PhD Oral Defense
(Summer 2014)

From Graphite to Graphene via Scanning Tunneling Microscopy

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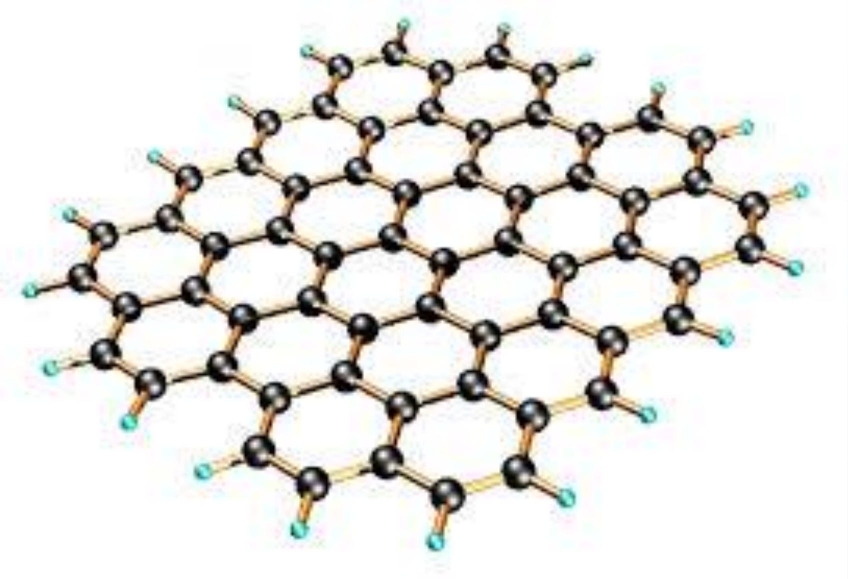
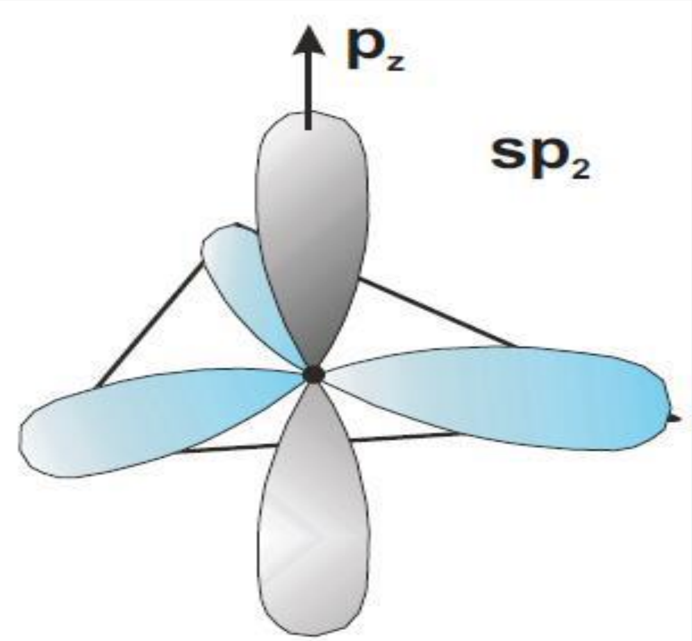
Outline

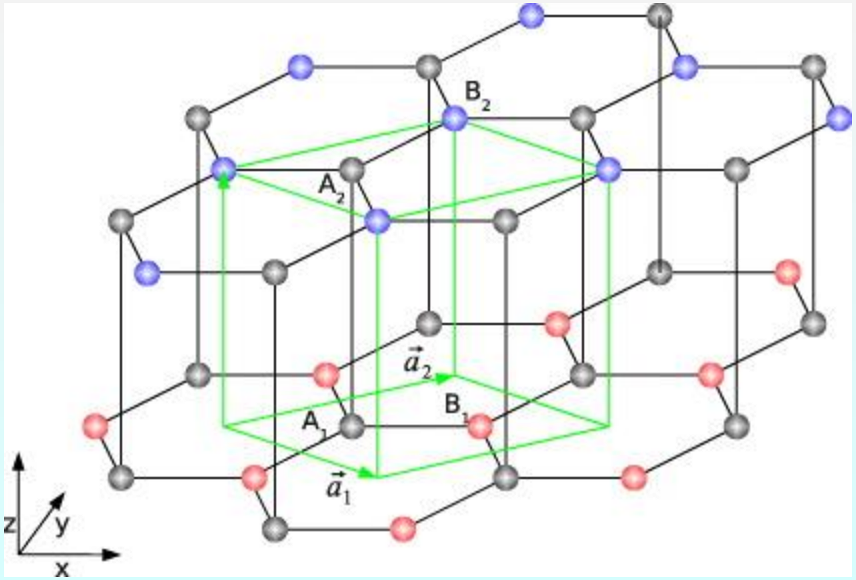
1. *Background and purpose (massive to massless)*
2. Scanning tunneling microscopy (STM)
3. Electrostatically lifting top layer of graphite
4. Vertical displacement properties
5. Summary, publications, acknowledgement, etc.

Graphene and graphite

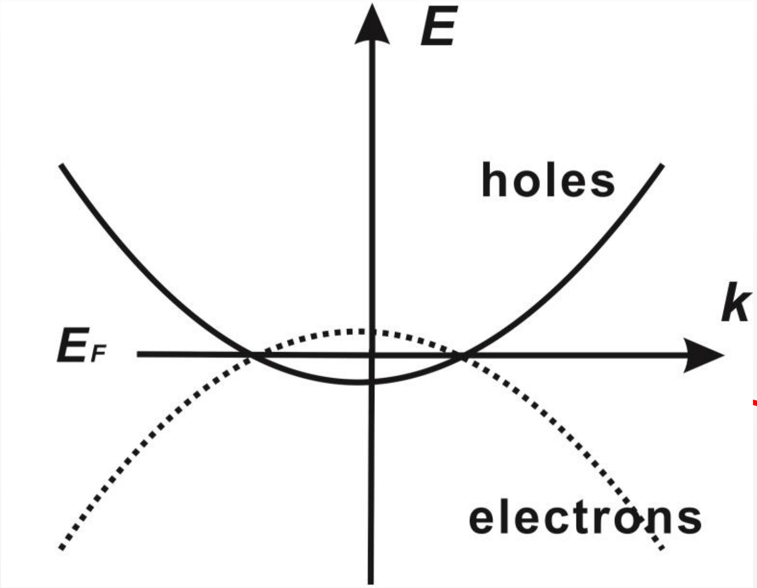
- Graphene: single layer carbon sheet
- Graphite: stacking of graphene sheets
- P_z orbits perpendicular to the palbne
- Bernal Stacking Pattern

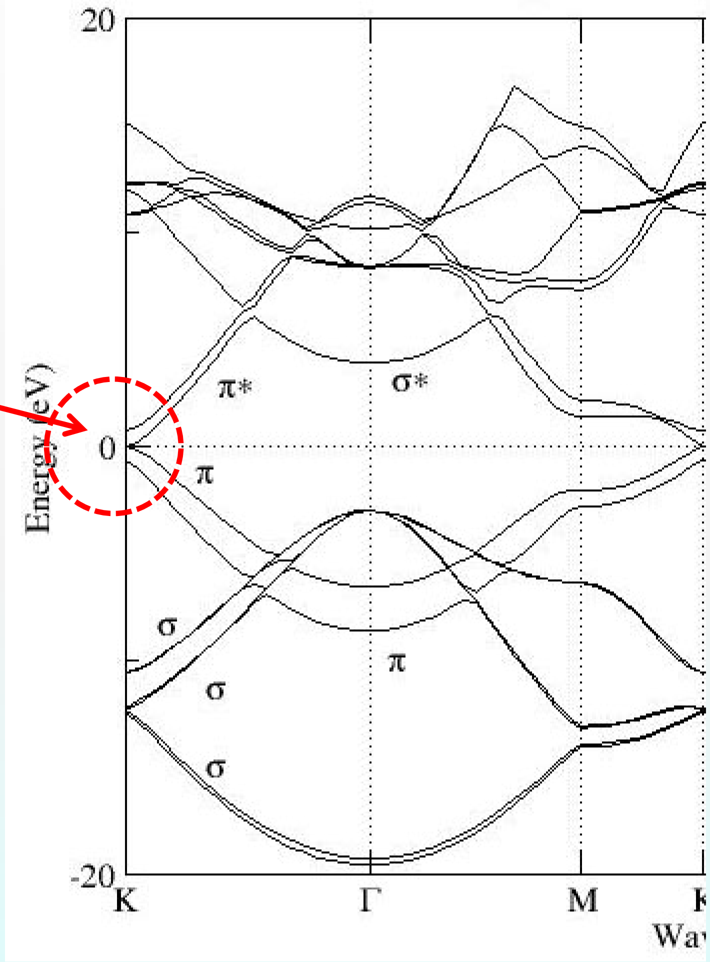






Band structure of Graphite



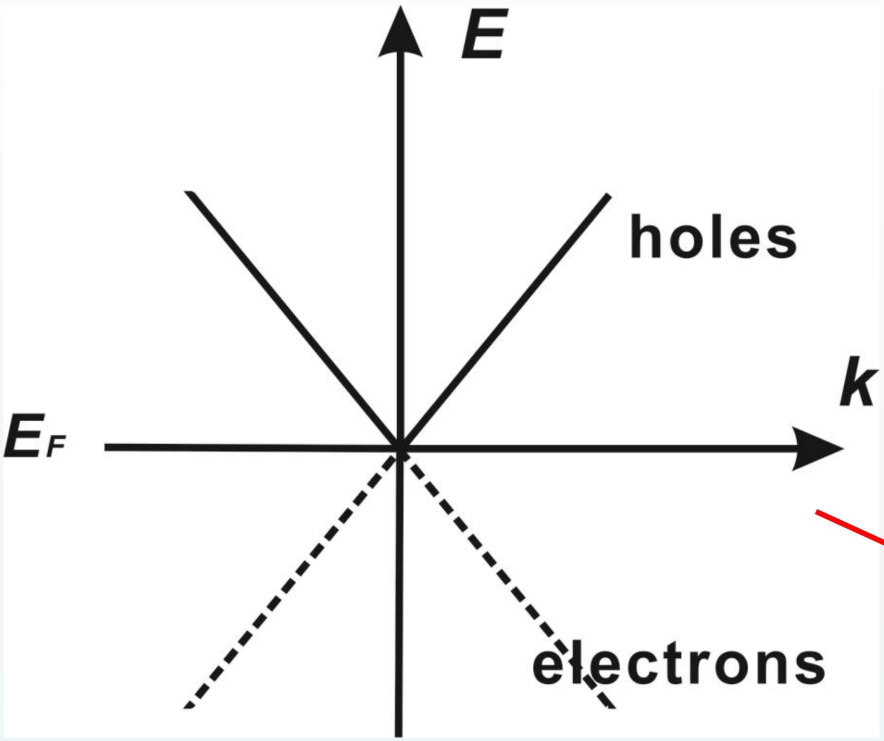


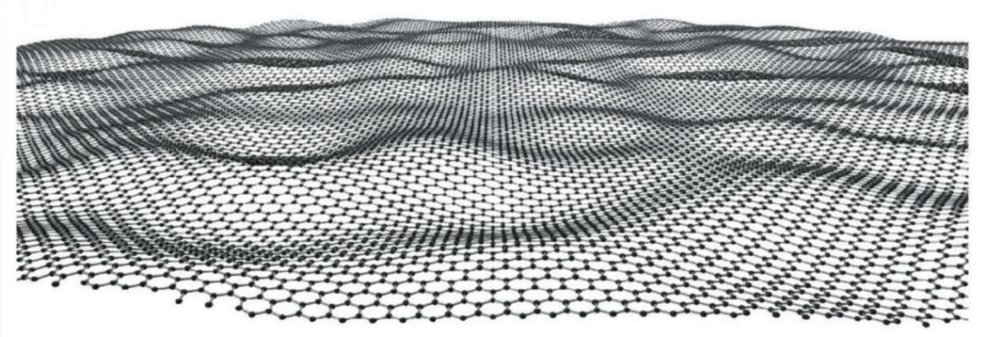
- ➢ No band gap
- ➢ Parabolic dispersion near *K* point for π and π* band

