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National Synchrotron Radiation Research Center

Angle-resolved photoemission spectroscopy on emergent quantum materials

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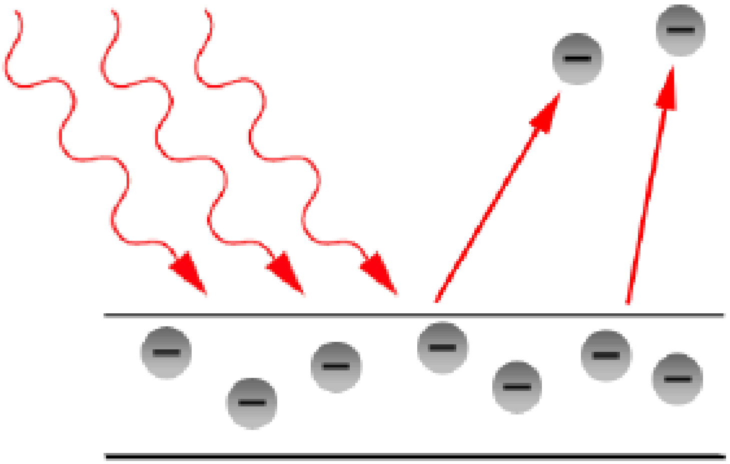
Outline

- Introduction to angle-resolved photoemission spectroscopy (ARPES)
  - The principle of ARPES
  - Current status of ARPES beamline at NSRRC

- The electronic structure of emergent materials
  - Surface states and quantum well states
  - Graphene based materials
  - Beyond graphene : 2D materials
  - Topological insulators (TIs)
  - Toward future electronic devices

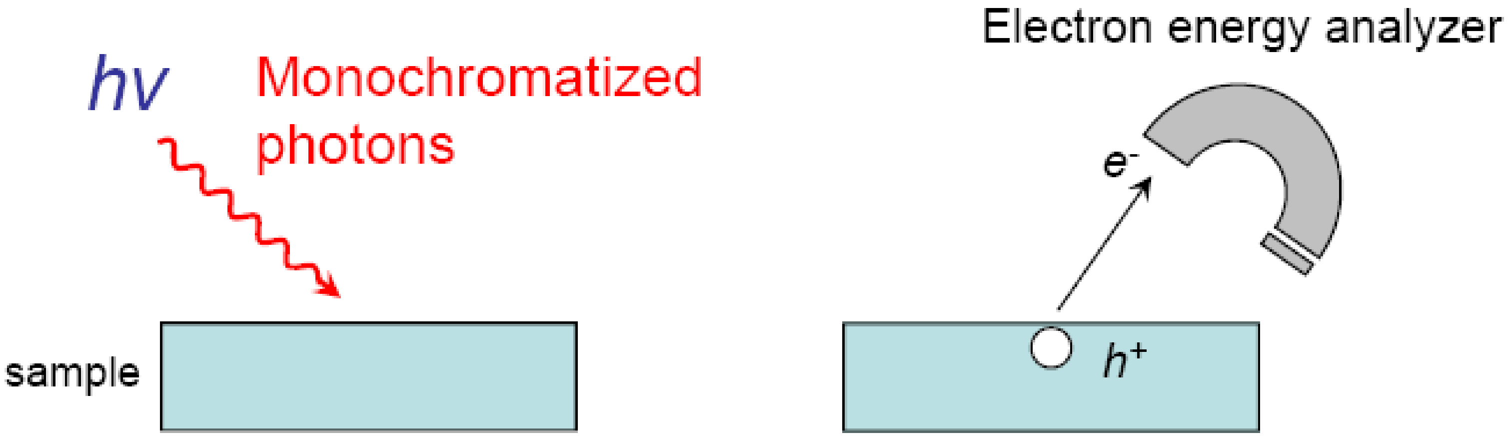
- Summary

What is photoemission?



Photon in –> electron out (emission)

What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)



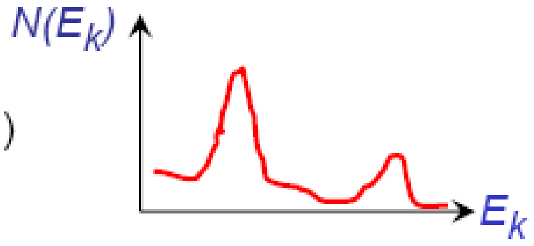
Initial state: ground (neutral) state

Final state: hole (excited) state

Conservation of energy

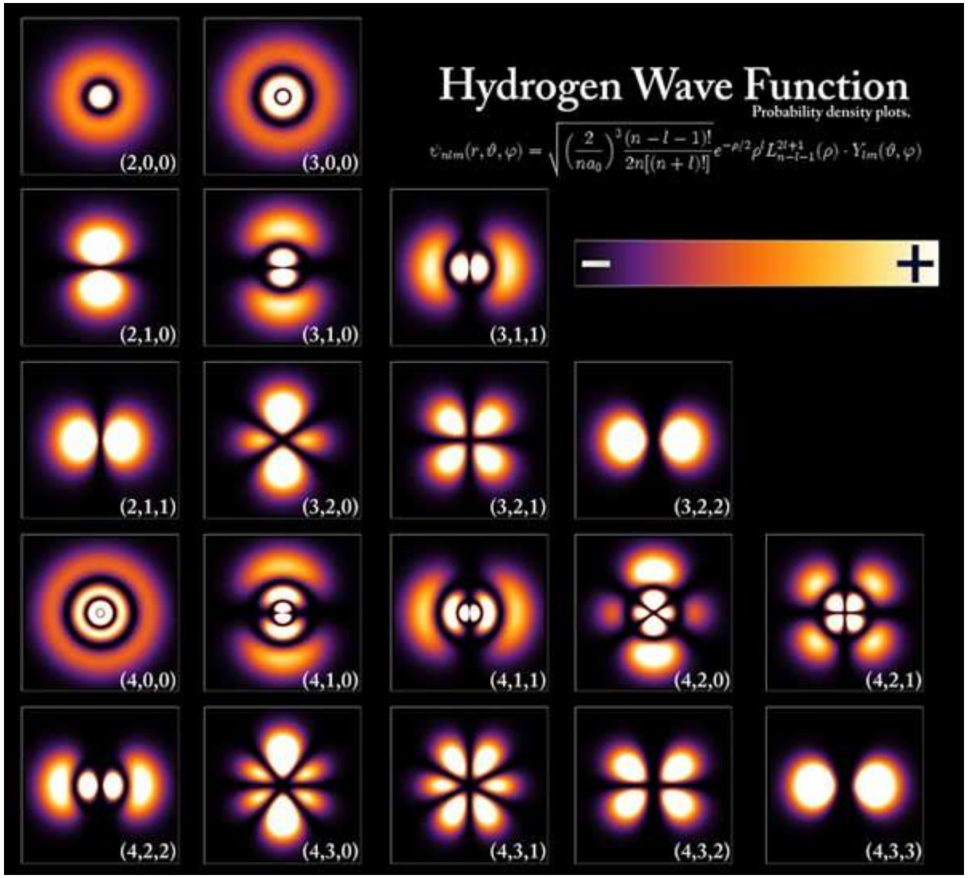
$E_k = h\nu + E_i - E_f$ (most general expression)

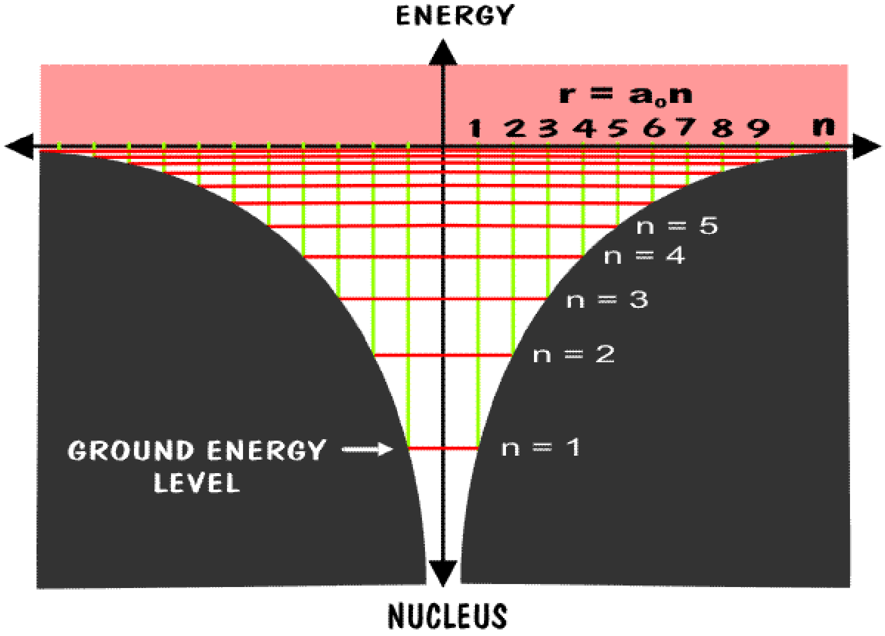
E_k : photoelectron kinetic energy
$E_i\,(N)$: total initial state system energy
$E_f\,(N\text{-}1)$: total final state system energy



Energy Distribution Curve (EDC) (Spectrum)

