SAND2013-10156C

Electronic dispersion in two overlapping graphene sheets: *Impacts of long-range atomic ordering and periodic potentials*

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9th International Symposium on Atomic Level Characterizations for New Materials and Devices '13
Dec. 2 – 7, 2013, Kailua-Kona, HI, USA.

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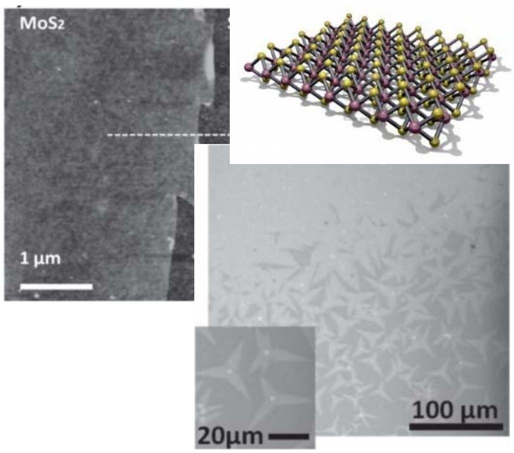
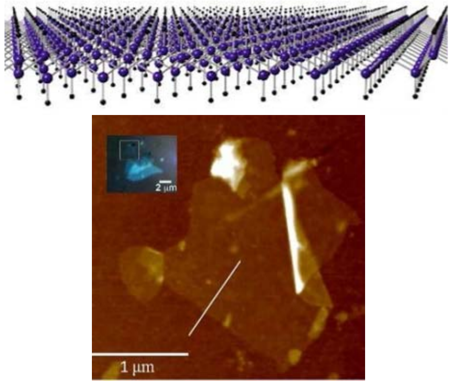
Stacked 2D-crystals: a new class of materials

- Various two-dimensional (2D) crystals



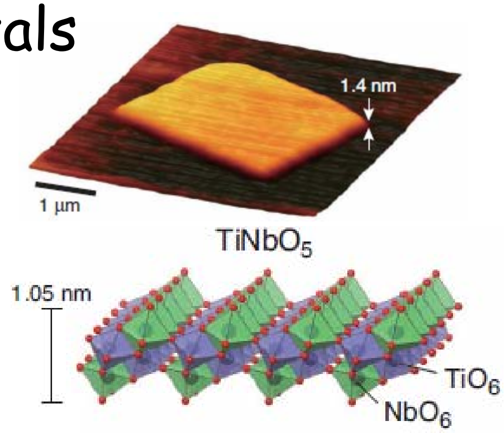
Molybdenum dichalcogenide

Lee et al., Advanced Materials, 24, 2320 (2012)



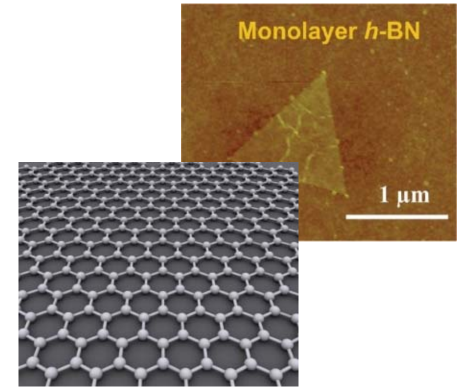
Germanane

Bianco et al., ACS Nano, 7, 4414 (2013)



Titanium Niobate

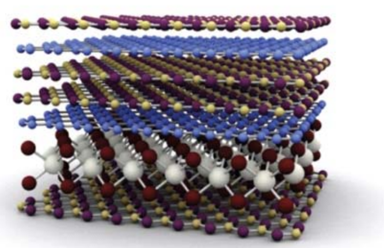
Osada et al., Adv. Funct. Mater. 21, 3482 (2011)



Graphene & h-BN

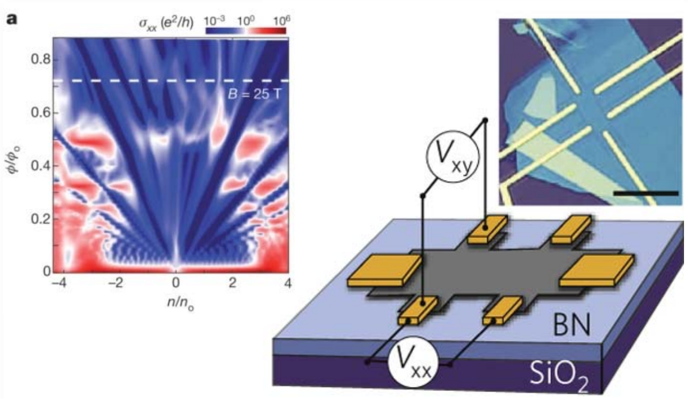
http://en.wikipedia.org/wiki/Graphene

- Hybrid 2D-solids can be realized
  - Combining materials
  - Emerging properties



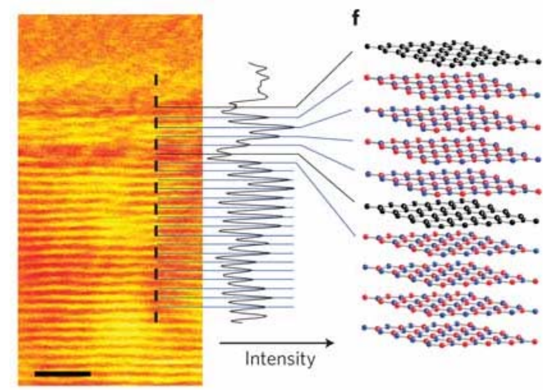
2D-based heterostructure

Novoselov et al., Nature 490, 192 (2012)



Graphene on BN

Dean et al., Nature Physics 7, 693 (2011); Dean et al., Nature 497, 598 (2013)



Graphene/BN superlattice

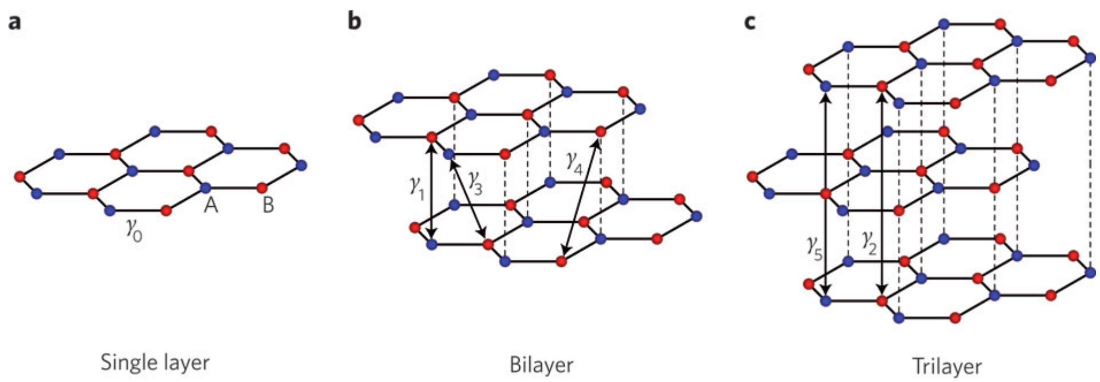
Haigh et al., Nature Materials 11, 764 (2012)

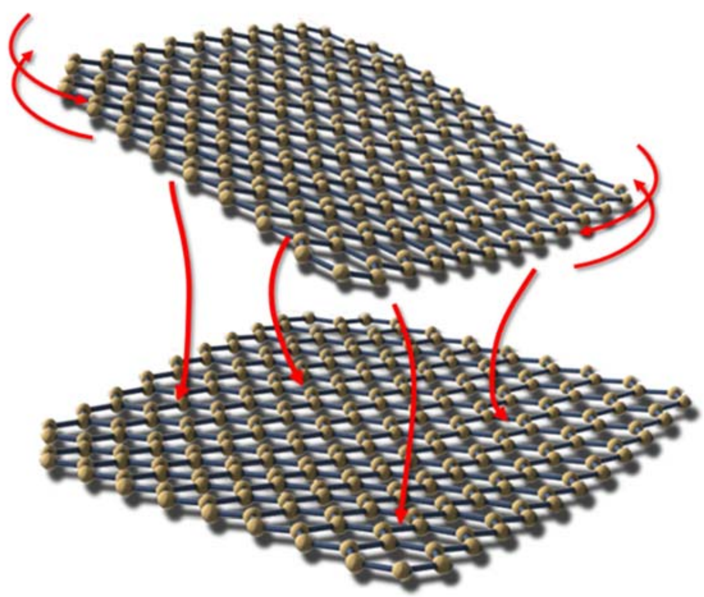
How would 2D-crystals interact electronically with each other?

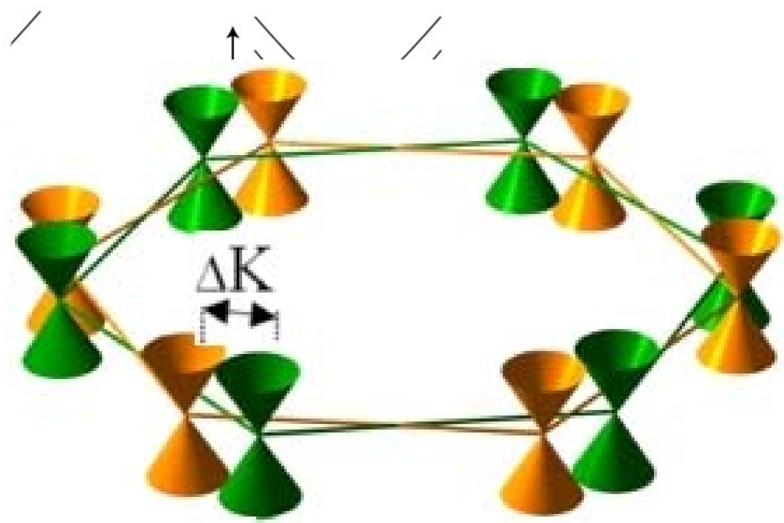
- We examine ***Twisted Bilayer Graphene (TBG)*** assembled via transfer process

How does azimuthal misorientation manifest itself in bilayer graphene?

- Bernal stacked graphene: strong interlayer interaction



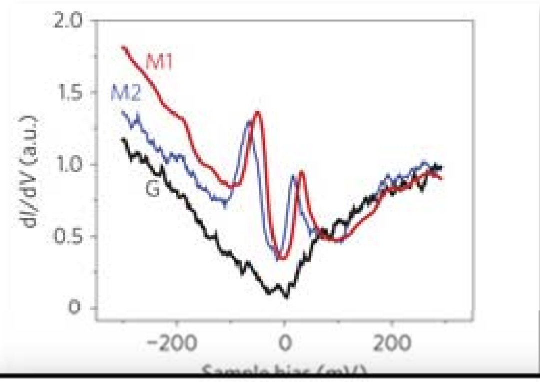




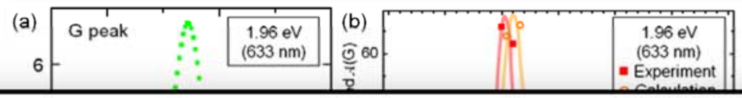
Li et al., Nature Physics 6, 109 (2010)

How does azimuthal misorientation manifest itself in bilayer graphene?