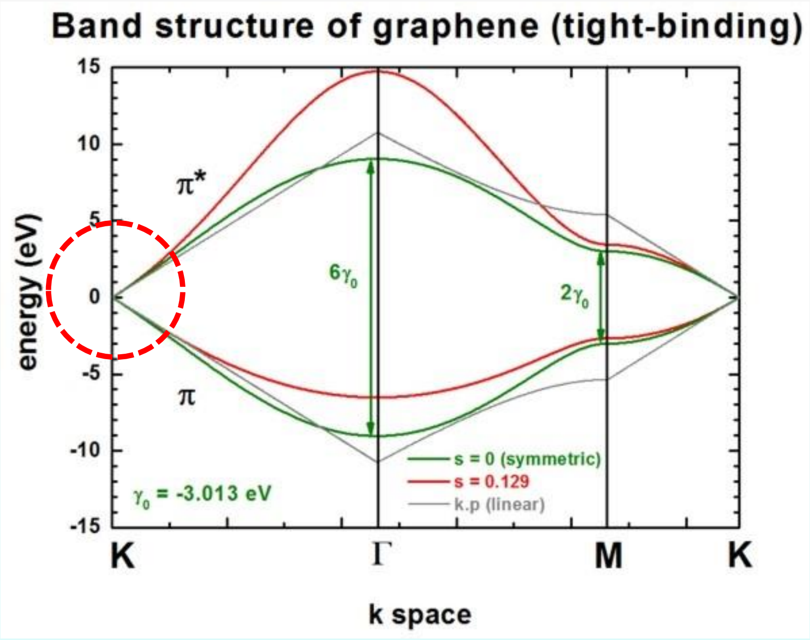
Nanotechnology ***23*** *(2012) 015701*

Physical Review B ***74****, 075404 2006*

Graphene and its band structure







- No band gap
- Linear dispersion near K point for π and π^* band

Overall band structure

From parabolic to linear

PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

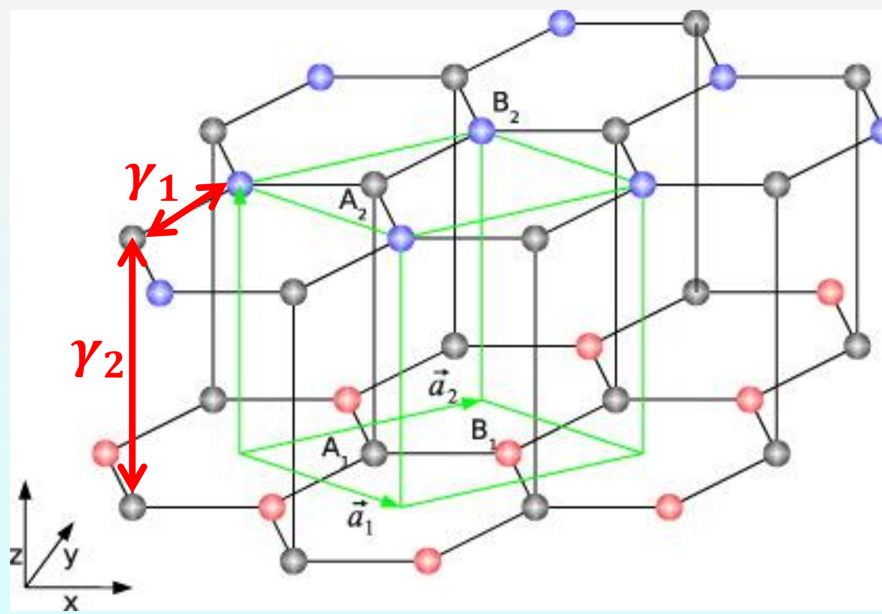
P. R. WALLACE*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

(Received December 19, 1946)

Near the cone (Fourier expansion):

$$E = E_0 + 3\boldsymbol{\gamma_2} \pm \sqrt{3}\pi\boldsymbol{\gamma_1}|k - k_c|a - 3\pi^2\boldsymbol{\gamma_2}|k - k_c|^2 a^2$$

$$\boldsymbol{\gamma_{1,2}} = \int \phi^*(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\mathbf{1,2}})H'\phi(\vec{\boldsymbol{r}})d\tau$$



Neglecting the γ_2:

$$|E - E_0| \approx \sqrt{3}\pi\boldsymbol{\gamma_1}|k - k_c|a$$

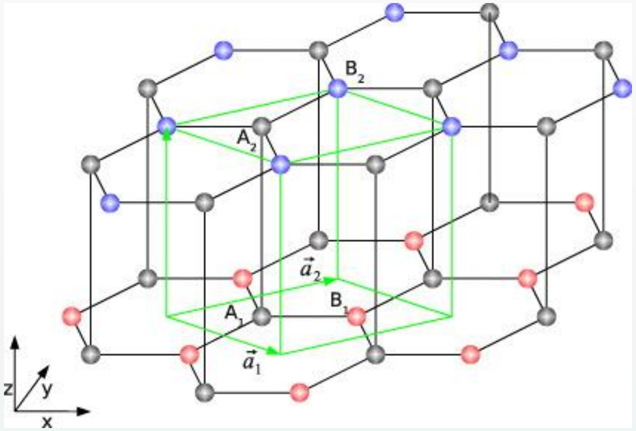
Giving rise to the linear dispersion

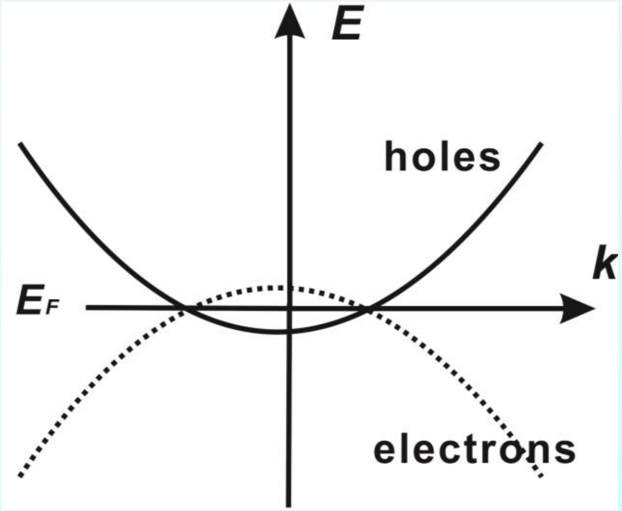
Normally we have: $E = \dfrac{\hbar^2 k^2}{2m}$

From graphite to graphene

$$E = mc^2\sqrt{1+\frac{\hbar^2k^2}{m^2c^2}} \approx mc^2 + \frac{\hbar^2k^2}{2m}$$

$m = \hbar^2(\nabla_k E(k))^{-1}$ (massive)

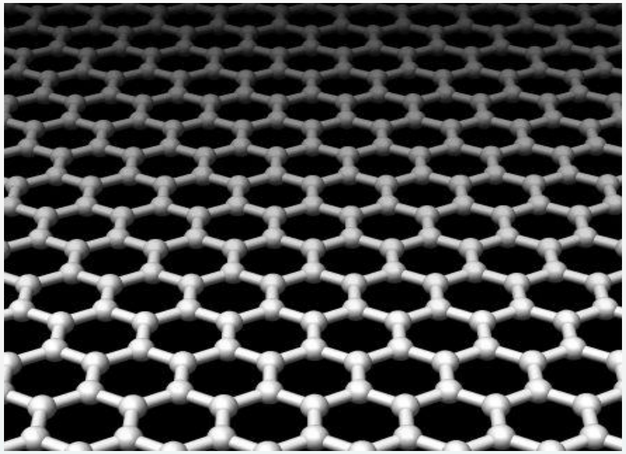


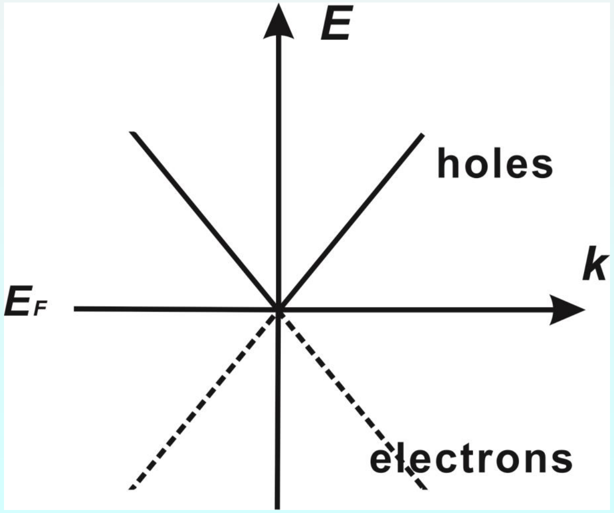


$$E \propto |k|$$

$$E = \sqrt{m^2c^4 + c^2\hbar^2k^2}$$

With $m = 0$ (massless)

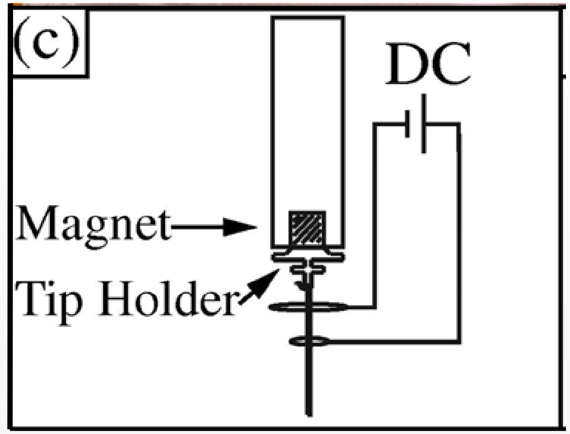




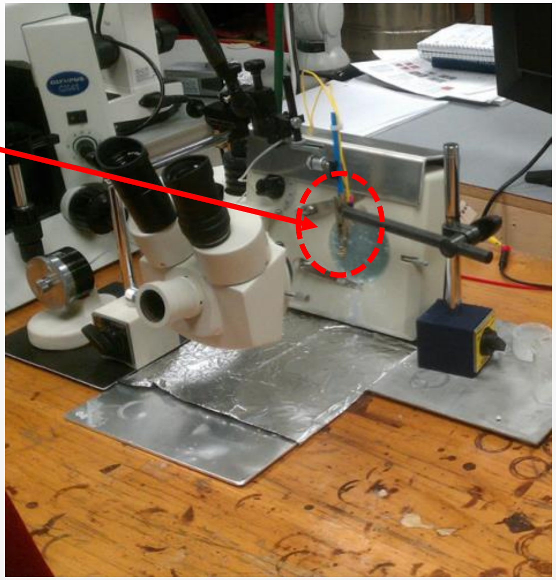
Outline

1. Background and purpose (massive to massless)
2. *Scanning tunneling microscopy (STM)*
3. Electrostatically lifting top layer of graphite
4. Vertical displacement properties
5. Summary, publications, acknowledgement, etc.

