SAND2013-2510C

Electronic dispersion from long-range atomic ordering and periodic potentials in two overlapping graphene sheets

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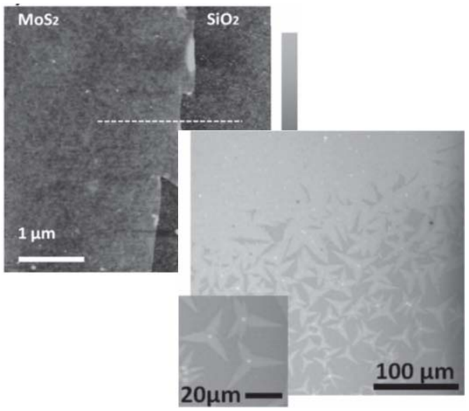
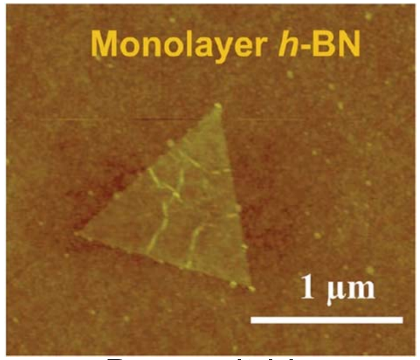
2D-crystals offer new scope of material

- Various two-dimensional (2D) crystals



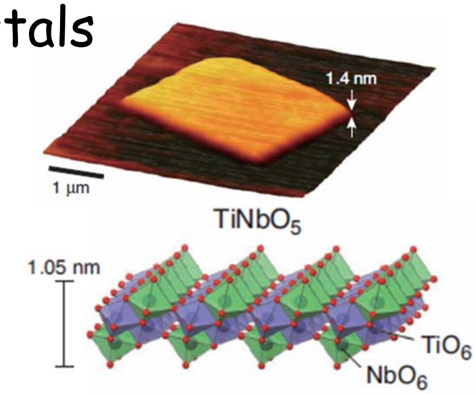
Molybdenum disulfide

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



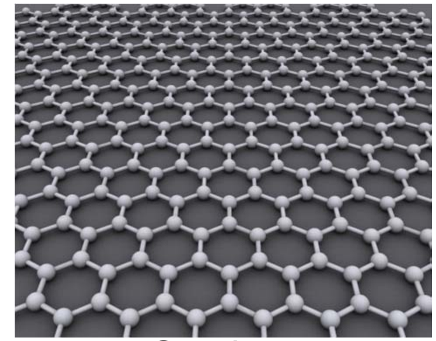
Boron nitride

Kim et al., Nano Lett., 12, 161 (2012)



Titanium Niobate

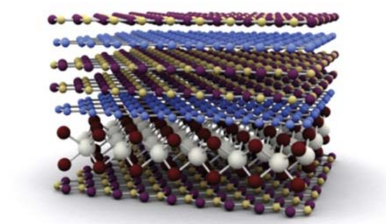
Osada et al., Adv. Funct. Mater. 21, 3482 (2011)



Graphene

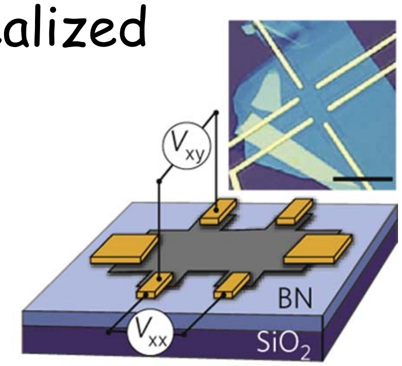
http://en.wikipedia.org/wiki/Graphene

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



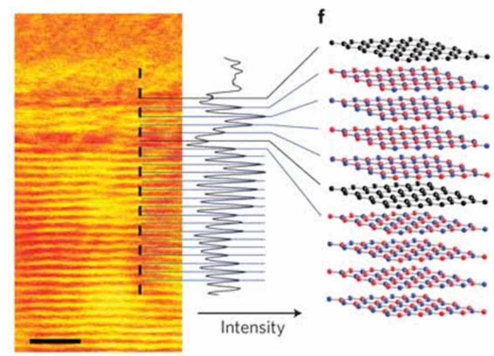
2D-based heterostructure

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



Graphene on BN

Dean et al., Nature Physics 7, 693 (2011)



Graphene/BN superlattice

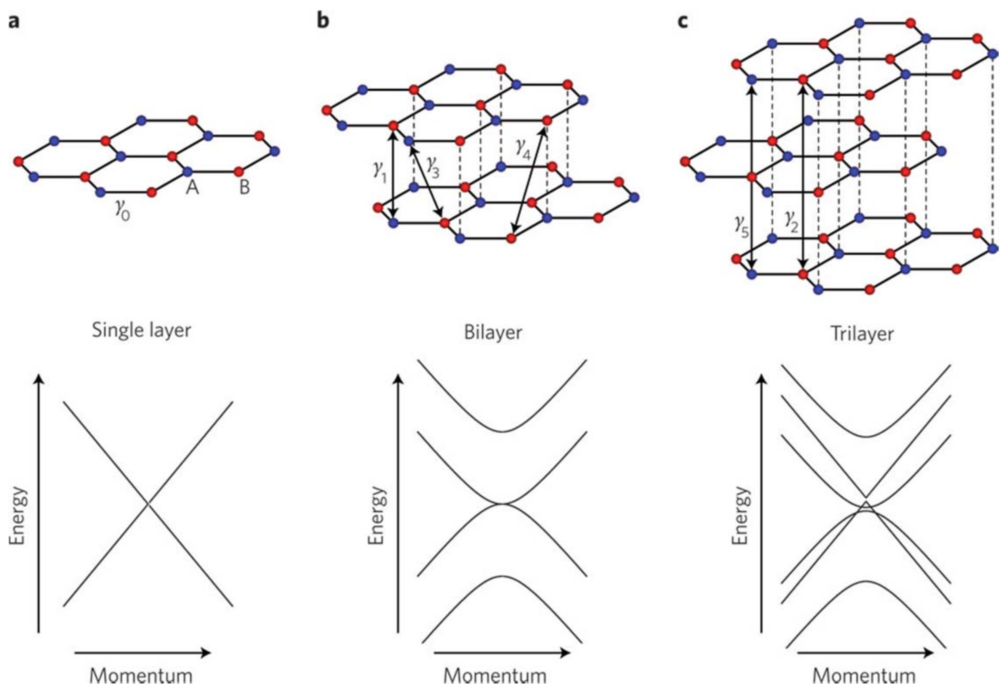
Haigh et al., Nature Materials 11, 764 (2012)

<u>How would 2D-crystals interact electronically with each other?</u>

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

How does misorientation manifest itself in bilayer graphene?

- Bernal stacked graphene: strong interlayer interaction

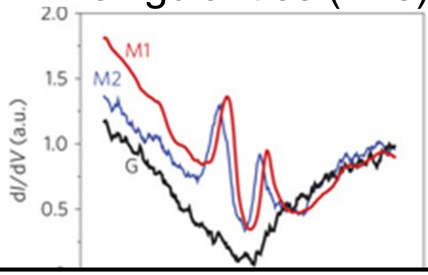


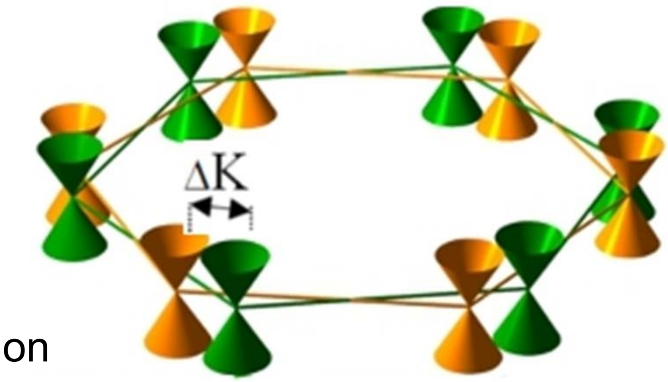
Freitag, Nature Physics 7 596 (2011)

How does misorientation manifest itself in bilayer graphene?

- What about twisted graphene?

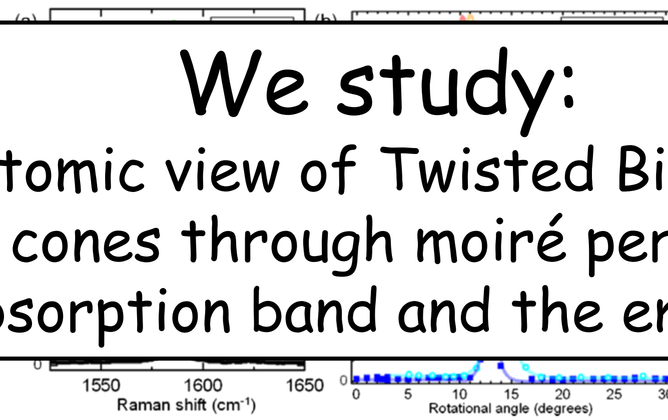
STS indicates van Hove singularities (vHs)





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

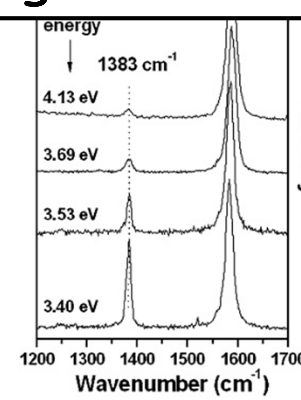
Raman shows resonant transition due to vHs or parallel states

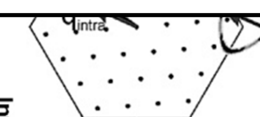


Kim et al., PRL 108, 246103 (2012)

We study:

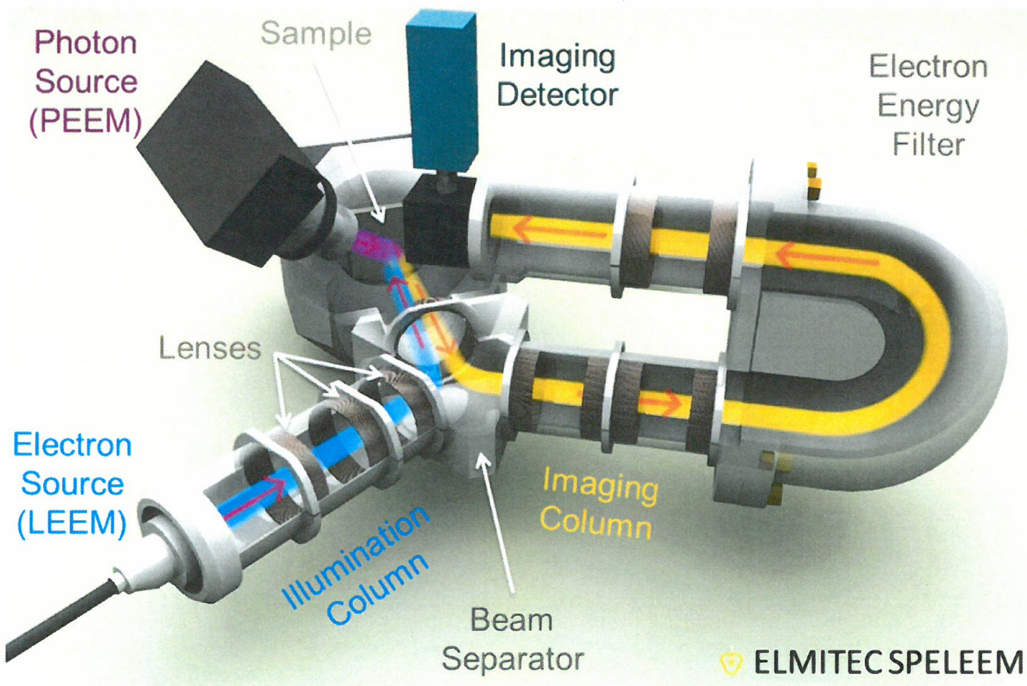
- Microscopic and atomic view of Twisted Bilayer Graphene (TBG)
- Interacting Dirac cones through moiré periodic potential
- Tunable optical absorption band and the emergence color domain





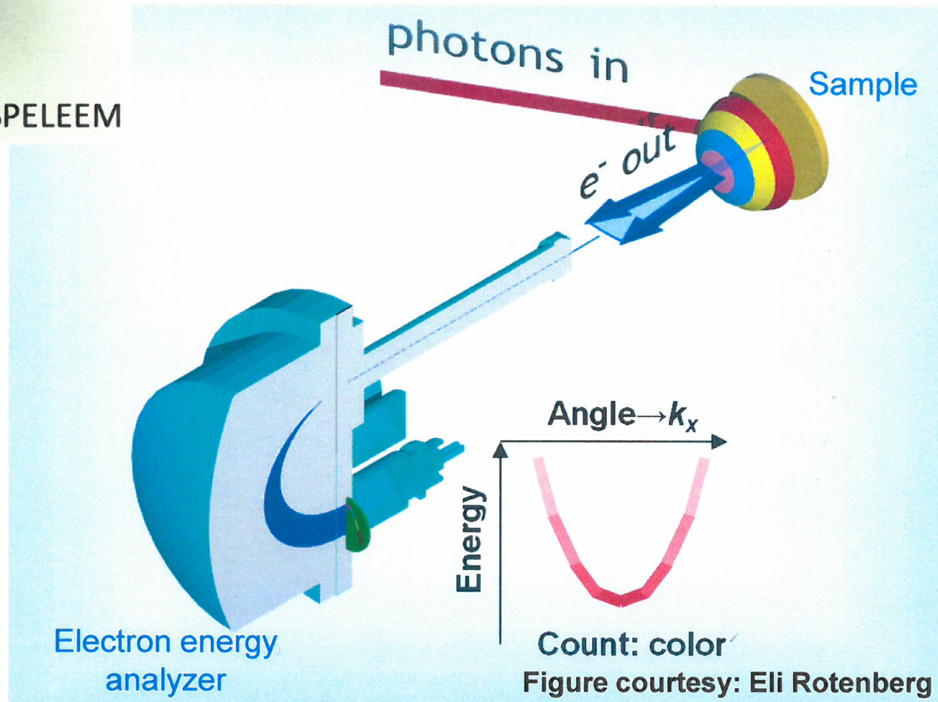
Righi et al., PRB 84, 241409(R) (2011)

LEEM/PEEM and ARPES



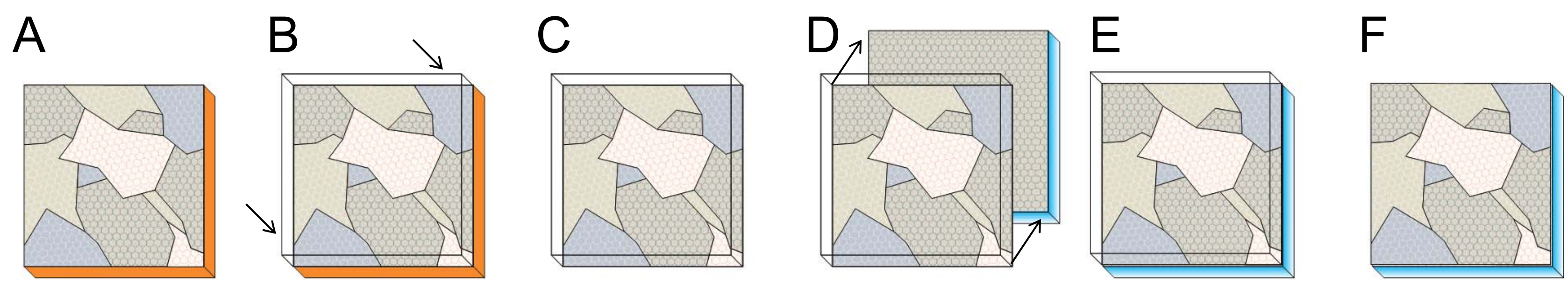
LEEM
(Low Energy Electron Microscopy)
– Surface-sensitive "reflection" electron microscopy

ARPES
(Angle-Resolved Photoemission Spectroscopy)
– Occupied electronic states' dispersion



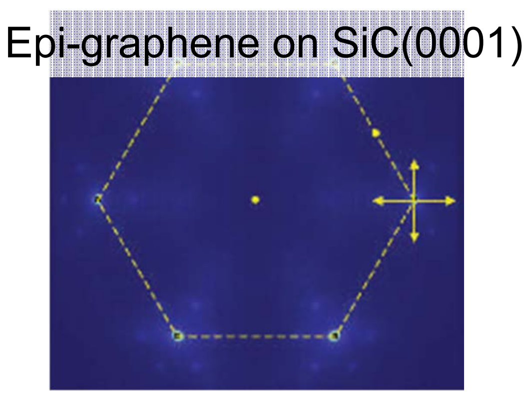
We make TBG by transfer

- Transferring CVD graphene onto epi-graphene (on SiC) yields large TBG domains with various twist angles

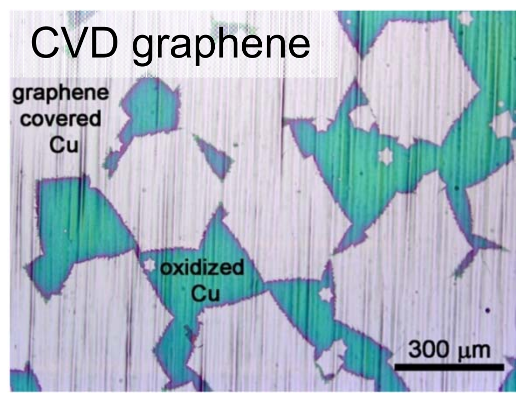


CVD grown graphene on Cu foil | Spin coat photoresist (PR) on CVD-graphene/Cu | Etch off Cu foil | Place PR/CVD-graphene on epi-graphene grown on SiC | Dissolve PR and clean the surface with H2

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

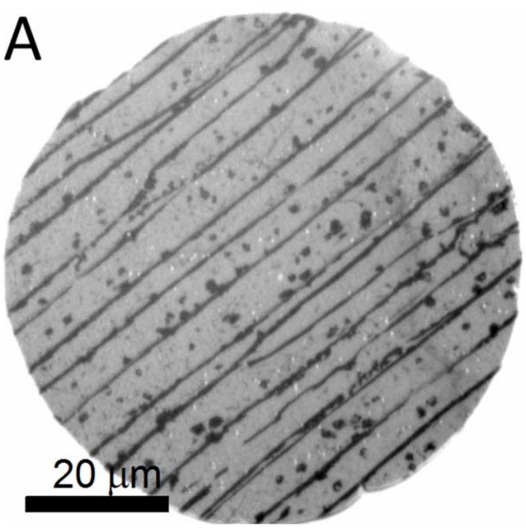


Bostwick et al., Nature Phys. 3, 36 (2007)

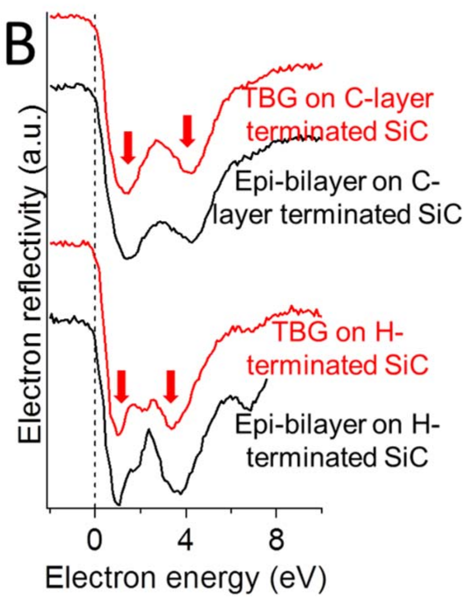


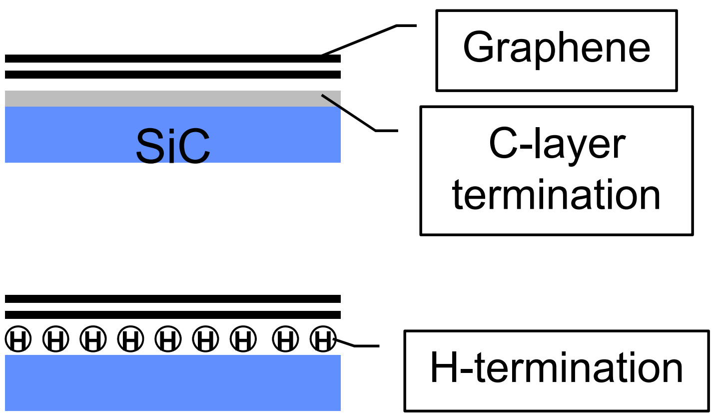
TBG shows characteristic electron reflectivity of bilayer graphene