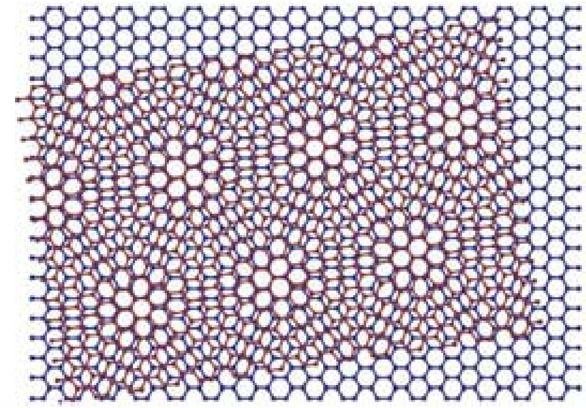
STS indicates van Hove singularities (vHs)



Raman shows resonant transition due to vHs or parallel states

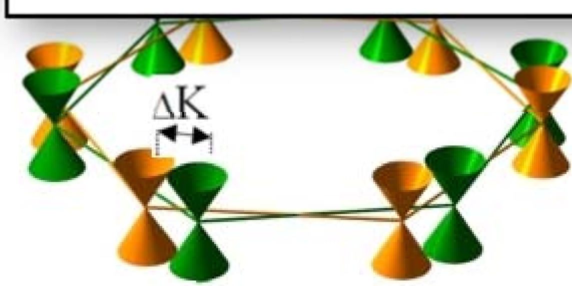


Moiré

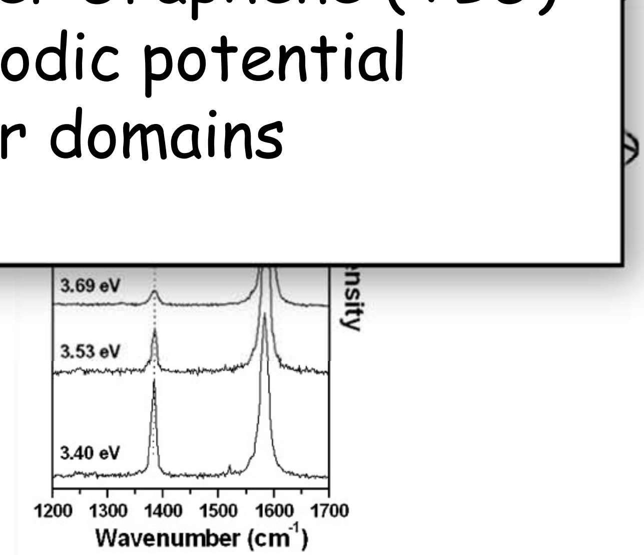


We study:

- Microscopic & atomic view of Twisted Bilayer Graphene (TBG)
- Interacting Dirac cones through moiré periodic potential
- Tunable optical absorption & emergent color domains
- Defects & inhomogeneities

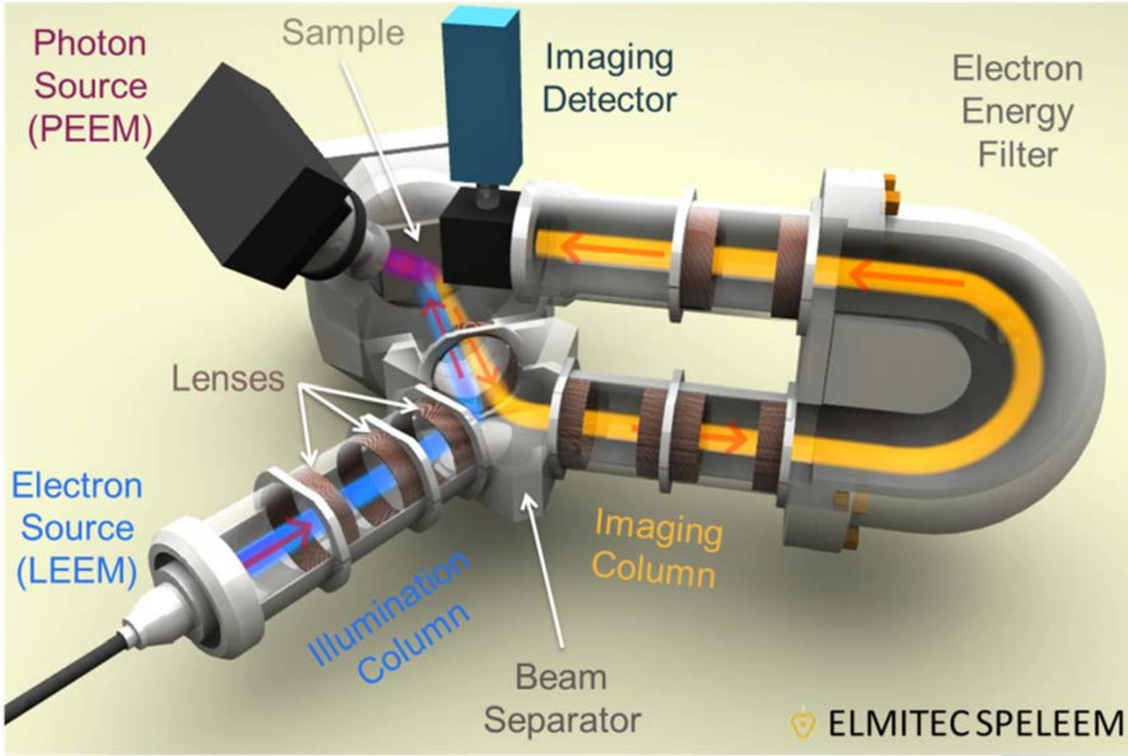


Li et al., Nature Physics 6, 109 (2010)



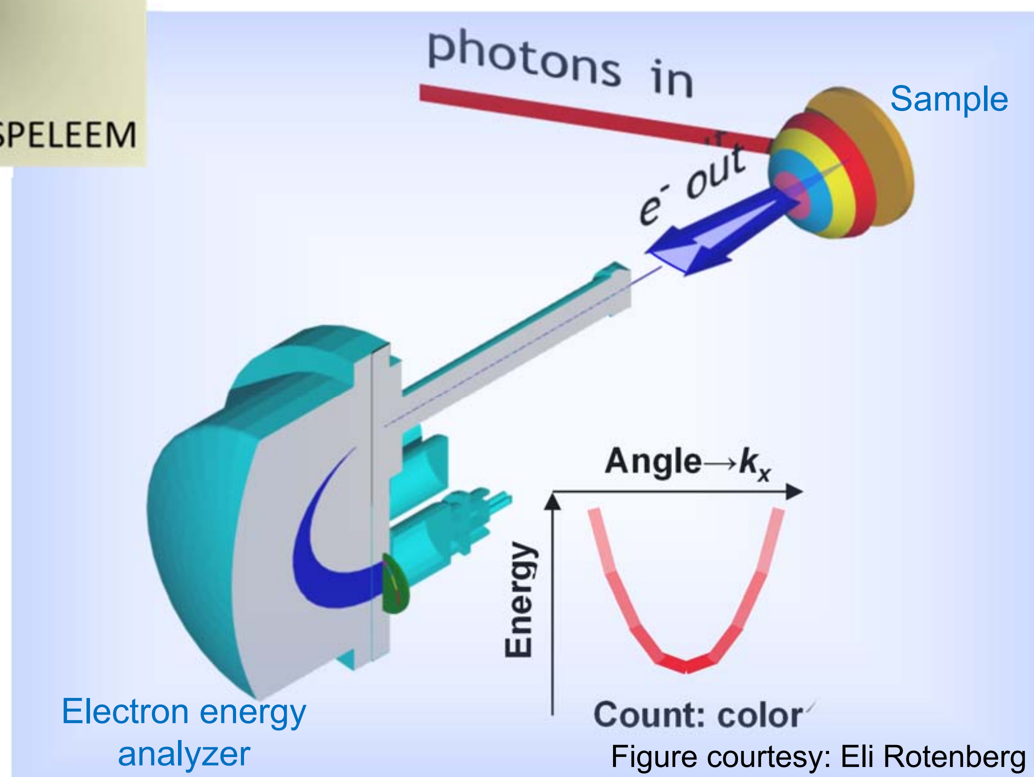
Righi et al., PRB 84, 241409(R) (2011)

LEEM/PEEM and ARPES



LEEM
(Low Energy Electron Microscopy)

– Surface-sensitive "reflection" electron microscopy

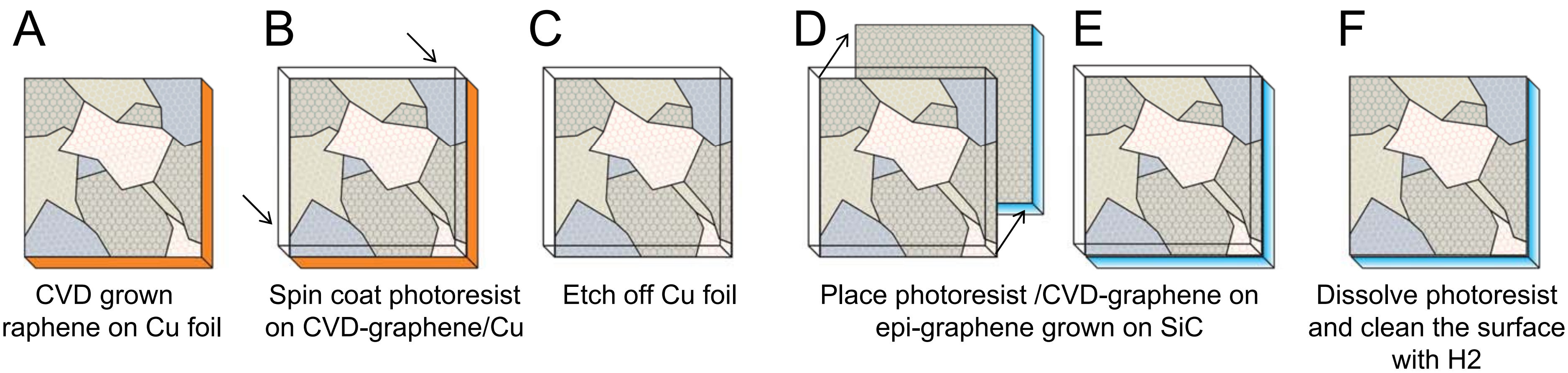


ARPES
(Angle-Resolved Photoemission Spectroscopy)

– Occupied electronic states' dispersion

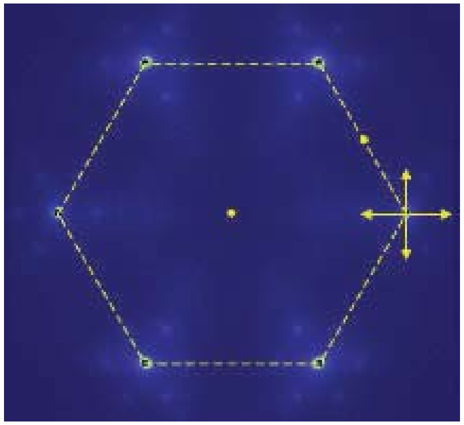
We make TBG by transfer

- Transferring CVD graphene onto epi-graphene (on SiC) yields large TBG domains with various twist angles
  - Carried out in collaboration with Jeremy Robinson at Naval Research Laboratory



  - Monolithic epi-graphene
  - Large-domain CVD graphene (>100um-size domain)

Epi-graphene on SiC(0001)



Bostwick et al., Nature Phys. 3, 36 (2007)

CVD graphene

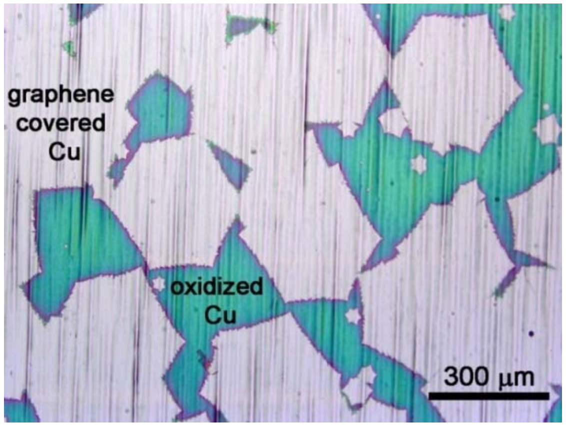
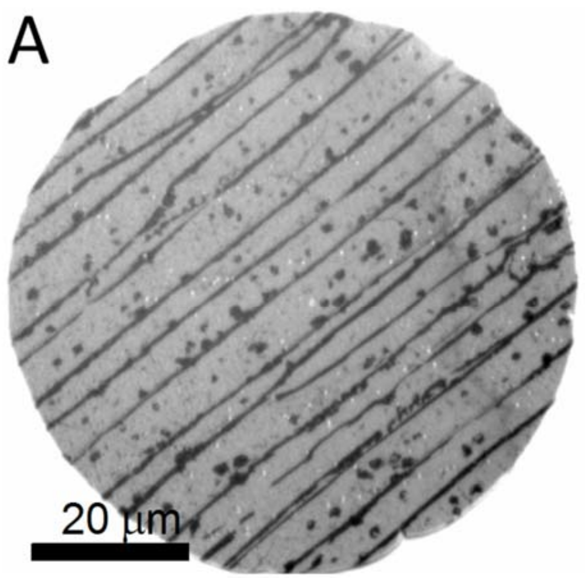


