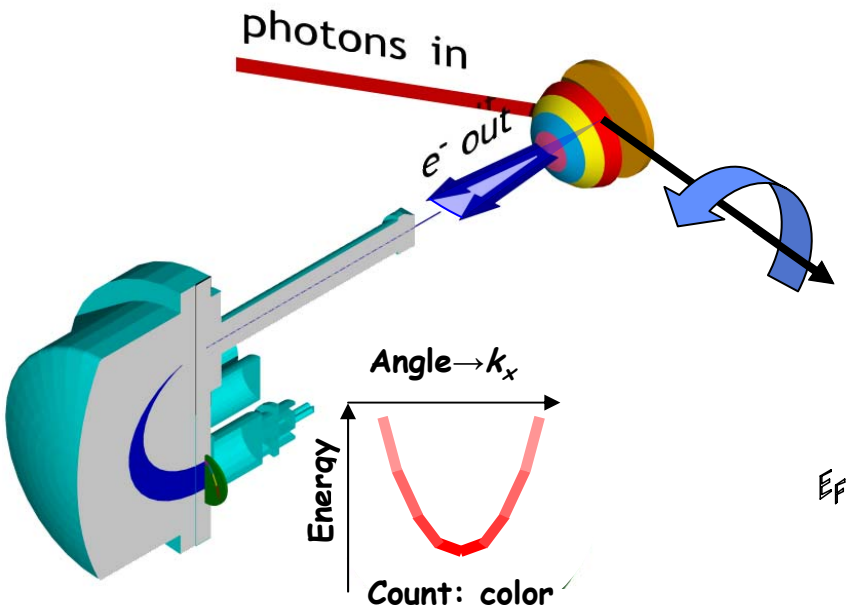


Figure courtesy: Eli Rotenberg

Photoemission spectroscopy (cont'd)

- **Electronic band structure (dispersion relation *E vs k*)**
  - **Angle resolved photoemission**
    - ➡ **Spectra: DOS as a function of** electron energy *E* **and** momentum *k*
      - **Light source: synchrotron radiation, ALS BL7**
      - **hv=80-220eV, energy resolution=25-30meV at hv=95eV**
      - **Angular resolution 0.1° (0.01Å^{-1})**



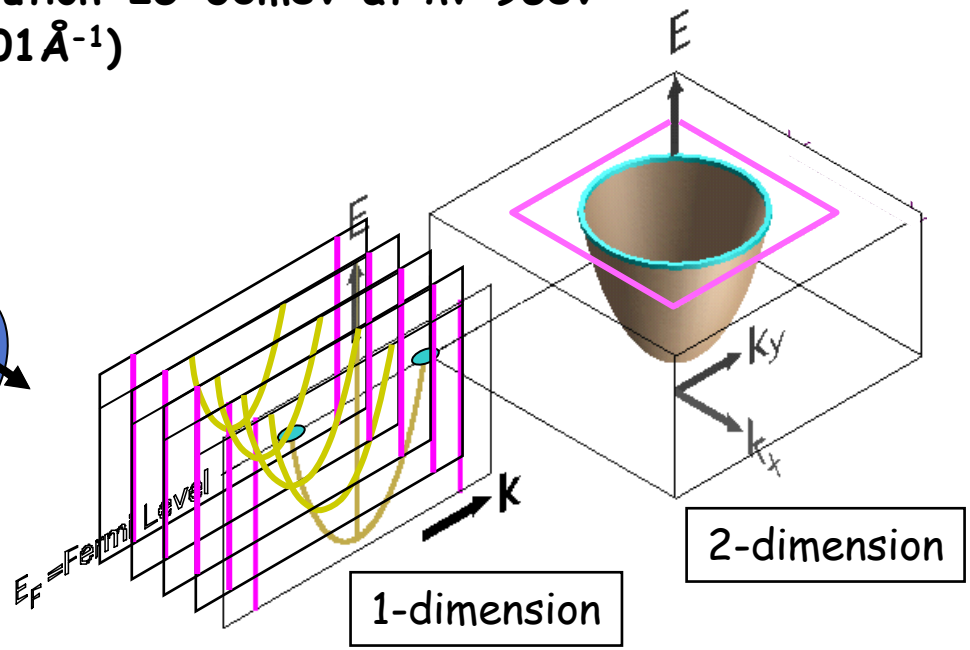


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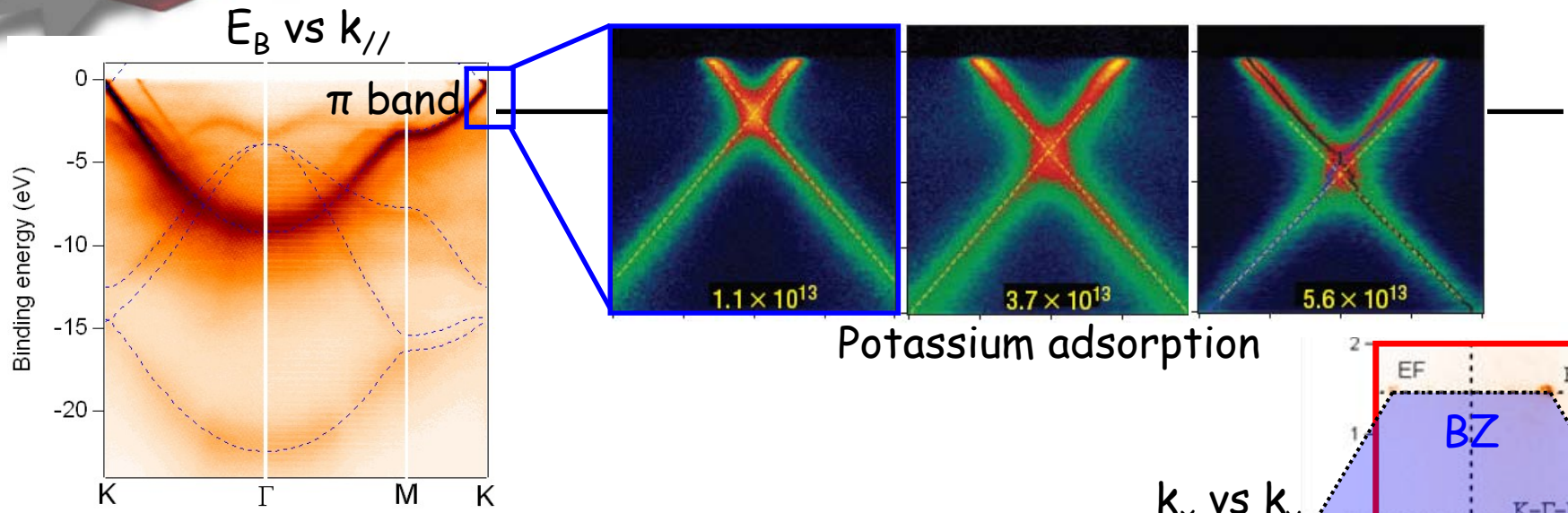
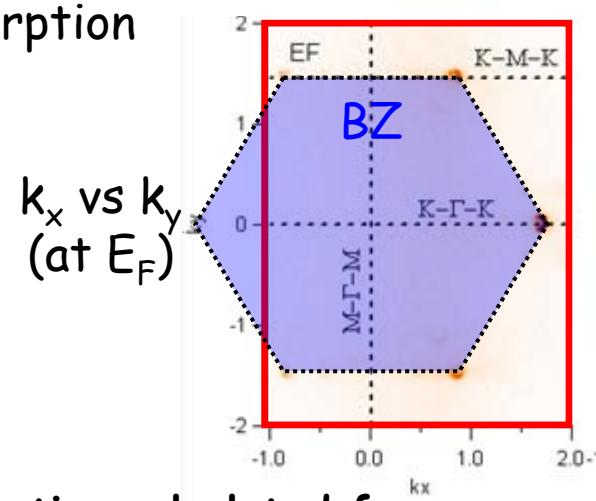
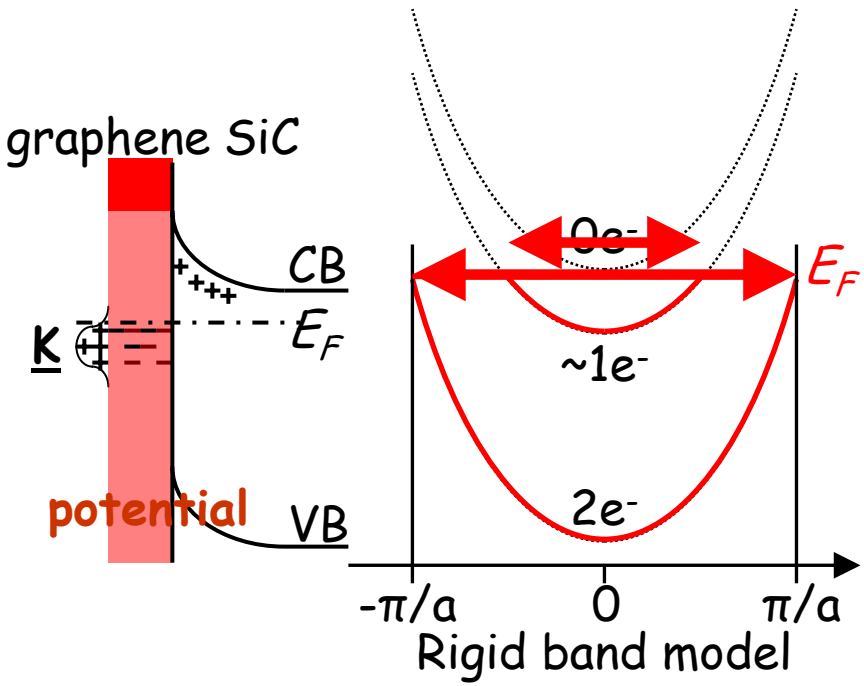
Figure courtesy: Eli Rotenberg