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



LEEM image of TBG

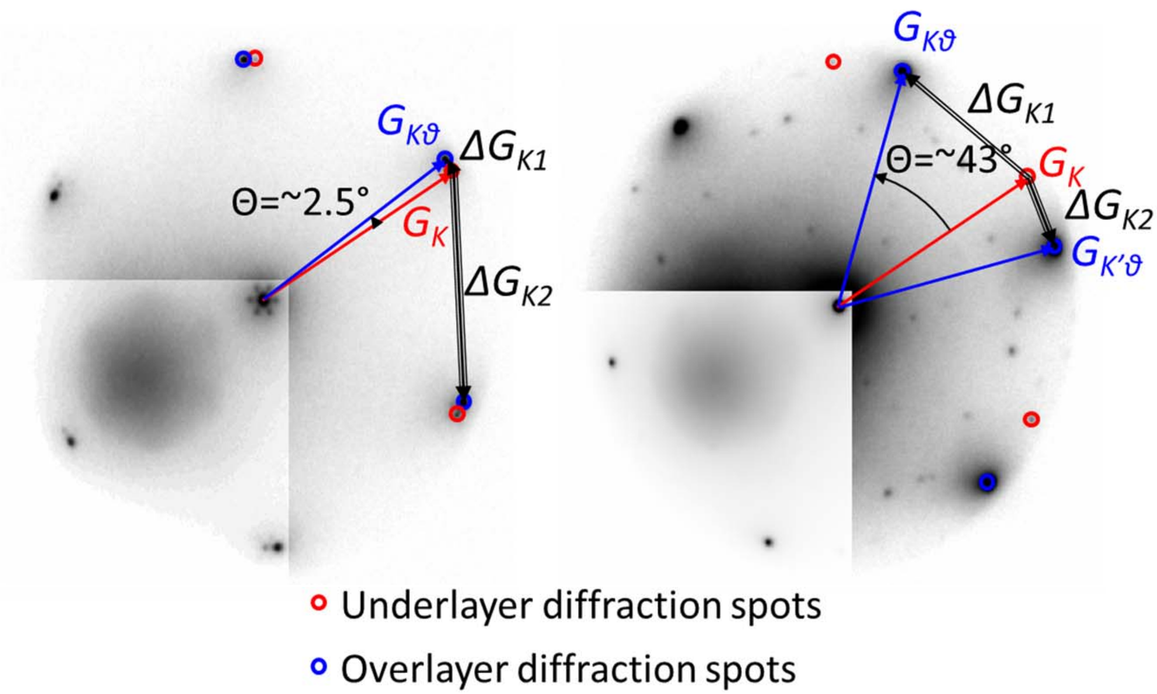


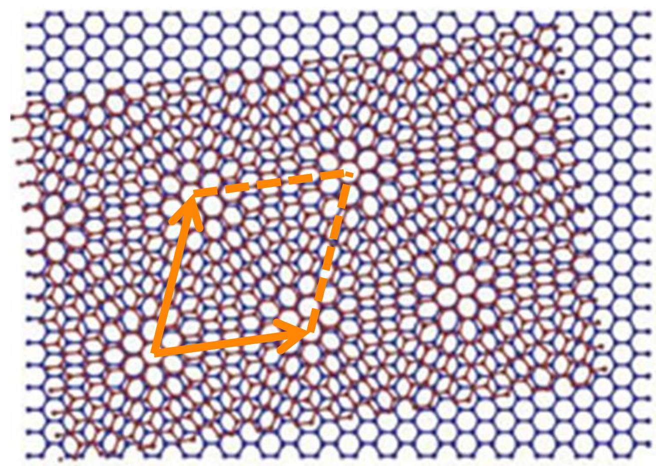


Ohta et al., PRB, 85, 075415 (2012)

TBG has long-range atomic ordering

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



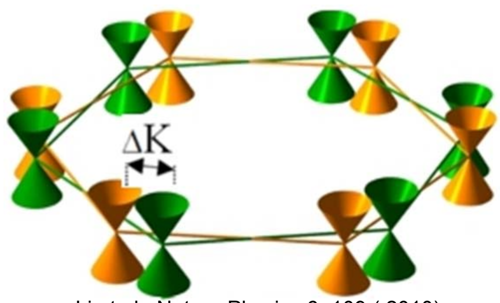


Real-space moiré vectors

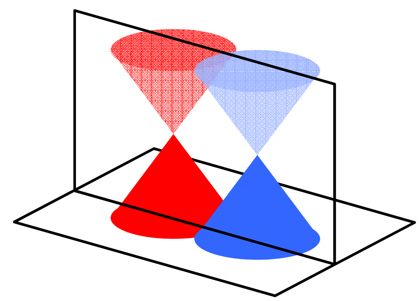
  - Minimum damage of graphene is confirmed using Raman spectroscopy
    - Please see PRB, 85, 075415 (2012) for detail

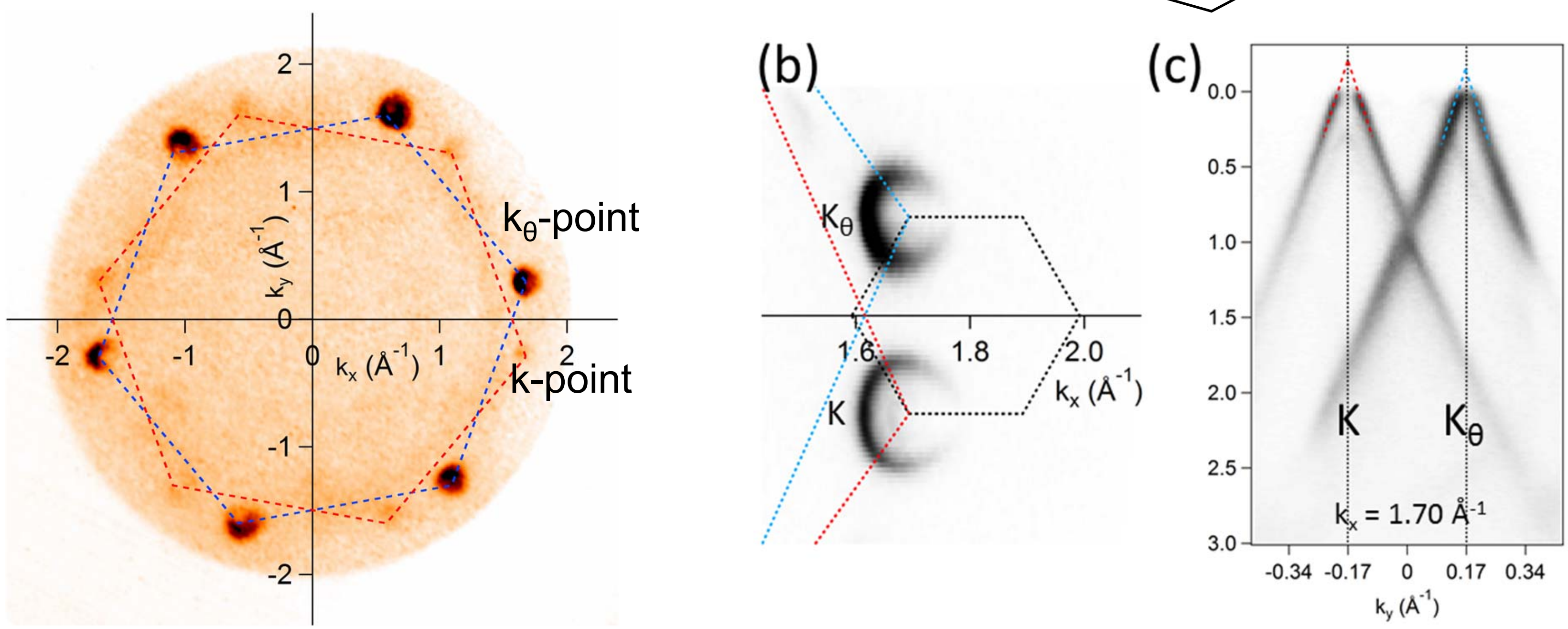
TBG has two sets of Dirac cones

- 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)