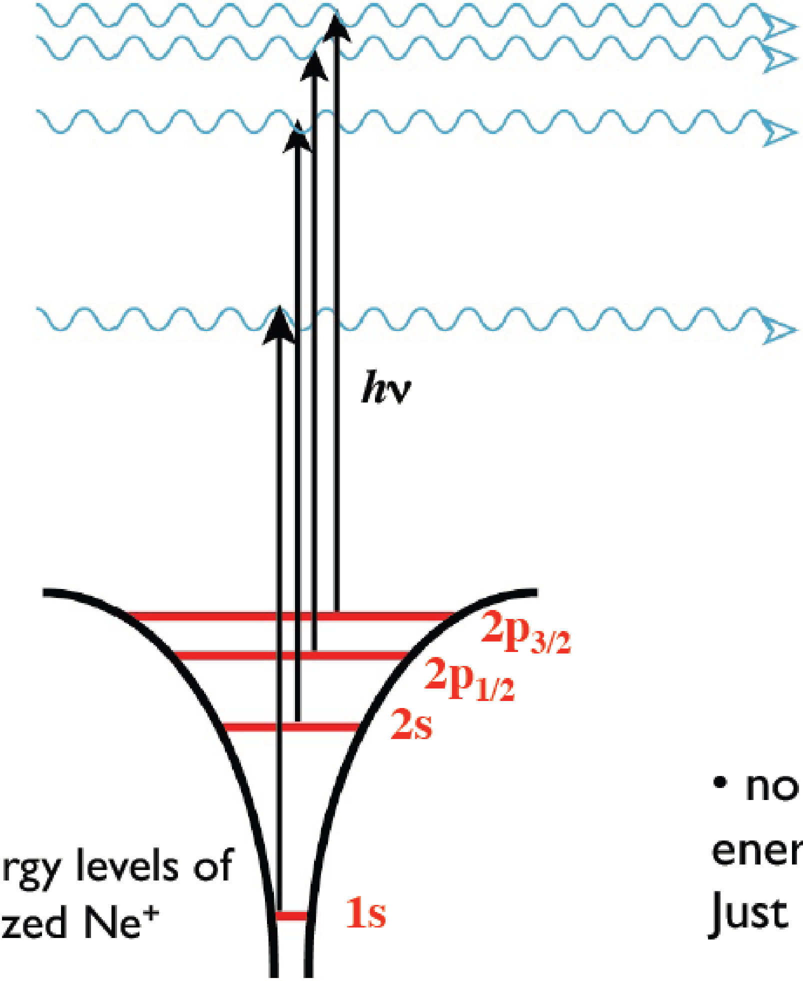
The energy level of hydrogen atom



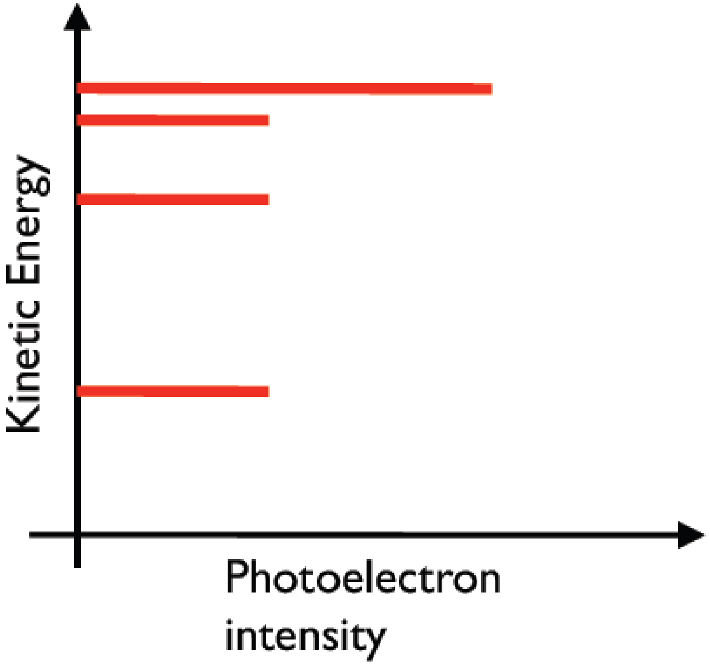


Electron ionization levels are formed from *discrete levels* in an atom

Energy conservation : $h\nu - E_I = KE$



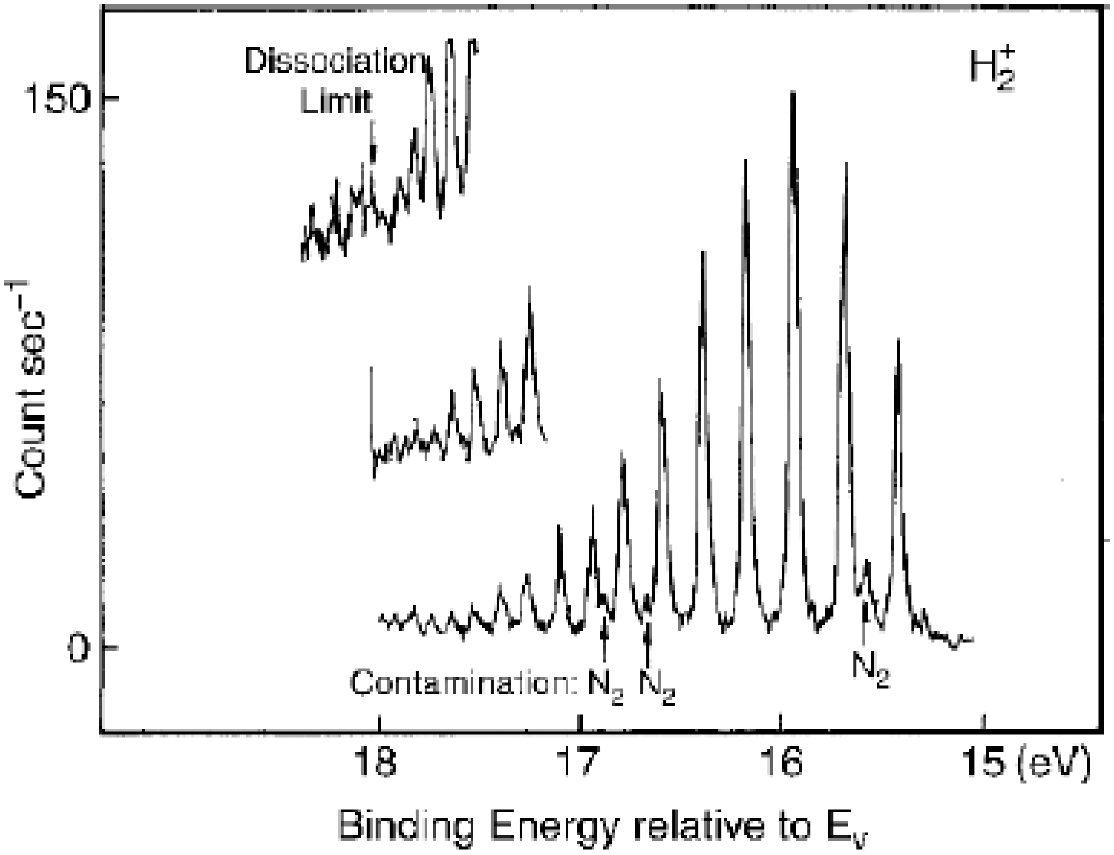
Energy levels of ionized Ne⁺

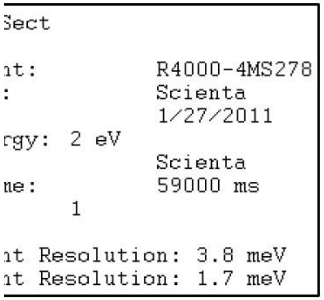


- no need to be on resonance or scan photon energies (e.g. NMR, optical measurements). Just need photons to have high enough energy!