Instruments and samples



Double Lamella method



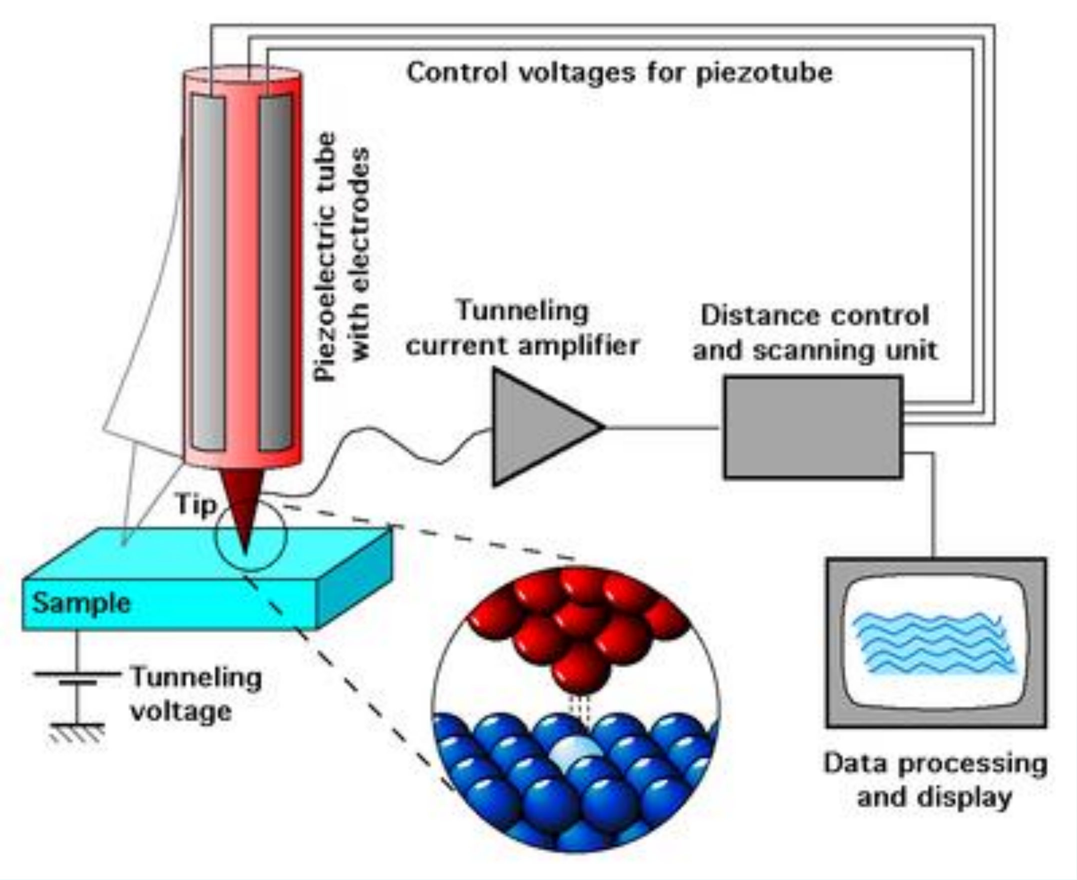
Optical
Microscope
STM Tip
Etching

UHV STM :

base pressure is 10^{-10} Torr

Highly ordered pyrolytic graphite (HOPG)

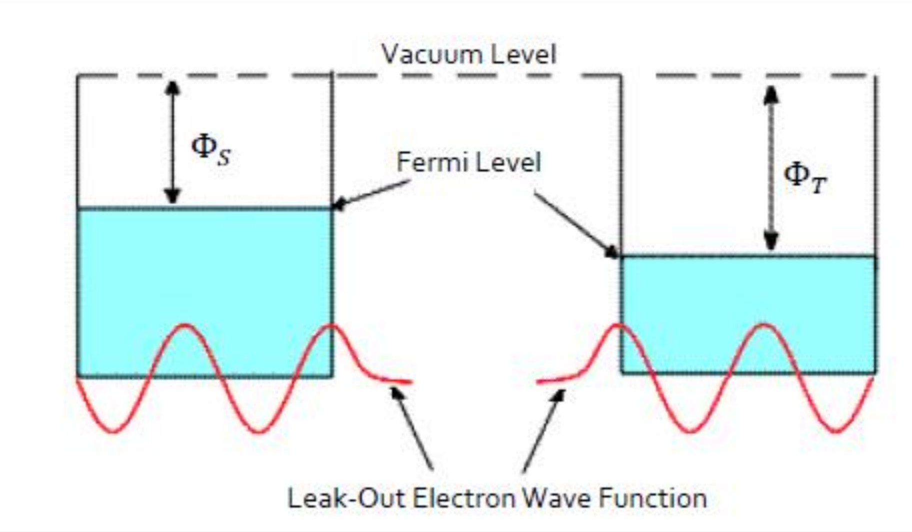
Research tool: Scanning Tunneling Microscope

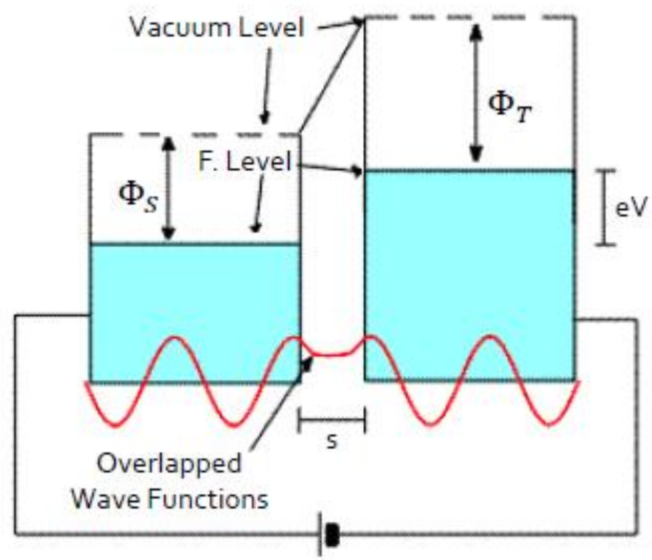


- ➢ Sharp metal tip
- ➢ Conductive sample
- ➢ Piezodrive
- ➢ Feedback loop
- ➢ Computer

- ➢ Tracks the topography of the sample.
- ➢ *Delivers* electronic structure of surfaces

Metal-insulator-metal tunneling





$$I = \frac{2\pi e}{\hbar} \sum_{T,S} f(E_T)[1 - f(E_S + eV)]\left|M_{T,S}\right|^2 \delta(E_T - E_S)$$

$$M_{T,S} = \frac{\hbar^2}{2m_e} \int (\psi_T \nabla \psi_S^* - \psi_S^* \nabla \psi_T) \cdot dS$$

$$\psi_S(z) = \psi_S^0 e^{-\kappa z} \text{ and } \psi_T(z) = \psi_T^0 e^{-\kappa(s-z)}$$

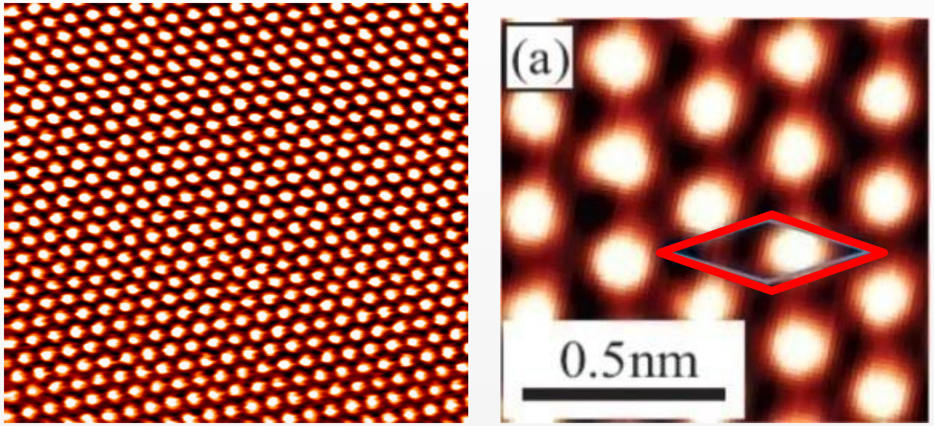
(The STM tip is stable)

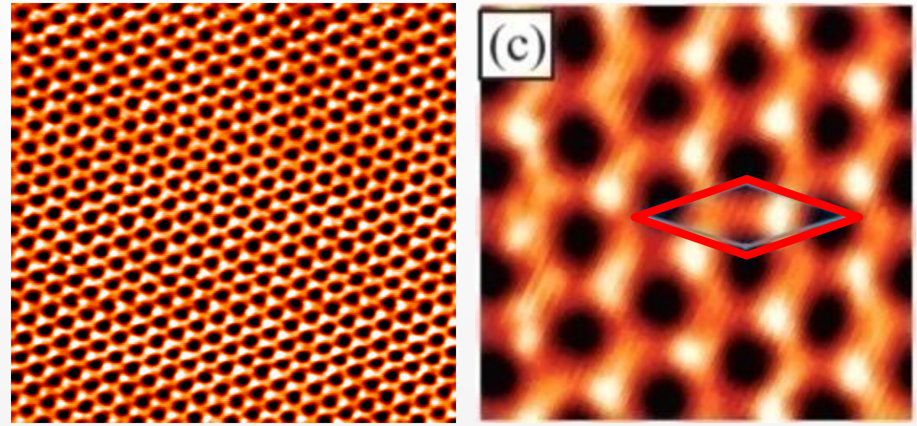
$$I \propto \left|\psi_S^0\right|^2 e^{-2\kappa s}$$