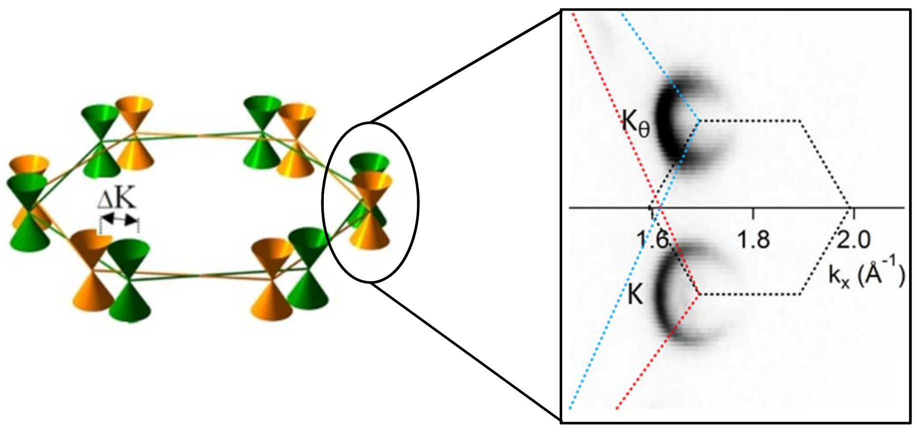


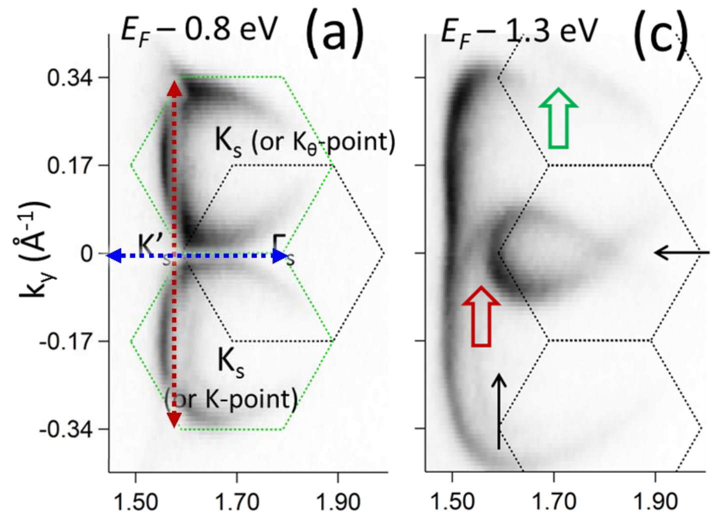


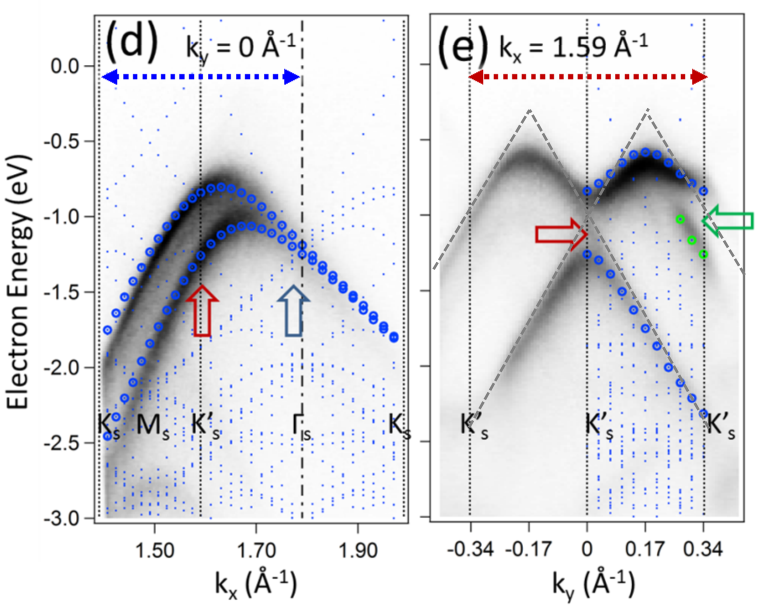
Ohta et al., PRL, 109, 186807 (2012)

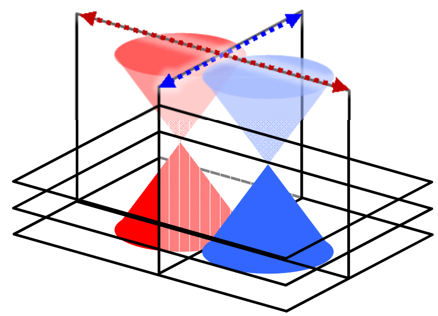
Two Dirac cones display anti-crossing

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







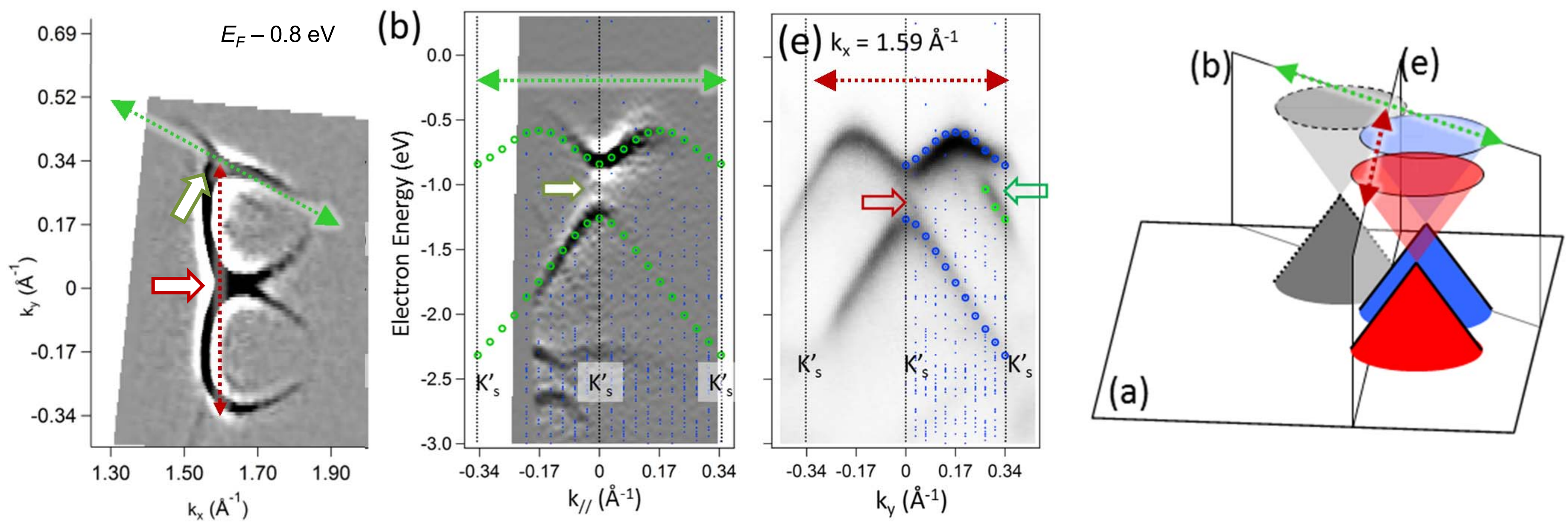


- Two cones' interaction leads to mini-gap and <u>van Hove singularities</u>
  - Match very well with DFT calculation

- Additional feature at the green arrow

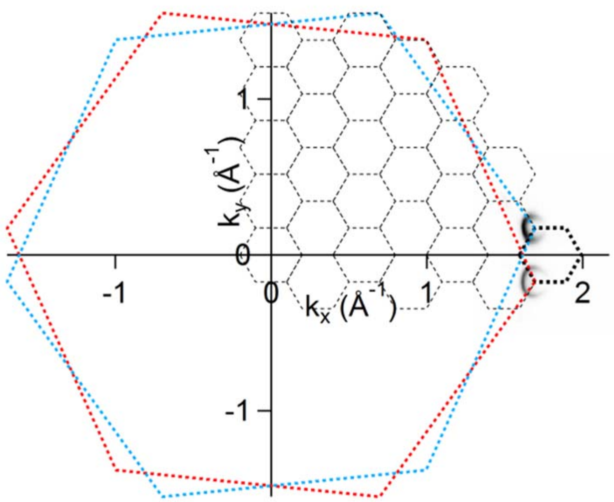
Additional Dirac cone emerges

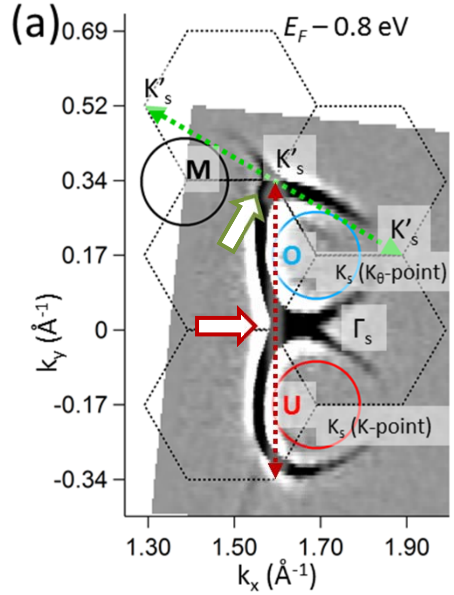
- Anti-crossing is found b/w the original and the additional Dirac cone

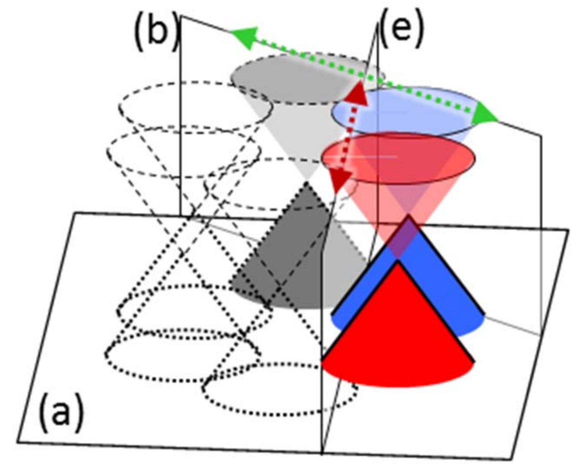


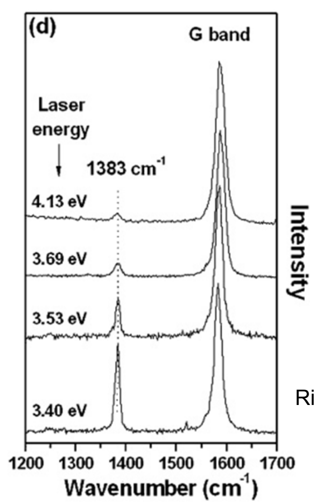
Moiré periodic potential produces Dirac cones

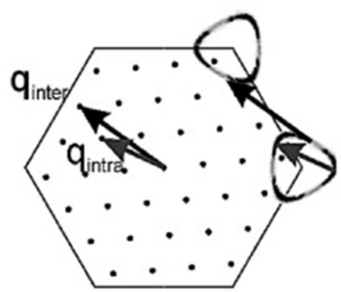
- Umklapp scattering by moiré periodic potential
  - Similar to moiré-induced Raman band and LEED spots



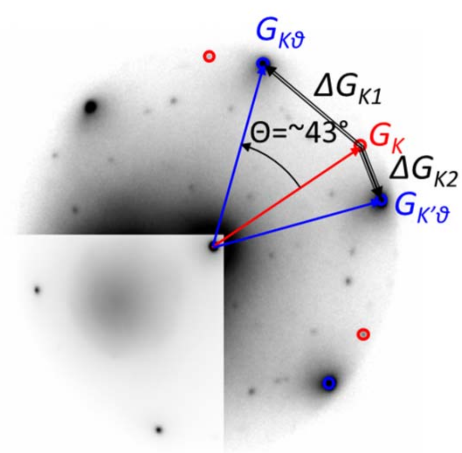








Righi et al., PRB 84, 241409(R) (2011)