Electr. Structure of Graphene Films







- Carrier concentration calculated from area of Fermi-surface/Brillouin Zone
  - Luttinger theorem
- E_D shift by charge transfer from SiC
  - Graphene excellent for sensor application

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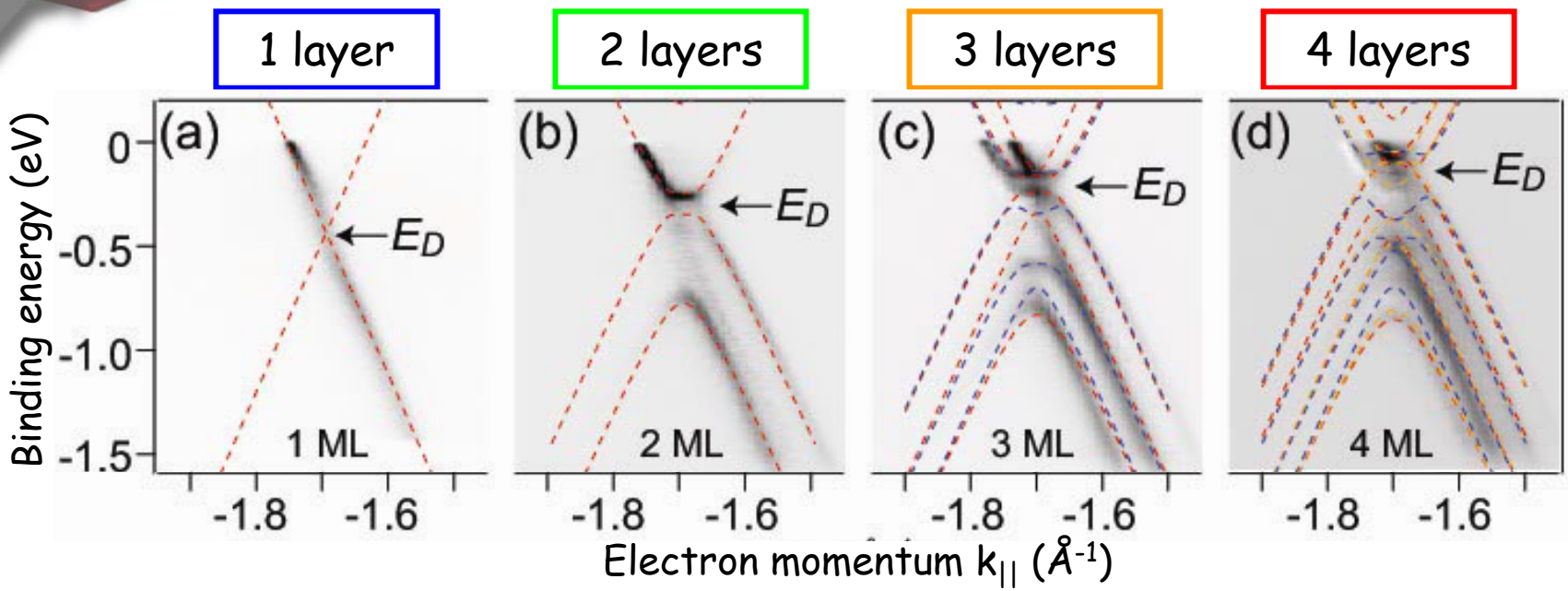
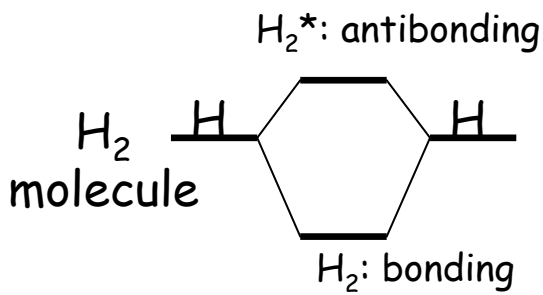
A. Bostwick, T. Ohta et al., Nature Phys., 3, 36, 2007

Evolution of π Band in Multilayer



- **π band splitting due to interlayer interaction**
- **E_D (crossing point) shift smaller for thicker graphene film**
  - **Same total charge transfer from SiC, but more bands crossing E_F**
- **Effect of stacking sequence**
  - **Bernal (ABA) and rhombohedral (ABC) stackings for 3 layers**
  - **Bernal type stackings (ABAB or ABAC) for 4 layers**
    - **Graphite: Bernal (ABAB) stacking ➡ toward bulk graphite**



Tight binding Hamiltonian from F. Guinea et al., cond-mat/0604396;
E. McCann cond-mat/0608221

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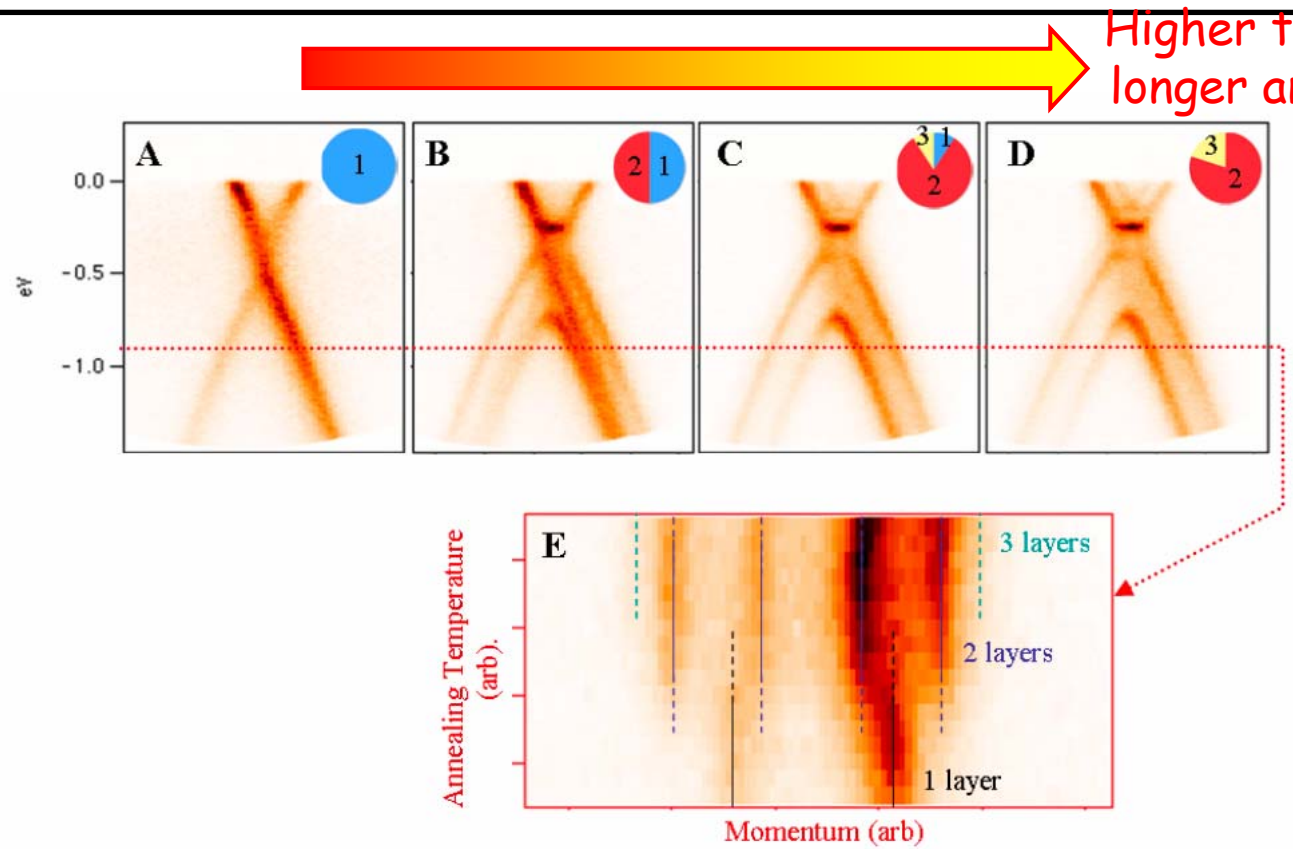
T. Ohta et al., Phys. Rev. Lett., 98, 206802, 2007

Evolution of π Band as a function of Annealing Temperature



- Thicker layers by higher temperature or longer anneal
- Counting the number of π states to determine the number of layers
- Mixture of n-1, n, n+1 layers beyond 2 layers
  - Isolation of a thicker layer component by subtraction of photoemission pattern