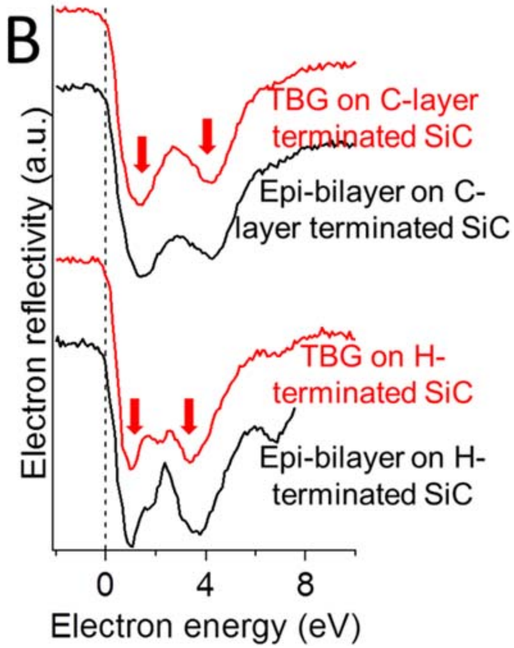
Figure courtesy: Jeremy Robinson

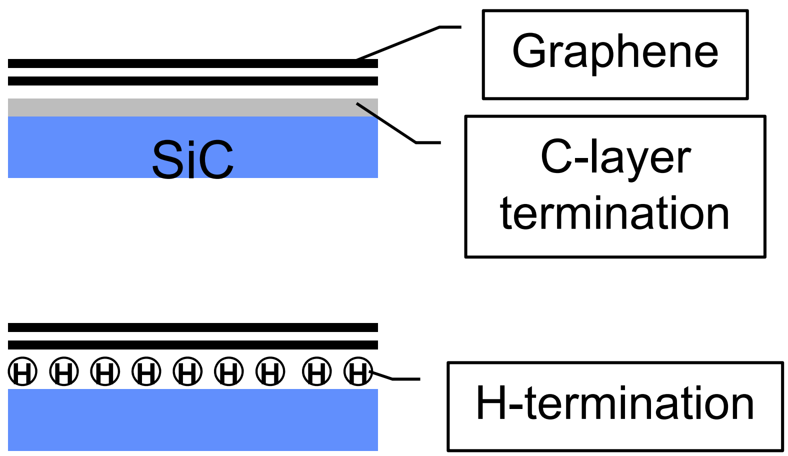
TBG shows electron reflectivity characteristic of bilayer graphene

- Two dips in electron reflectivity spectra: bilayer graphene on SiC
  - Low energy electron microscopy (LEEM) measurement



LEEM image of TBG



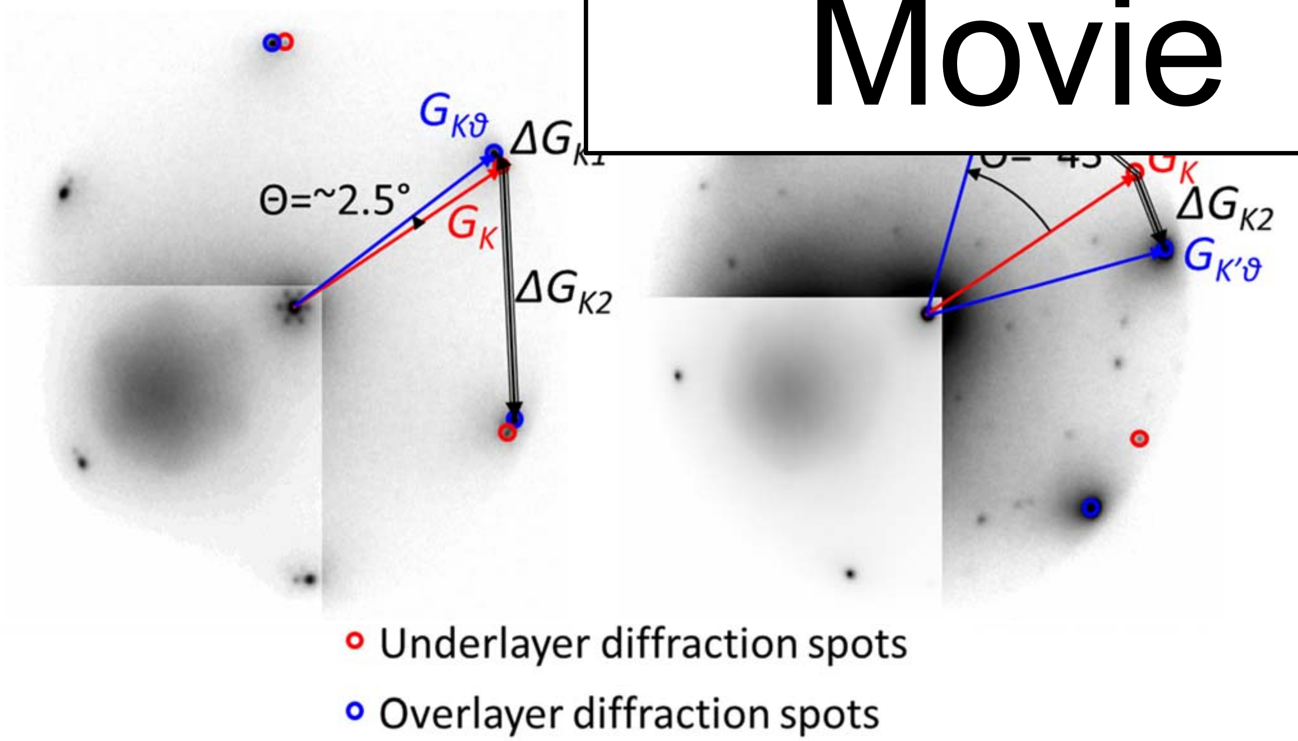


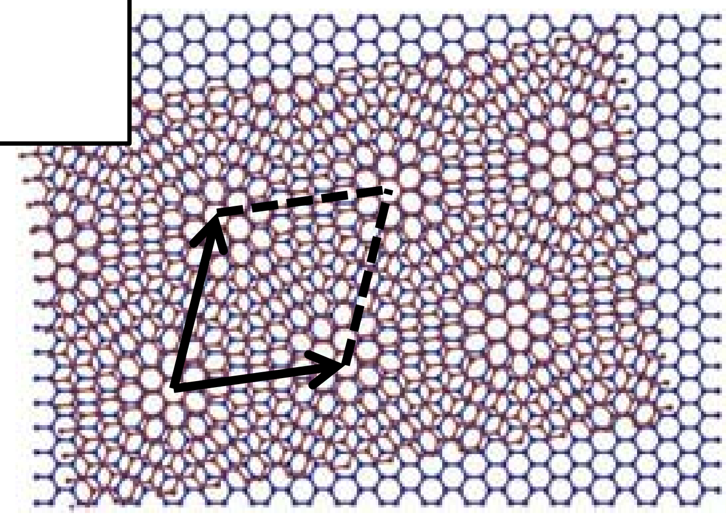
Ohta et al., PRB, 85, 075415 (2012)

TBG has long-range atomic order

- Diffraction patterns from TBG with a small and a large twist angles
  - Diffraction spots due to moiré

Movie



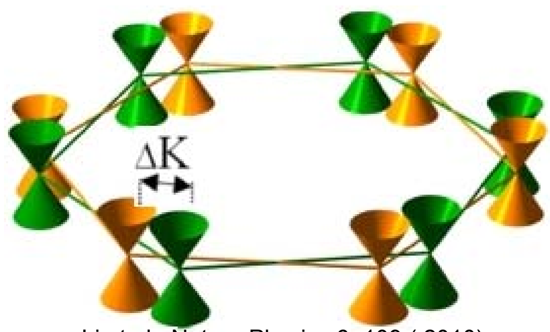


Real-space moiré vectors

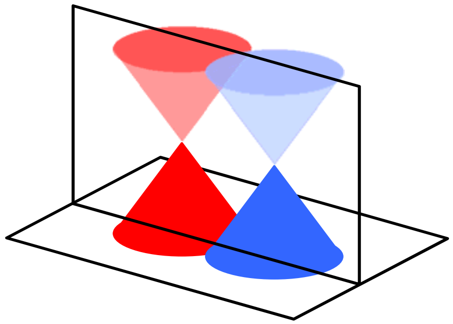
  - Minimum damage of graphene was confirmed using Raman spectroscopy
    - Please see PRB, 85, 075415 (2012) for detail

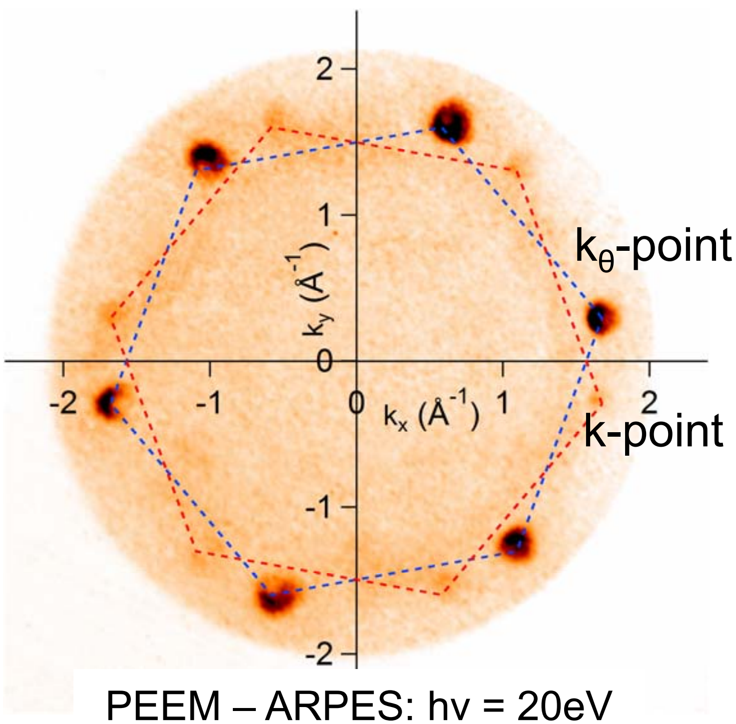
TBG has two sets of Dirac cones

- Electronic dispersion is measured using PEEM (photoemission electron microscopy) and ARPES (angle-resolved photoemission spectroscopy)
  - Upper (blue hexagon) and lower (red hexagon) graphene sheets create two sets of Dirac cones

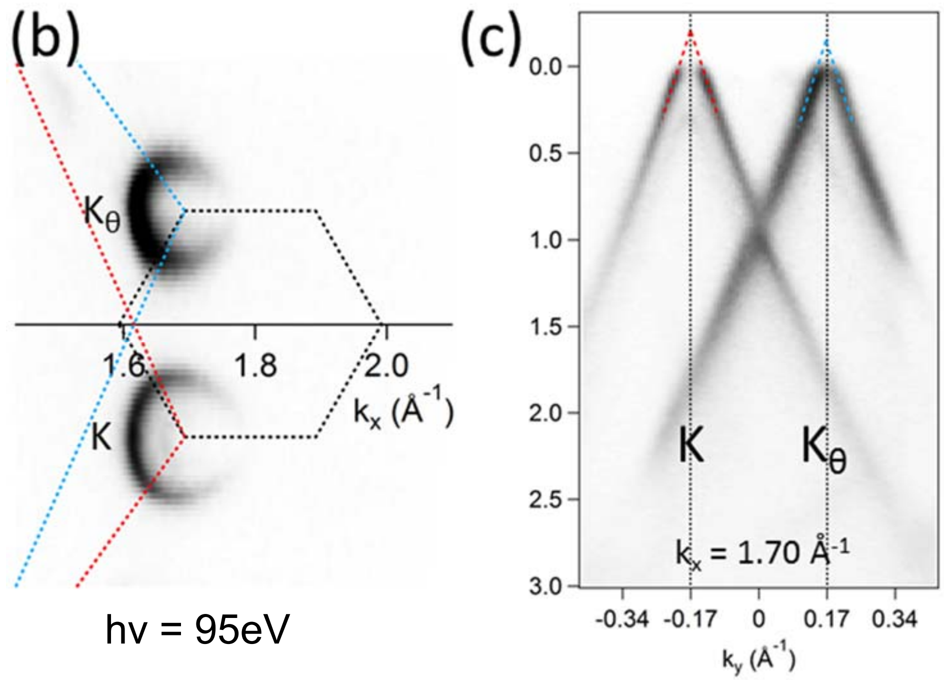


Li et al., Nature Physics 6, 109 (2010)