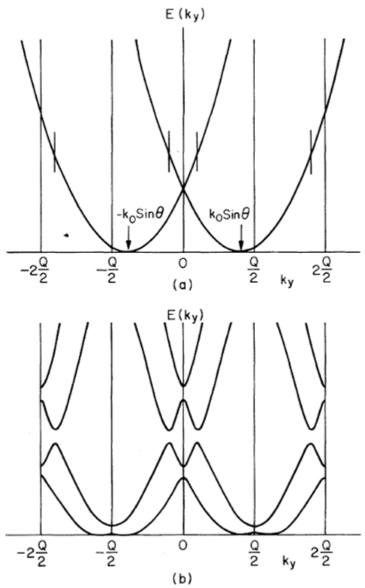


Superlattice changes electronic dispersion

- Substrate or neighboring material provides periodic potentials

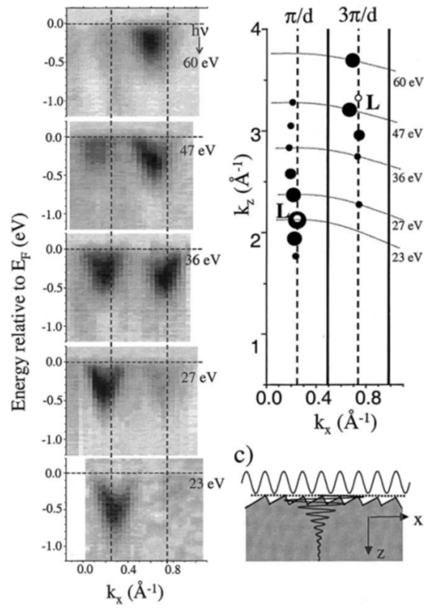
Surface superlattice

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



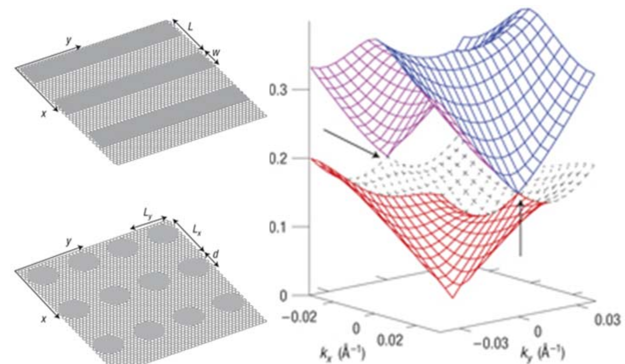
Tsui et al., PRL 40, 1667 (1978)

Surface state on Au(322) vicinal surface



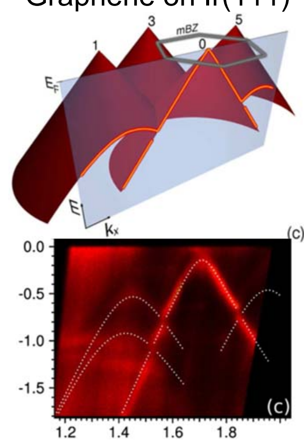
Ortega et al., Materials Science and Engineering B96 154 (2002)

Graphene superlattice



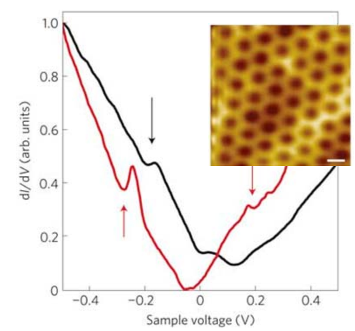
Park et al., Nature Physics 4, 213 (2008)

Graphene on Ir(111)



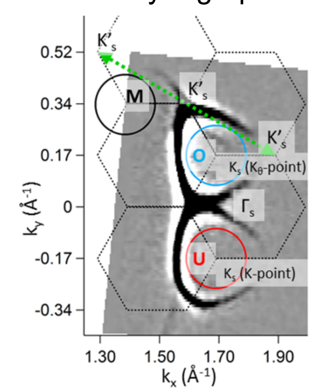
Pletikosic et al., PRL 102, 056808 (2009)

Graphene on hBN



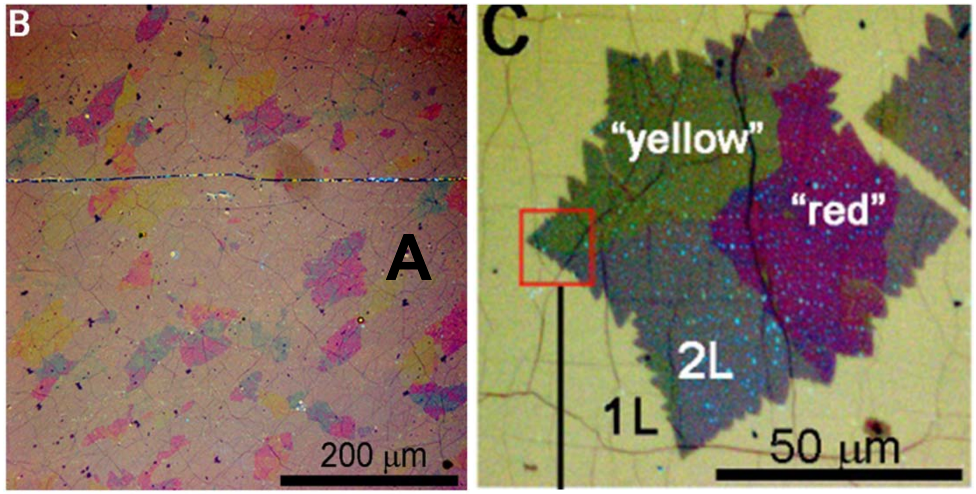
Yankowitz et al., Nature Physics 8, 382 (2012)

Twisted bilayer graphene

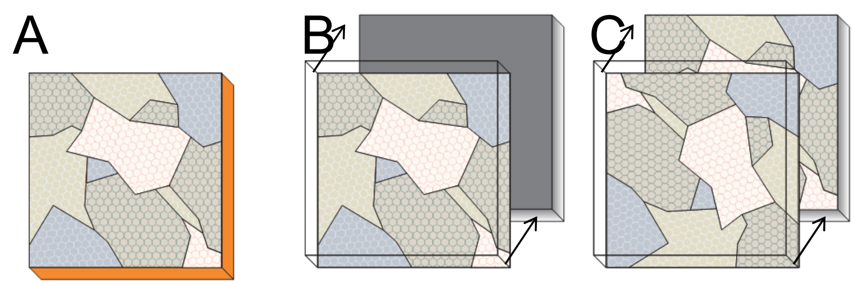


Moiré is ubiquitous in hybrid 2D-crystal stacks with misorientation!

How does the band renormalization affect the properties of TBG?

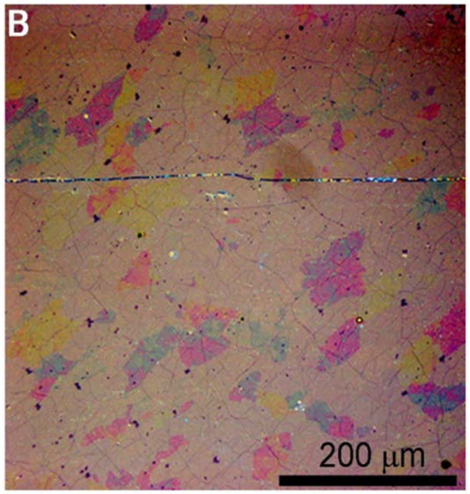


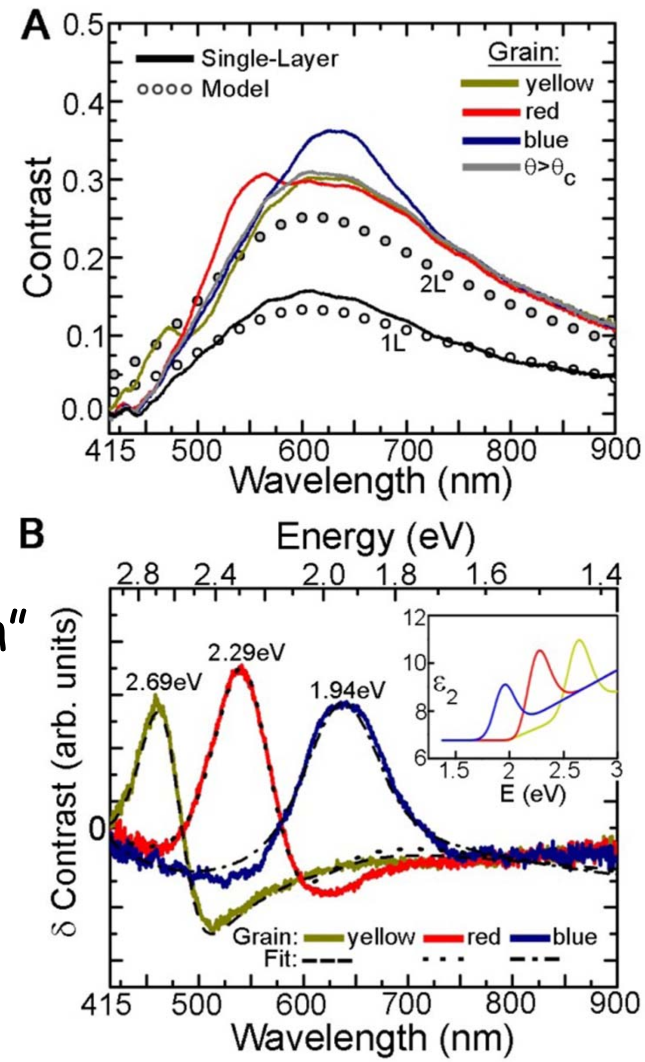
- Patches of "colored grain" observed in optical microscope
  - <u>TBG on SiO_2/Si substrate</u>



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

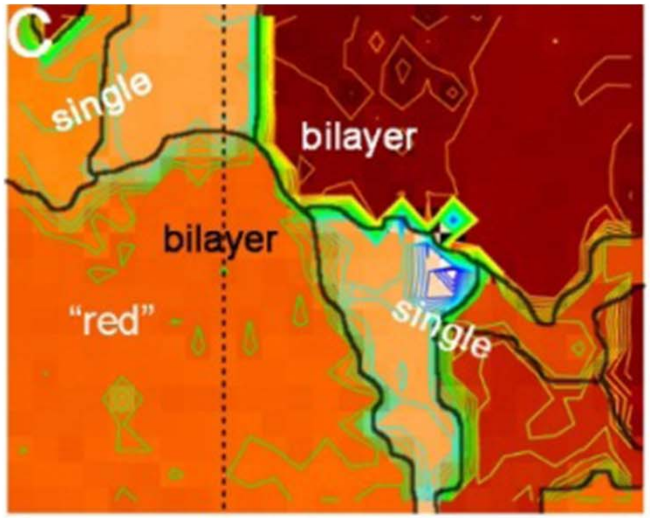
Emerging absorption band is responsible for "Colored grain"