- $f(E_i)$ is the Fermi function
- Matrix element :overlap of wave functions
- Integral gives exponential dependence on s

Difference between graphite and graphene in STM

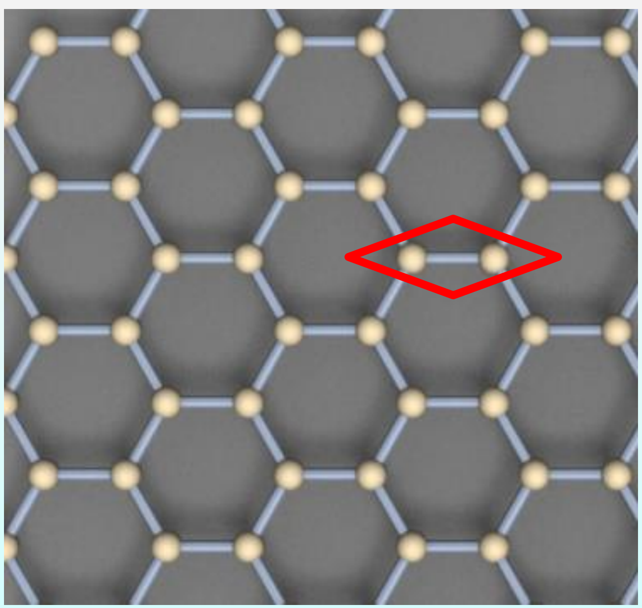
From graphite to graphene

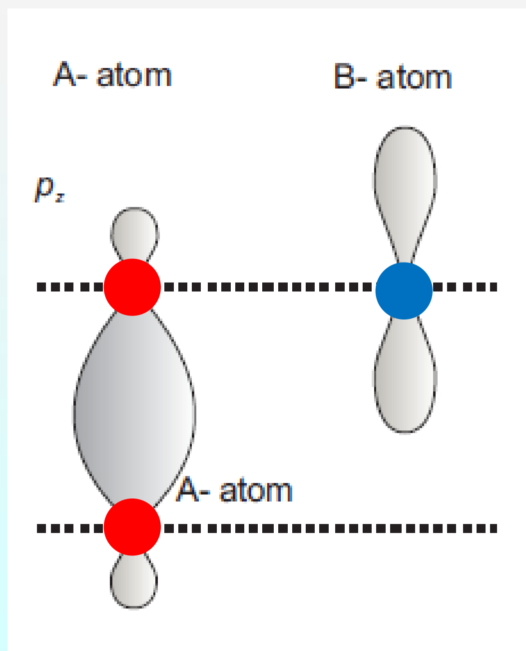


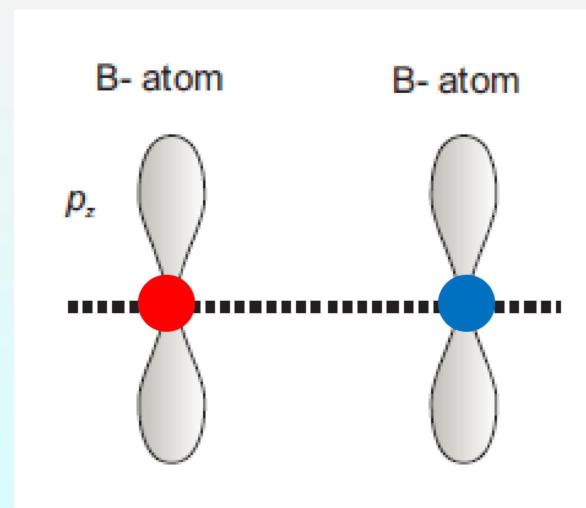


Graphite:Triangular symmetry

Graphene: Hexagonal symmetry







Outline

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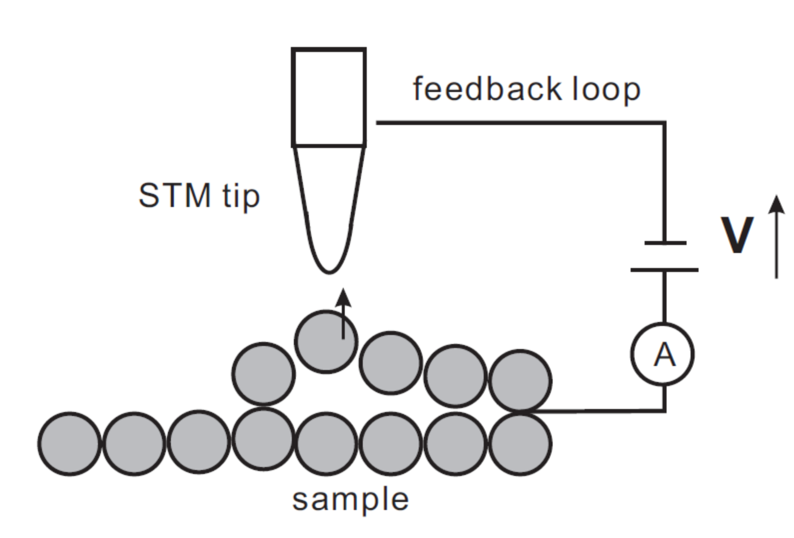
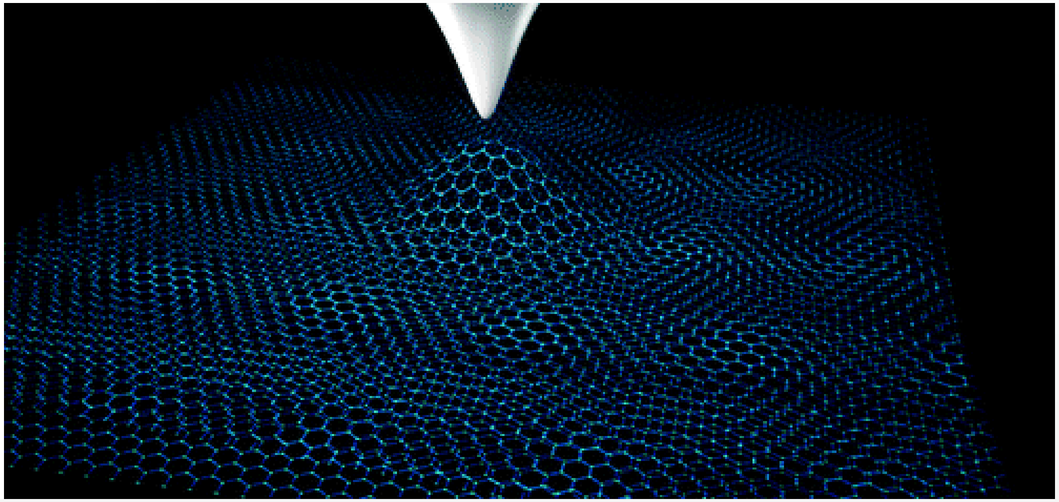
Electrostatic manipulation STM (EM-STM)

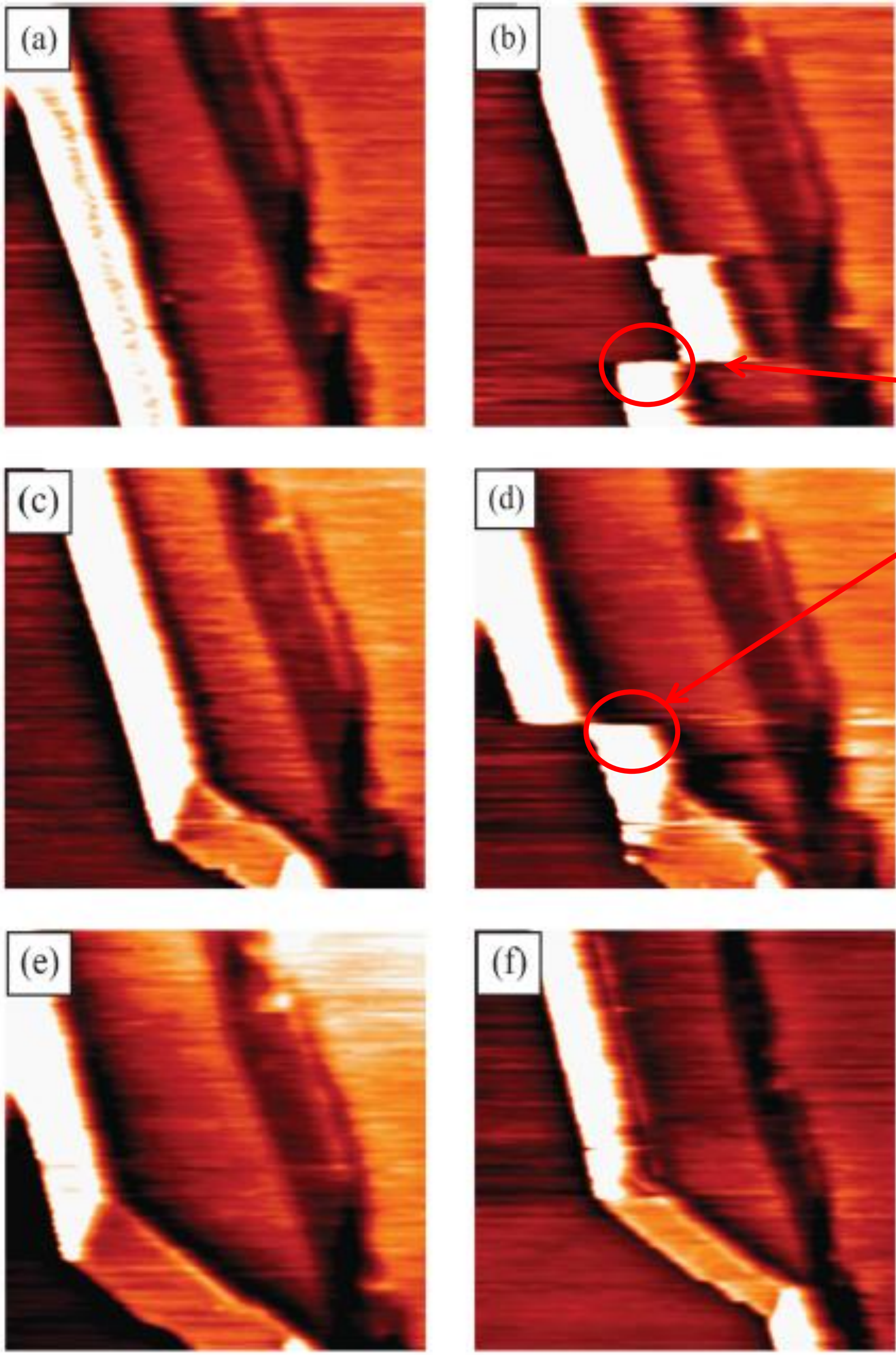




ACS Nano, **3** (11), 3455 (2009)

- Feedback loop on
- Constant tunneling constant current maintained
- Bias voltage increase with the scan is paused
- STM tip induces perturbation on sample surface