PEEM – ARPES: hv = 20eV

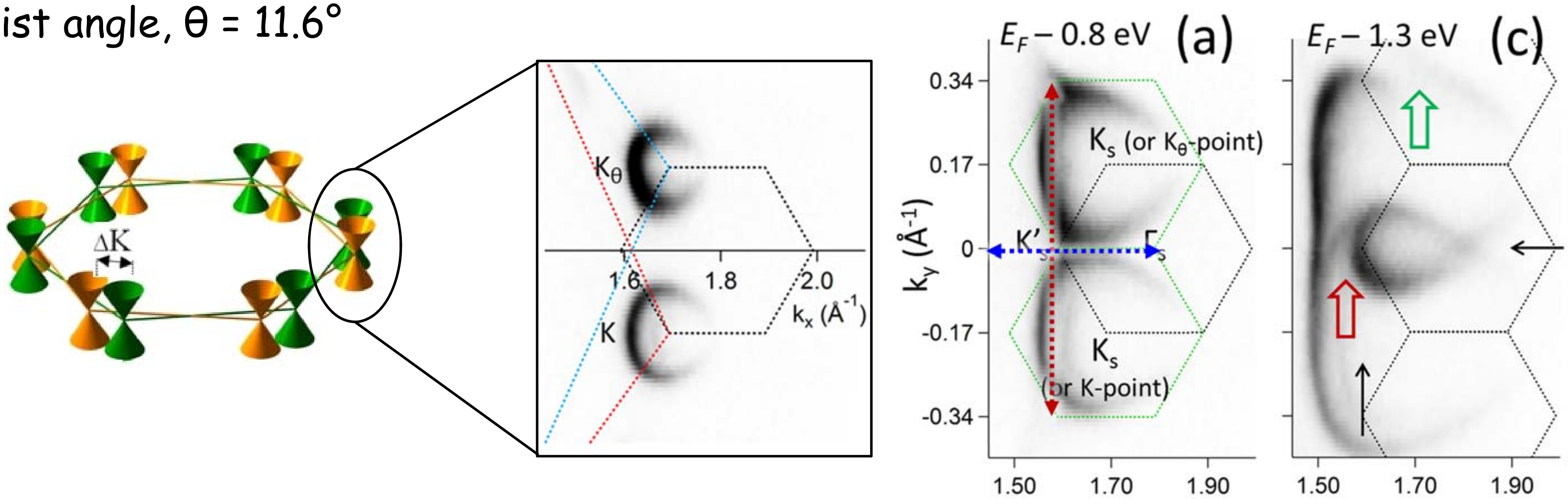


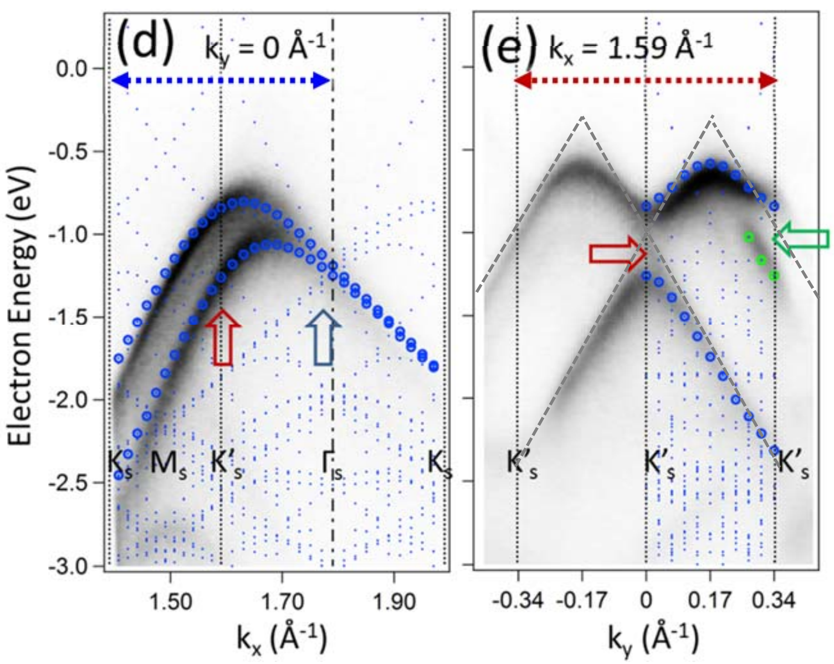
hv = 95eV

Ohta et al., PRL, 109, 186807 (2012)

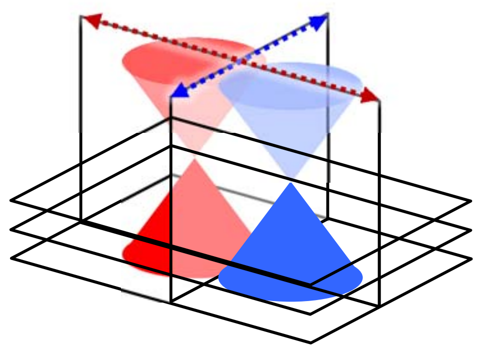
Two Dirac cones display anti-crossing

- Departure from the simple Dirac cone picture
  - Twist angle, θ = 11.6°





Blue dots/circles: DFT calculation

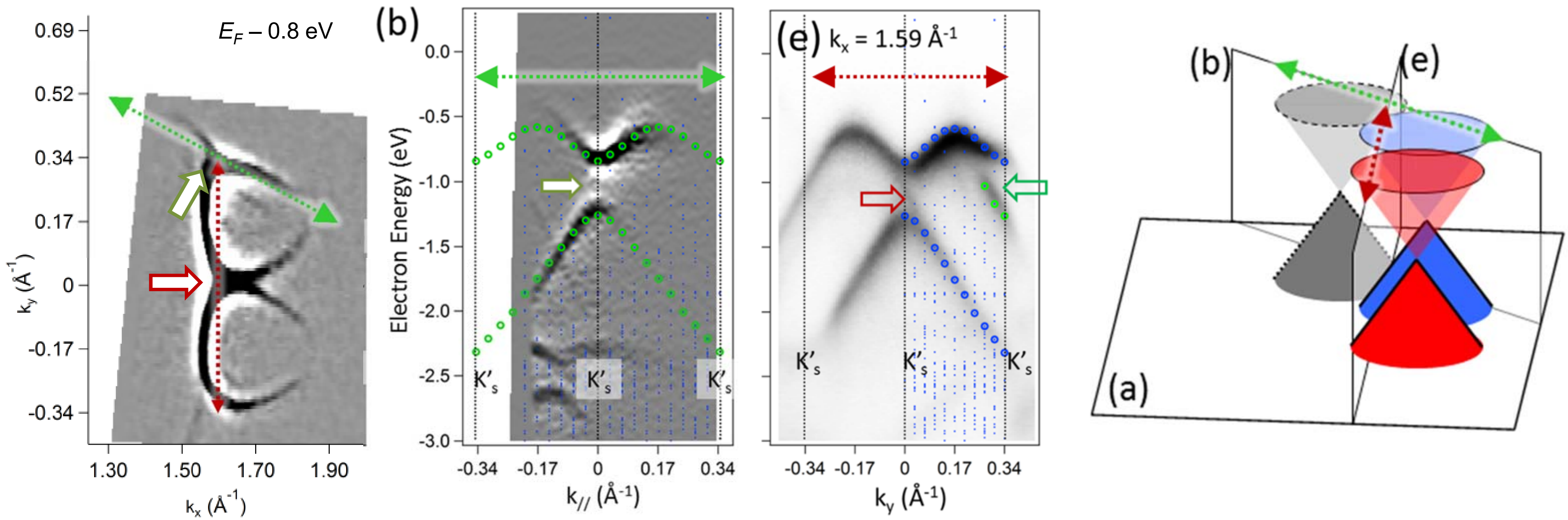


- Two cones' interaction leads to mini-gap and <u>van Hove singularities</u>
  - *Match very well with DFT calculation*

- Additional feature at the green arrow

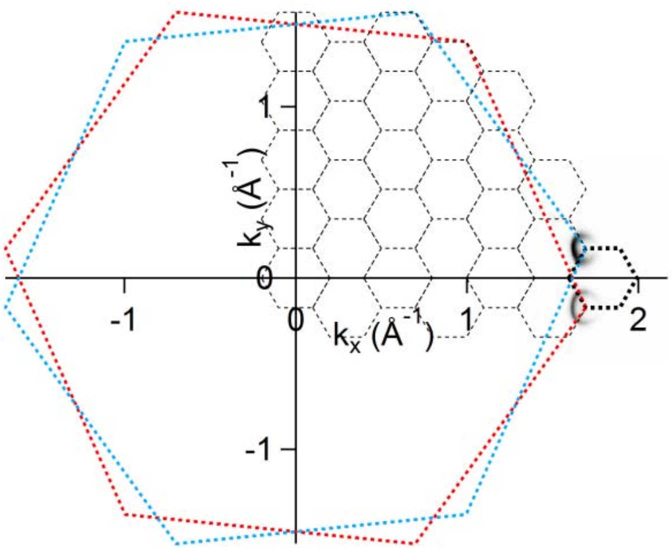
Additional Dirac cone emerges

- Anti-crossing is found b/w the original and the additional Dirac cone

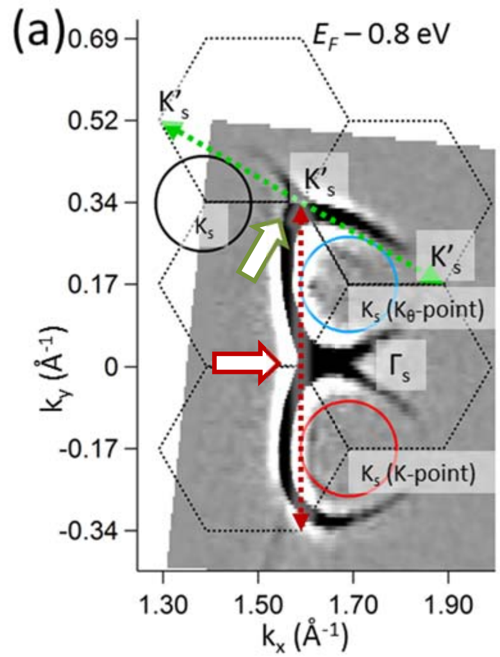


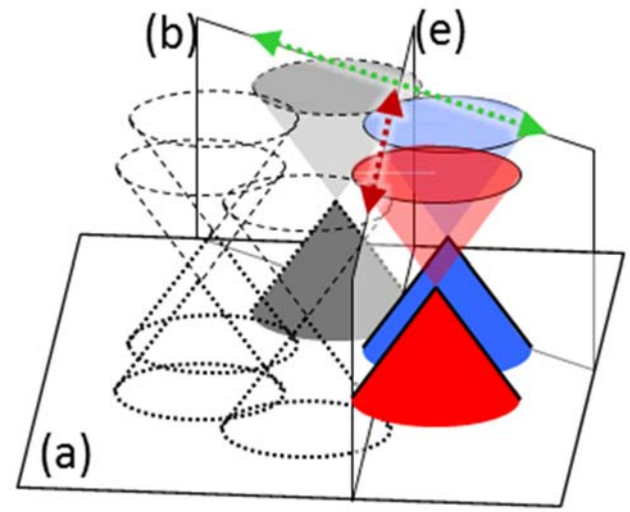
Moiré periodic potential produces Dirac cones

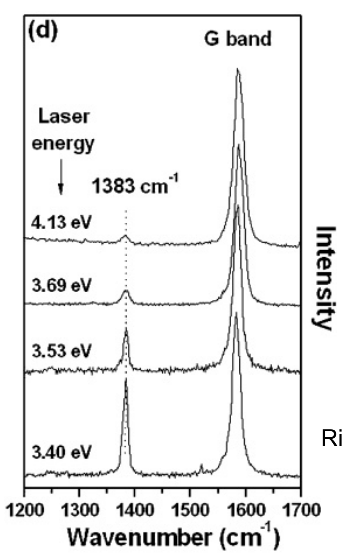
- Umklapp scattering by moiré periodic potential
  - Similar to moiré-induced Raman band and LEED spots

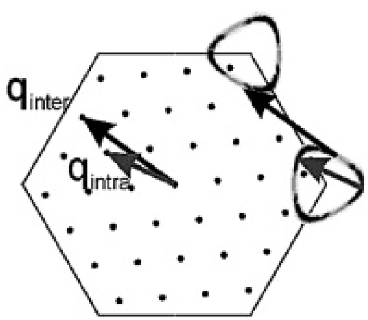


θ = 11.6°

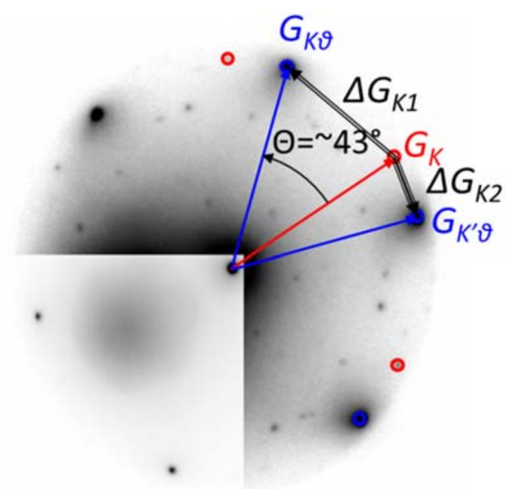








Righi et al., PRB 84, 241409(R) (2011)