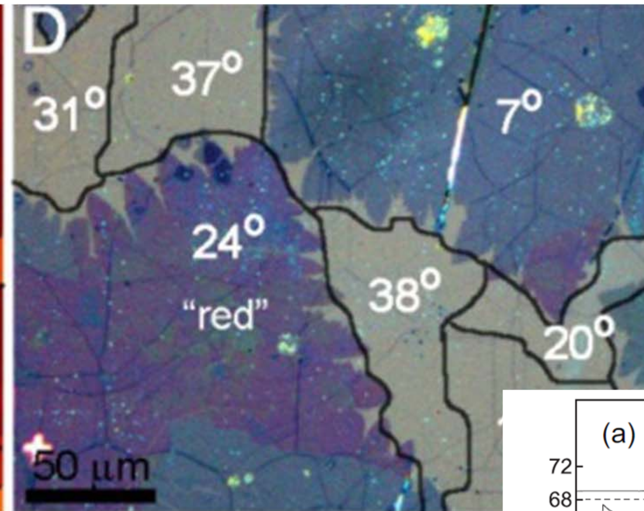


- Optical spectroscopy reveals an absorption band for "colored grain"

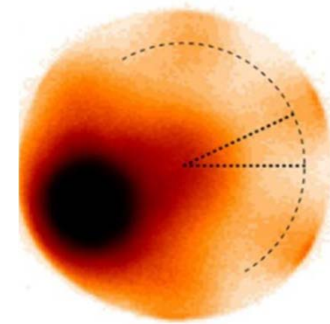
Optical absorption depends on the twist angle



Map of LEED pattern orientations across the sample surface

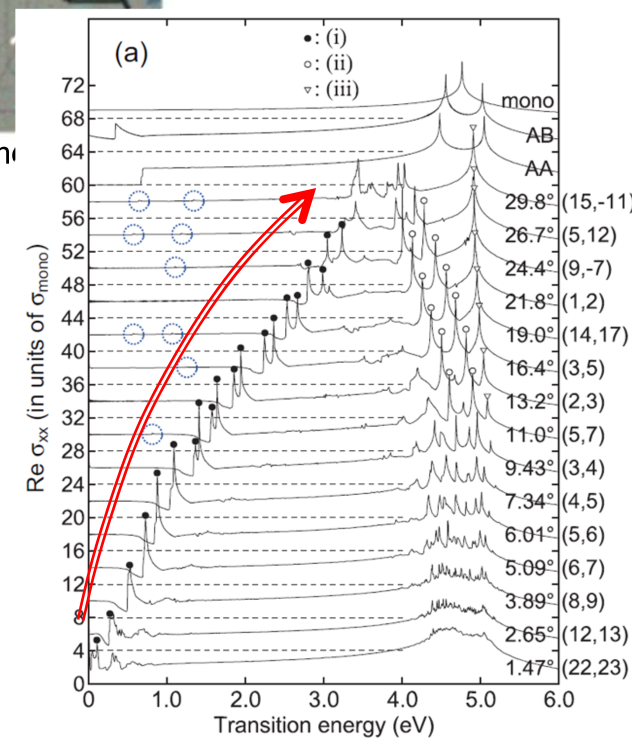


Optical micrograph of the sam



Typical LEED pattern of TBG

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

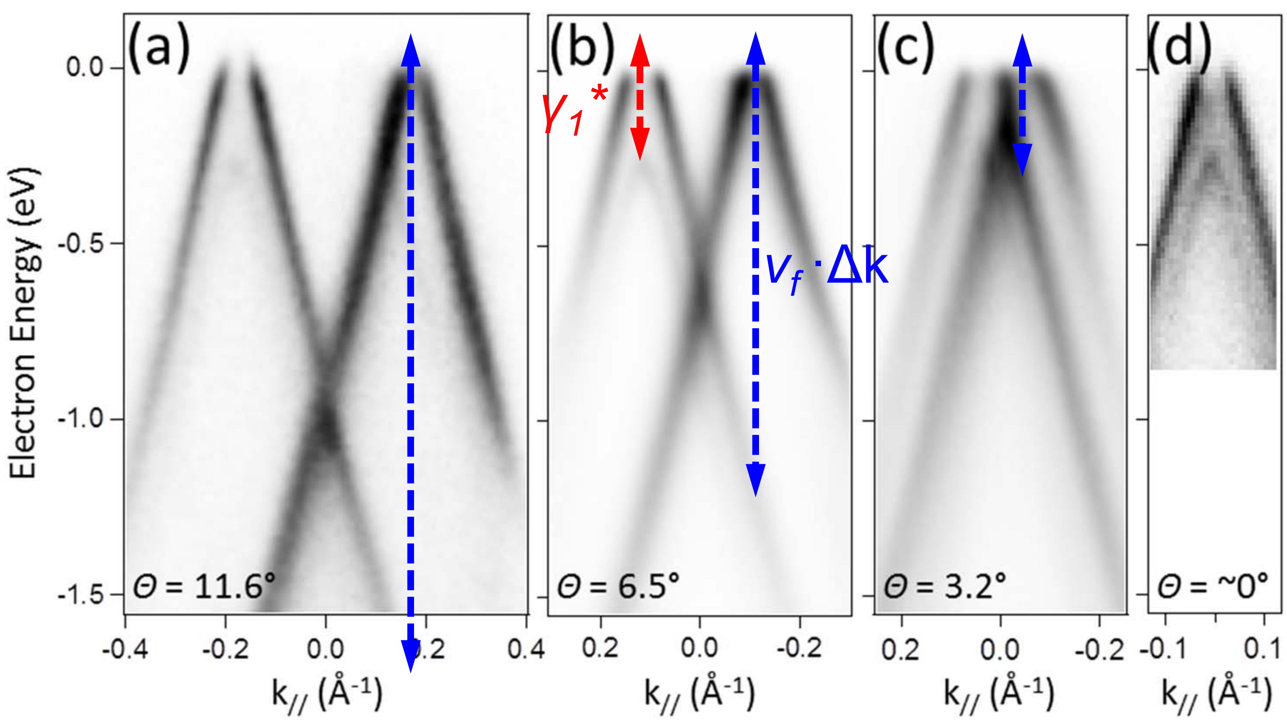


Moon & Koshino, arXiv:1302.5218 (2013)

- Confirmed theoretically

Interlayer overlap and characteristic energy $v_f \cdot \Delta k$ dictate band renormalization

- The energy scale of interlayer overlap integral (γ_1*) and the characteristic energy ($v_f \cdot \Delta k$) crossover at twist angle, θ = ~3°

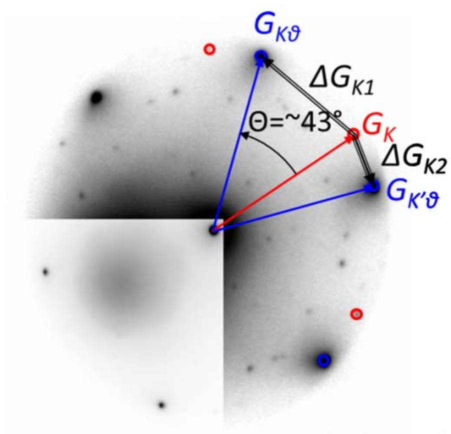


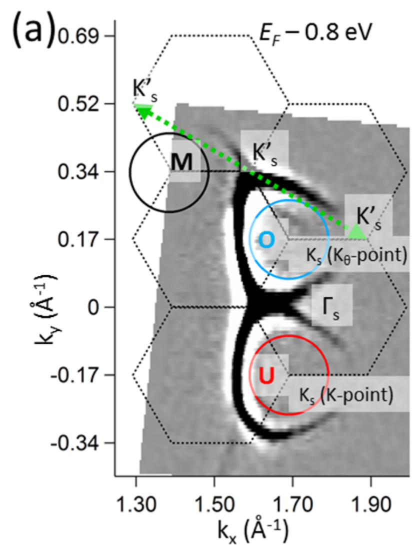
Ohta et al., unpublished (2012)

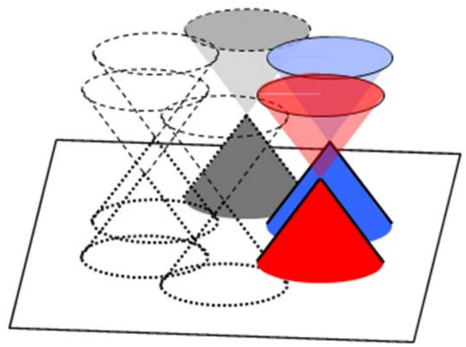
Summary

Moiré influences the electronic structure of TBG and 2D-solids

- 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
- Moiré is ubiquitous feature in 2D-solids: handle to tailor electronic properties







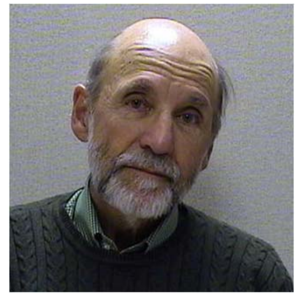
For details of our work, please see the following publications:

- 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."