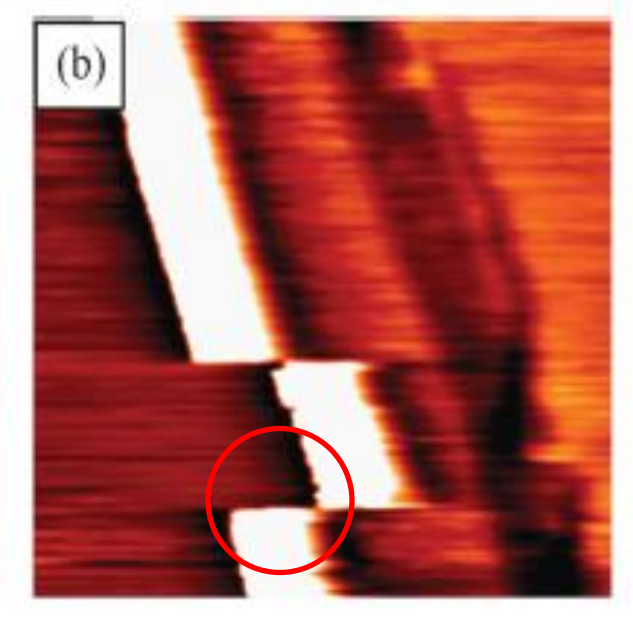
EM-STM on graphite strip

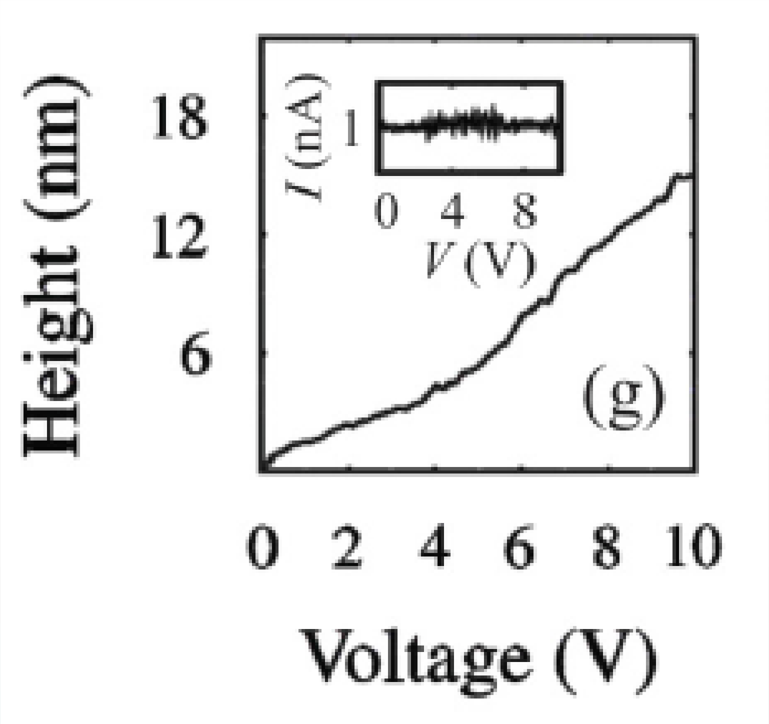


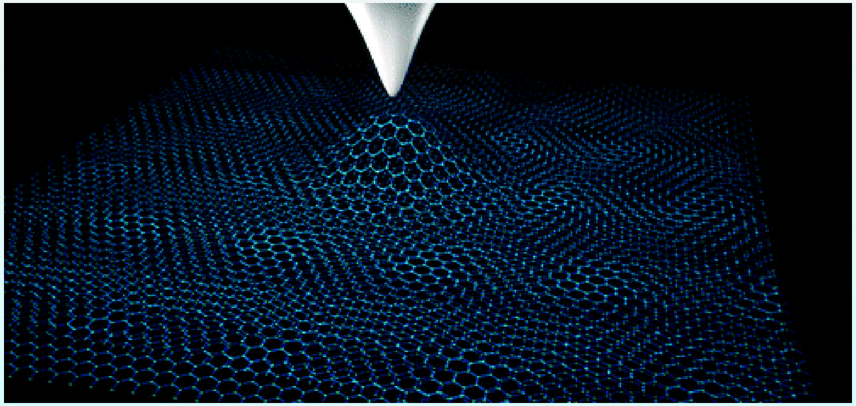
Two pulses of bias voltage
Form 0 V-10 V

- Surface morphology is alterted by STM tip
- 150 nm × 150 nm filled-state STM images of one location on graphite
- Constant tunneling current I=1.0 *nA*.

Recording the tip's height and tunneling current



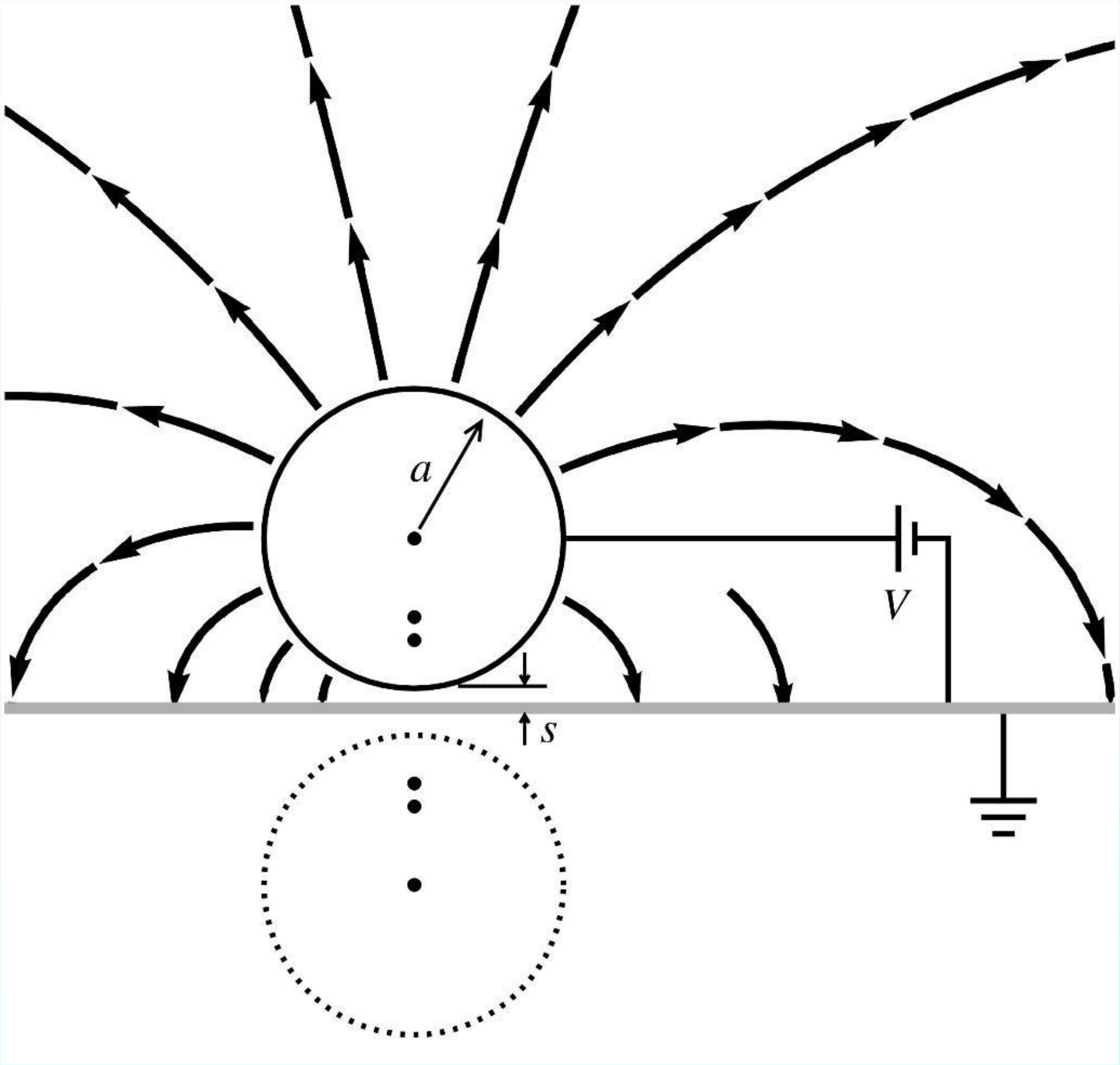




- Tunneling current remain constant
- continuous increase in the height of the STM tip with increase in bias voltage

Role of the bias voltage (Image charge model)

Staring by replacing sphere with point charge: $q_0 = 4\pi\varepsilon_0 aV$ at $x_0 = a + s$



$$q_i = \left(\frac{a}{x_0 + x_{i-1}}\right) q_{i-1}$$

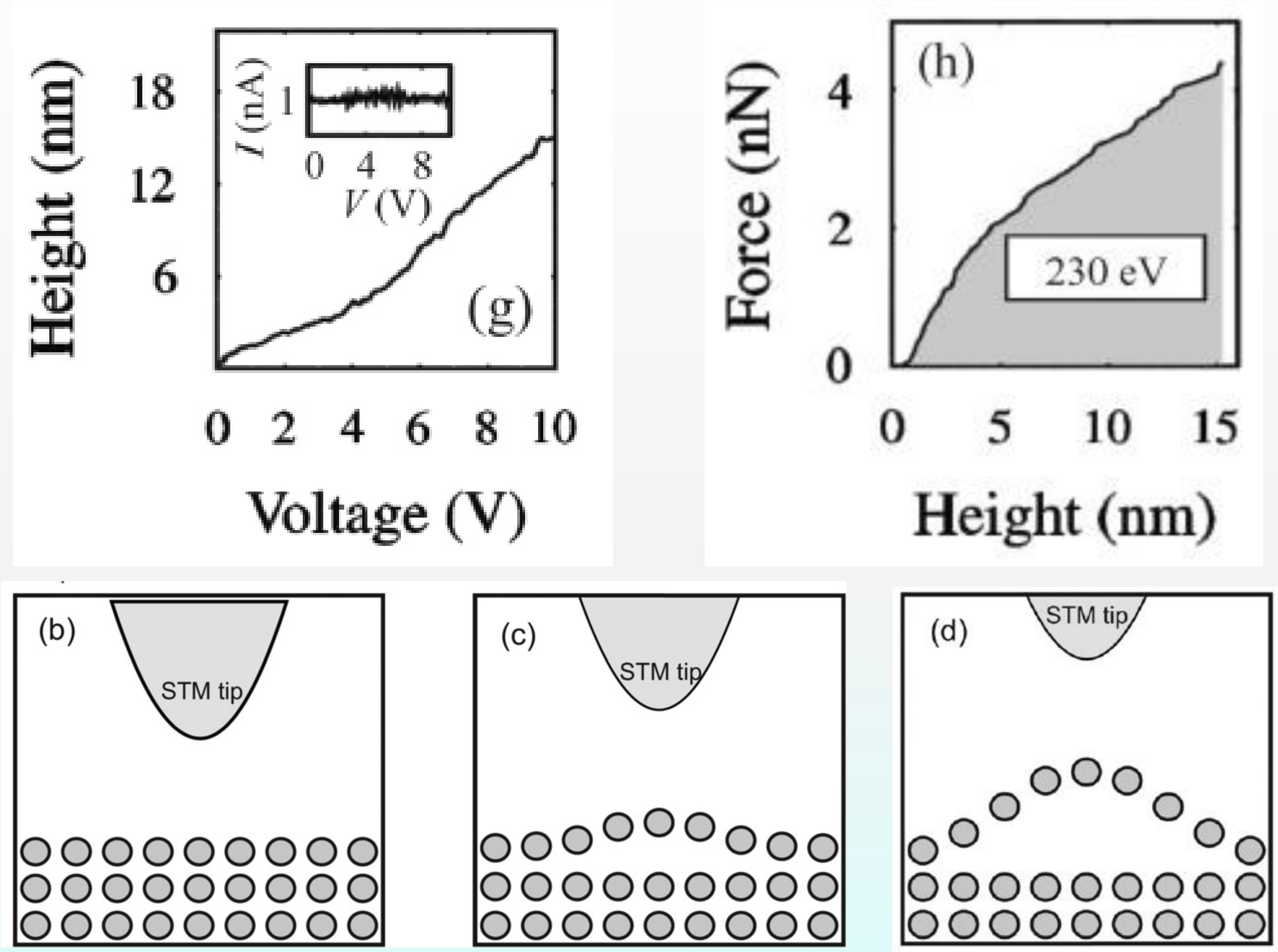
$$x_i = x_0 - \frac{a^2}{x_0 + x_{i-1}}$$