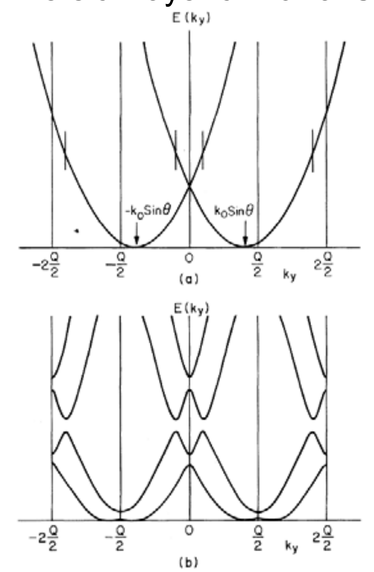


Superlattice changes electronic dispersion

- Substrate or neighboring material provides periodic potentials

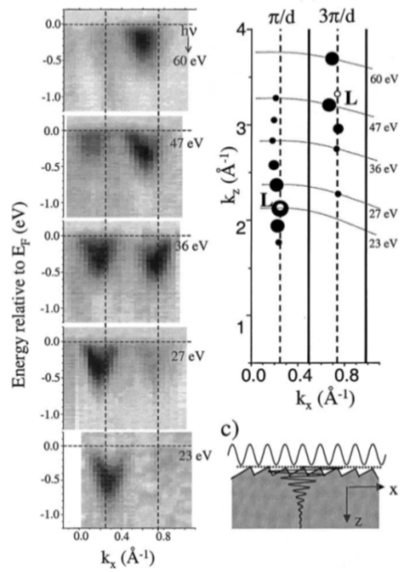
Surface superlattice

Mini-bands & gaps formed in inversion layer of vicinal Si



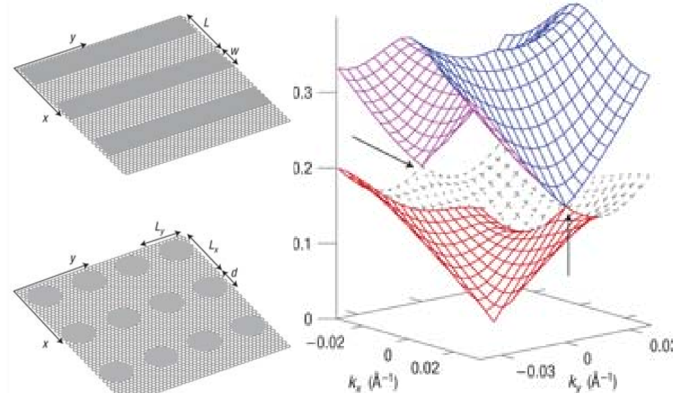
Tsui et al., PRL 40, 1667 (1978)

Surface state on Au(322) vicinal surface



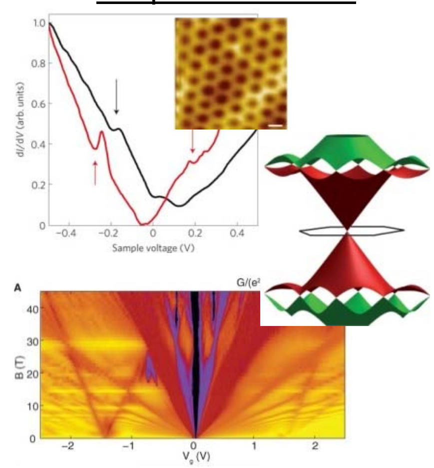
Ortega et al., Materials Science and Engineering B96 154 (2002)

Graphene superlattice



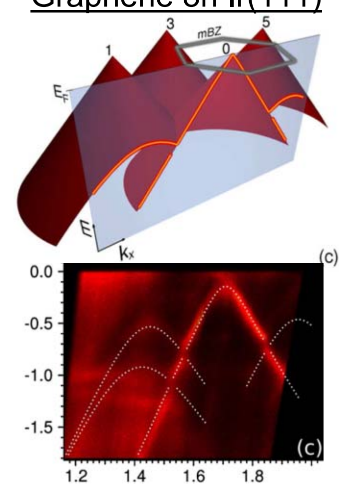
Park et al., Nature Physics 4, 213 (2008)

Graphene on hBN



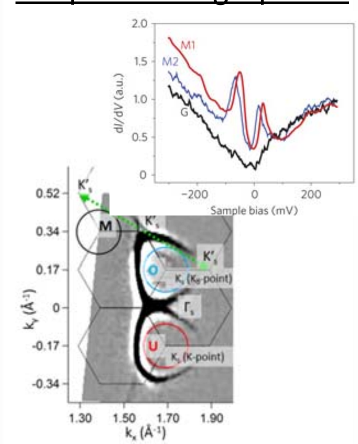
Yankowitz et al., Nature Phys. 8, 382 (2012); Ponomarenko et al., Nature, 497, 594 (2013); Hunt et al., Science 340, 1427 (2013)

Graphene on Ir(111)



Pletikosic et al., PRL 102, 056808 (2009)

Graphene on graphene

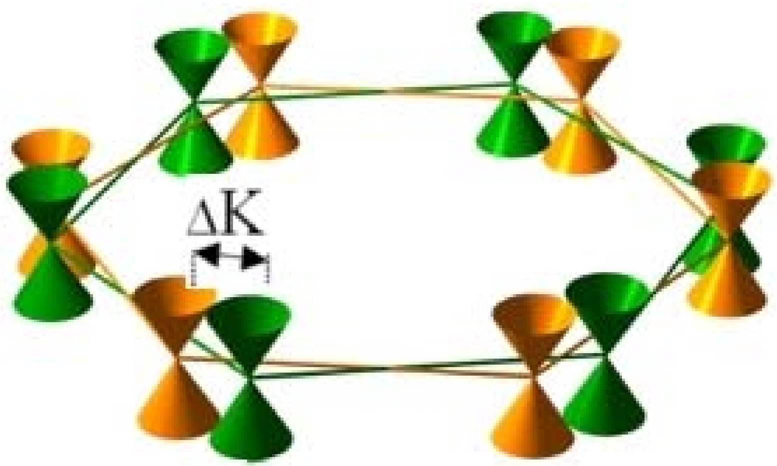


Li et al., Nature Physics 6, 109 (2010); Ohta et al., PRL, 109, 186807 (2012)

Moiré is ubiquitous in hybrid 2D-crystal stacks!

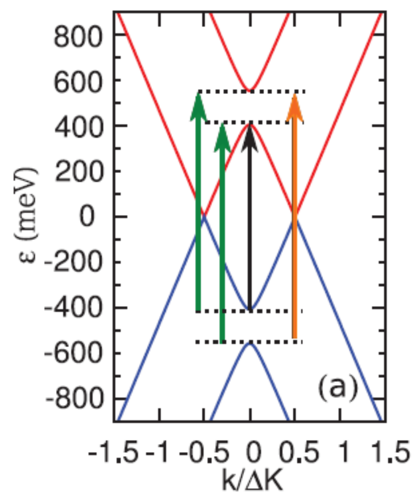
How does the band renormalization affect the properties of TBG?

- Does interlayer interaction lead to changes in properties of TBG other than electronic dispersion?
  - How does it vary as a function of twist angle?

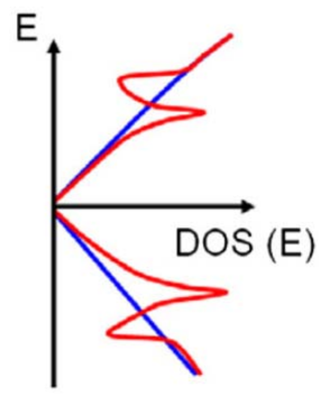


Li et al., Nature Physics 6, 109 (2010)

- Color variation is found in TBG!



Tabert et al., PRB 87, 121402(R) (2013)

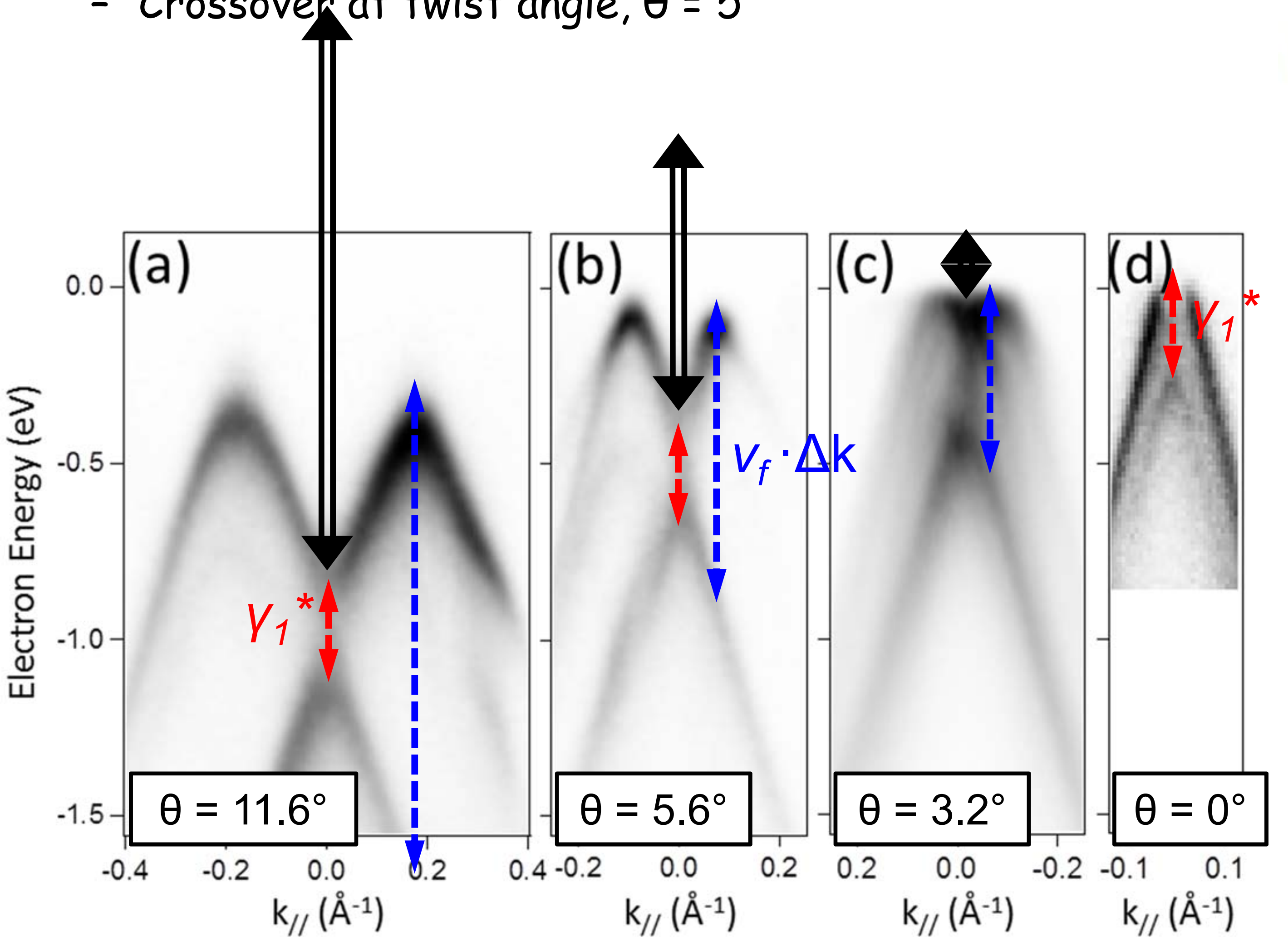


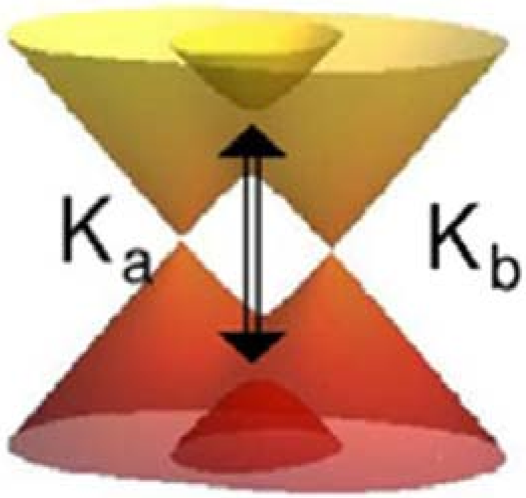
Kim et al., PRL 108, 246103 (2012)