Acknowledgements

- Jeremy T. Robinson (Naval Research Laboratory)
- Thomas E. Beechem, Peter J. Feibelman, Bogdan Diaconescu (Sandia National Laboratories)






- Collaborators:
  - 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)
  - Aaron Bostwick, Eli Rotenberg (Advanced Light Source, Lawrence Berkeley National Laboratory)

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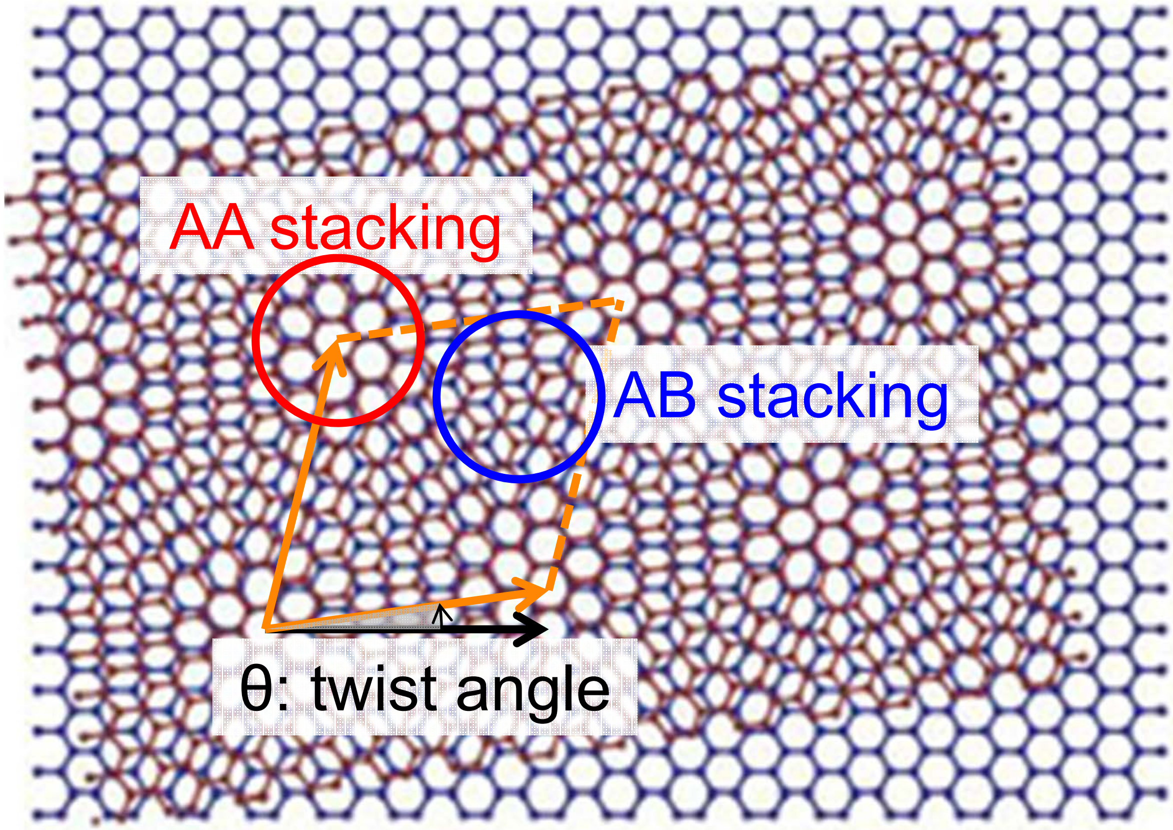
  - NTM and New Idea LDRD programs, Sandia National Laboratories

Following include supplemental slides

Two graphene lattices form moiré

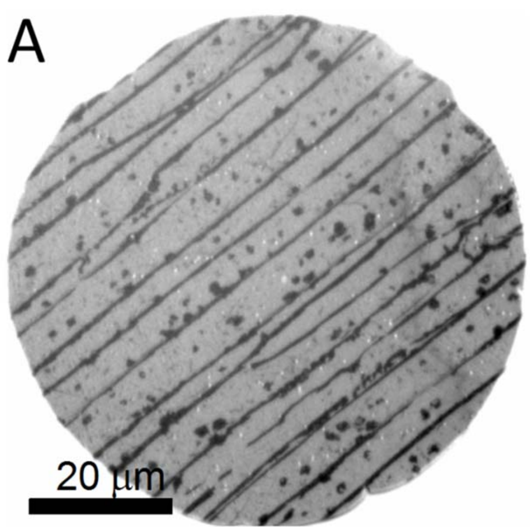
- Two layers of graphene stacked with an azimuthal (in-plane) misorientation



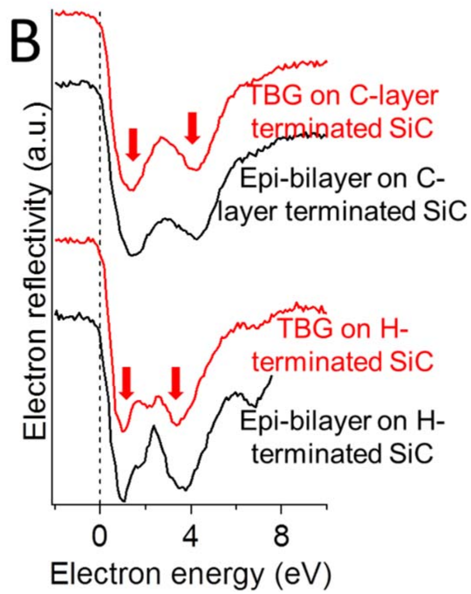
http://www.nist.gov/cnst/epg/sds_graphene.cfm

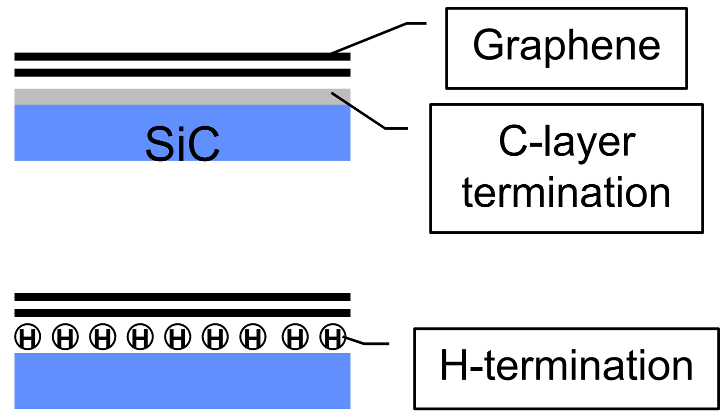
TBG shows characteristic electron reflectivity of bilayer graphene

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

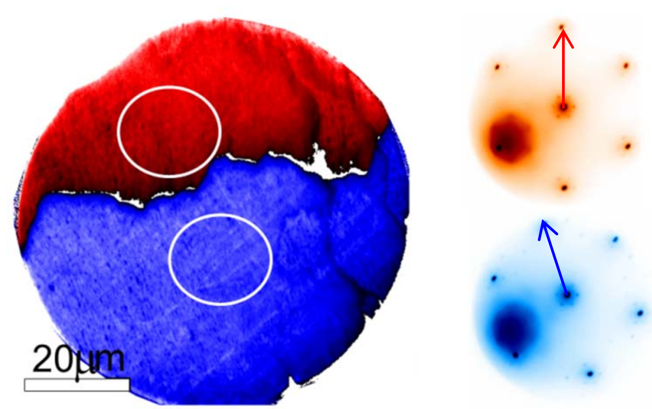


LEEM image of TBG





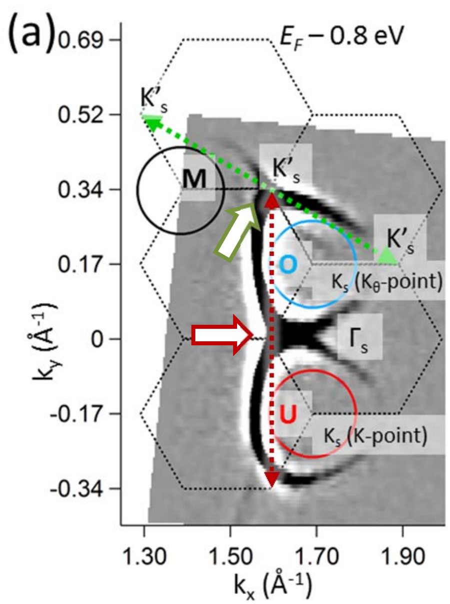
  - Diffraction experiments and dark-field imaging show large domain each with an unique twist angle

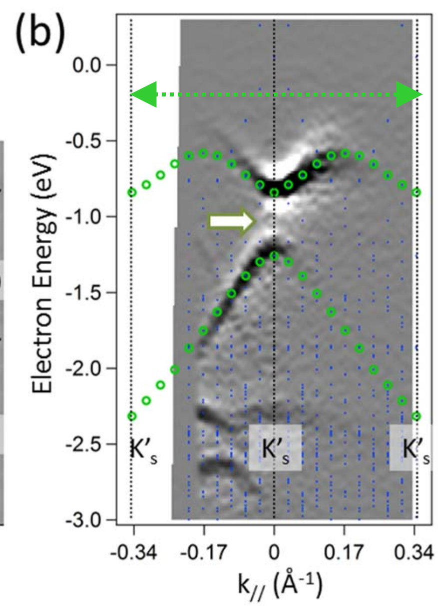


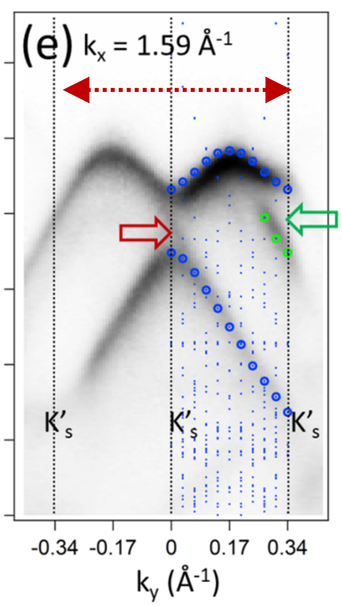
Ohta et al., PRB, 85, 075415 (2012)

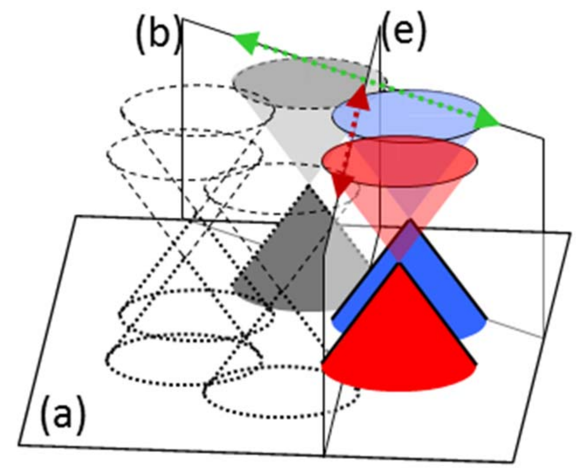
Umklapp scattering due to moiré periodic potential produces additional Dirac cones