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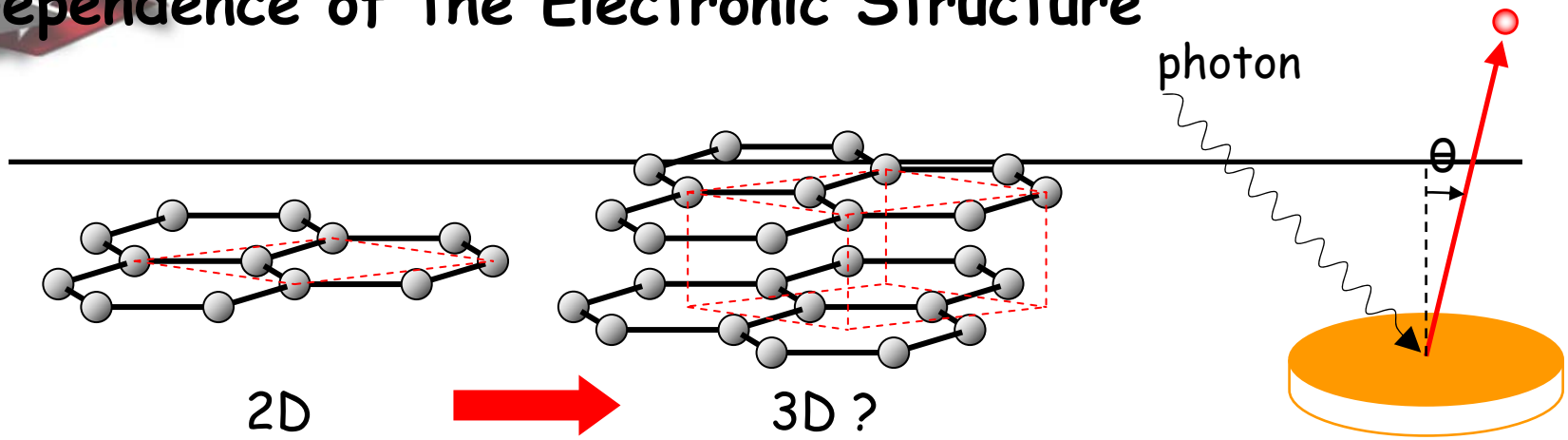
T. Ohta et al., Science, 313, 951 (2006)

$k_\perp$ Dependence of the Electronic Structure



- $k_\perp$ can be tuned by photon energy dependent PES
  - Electron momentum $k_\perp$ depend on electron kinetic energy

$$E_{kin} = h\nu - \phi - E_B$$

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2}(E_{kin} + V_0)}$$

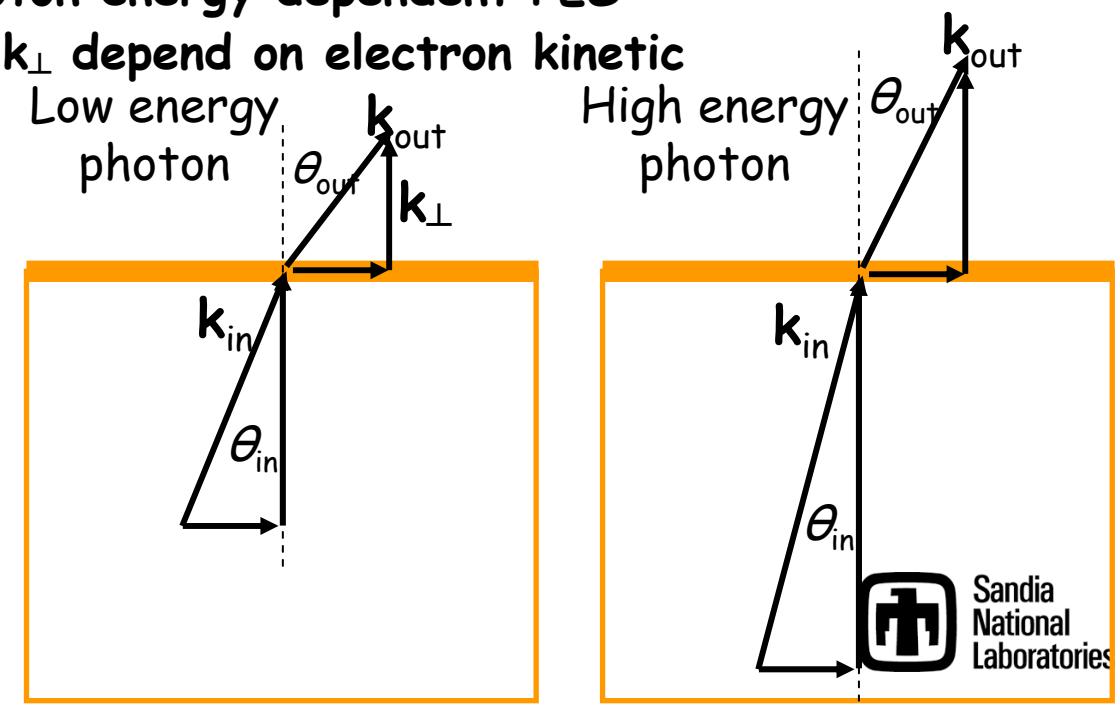
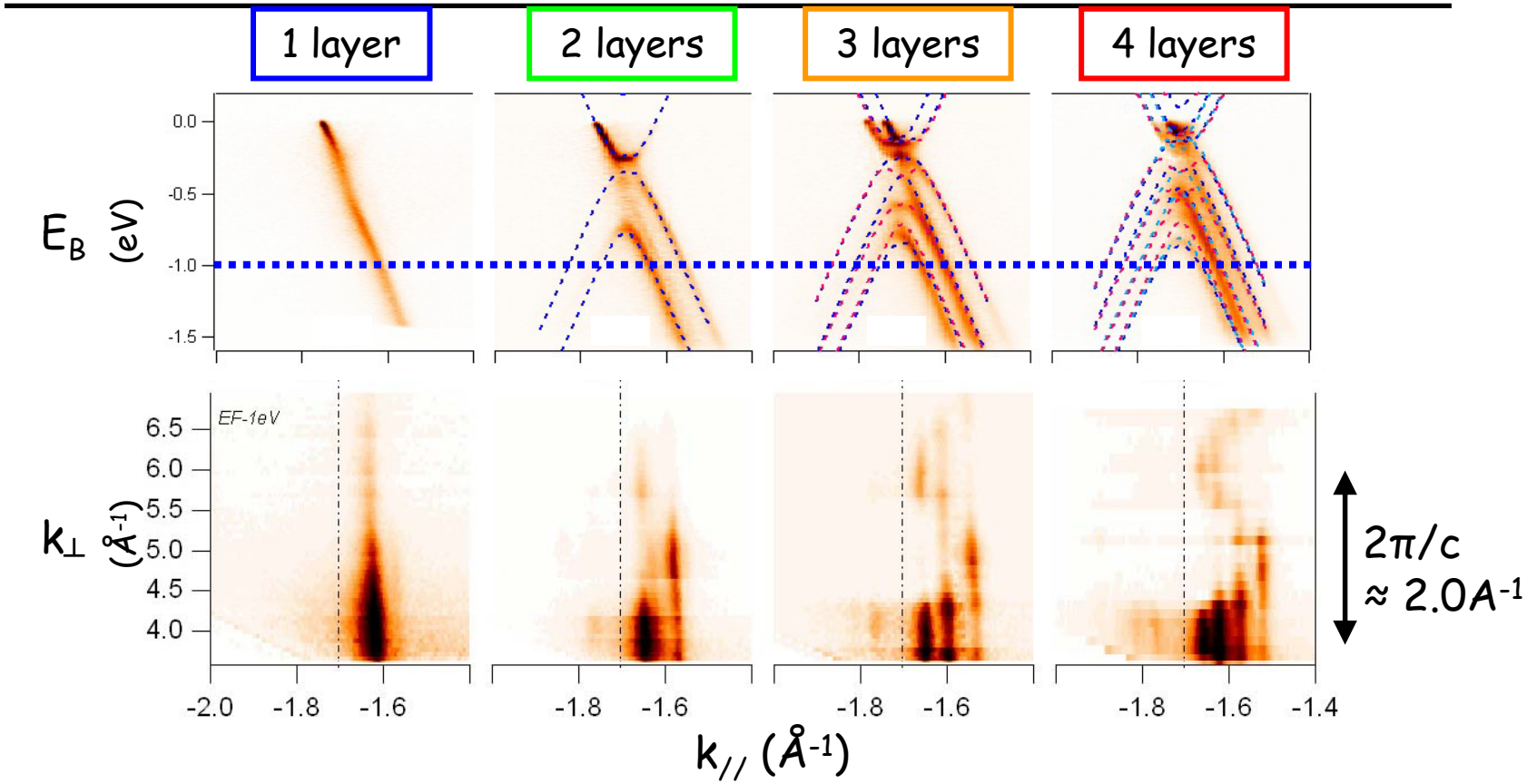


Figure courtesy: Eli Rotenberg

2D to 3D Transition



- Non-dispersing π bands: 2-D system
- Alternating photoemission intensity from split π bands
  - Periodicity matches to interlayer distance of bulk graphite