Graphene in Color, Science 152, 374 (2013)

Electronic dispersion changes as a function of twist angle

- Interlayer overlap integral (γ_1*) and the characteristic energy ($v_f \cdot \Delta k$) dictate band renormalization
  - Crossover at twist angle, θ = 5°

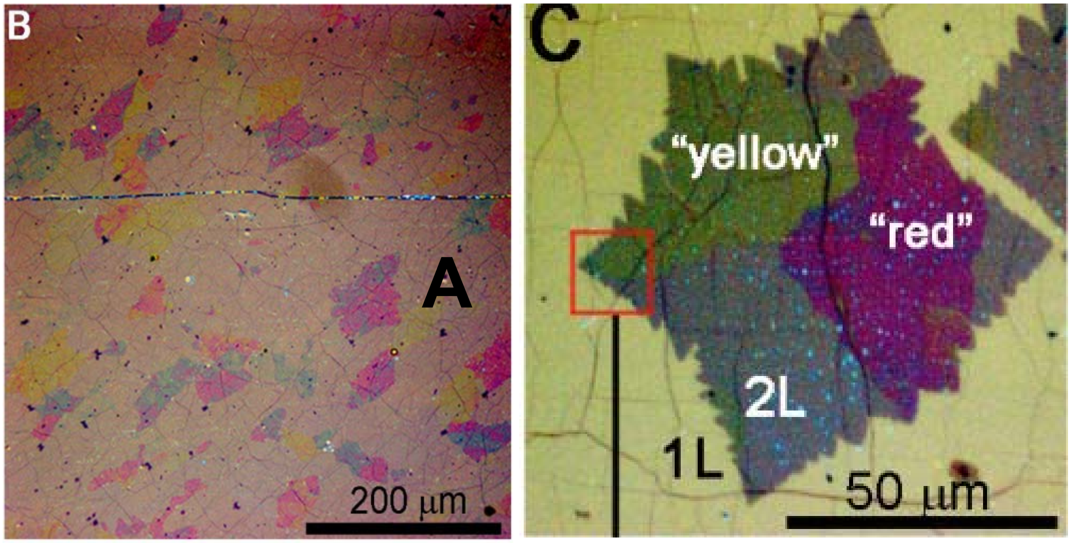




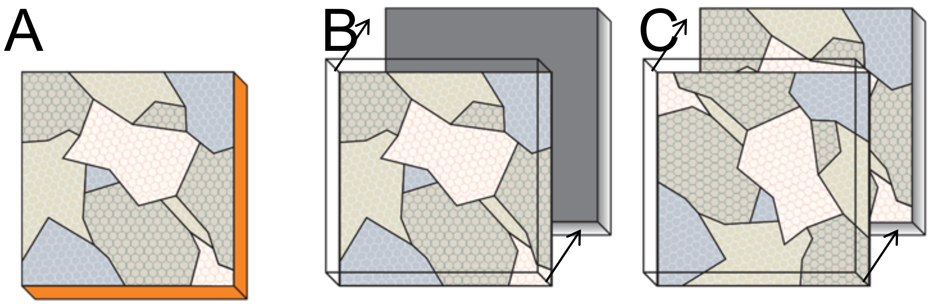
Kim et al., PRL 108, 246103 (2012)

Ohta et al., unpublished (2012)

"Colored grain" are observed for TBG on SiO_2/Si substrate

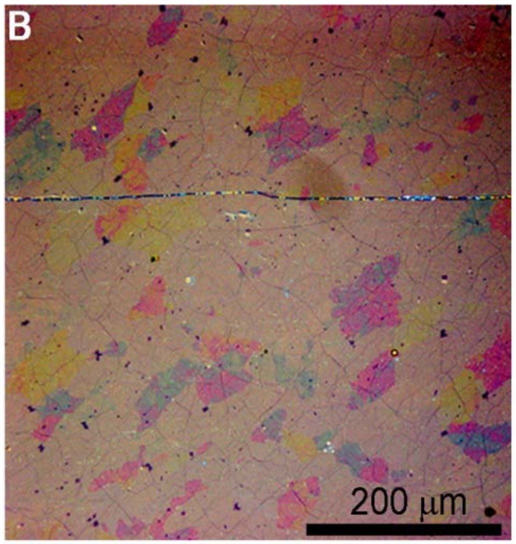


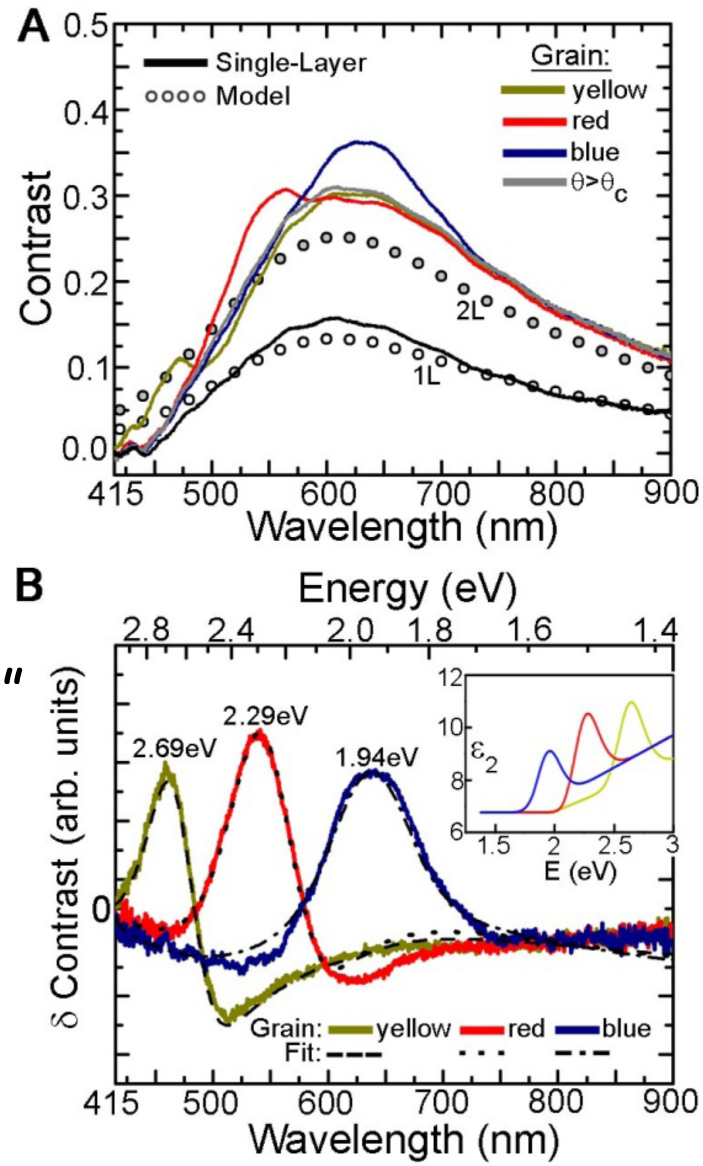
- Patches of "colored grain" observed in optical microscope
  - <u>TBG on SiO_2/Si substrate</u>



Robinson et al., ACS Nano, 7, 637 (2013) & Science 152, 374 (2013)

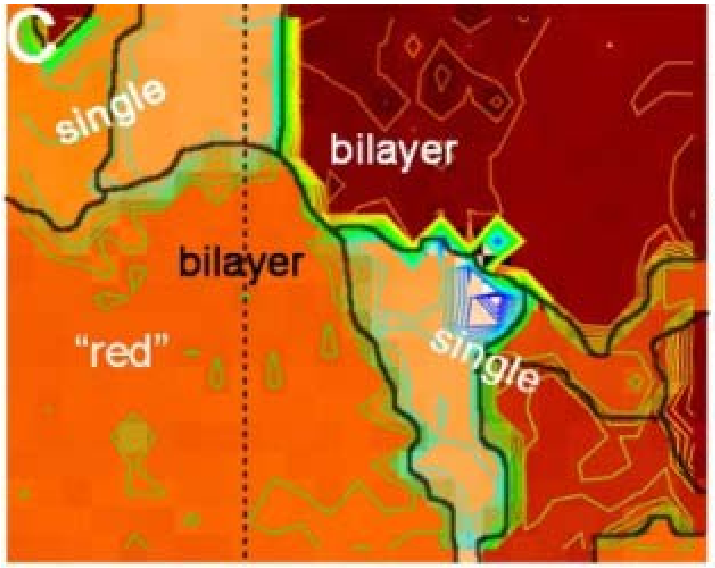
Emerging absorption band is responsible for "Colored grain"



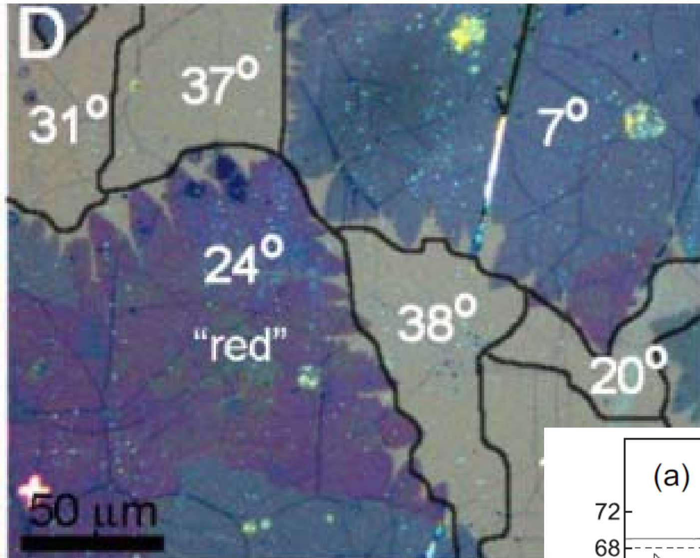


- Optical spectroscopy reveals an absorption band for "colored grain"

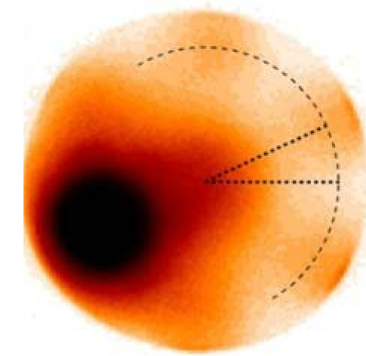
Optical absorption depends on the twist angle



Map of LEED pattern orientations across the sample surface

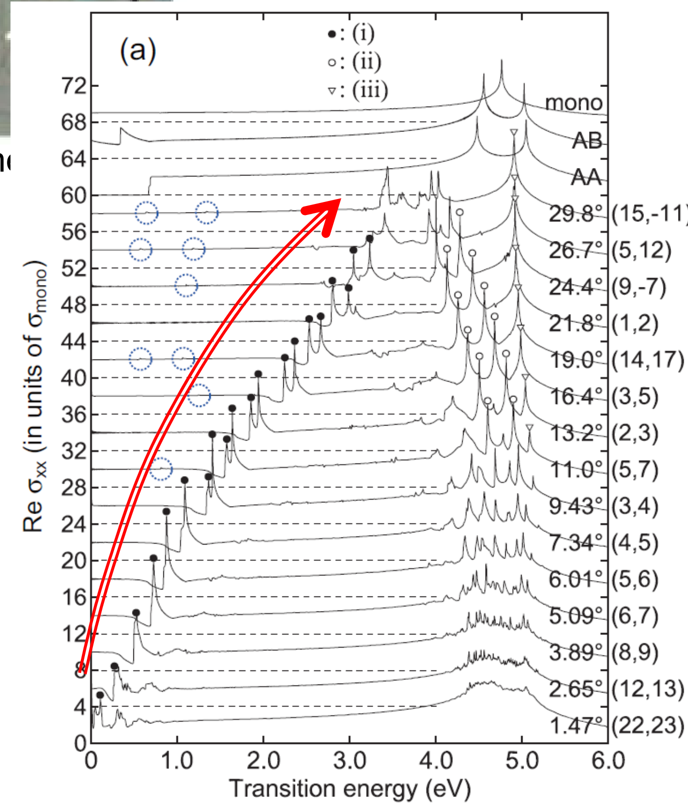


Optical micrograph of the sam



Typical µ-LEED pattern of TBG

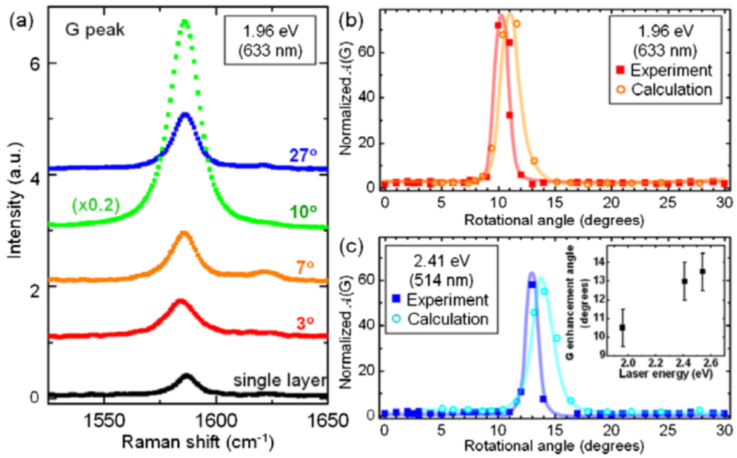
- LEED correlates the color to the twist angle
  - LEED sensitive to the top layer only