$$U = \frac{1}{2}\left(q_0 + \sum_{i=1}^{N} q_i\right) V$$

$$F = -\frac{\partial U}{\partial x_0} = -\frac{V}{2}\sum_{i=1}^{N}\frac{\partial q_i}{\partial x_0}$$

$$F = -2\pi\varepsilon_0 aV^2 \sum_{i=1}^{N}\frac{\partial Q_i}{\partial x_0} \propto V^2$$

EM-STM measurement on graphite



- STM tip vertically lifted up the surface layer.
- Constant tunneling current is shown as an inset.

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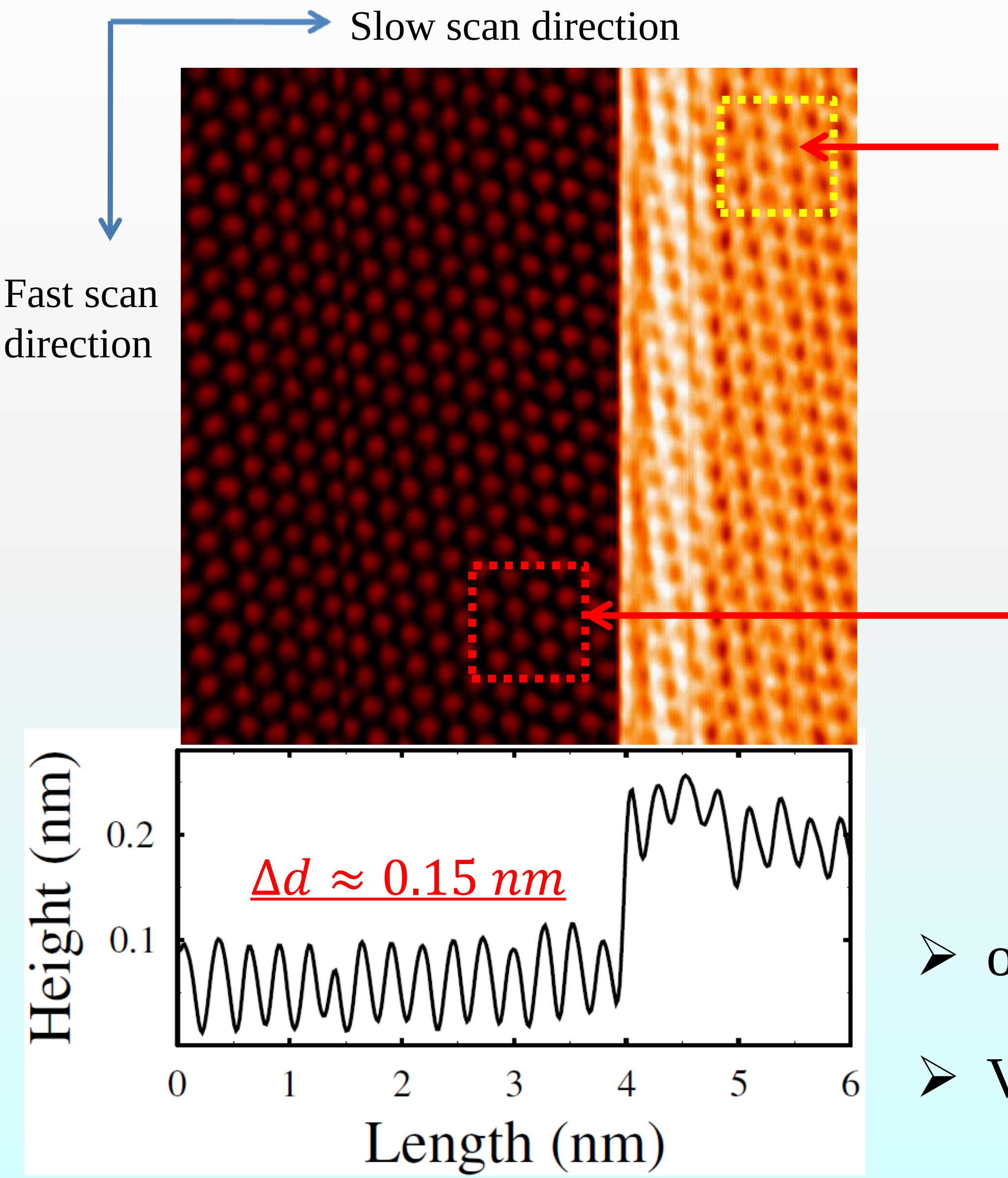
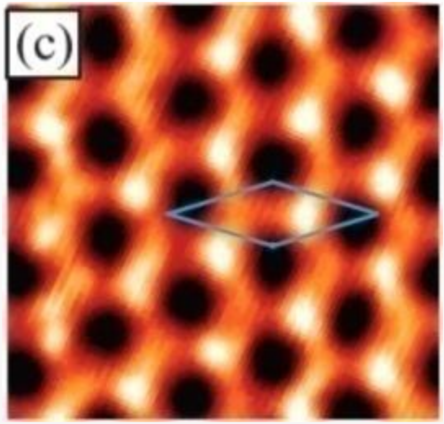
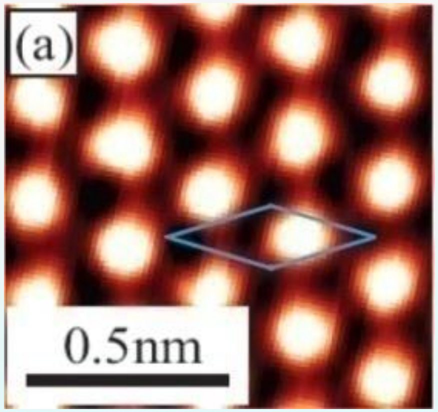
Vertical Jump Caught in Mid-Scan