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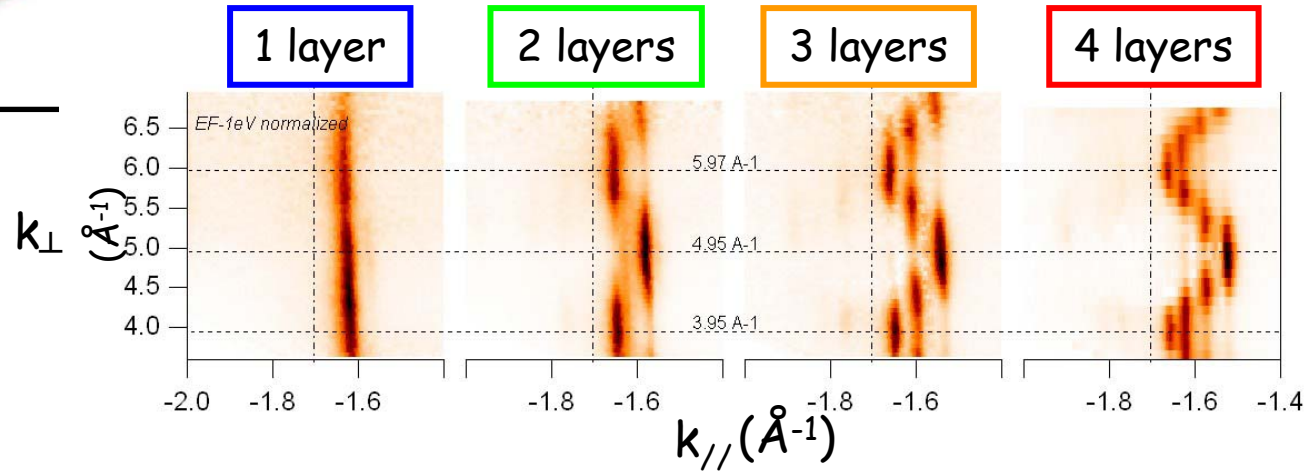
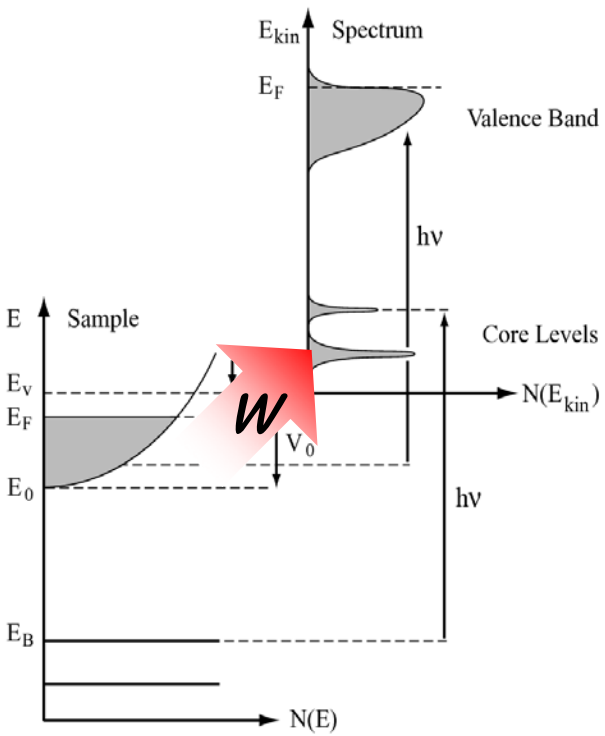
T. Ohta et al., Phys. Rev. Lett., 98, 206802, 2007

2D to 3D Transition (cont'd)





$$w \propto \frac{2\pi}{\hbar}\left|M_{fi}\right|^2 \delta(E_f - E_i - \hbar\omega)$$

w: transition probability (for photoemission)

H_{int}: interaction between electromagnetic field and electron

M_{fi}: transition matrix

Projection of initial states onto final states

Final state: free-electron approximation

- **What makes intensity oscillation $\left|M_{fi}\right|^2 \propto \left|\langle \psi_f | H_{\text{int}} | \psi_i \rangle\right|^2$**
  - **➡ Character of initial state wave function**

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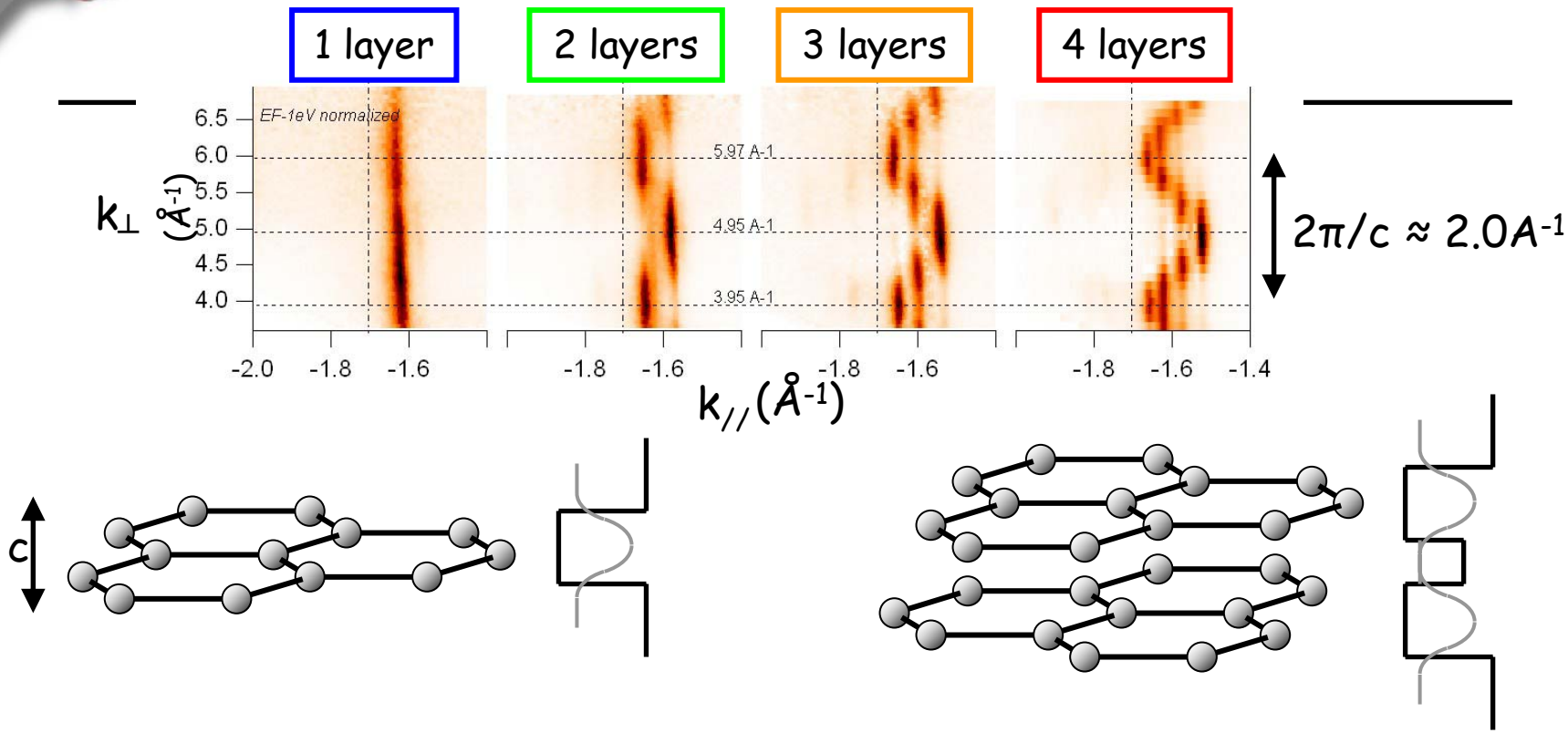
2D to 3D Transition (cont'd)



- Intensity oscillation matches out-of-plane periodicity of graphene layers
  - ➡ Eventually develops into $k_\perp$ band dispersion for infinite thickness (3D material)
- ➡ Transition from 2D to 3D by interlayer interaction
  - Interference of the wave functions in out-of-plane direction
  - Analogous to maximum photoemission intensity for quantum well states and surface states near vertical transition

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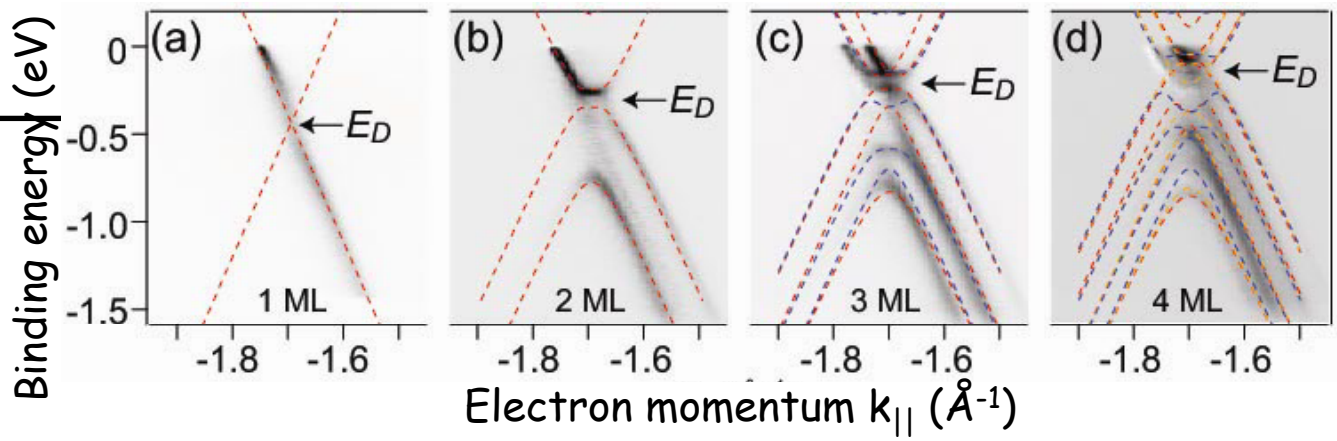
TB Modeling of π Band for Multilayer



- **Single layer**

$$H = \begin{pmatrix} 0 & v_F\pi^\dagger \\ v_F\pi & 0 \end{pmatrix}, \qquad \pi = p_x + ip_y$$

- **Multilayer**
  - **Bernal and rhombohedral stackings**
  - **With potential**

$$H = \begin{pmatrix} \alpha_1 & \beta & & & & \\ \beta^T & \alpha_2 & \beta^T & & & \\ & \beta & \alpha_3 & \beta & & \\ & & \beta^T & \alpha_4 & \beta^T & \\ & & & \beta & \ddots & \\ & & & & & \alpha_N \end{pmatrix}$$

$$\alpha_i \equiv \begin{pmatrix} 0 & v\pi^+ \\ v\pi & 0 \end{pmatrix} \quad \beta \equiv \begin{pmatrix} 0 & 0 \\ \gamma_1 & 0 \end{pmatrix}$$

$$\beta_s \equiv \gamma_1 \begin{pmatrix} 0 & s \\ 1-s & 0 \end{pmatrix}$$

$$s = \begin{cases} 0 & \text{Bernal} \\ 1 & \text{Rhombohedral} \end{cases}$$

$$\alpha_i \equiv \begin{pmatrix} E_i & v\pi^+ \\ v\pi & E_i \end{pmatrix}$$

E_i= onsite Coulomb energy

- **TB formalism from**
  - **F. Guinea, A. H. Castro Neto, and N. M. R. Peres, Phys. Rev. B 73, 245426 (2006)**
  - **E. McCann and V. I. Fal'ko, Phys. Rev. Lett. 96, 086805 (2006)**