Kyle Shen, IGERT Lecture 2008

Xeon gas phase test



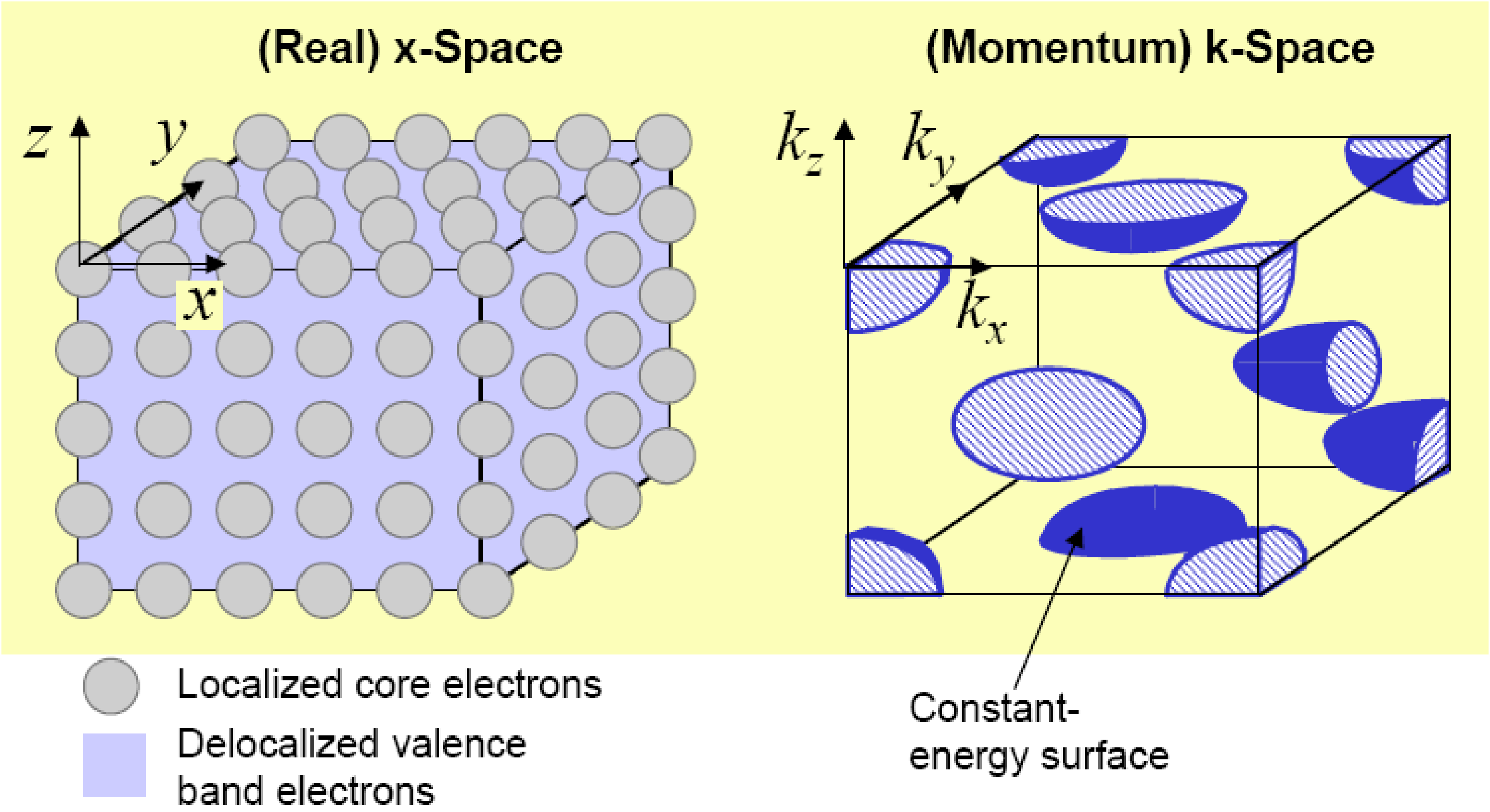


```
Sect

nt:            R4000-4MS278
:              Scienta
               1/27/2011
rgy:  2 eV
               Scienta
me:            59000 ms
          1

nt Resolution: 3.8 meV
nt Resolution: 1.7 meV
```

The crystal structure and momentum space



(Real) x-Space

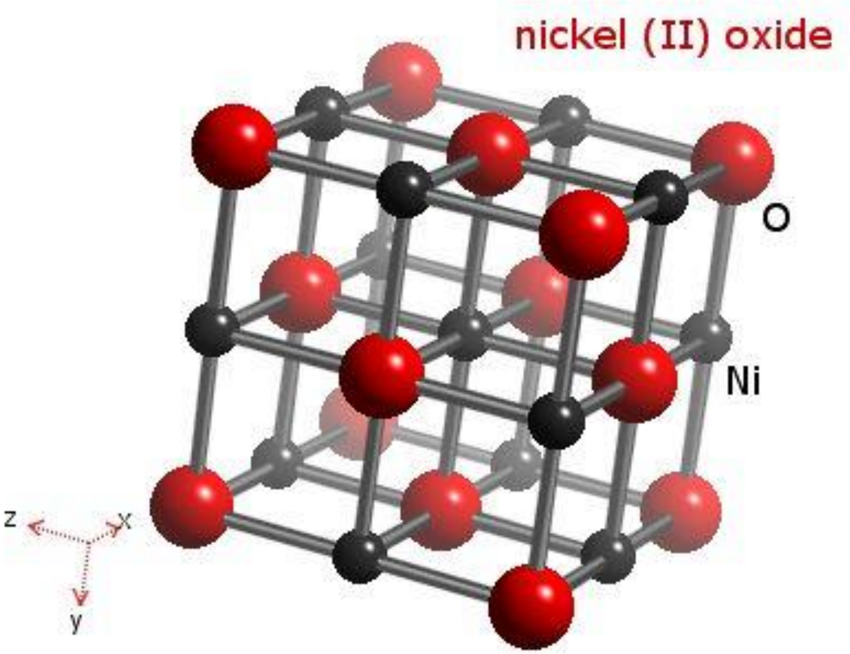
(Momentum) k-Space

● Localized core electrons

▨ Delocalized valence band electrons

Constant-energy surface

Z. Hussain, ALS summer school



primitive vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$

reciprocal lattice vector $\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{V}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{V}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{V}$$

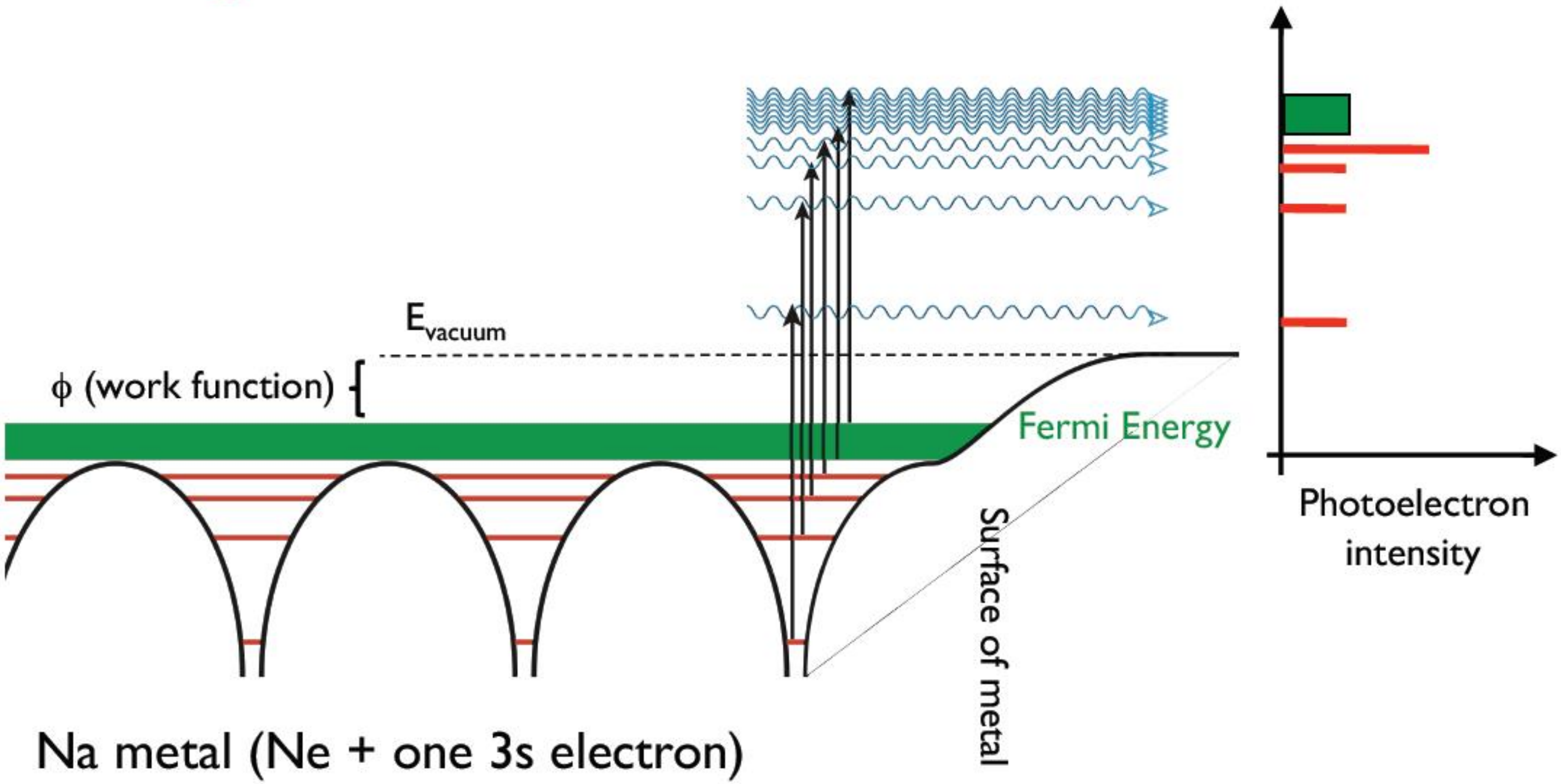
$$V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$$

reciprocal lattice **G** :

$$\vec{G} = l\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3$$

l,m,n are any integers

- Deeply bound "*core*" electrons remain basically unchanged
- Outermost "*valence*" electrons hybridize forming continuous "*energy bands*"



Na metal (Ne + one 3s electron)

Kyle Shen, IGERT Lecture 2008

Band theory

Two approximations

Nearly free electrons. Electrons are non-interacting in a periodic crystal potential which is relatively weak and can be treated as a perturbation. As in the free-electron-gas model, they are still subject to the Pauli exclusion principle.

Free electron gas :
The interactions between electrons and between electrons and nuclei are turned off, subject only to the Pauli exclusion principle.

Tightly-bonding approximation

Electrons are tightly bound to particular atoms, overlapping only weakly with neighbors.