Moon & Koshino, PRB 87, 205404 (2013)

- Supported theoretically

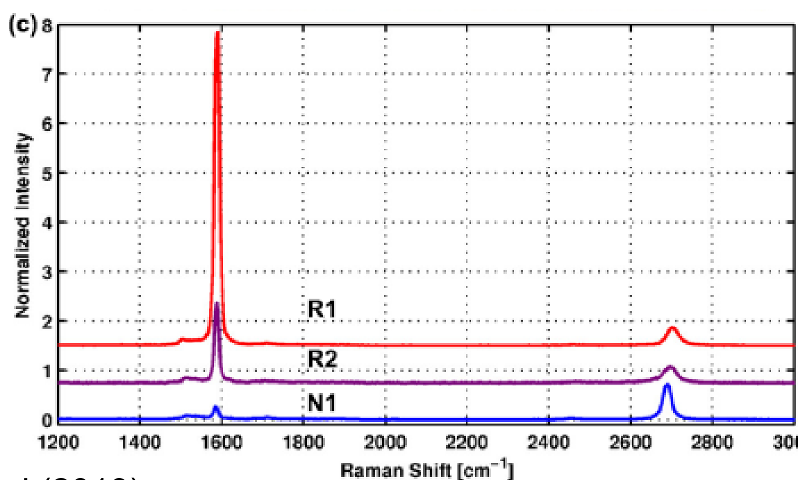
We study local inhomogeneities using Raman G-mode



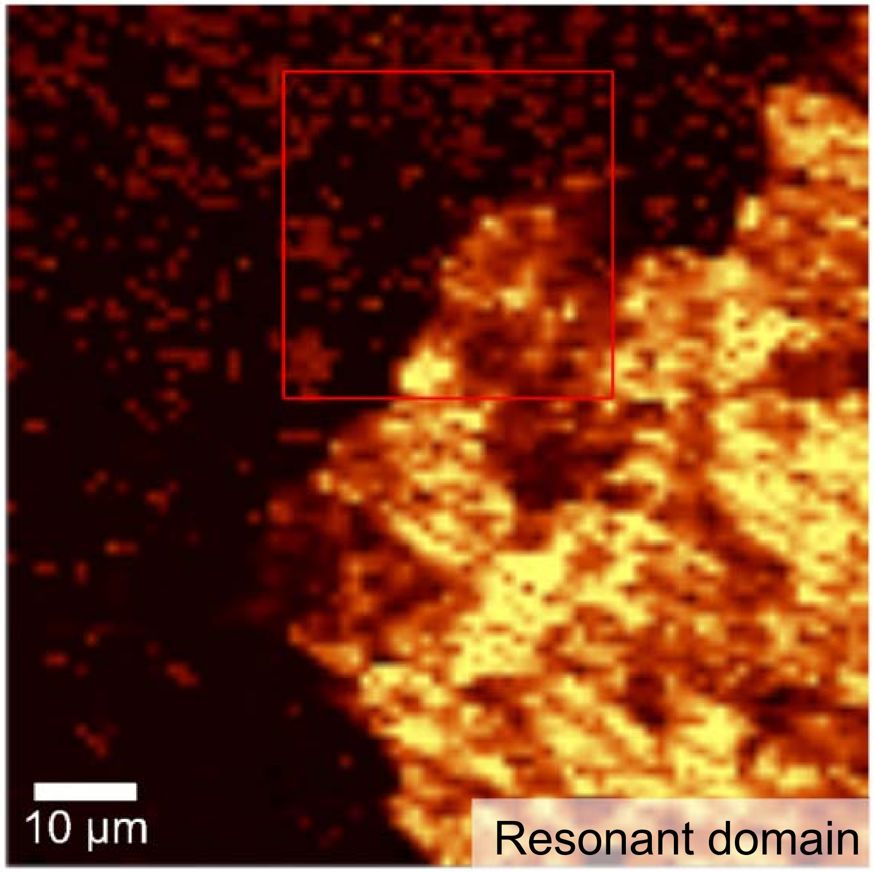
Kim et al., PRL 108, 246103 (2012)

- Enhanced optical absorption correlates with giant Raman G-mode

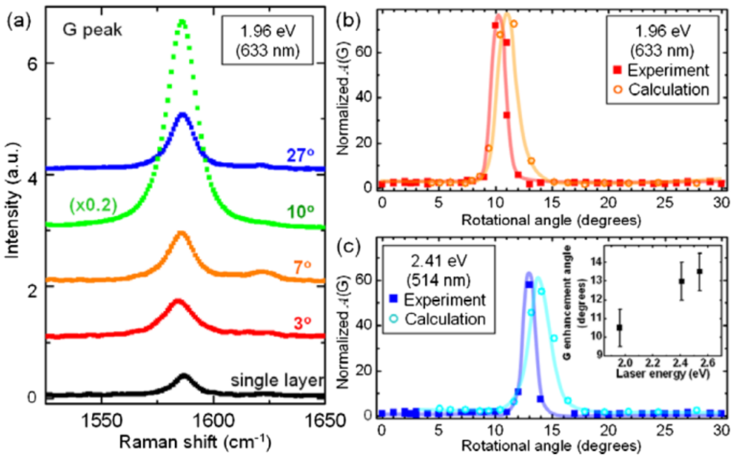
- Grains with giant Raman G-mode are found in TBG on SiC



Beechem et al., submitted (2013)

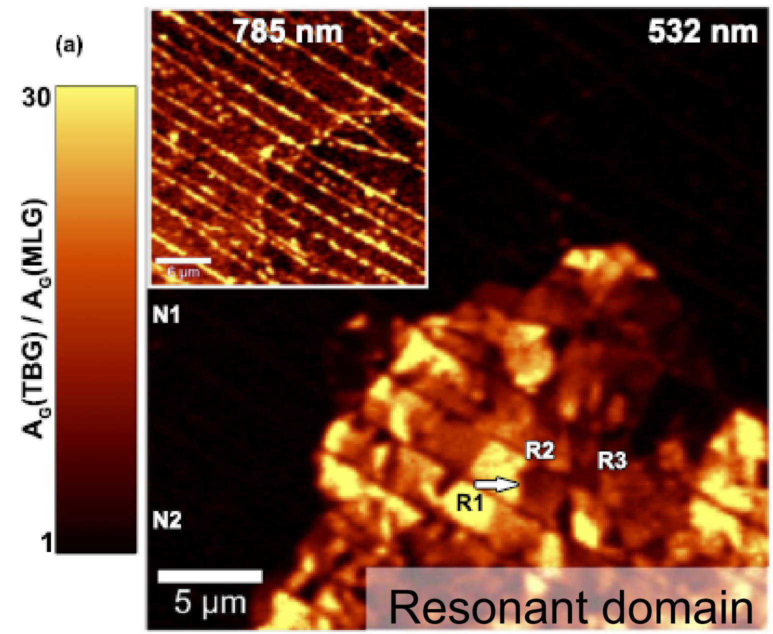


We study local inhomogeneities using Raman G-mode



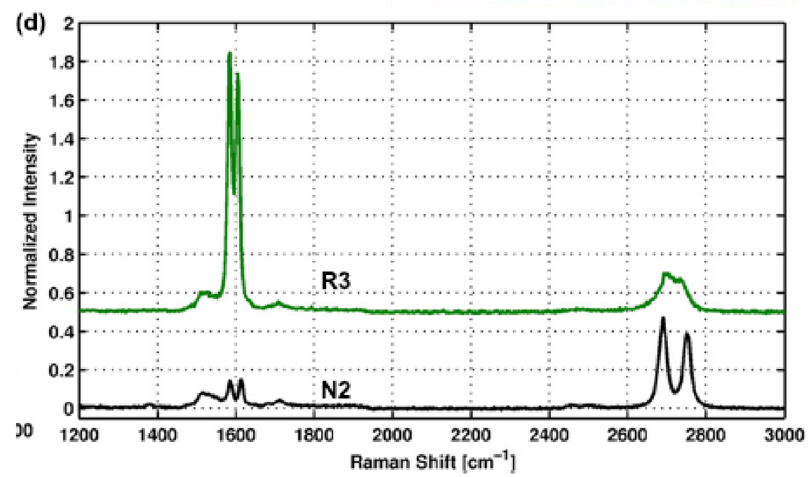
Kim et al., PRL 108, 246103 (2012)

- Enhanced optical absorption correlates with giant Raman G-mode

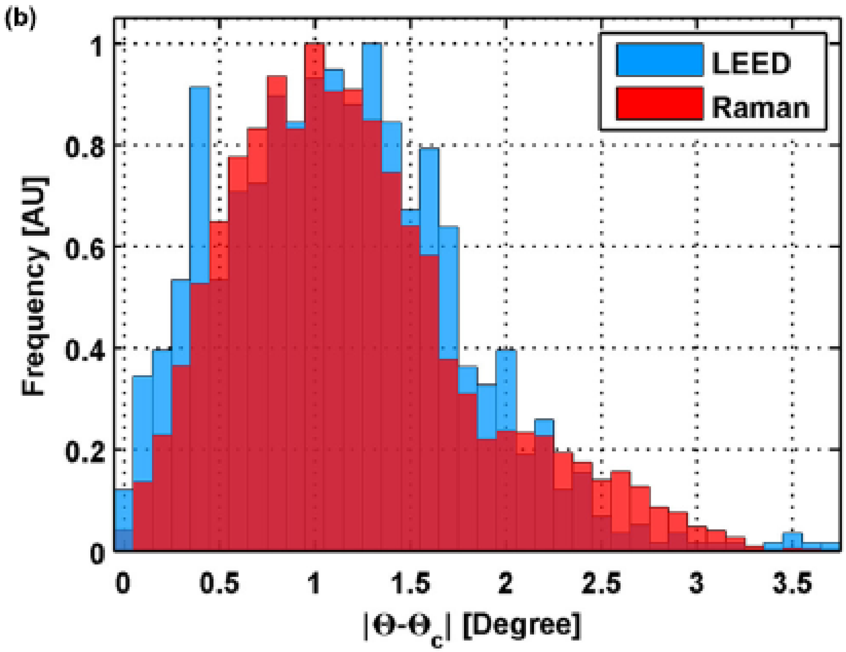


- Sub-grains separated by wrinkles and blisters
  - Rotation disorders make Raman G-mode intensity variation

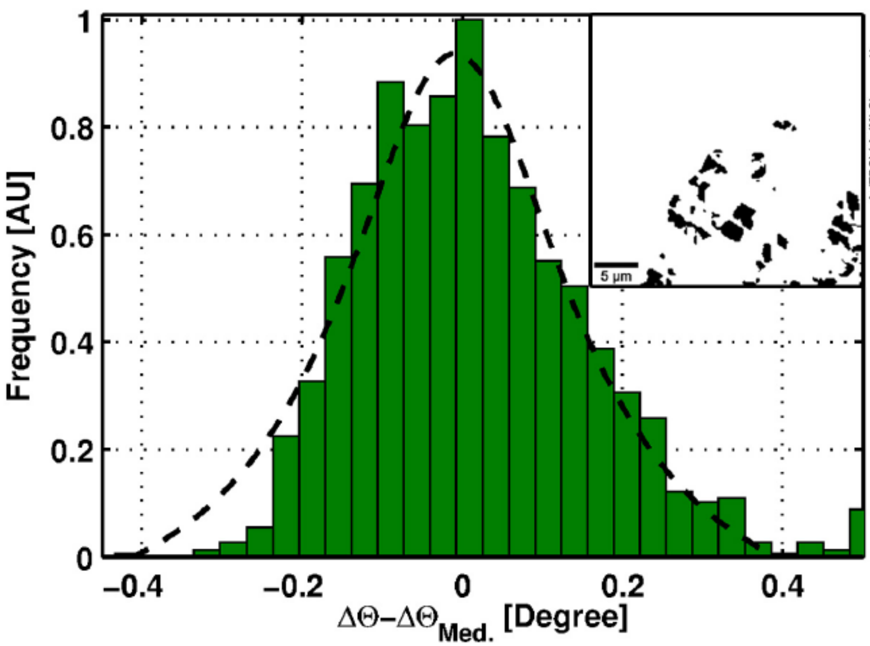
- Non-equivalent strain in two layers creates splitting
  - <u>Robust giant G-mode and hence band renormalization</u>