T. Ohta et al., Phys. Rev. Lett., 98, 206802, 2007

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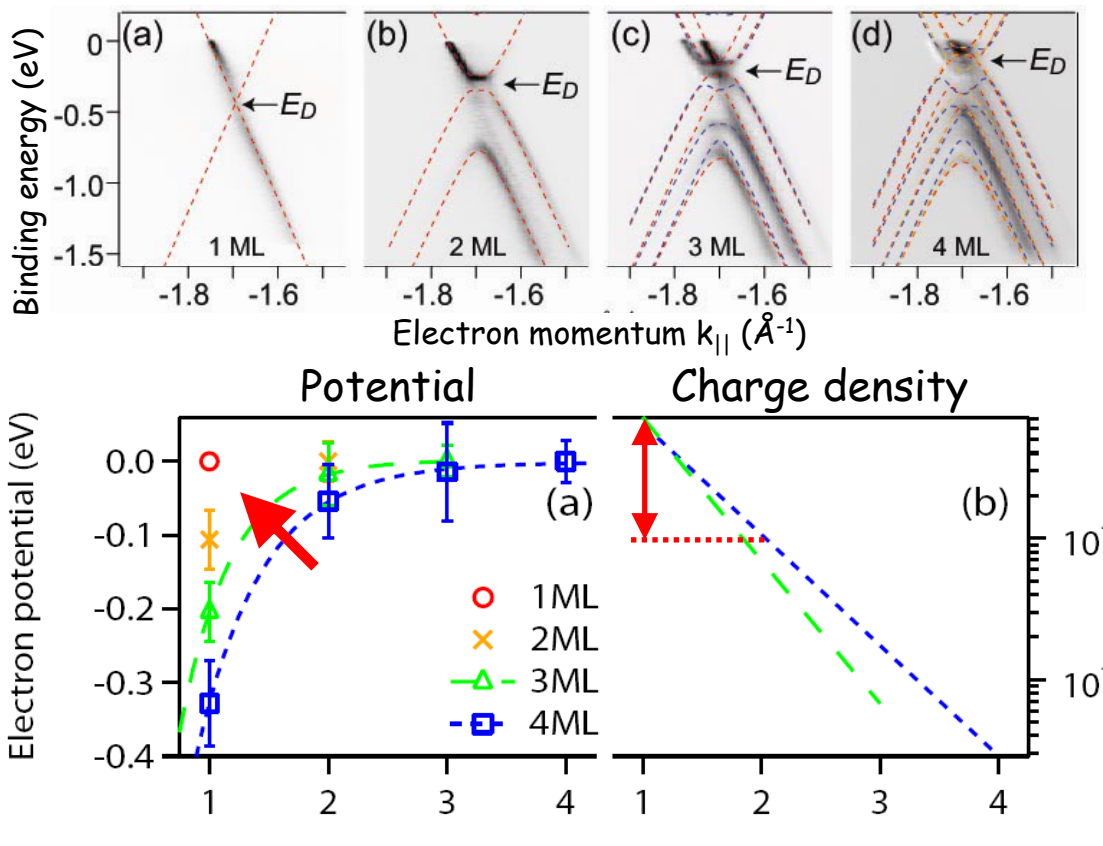
Potential and Carrier Concentration Profiles in Multilayer



- Screening length l_S : ~1.4-1.9Å
  - Exponential decay assumed for potential profile

$$V(z) = \exp(-\frac{z}{l_S})$$

- More charge carrier than graphite (3.8-5Å)
  - Metal(Cu): ~0.5Å, semiconductor(Si): Å-μm

➡ Semiconductor-like electron screening in graphene

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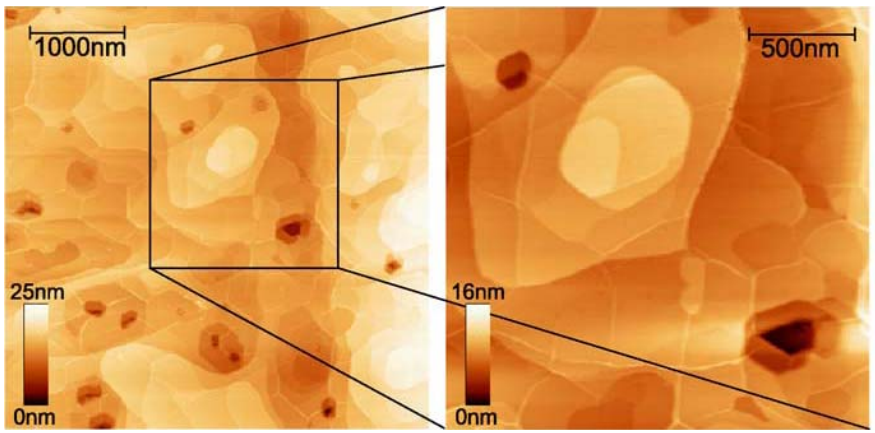
Morphology of Graphene Films on SiC

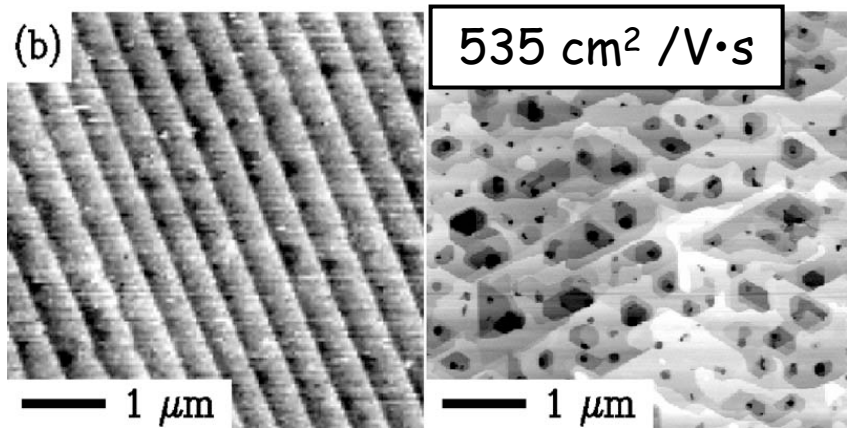
- Small domain size
- Low carrier mobility
  - Rough morphology of the graphene layer?

➡ Need to improve!



2nm thick graphene film

Th. Seyller et al., Surface Science 600 (2006) 3906



4H-SiC 2.5ML graphene film

G. Gua et al., Appl. Phys. Lett. 90, 253507 (2007)

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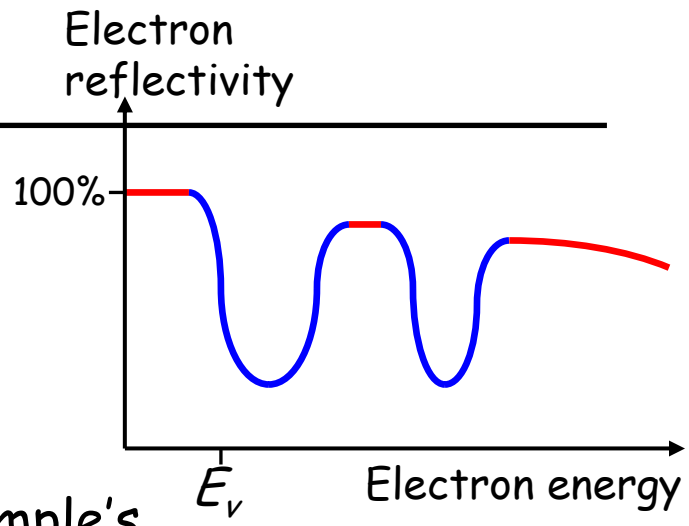
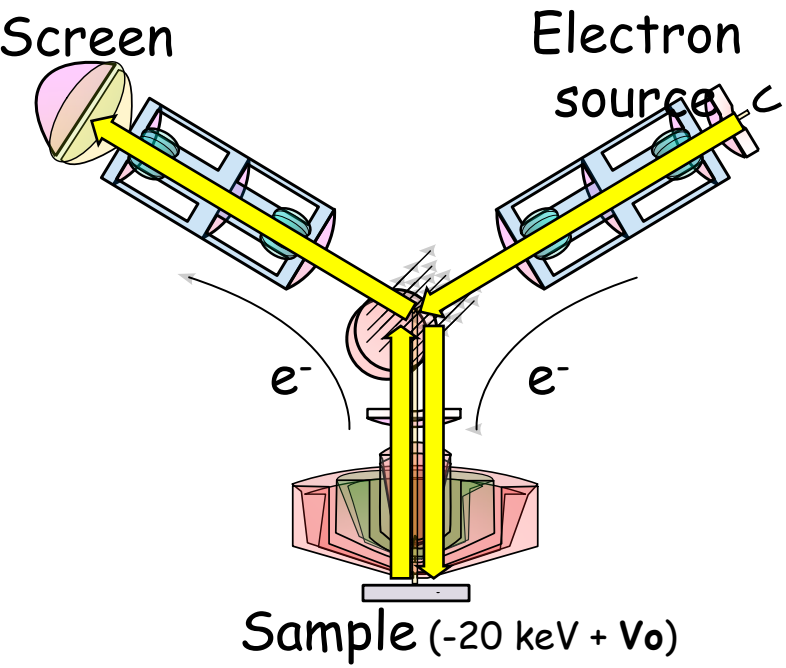
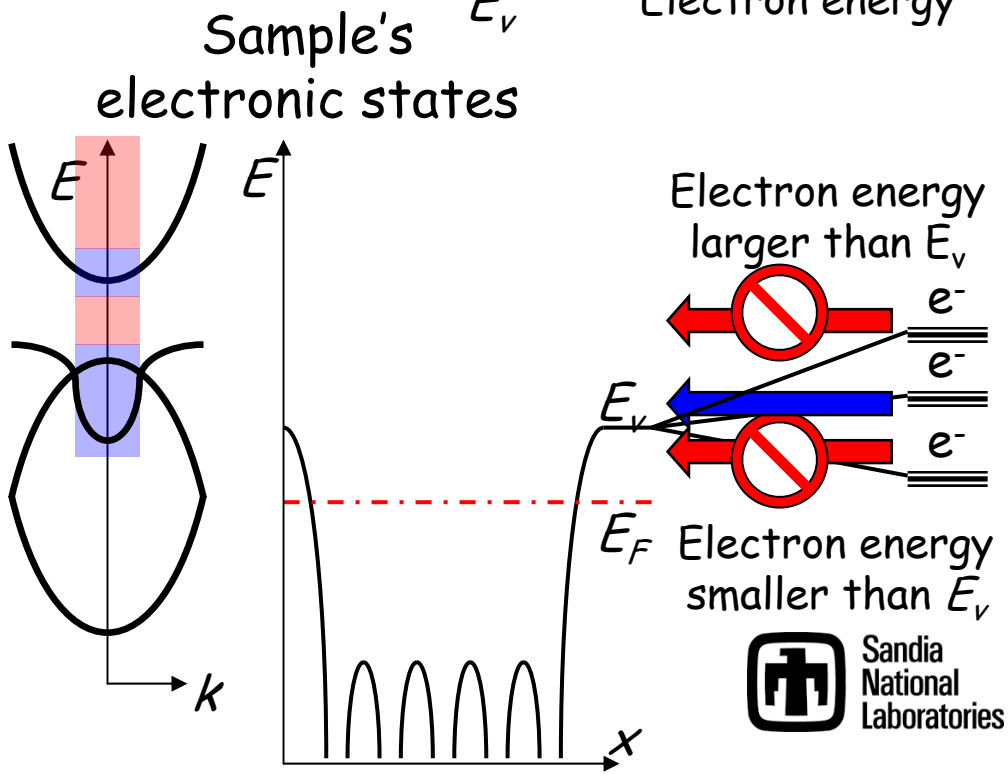
LEEM Contrast and LEEM I-V