Fermi-Dirac Distribution

Thermal Properties of Free Electron Gas:

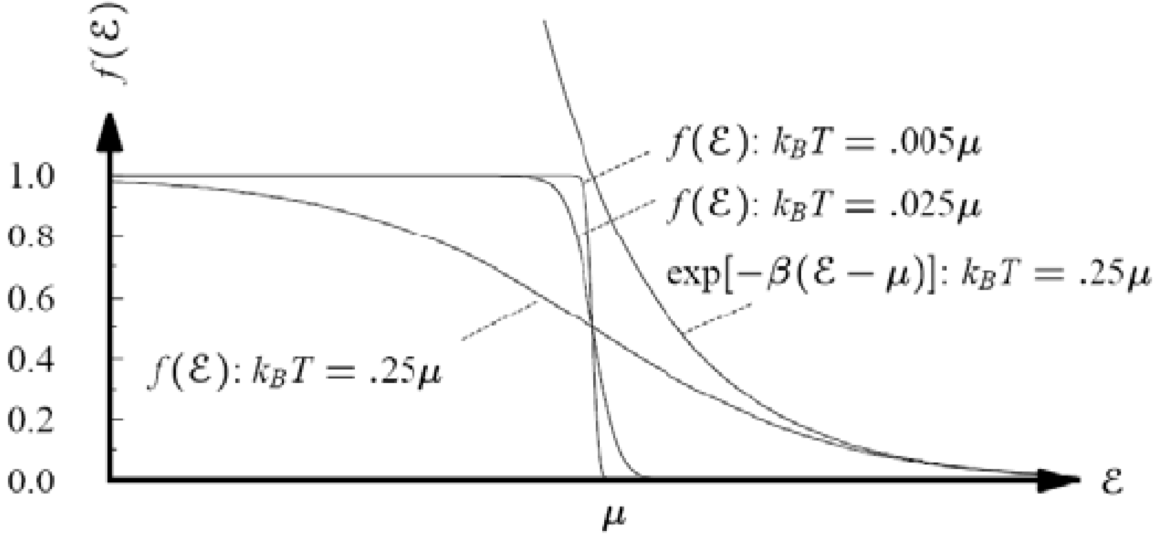
Almost every electronic transport property of solids is proportional to $D(\mathcal{E}_F)$.

Fermi function

(Fermi-Dirac distribution)

$$f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/k_B T} + 1}$$

RT ~ 25 meV



Hufner, Very high resolution photoelectron spectroscopy

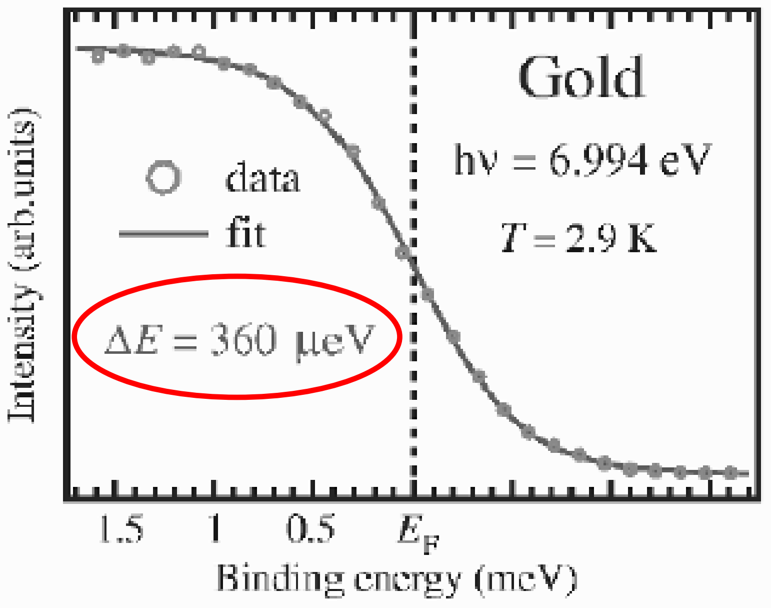


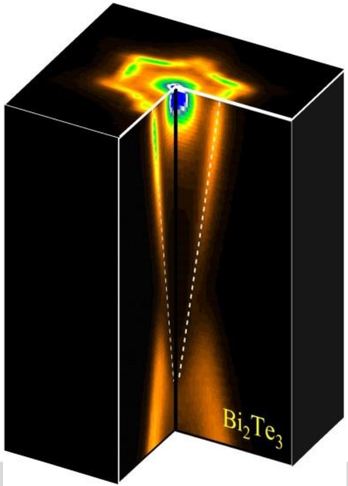
Fig. 2.3. Ultra-high resolution photoemission spectrum on a polycrystalline gold sample (evaporated Au film) for the determination of the energy resolution. The Fermi edge was measured at $T = 2.9$ K using a frequency tripled ($KBe_2BO_3F_2$ crystal, KBBF) YVO_3 laser for the photoexcitation ($h\nu = 6.994$ eV) [15]

Hufner, Very high resolution photoelectron spectroscopy

Why ARPES - key technique for the electronic structure mapping

- Angle-resolved photoemission spectroscopy (ARPES) is the most general tool to probe band structure, electronic interactions or spectral function mapping.

- Broad applications: surfaces, thin films, bulk materials, superconductors, magnetic/spin systems, complex materials, topological insulators, graphene based materials, charge density wave materials, low-dimensional systems, artificial stacks, device configurations, etc.



Example: the electronic structure of graphene

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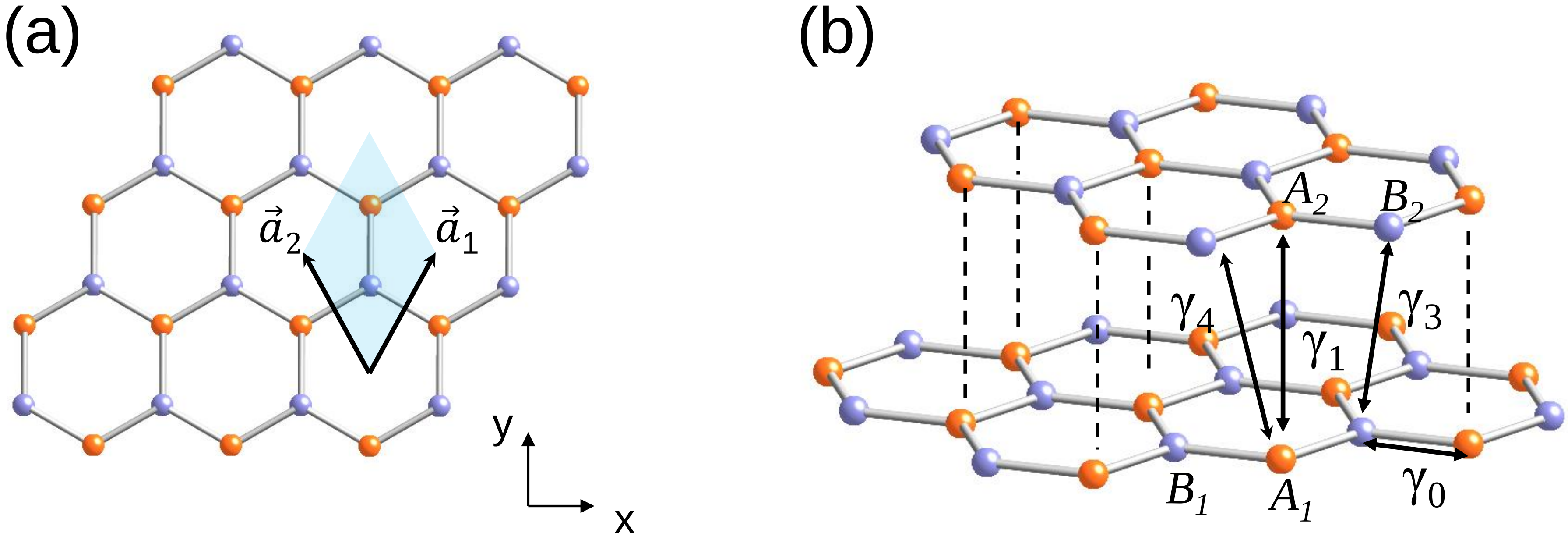
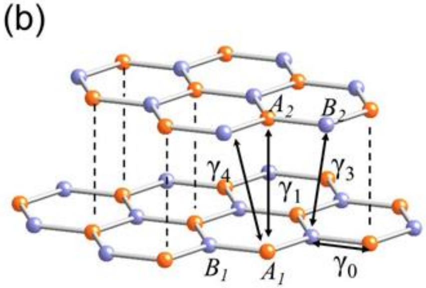
The unit cell of graphene



SWMc Hamiltonian of bilayer graphene

$$\mathrm{H}(\vec{k}) = \begin{pmatrix} E_0+\Delta & \gamma_0 f(\vec{k}) & \gamma_1 & \gamma_4 f^*(\vec{k}) \\ \gamma_0 f^*(\vec{k}) & E_0 & \gamma_4 f^*(\vec{k}) & \gamma_3 f(\vec{k}) \\ \gamma_1 & \gamma_4 f(\vec{k}) & E_0+\Delta & \gamma_0 f^*(\vec{k}) \\ \gamma_4 f(\vec{k}) & \gamma_3 f^*(\vec{k}) & \gamma_0 f(\vec{k}) & E_0 \end{pmatrix}$$