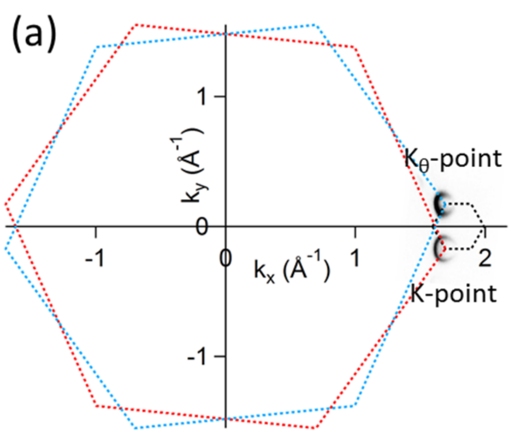
- Similar to moiré-induced LEED spots





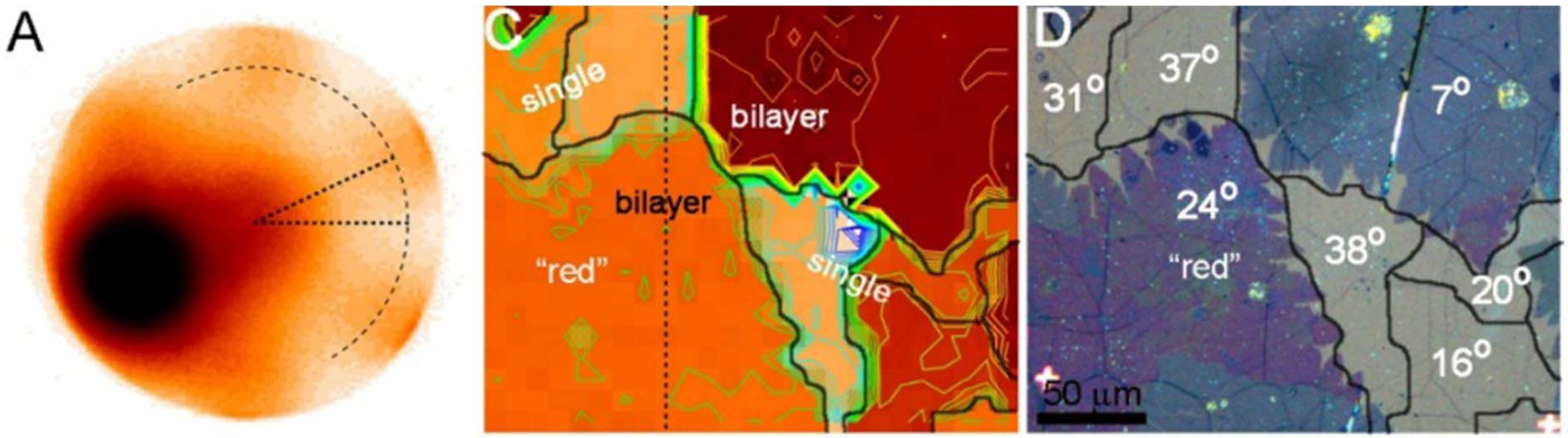






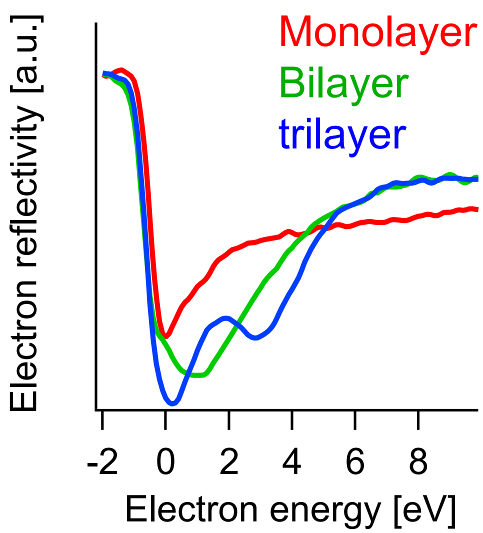
We confirmed the twist angle using LEED

- Twist angle was determined by comparing LEEM pattern orientation and the information of thickness using optical image
  - LEED is sensitive to only the top layer



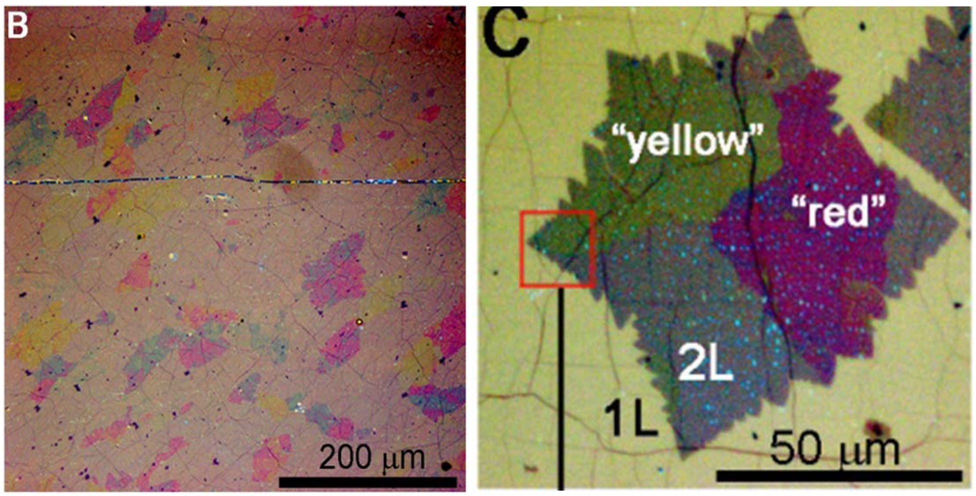
Typical LEED pattern of TBG | Map of LEED pattern orientations across the sample surface | Optical micrograph of the same area

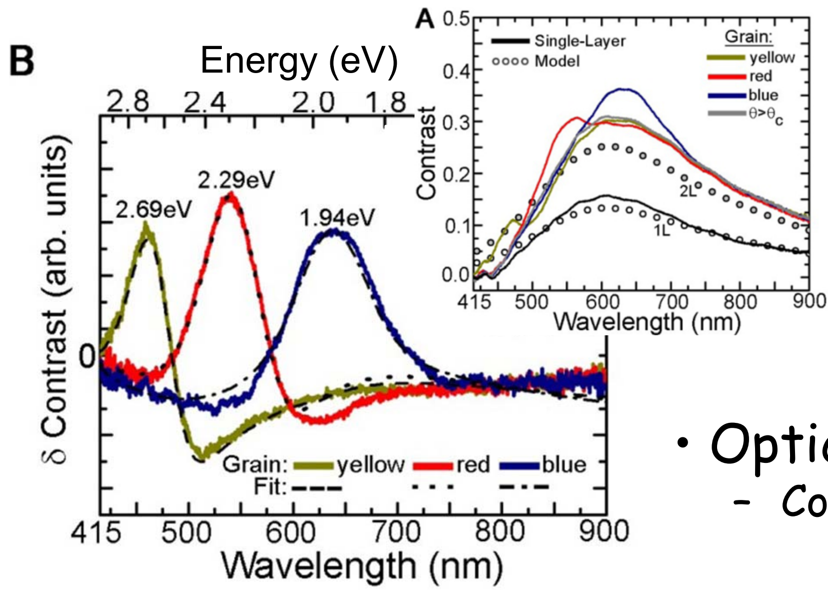
  - Graphene thickness confirmed using LEEM-IV

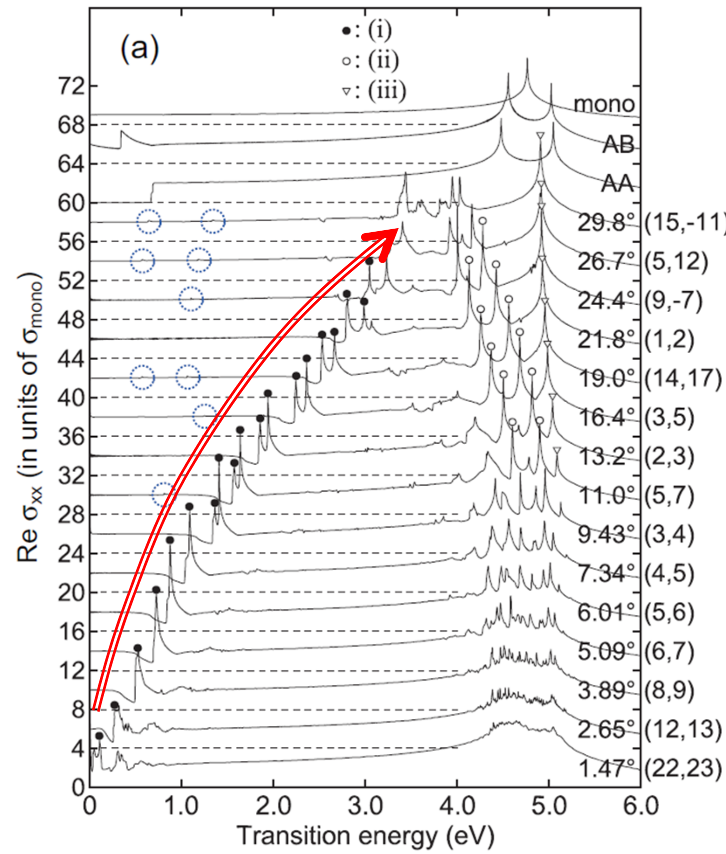


TBG gains color by electronic hybridization

- Optical microscope images of <u>TBG on SiO_2/Si substrate</u>
  - Blue: θ_{blue} = 11°, red: θ_{red} = 13°, yellow: θ_{yellow} = 15°







Moon & Koshino, arXiv:1302.5218 (2013)

- Optical absorption depends on the twist angle
  - Confirmed using Raman spectroscopy and LEED

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

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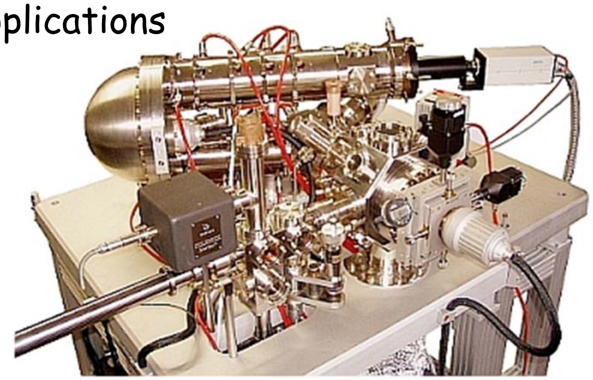
Postdoc opportunities at Sandia National Labs

- LEEM-PEEM research program
  - Properties of 2D-crystals and their stacked structures
  - Understanding defects in indium gallium-nitrides for lighting applications
- New capability: energy-filtered LEEM-PEEM
  - Real-time surface imaging and diffraction
  - Electronic structure study using EELS and ARPES



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