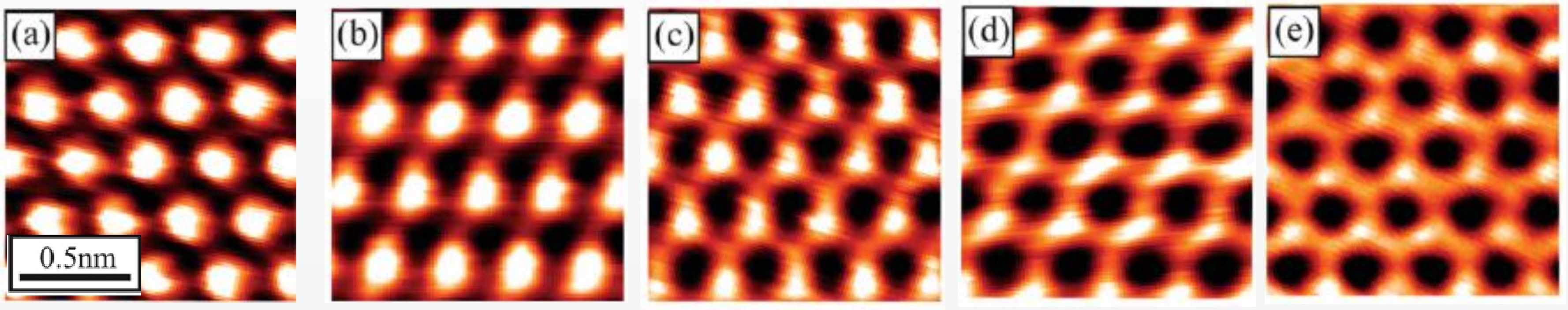




- observing the transition
- Vertical jump is caught

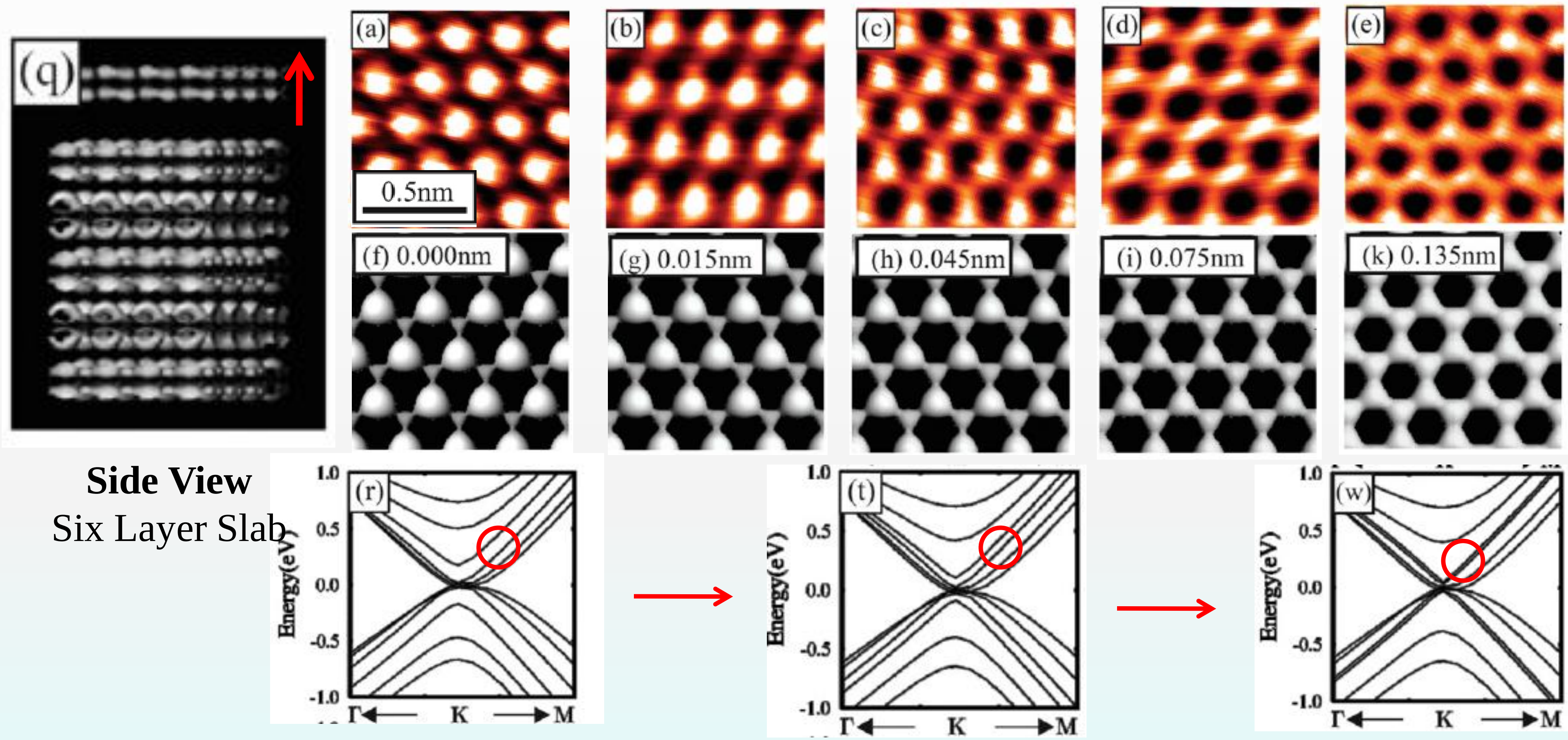
Full triangular to full hexagonal symmetry

Realized by performing EM-STM measurements



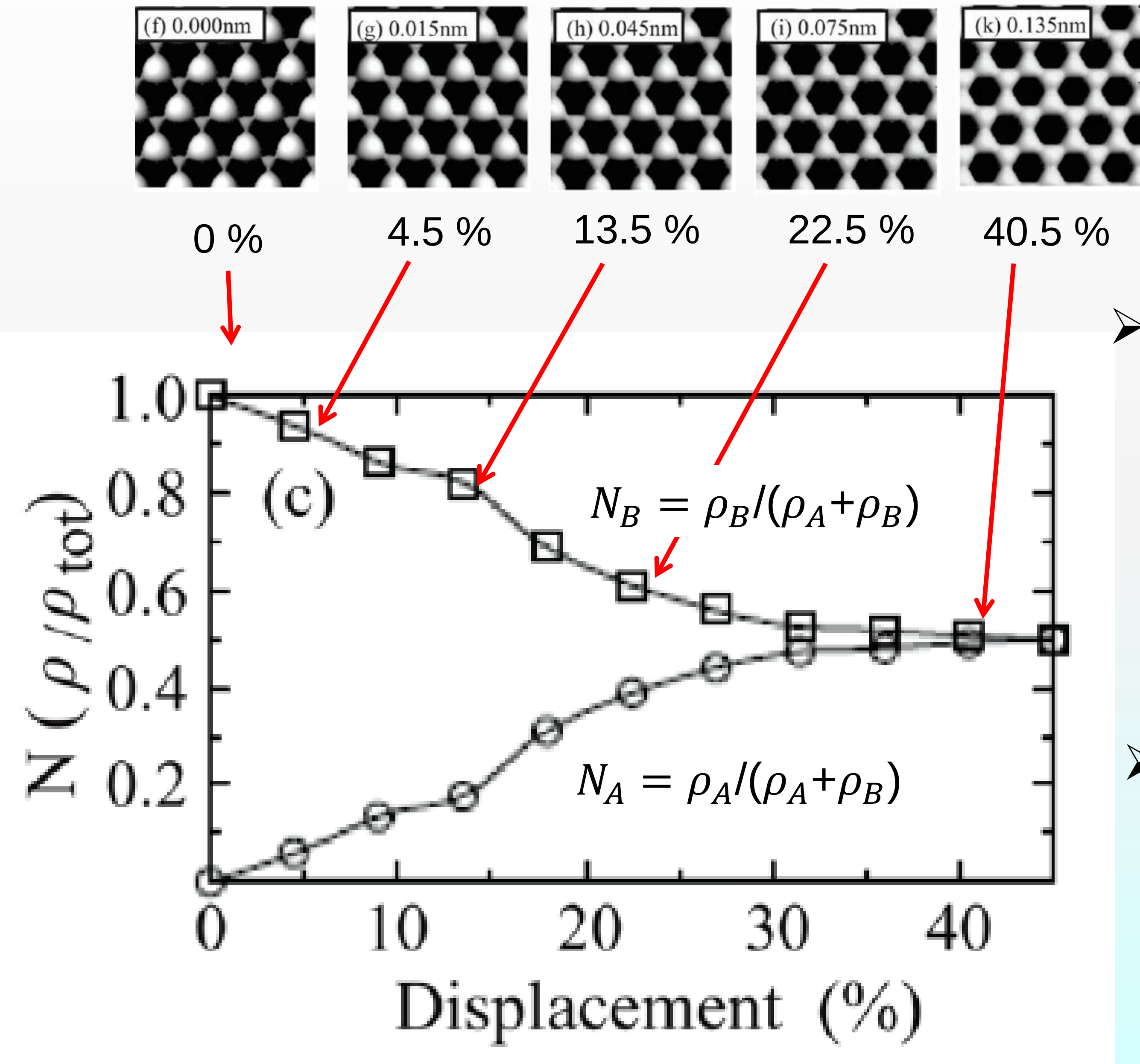
a) Big bright circle--- *Pz* orbitals of B atom
b) Weak visible A-atom
c) Asymmetrical hexagonal appears
d) More balanced hexagonal symmetry
e) Nearly perfect hexagonal symmetry

Vertical displacement of top layer of graphite



- Simulated STM images without tip.
- Isocontour Surfaces
- Extracted at incrementally higher values of the LDOS.
- DFT implemented in the plane-wave basis set VASP.

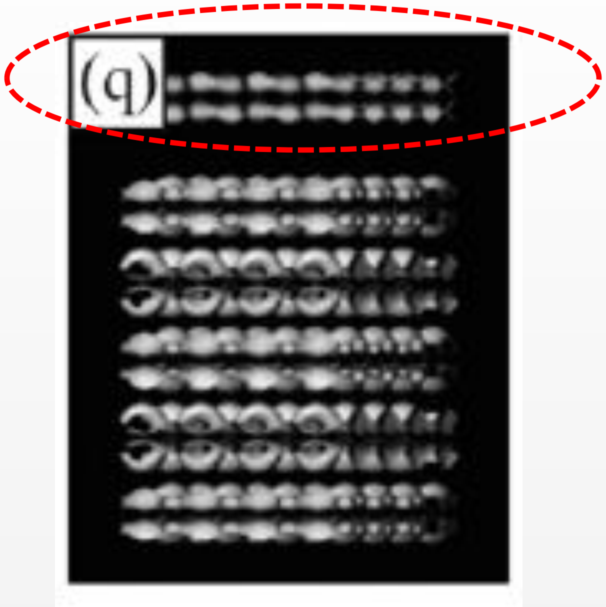
Surface charge reconstruction

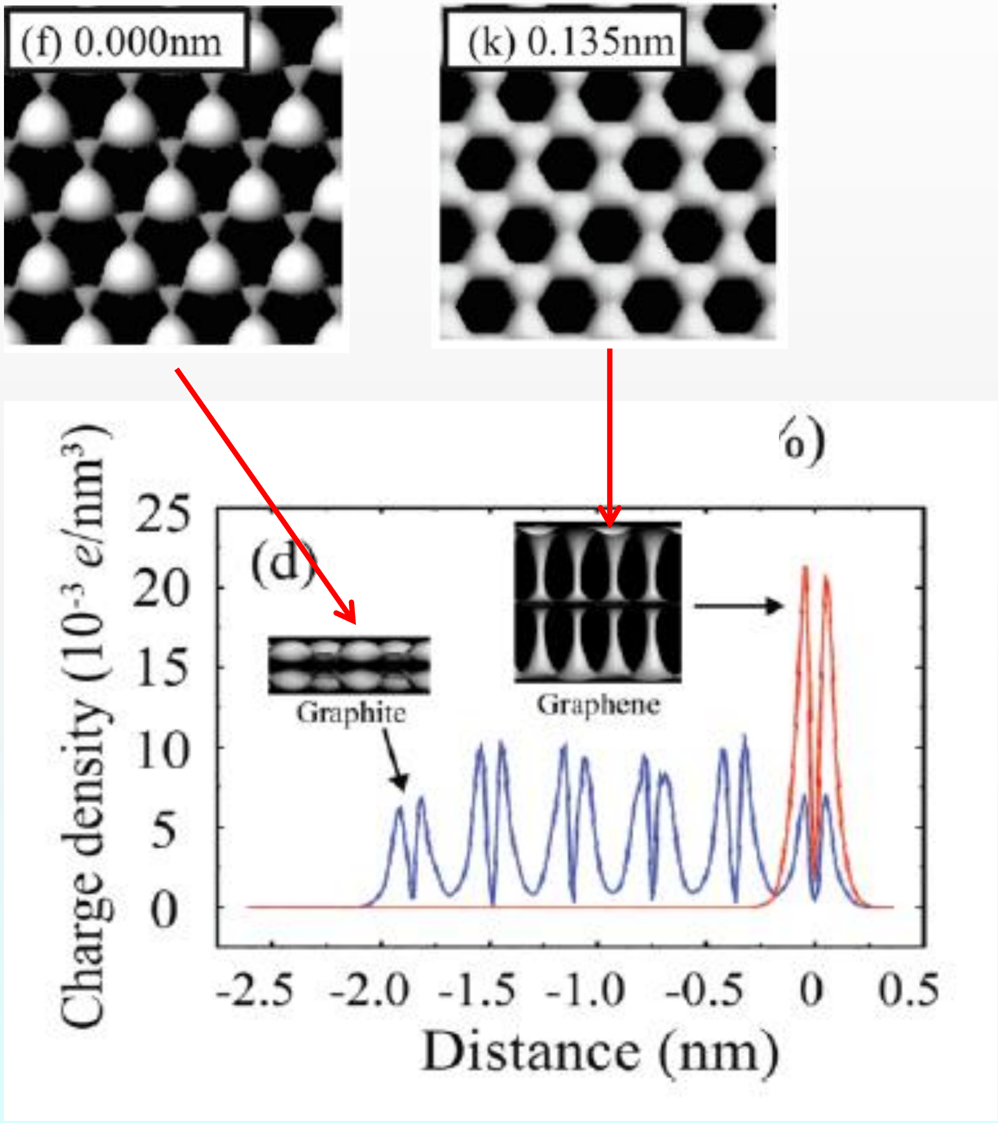


- Charged densities reconstruct with displacement

- Effective mass scaling parameter.