- **Morphology: important for device fabrication**
- **Probing unoccupied electronic states near Brillouin zone center**







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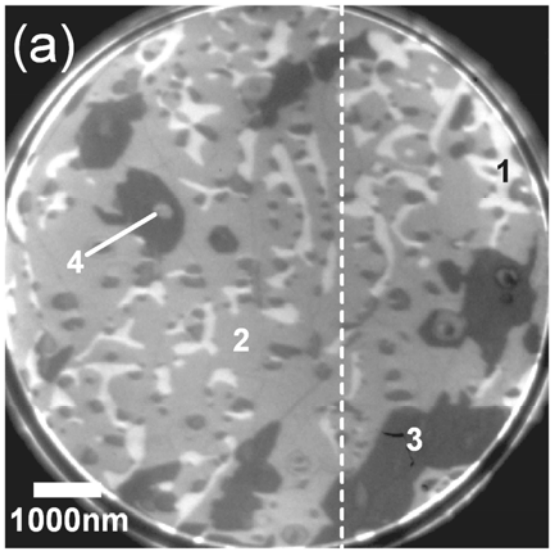
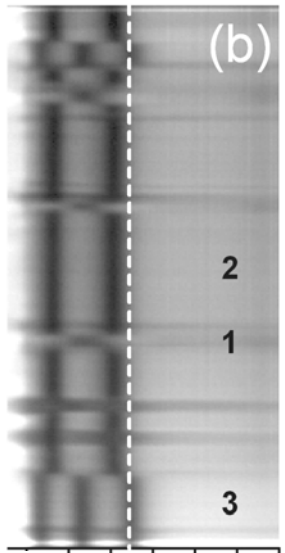
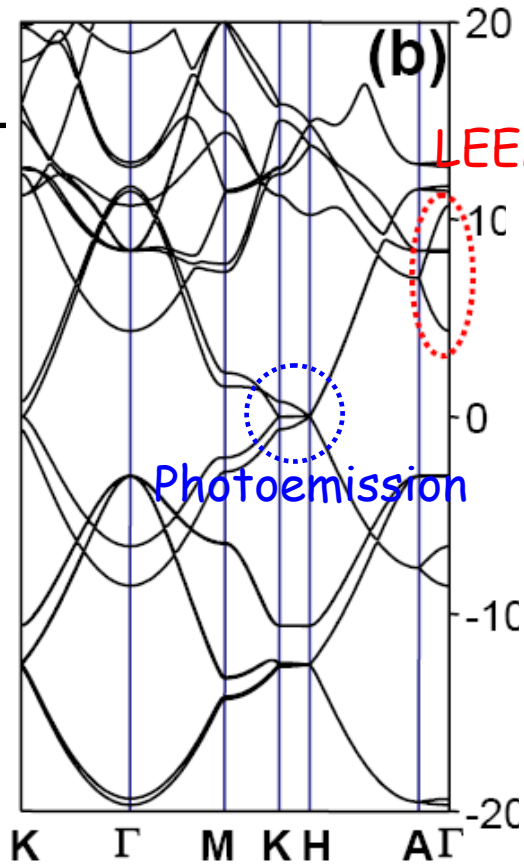
LEEM I-V Study of Graphene Film

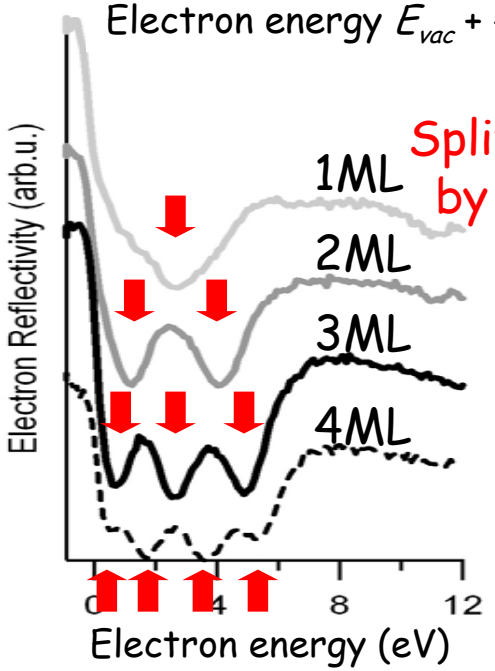




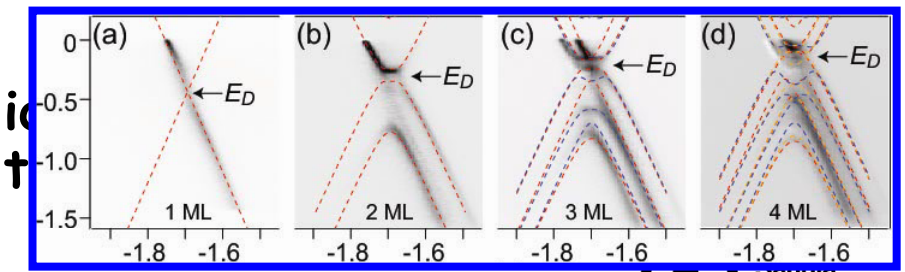
Electron energy E_{vac} + 4.88eV



Splitting of the band (Γ-A) by interlayer interaction



- Local ic
  layer t



Theoretical band structure from H. Hibino et al., accepted to Phys. Rev. B
T. Ohta et al., New Journal of Physics 10 (2008) 023034

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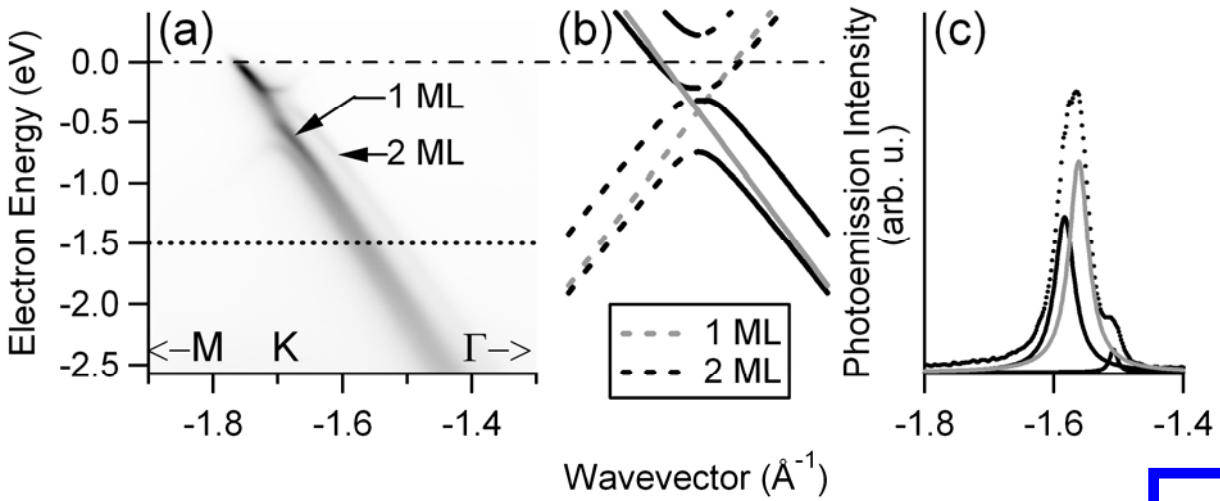
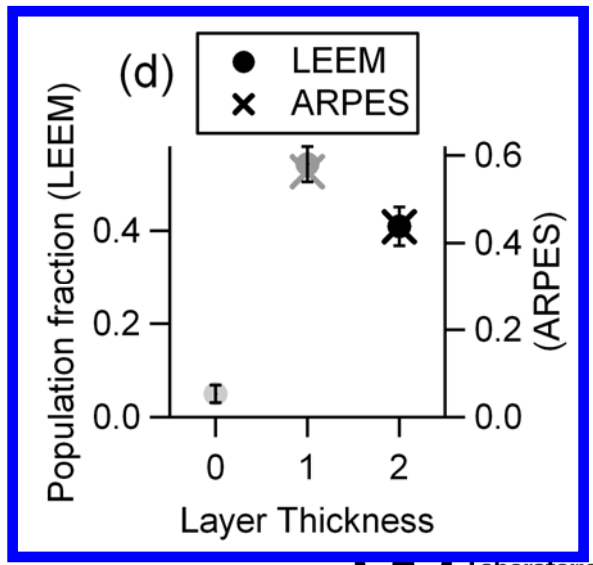
LEEM vs ARPES Thickness Calibration