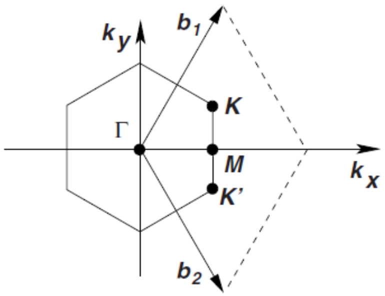


$$f(\vec{k}) = \exp\left(ik_x a_0/2\sqrt{3}\right) + 2\exp(-ik_x a_0/2\sqrt{3})\cos(k_y/2)$$

$$\vec{k} = (k_x, k_y)$$

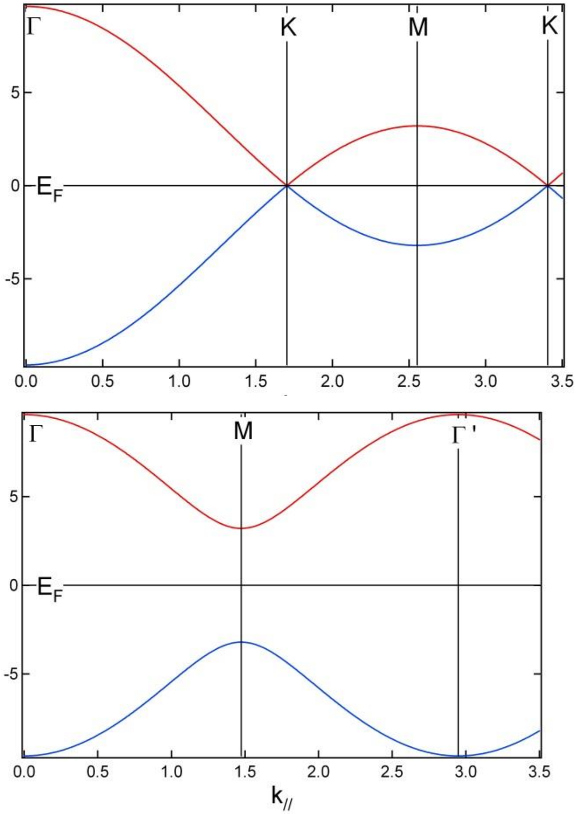
A. Gruneis et al., PRB (2008)

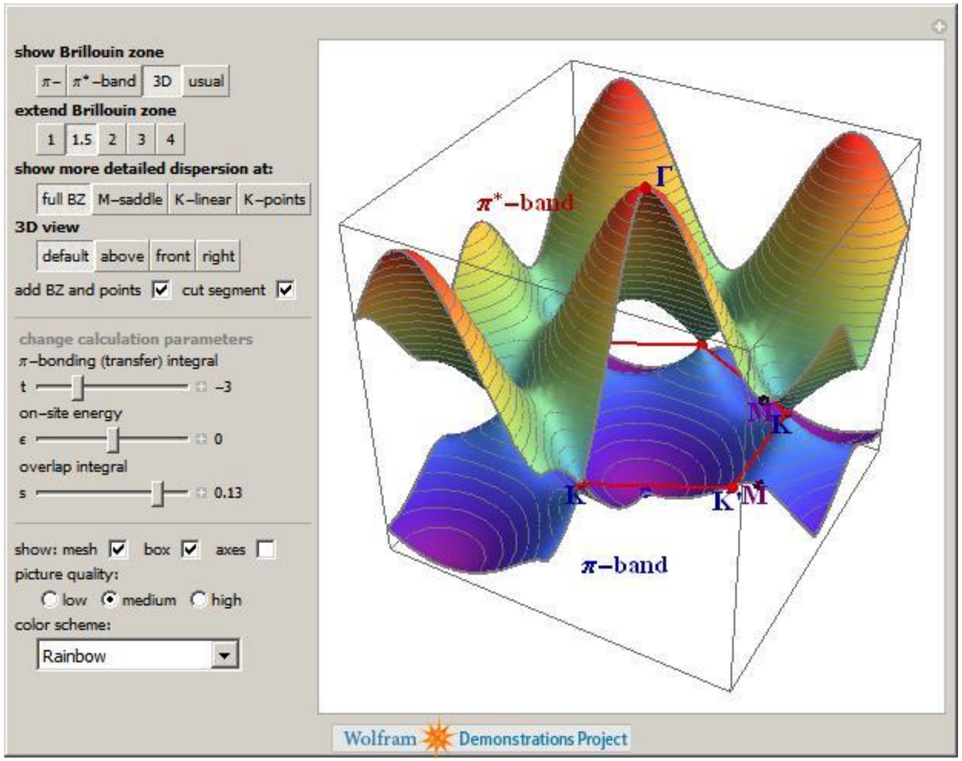
Pure 2D material : graphene



$$\boldsymbol{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3}), \quad \boldsymbol{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3})$$

$$\boldsymbol{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \boldsymbol{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right)$$