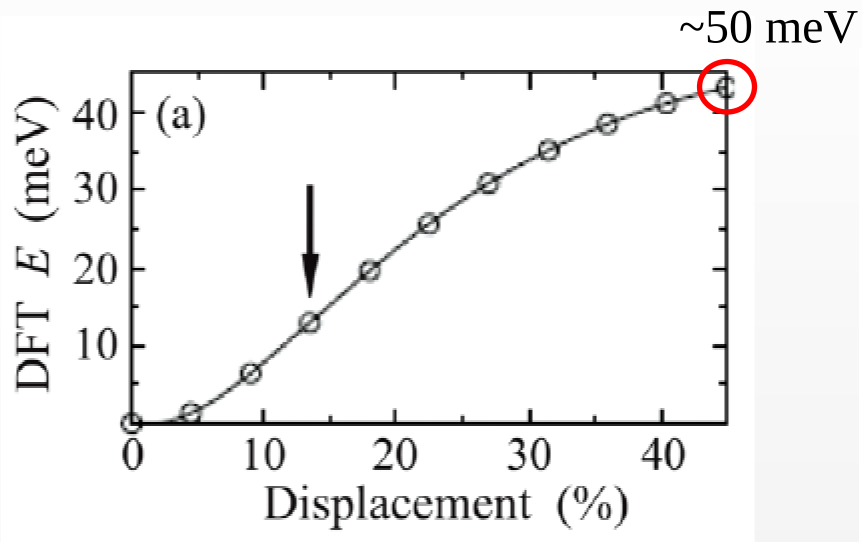
Giant surface charge density



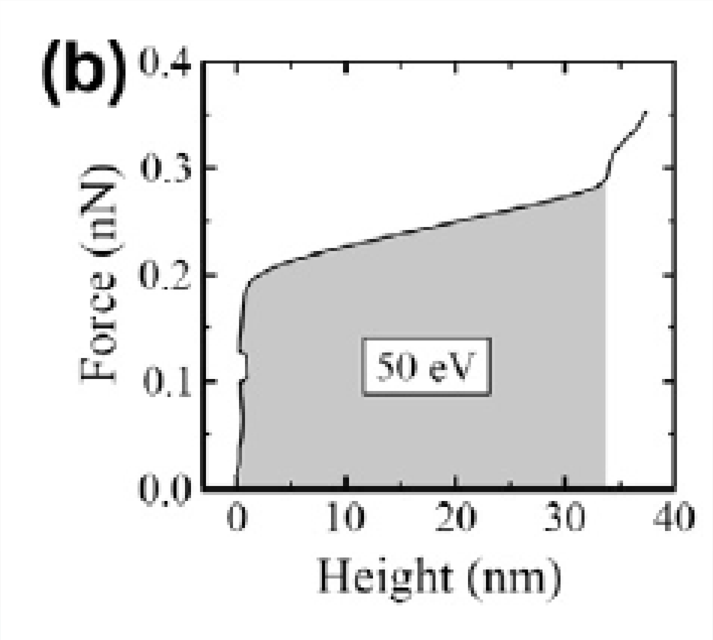


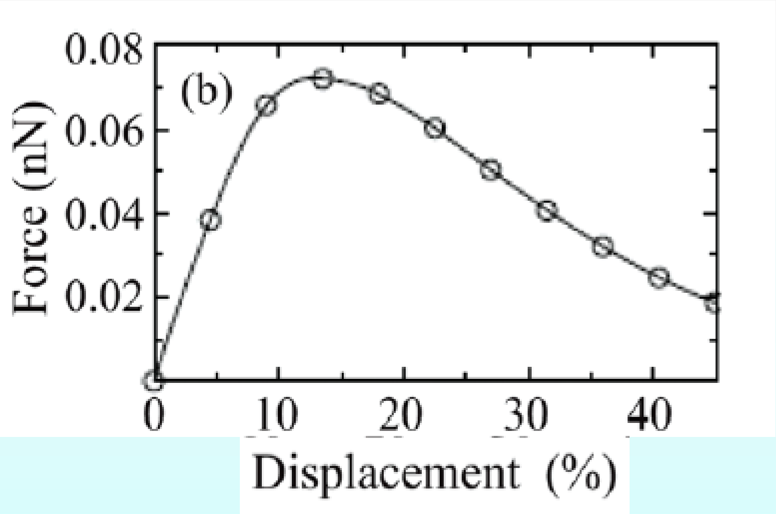
- ➢ Giant charge density of graphene
- ➢ High current carrying capacity and thermal conductivity

Vertical displacement total energy consideration



Total energy vs. displacement





Force vs. displacement

- 50 meV to separate one unit cell
- Region with 10 nm × 10 nm size was affected

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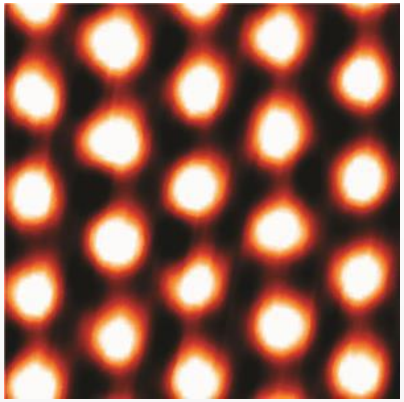
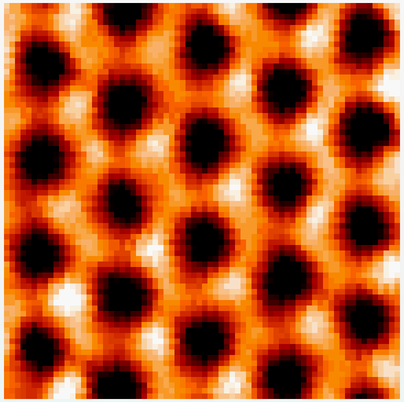
Summary

- ➢ EM-STM technique broadens the abilities of the STM;
- ➢ Surface graphite displacement induces a charge redistribution;
- ➢ The graphite to graphene transition was quantified;





1. ***Electronic Transition from Graphite to Graphene via Controlled Movement of The top Layer with Scanning Tunneling Microscopy*** P. Xu, Y. Yang, D. Qi, S. D. Barber, J. K. Schoelz, M. L. Ackerman, L. Bellaiche, and P. M. Thibado Physical Review B 86, 085428L.

2. ***New scanning tunneling microscopy technique enables systematic study of the unique electronic transition from graphite to graphene*** P. Xu, Y. Yang, S. D. Barber, J. K. Schoelz, D. Qi, M. L. Ackerman, L. Bellaiche, and P. M. Thibado, Carbon 50, 4633

3. ***A pathway between Bernal and rhombohedral stacked graphene layers with scanning tunneling microscopy*** P. Xu, Y. Yang, D. Qi, S. D. Barber, M. L. Ackerman, J. K. Schoelz, T. B. Bothwell, S. Barraza-Lopez, L. Bellaiche, and P. M. Thibado, Applied Physics Letters 100, 201601

Publications

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2013 P. Xu, S. D. Barber, J. K. Schoelz, M. L. Ackerman, D. Qi, P. M. Thibado, V. D. Wheeler, L. O. Nyakiti, R. L. Myers-Ward, C. R. Eddy, Jr., and D. K. Gaskill, "*Atomic-scale movement induced in nanoridges by scanning tunneling microscopy on epitaxial graphene grown on 4H-SiC(0001)*" Journal of Vacuum Science and Technology B 31(4), 04D101

P. Xu, M. L. Ackerman, S. D. Barber, J. K. Schoelz, D. Qi, P. M. Thibado, V. D. Wheeler, L. O. Nyakiti, R. L. Myers-Ward, C. R. Eddy, Jr., and D. K. Gaskill, "*Graphene Manipulation on 4H-Sic(0001) using Scanning Tunneling Microscopy*" Japanese Journal of Applied Physics 52, 035104

2012 P. Xu, Y. Yang, D. Qi, S. D. Barber, J. K. Schoelz, M. L. Ackerman, L. Bellaiche, and P. M. Thibado, "*Electronic Transition from Graphite to Graphene via Controlled Movement of The top Layer with Scanning Tunneling Microscopy*" Physical Review B 86, 085428

L. Dong, J. Hansen, P. Xu, M. L. Ackerman, S. D. Barber, J. K. Schoelz, D. Qi, and P. M. Thibado, "*Electromechanical properties of freestanding graphene functionalized with tin oxide (SnO_2) nanoparticles*" Applied Physics Letters 101, 061601

P. Xu, Y. Yang, S. D. Barber, J. K. Schoelz, D. Qi, M. L. Ackerman, L. Bellaiche, and P. M. Thibado, "*New scanning tunneling microscopy technique enables systematic study of the unique electronic transition from graphite to graphene*" Carbon 50, 4633

P. Xu, Y. Yang, D. Qi, S. D. Barber, M. L. Ackerman, J. K. Schoelz, T. B. Bothwell, S. Barraza-Lopez, L. Bellaiche, and P. M. Thibado, "*A pathway between Bernal and rhombohedral stacked graphene layers with scanning tunneling microscopy*" Applied Physics Letters 100, 201601

J. K. Schoelz, P. Xu, S. D. Barber, D. Qi, M. L. Ackerman, G. Basnet, C. T. Cook, and P. M. Thibado, "*High-percentage success method for preparing and pre-evaluating tungsten tips for atomic-resolution scanning tunneling microscopy*" Journal of Vacuum Science and Technology B 30(3), 033201

P. Xu, Y. Yang, S. D. Barber, M. L. Ackerman, J. K. Schoelz, D. Qi, I. A. Kornev, L. Dong, L. Bellaiche, S. Barraza-Lopez, and P. M. Thibado, "*Atomic control of strain in freestanding graphene*" Physical Review B 85, 121406(R)

2011 P. Xu, D. Qi, S. D. Barber, C. T. Cook, M. L. Ackerman, and P. M. Thibado, "S*treamlined inexpensive integration of a growth facility and scanning tunneling microscope for in-situ characterization*" Journal of Vacuum Science and Technology B 29(4), 041804

P. Xu, D. Qi, M. L. Ackerman, S. D. Barber, and P. M. Thibado, "*Controlling Mn depth profiles in GaMnAs during high-temperature molecular beam epitaxial growth*" Journal of Crystal Growth 327, 42

In the future…

Moving to Chicago, IL

(Late August, 2014)
Software Engineering (MS program)

College of Computing and Digital Media

DePaul University

To be continued…

Acknowledgements

Principal investigator:

Dr. Paul Thibado

Group members:

Dr. Peng Xu, Dr. Steven Barber, Matt Ackerman, and Kevin Schoelz

Collaborators:

Dr. Laurent Bellaiche, Dr. Yurong Yang

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THANK YOU!