- Very good agreement between LEEM and ARPES for thickness calibration

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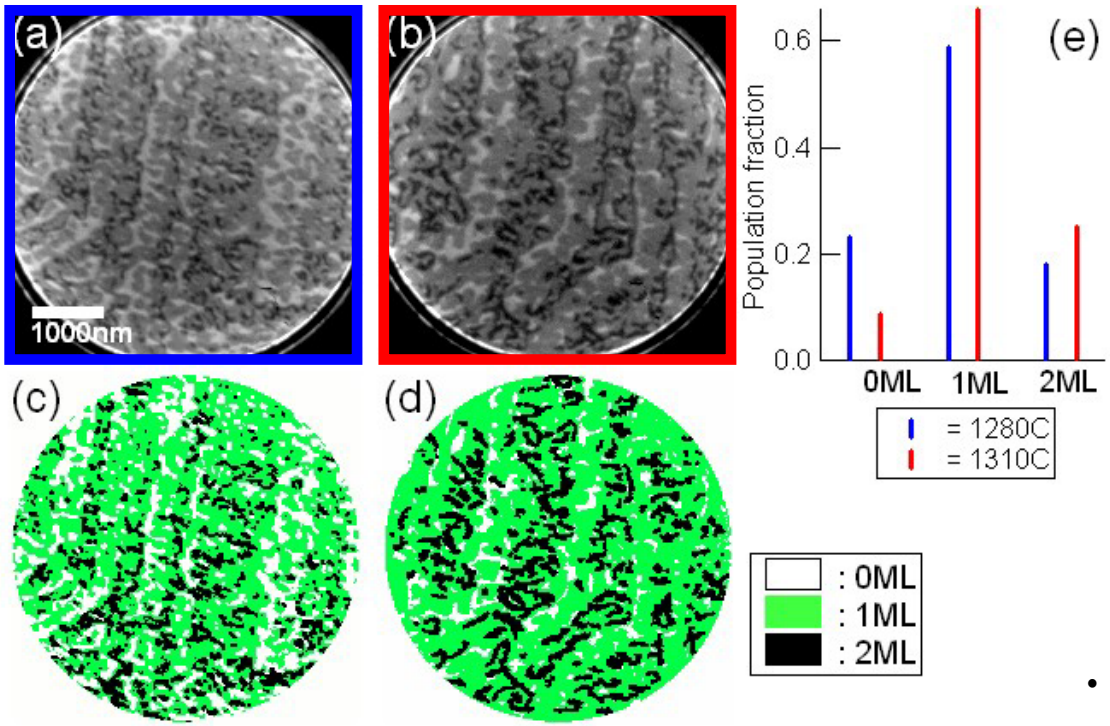
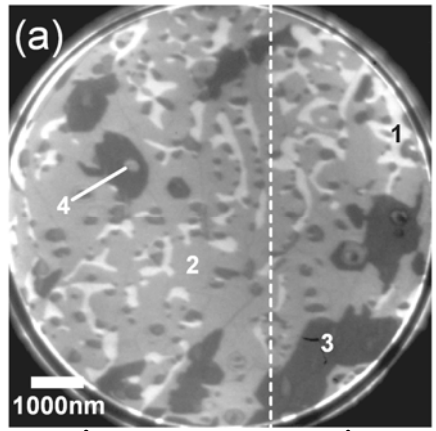
Morphology Evolution of Graphene Film





Mainly 2ML graphene

- **Determining domain size and local thickness**
- **Small domains started from rough interface-carbon layer's morphology**
  - **See also C. Riedl et al., Phys. Rev. B 76, 245406 (2007)**

Interface carbon layer
SiC
~1000 C

Interface layer formation

1st graphene sheet
Interface carbon layer
SiC
~1200 C

1st graphene sheet formation

2nd graphene sheet
1st graphene sheet
Interface carbon layer
~1300 C

2nd graphene sheet formation

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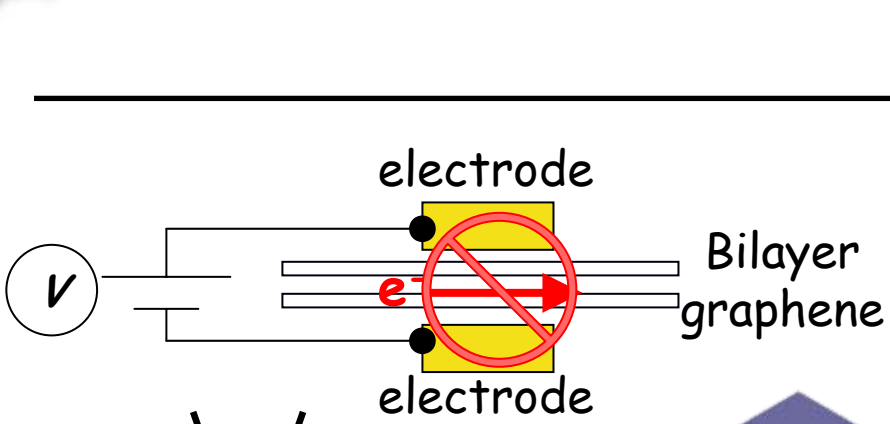
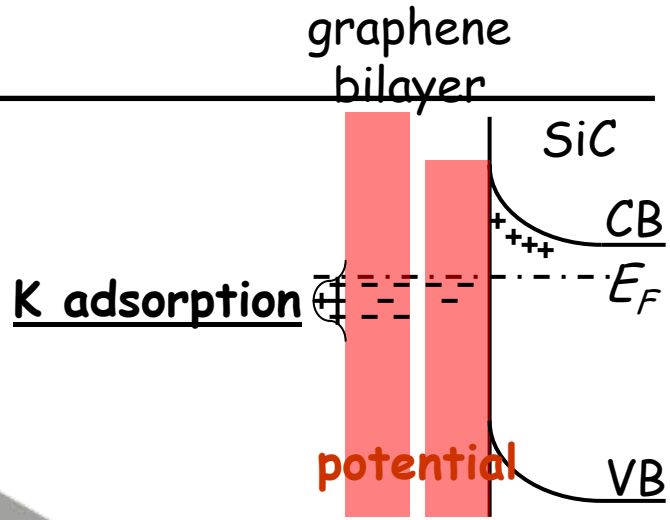
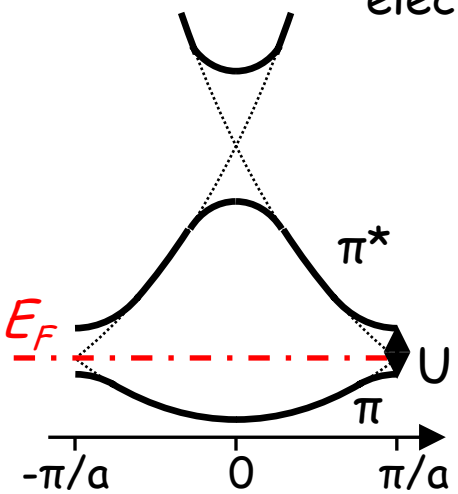
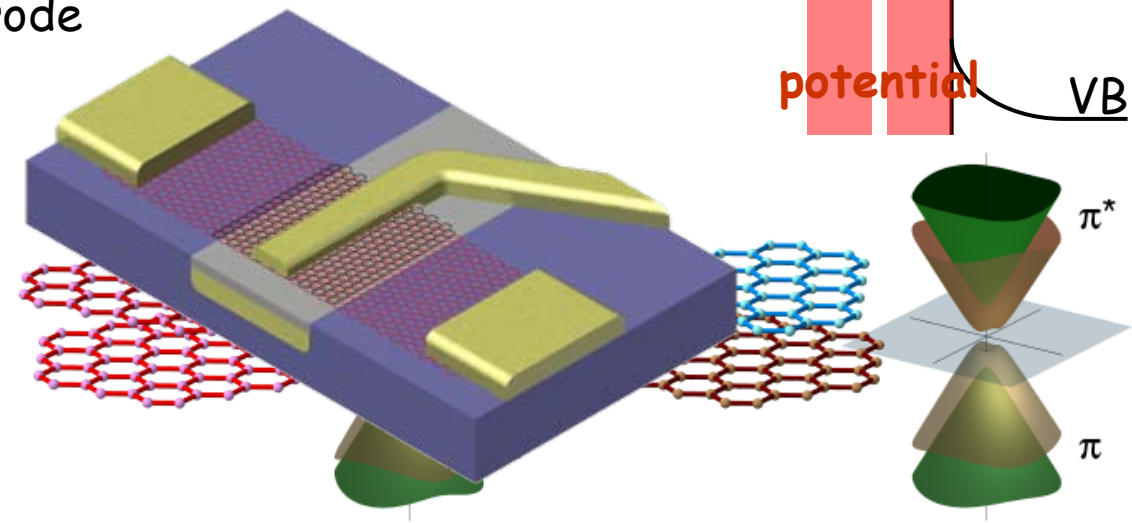
Switching Functionality using Bilayer Graphene