show Brillouin zone: 3D

extend Brillouin zone: 1.5

show more detailed dispersion at: full BZ

3D view: default

add BZ and points ☑ cut segment ☑

change calculation parameters

π–bonding (transfer) integral

t –3

on–site energy

ϵ 0

overlap integral

s 0.13

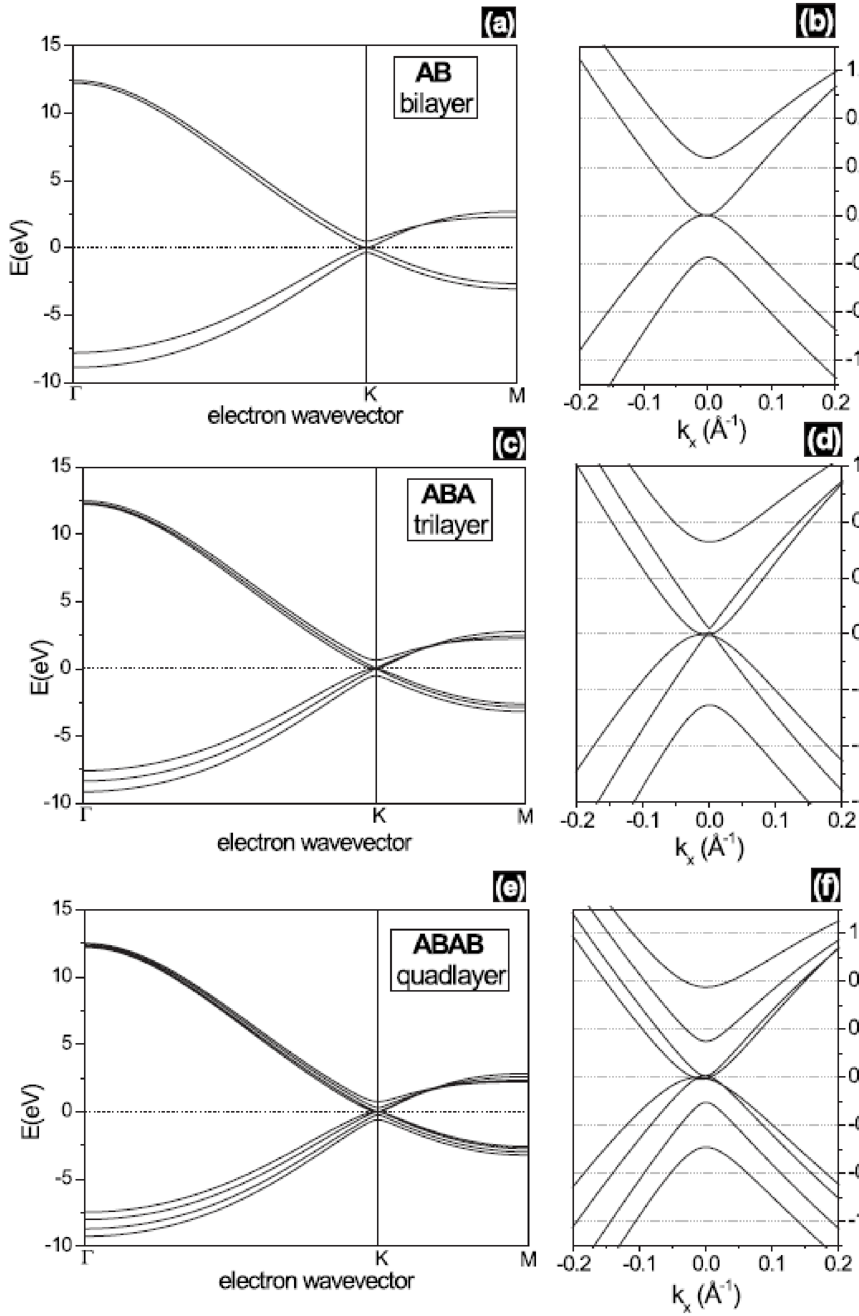
show: mesh ☑ box ☑ axes ☐

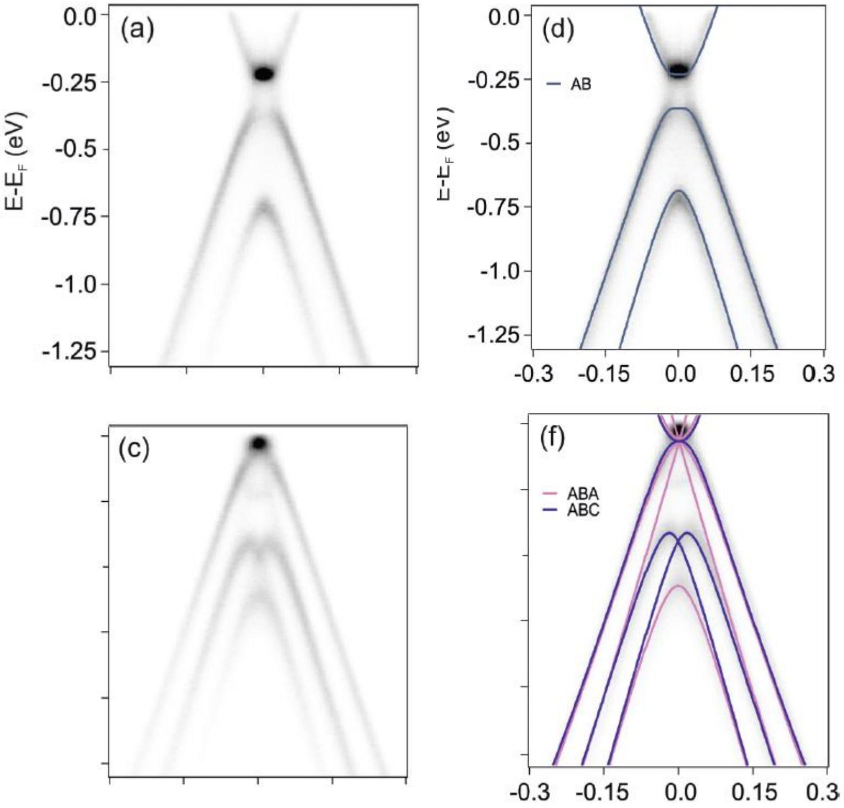
picture quality:

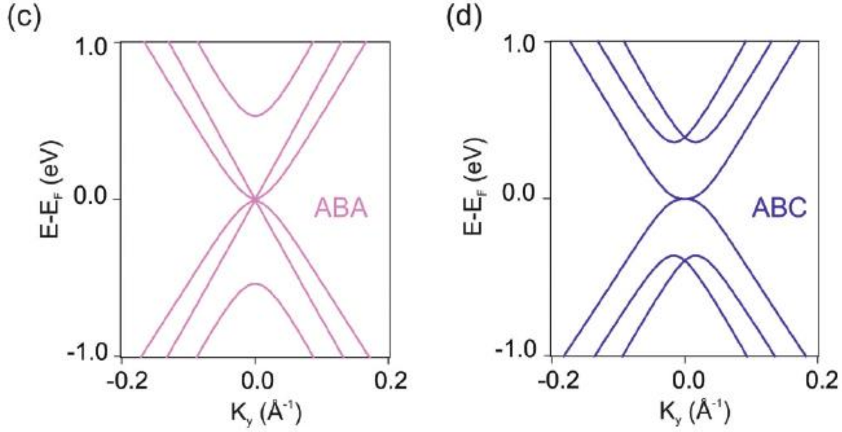
○ low ● medium ○ high

color scheme:

Rainbow

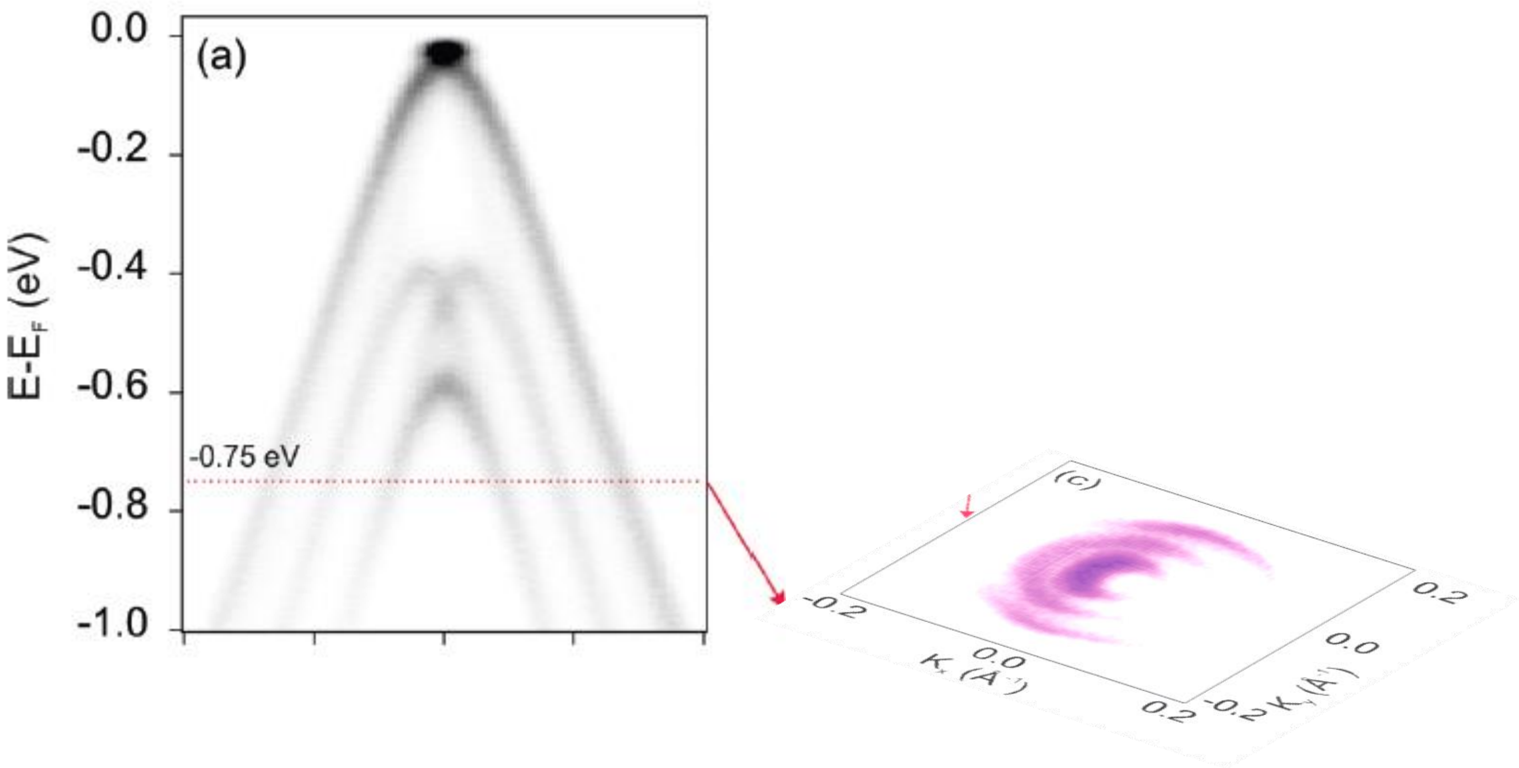






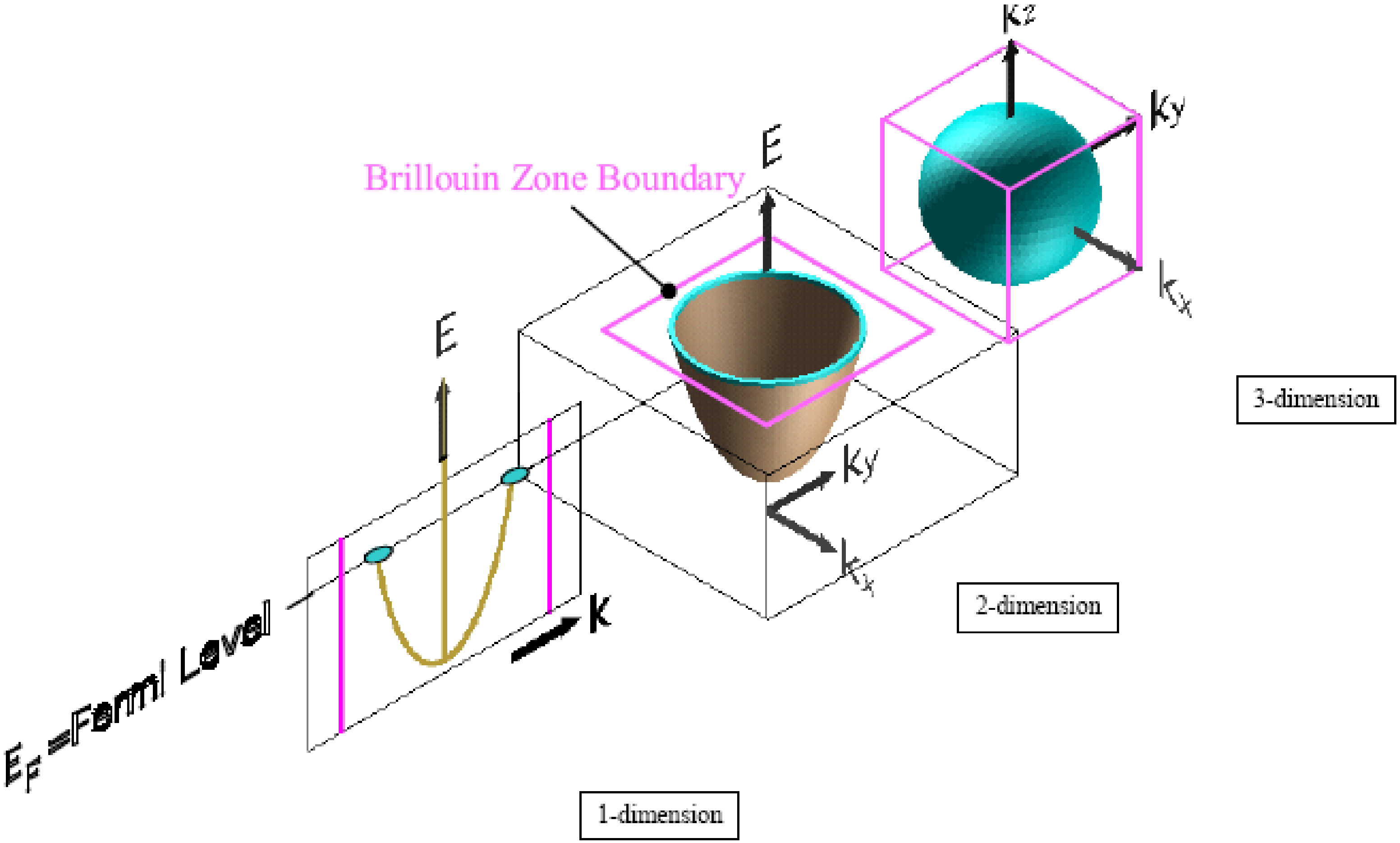
Coletti et al., PRB (2013)