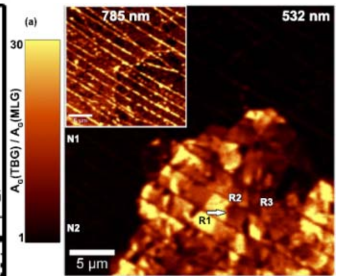


Rotational disorder is quantified using Raman



- Twist angle varies by ~1° within CVD graphene domain
- Twist angle variations from Raman and LEED match





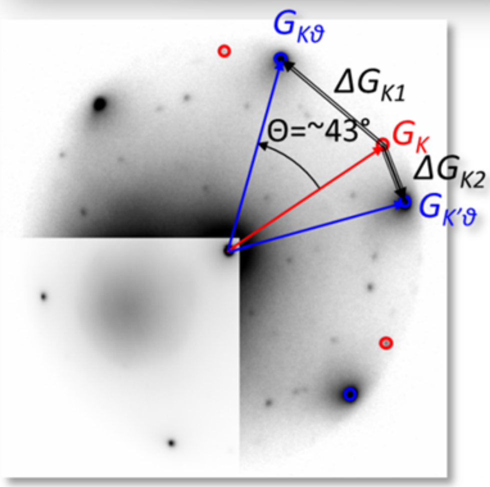
- Sub-grains show ~0.1° twist angle variation (below measurement limit)
  - <u>Future opportunity to improve the properties of stacked 2D-crystals</u>

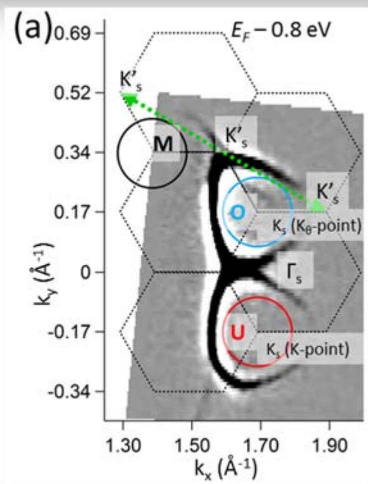
Summary

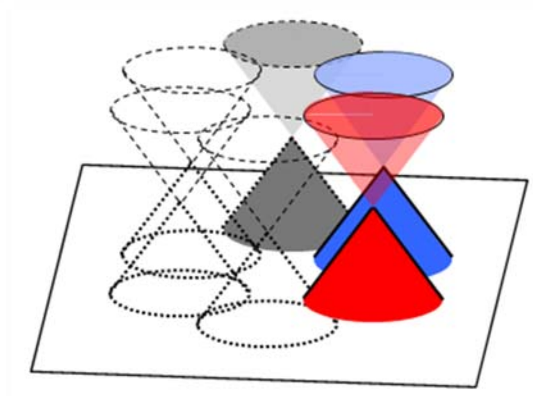
Moiré influences the electronic structure of TBG

- Twisted Bilayer Graphene (TBG) can be produced using transfer approach
- Electronic dispersion is altered by moiré (long-range periodicity)
- Optical properties can be tuned by the twist angle
- Band renormalization is relatively robust against rotational disorders

<u>Moiré is ubiquitous in 2D-solids: handle to tailor electronic properties</u>





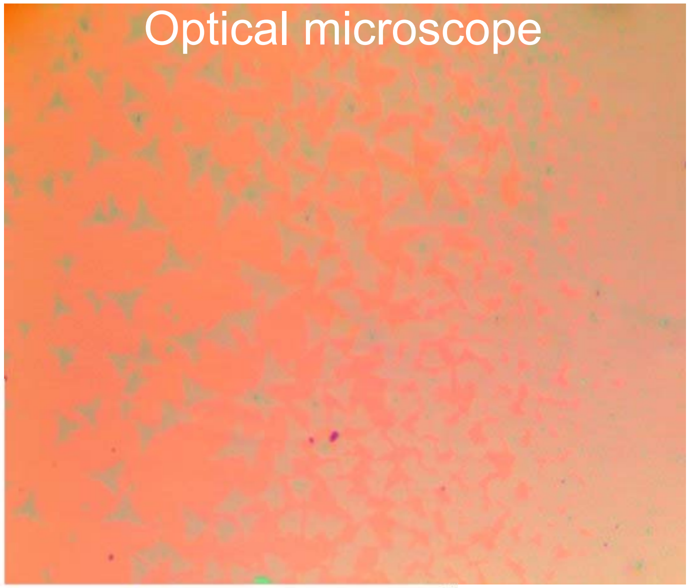


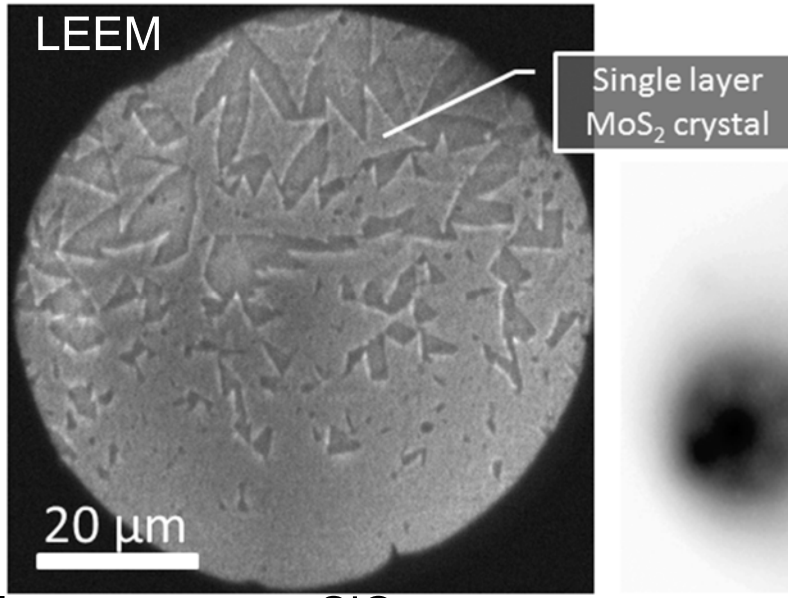
For details of our work, please see the following publications:

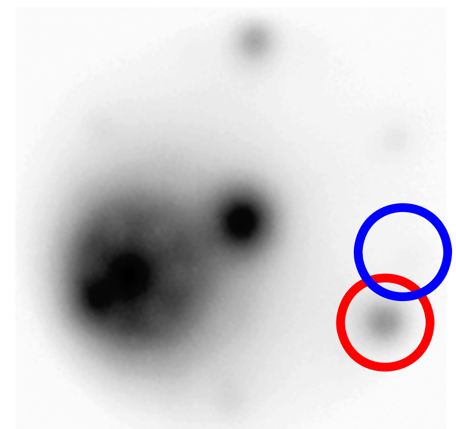
- T. Ohta, T. E. Beechem, J. Robinson, G. L. Kellogg, *Long-range atomic ordering and variable interlayer interactions in two overlapping graphene lattices with stacking misorientations*, Phys. Rev. B, 85, 075415, 2012.
- T. Ohta, J. T. Robinson, P. J. Feibelman, A. Bostwick, E. Rotenberg, T. E. Beechem, *Evidence for interlayer coupling and moiré periodic potentials in twisted bilayer graphene*, Phys. Rev. Lett. 109, 186807, 2012.
- J. T. Robinson, S. W. Schmucker, C. B. Diaconescu, J. P. Long, J. C. Culbertson, T. Ohta, A. L. Friedman, T. Beechem, *Electronic Hybridization of Large-Area Stacked Graphene Films*, ACS Nano, 7, 637, 2013.
- *Graphene in Color*, Science 152, 374, 2013 "editor's choice."
- R. M. Feenstra, N. Srivastava, Q. Gao, M. Widom, B. Diaconescu, Taisuke Ohta, G. L. Kellogg, J. T. Robinson, I. V. Vlassiouk, *Low-energy Electron Reflectivity from Multilayer Graphene*, Phys. Rev. B Rapid Communications, 87, 041406(R), 2013.

We study MoS_2 using LEEM

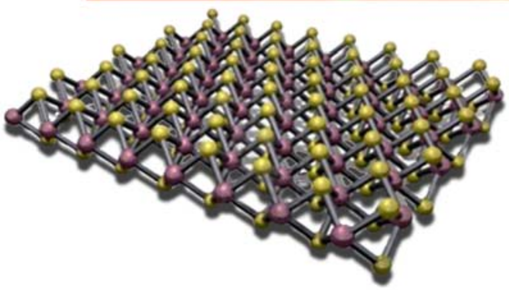
- Identifying the crystallographic orientation and the domain size of single-crystal MoS_2 monolayer

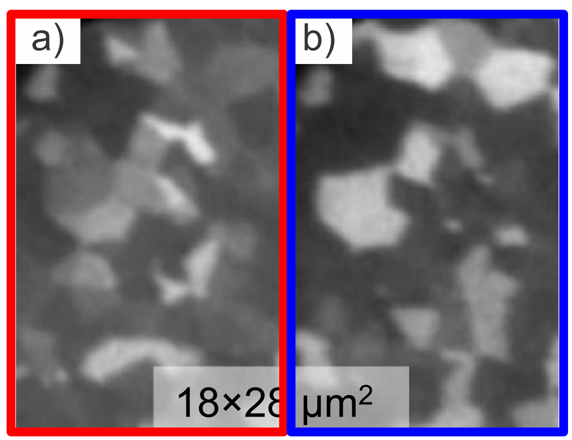






MoS_2 monolayer grown on SiO_2





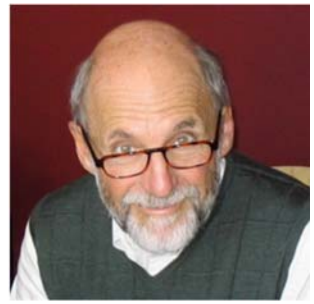
– Dark-field images of MoS_2 film

Mann, Bartels, et al., European Phys. J. B 86, 226 (2013)

Acknowledgements

- Main contributors to twisted bilayer graphene work:
  - Jeremy T. Robinson (Naval Research Laboratory)
  - Thomas E. Beechem, Peter J. Feibelman, Bogdan Diaconescu (Sandia National Laboratories)






- Collaborators in twisted bilayer graphene work:
  - G. L. Kellogg, R. G. Copeland, A. McDonald, N. C. Bartelt (Sandia National Laboratories)
  - S. Schmucker, J. C. Culbertson, J. P. Long, A. Friedman (Naval Research Laboratory)
  - A. Bostwick, E. Rotenberg (Advanced Light Source, Lawrence Berkeley National Laboratory)

- MoS_2 work:
  - J. Mann, L. Bartels (University of California, Riverside)

- User facility:
  - B. Swartzentruber, D. Pete through CINT at SNL/LANL (Contract No. DE-AC04-94AL85000)
  - ALS, LBNL, supported by the U.S. DOE, BES (Contract No.DE-AC02-05CH11231)

- Funding:
  - LDRD program, Sandia National Laboratories
  - U.S. DOE Office of Basic Energy Sciences, Division of Materials Science and Engineering (Contract No. DE-AC04-94AL85000)

LEEM-PEEM research opportunities

- Postdoc in LEEM group at Sandia National Laboratories, Albuquerque
  - Defects and 2D-electron gas in nitride semiconductor heterostructures
  - Electronic properties of 2D-crystals and their stacked structures

Job posting: 644053
http://www.sandia.gov/careers/index.html

- New research capabilities: energy-filtered LEEM-PEEM
  - Real-time surface imaging and diffraction
  - Electronic structure study using EELS and ARPES (UV-light sources)

For further information, please contact
Taisuke Ohta (tohta@sandia.gov)

LEEM-PEEM with electron energy filter