- Controlling gap between π and π* bands by on-site Coulomb potential
  - Analogous to metal-insulator transition for transition metal oxides
    - Tuning Coulomb repulsion in Zaanen-Sawatzky-Allen diagram
- High current switching (~nA per atom)

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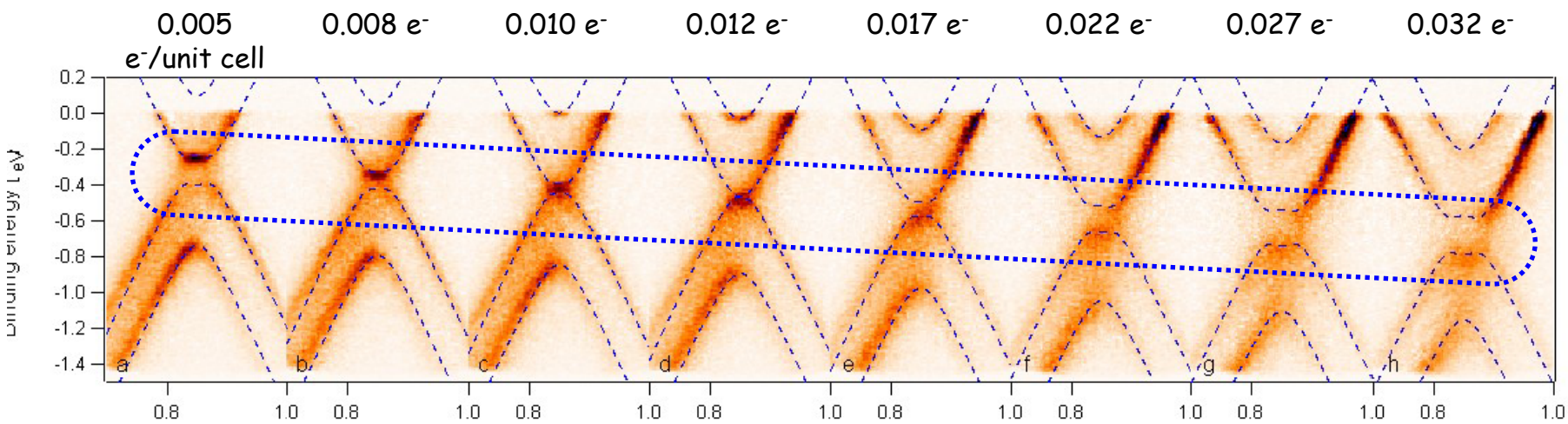
T. Ohta et al., Science, 313, 951 (2006)

Evolution of π Bands by Surface Doping

K



- **Shift of π bands due to increased total carrier density**
- **Continuous** closing/reopening of the gap

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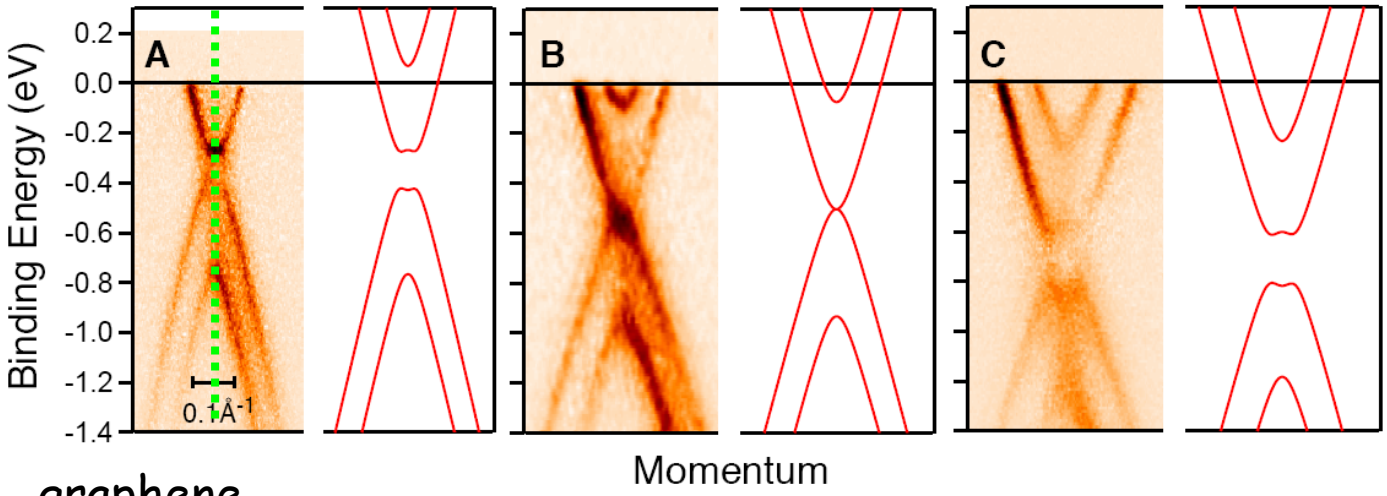
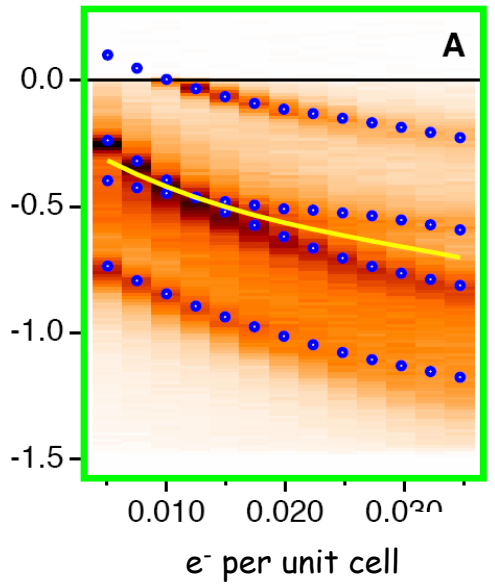
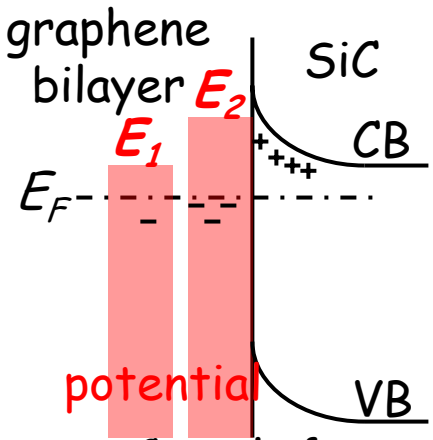
Closing and Opening of Gap between π and π* Bands







- **Control of potential difference**
  - $E_1 = E_2$: no gap –delocalized
  - $E_1 \neq E_2$: gapped – localized
  - E_1 and E_2 extracted from TB calculation

TB Hamiltonian: McCann and Fal'ko, Phys. Rev. Lett. 96, 086805 (2006)

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Sensitive Gas Sensor

- Shift of π bands due to increased total carrier density

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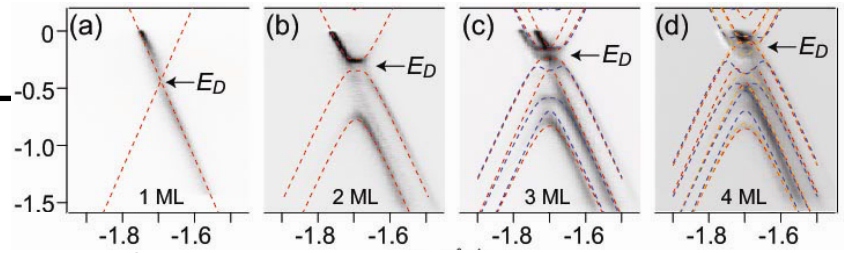
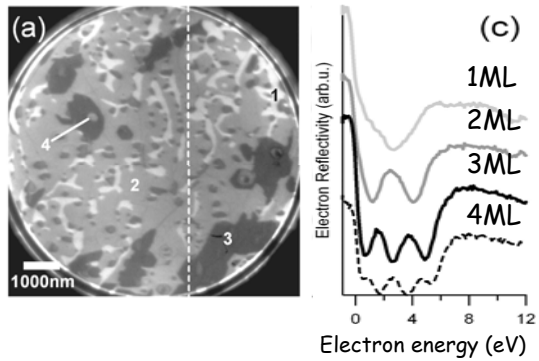
Summary





- We have shown
  - Electronic band structure of graphene
    - Dirac fermion spectrum
    - Layer-dependent electronic band structure of single and multilayer
    - Potential and carrier concentration profiles in multilayer
  - Morphology of graphene films on SiC
    - Determining domain size and local thickness
    - Importance of interface-carbon layer on the formation of graphene
  - Controlling the electronic structure in graphene bilayer

- Issues
  - Small graphene domains
    - We can determine
      - layer-dependent electronic structures
      - Symmetry breaking and gap control in bilayer
    - Too small for routine device fabrication
  - Interface-carbon layer
    - Symmetry breaking in monolayer (?)
    - Graphene formation process

- Experimental tools
  - ARPES
  - LEEM
  - Raman spectroscopy
  - IR spectroscopy
  - etc

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Thank you!

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