Constant energy mapping



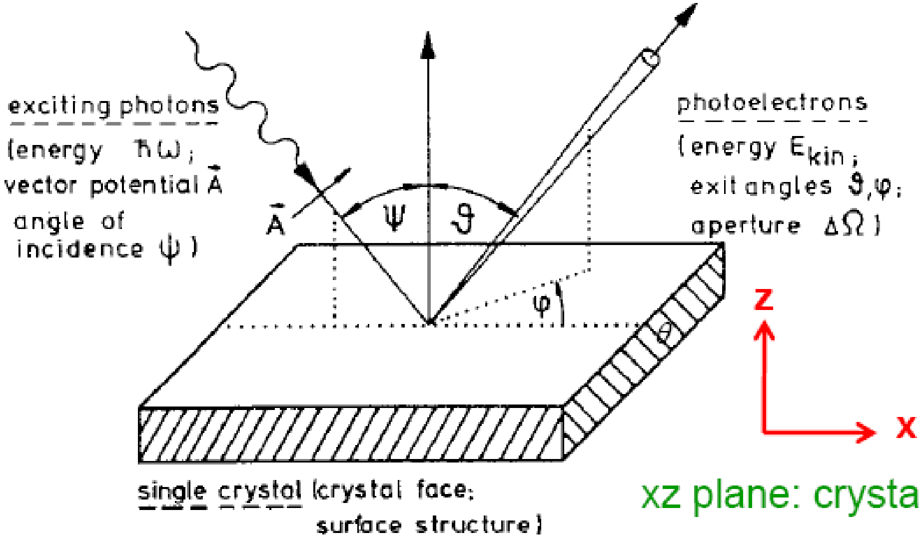
Coletti et al., PRB (2013)

Fermi Surface



How to probe the electronic structure of solids

Angular Resolved Photoemission Spectroscopy(ARPES)



xz plane: crystal symmetry plane

Electron emission angle: *θ*

Photon incident angle: *ψ*, *s*- and *p*-polarization

$$k_{//} = \sqrt{\frac{2m}{\hbar^2}E_k}\cdot\sin\theta$$

$$k_{//}(\text{Å}^{-1}) = 0.5123\sqrt{E_k(eV)}\cdot\sin\theta$$

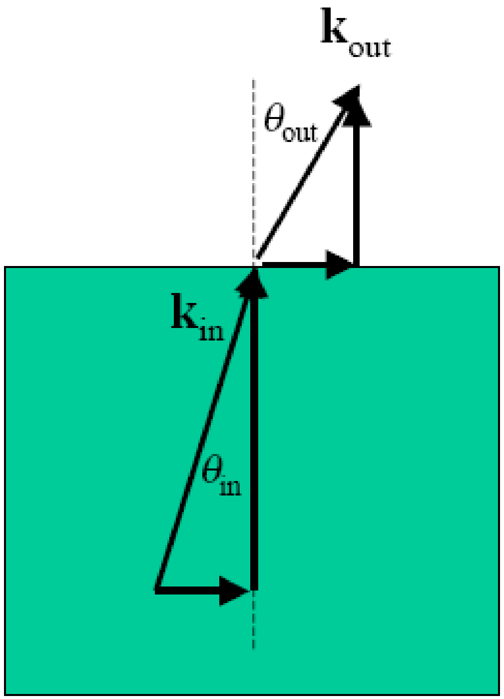
$k_{||}$(inside) = $k_{||}$(outside)

Conservation of liner momentum

Important for 3D and 2D band mapping

$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

Conservation of linear momentum parallel to the surface



Kinematic relations

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

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

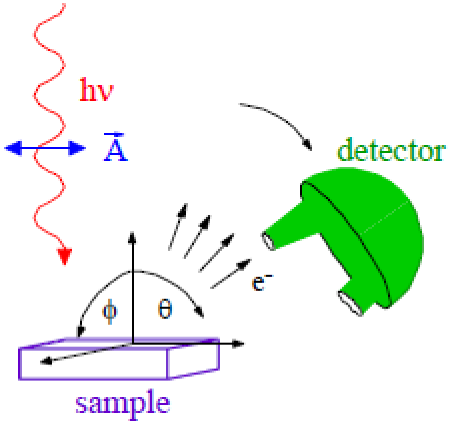
$$k_{out,\|} = k_{in,\|} \equiv k_{\|}$$

"Snell's Law"

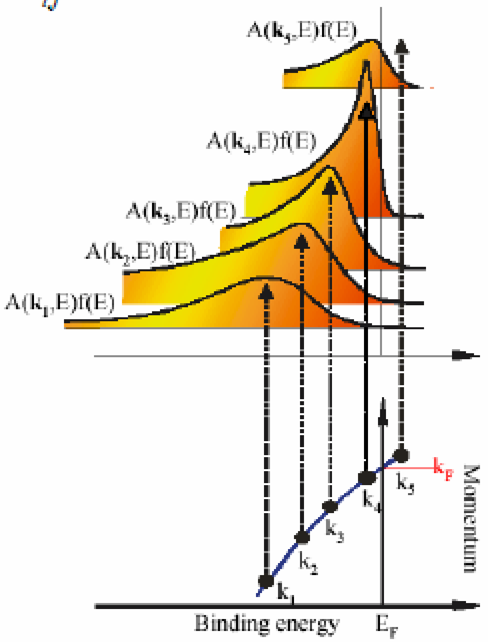
$$k_{\|} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission

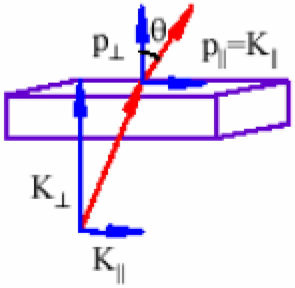
$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$



Intensity $\propto \sum_{i,f} \left|\langle f|\vec{\mathbf{p}}\bullet\vec{\mathbf{A}}|i\rangle\right|^2 A(\vec{\mathbf{k}},E)f(E)$



Electron momentum
Parallel to the surface is
conserved

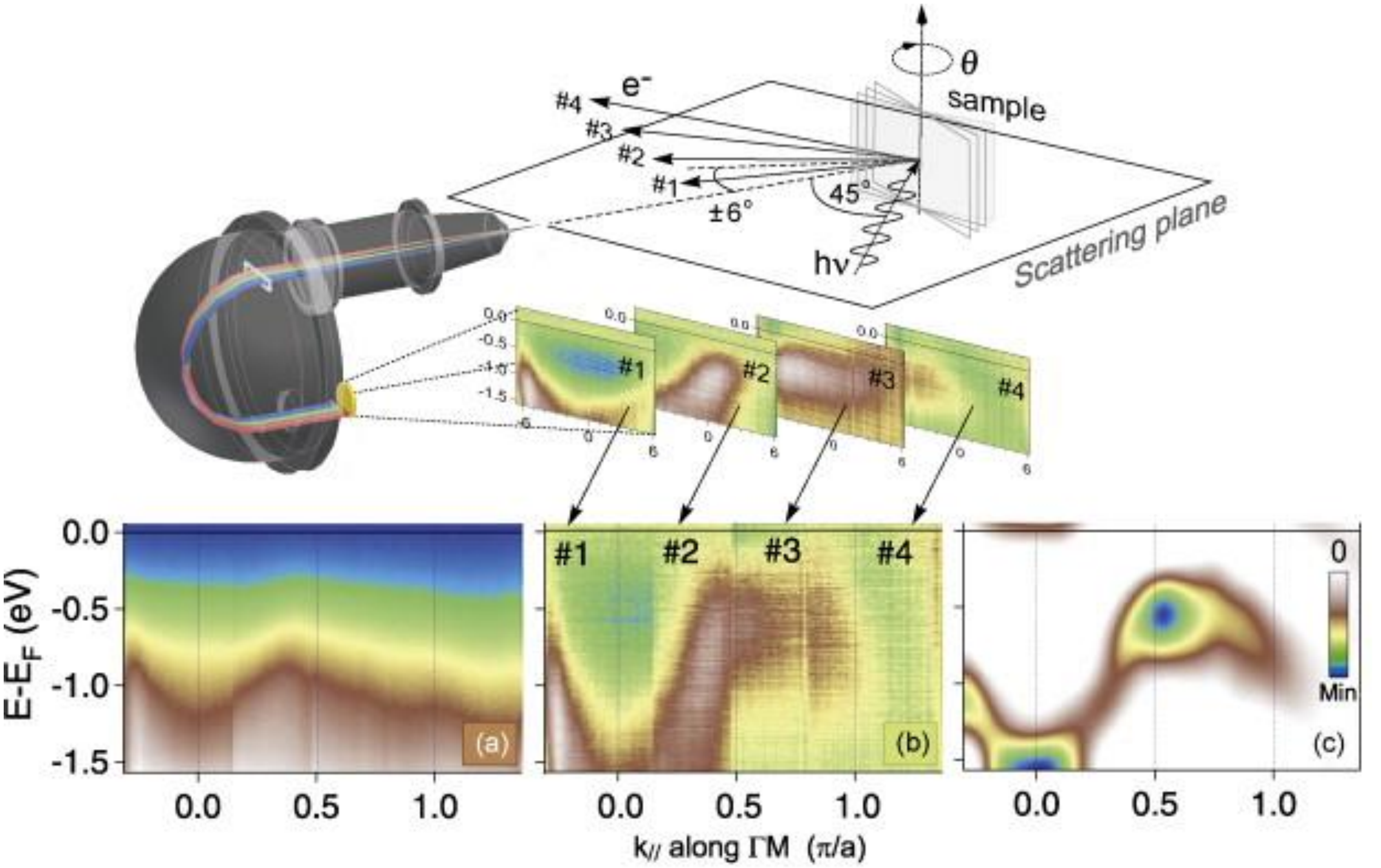


$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

- Low photon energy provides better momentum resolution, but the covering range of BZ is also small.

- We expect to study the electronic structure of solids at VUV region (10 eV~ 100 eV).



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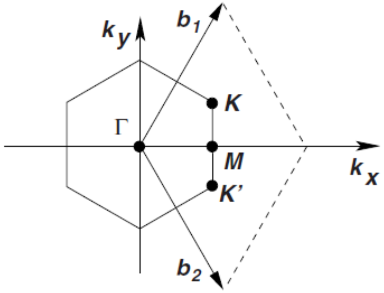
Krempasky et al., JESRP (2010)

$$k_\perp = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$



Lattice constant :
Graphene : 2.46 Å
Cu(111) : 2.08 Å
MoS_2 : 3.12 Å

- ✓ Assume the work function is 4.3 eV , please estimate the largest covering range of BZ at the Fermi level at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy.
  Answer: 0.67 $Å^{-1}$, 2.11 $Å^{-1}$,3.46 $Å^{-1}$, 5.01 $Å^{-1}$, 11.4 $Å^{-1}$

- ✓ The angle between the incident beam and spectrometer is 50 degree, please estimate the covering range of BZ at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy.
  Answer: 0.51 $Å^{-1}$, 1.61 $Å^{-1}$, 2.65 $Å^{-1}$, 3.83 $Å^{-1}$, 8.45 $Å^{-1}$

- ✓ The BZ in single layer graphene, the magnitude of ΓK is 1.703 $Å^{-1}$. If you plan to probe the band structure of graphene near the K-point, what are the required angle between the surface normal and spectrometer at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy?
  Answer: mission impossible, 54 degree, 29.5 degree, 19.9 degree, 8.6 degree

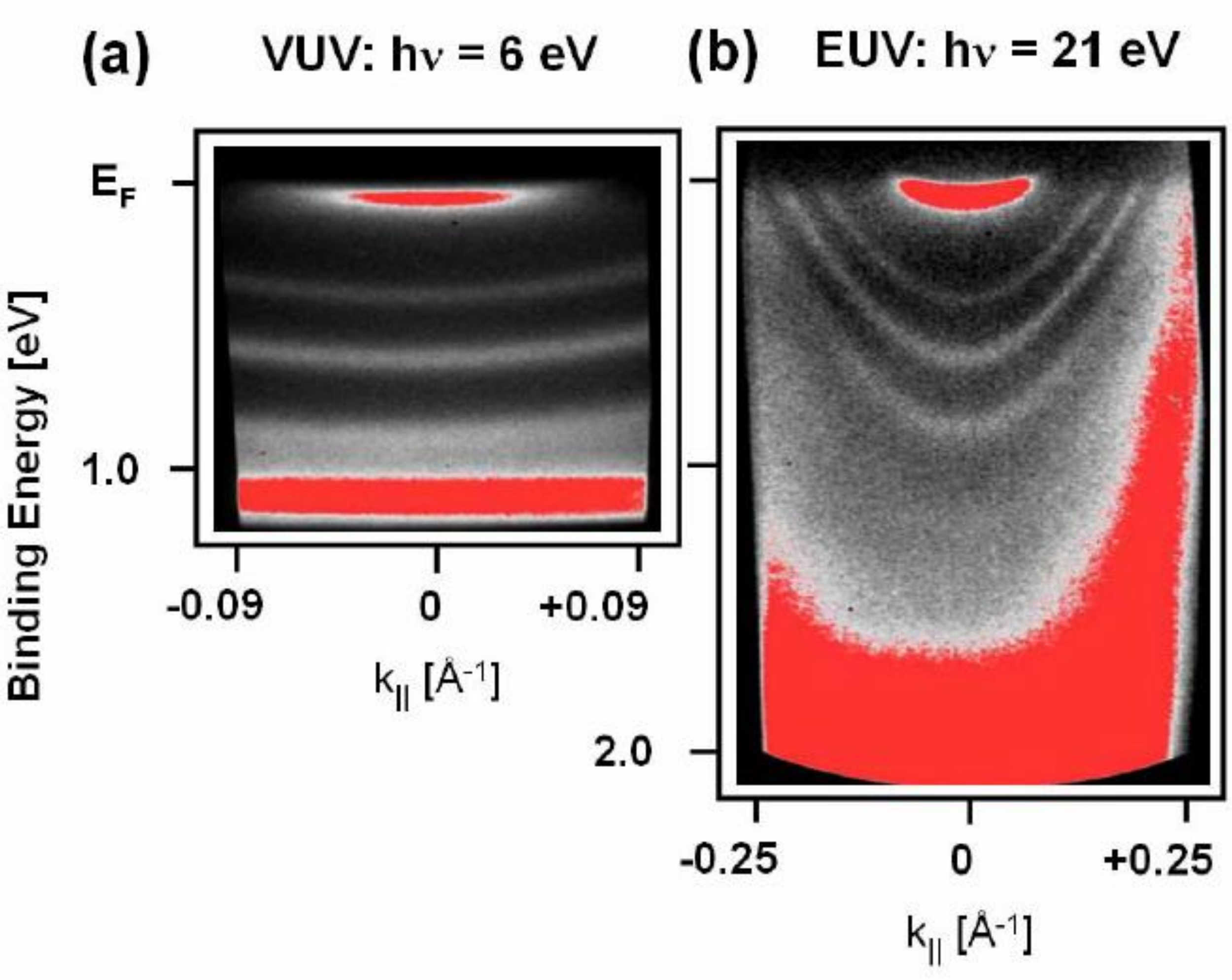
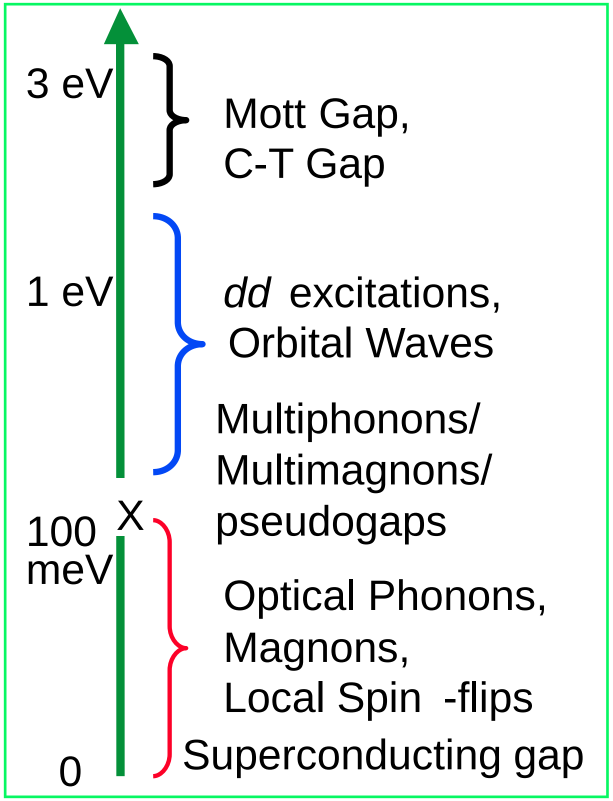


Figure 3. Angle-resolved photoemission spectra of the Shockley surface state and a series of quantum well states of 40 ML Ag/Cu(111) recorded at photon energies of 6 eV (fourth harmonic of the Ti:sapphire oscillator, 4(a)) and 21.22 eV (He I line of a discharge VUV lamp, 4(b)), respectively.

S Mathias et al., J. Physics : Conference series (2009)

- You need to understand the crystal structure of solids.
- The sample characterization, such as the orientation and crystalline, is quite important before the experiment.
- XRD, Laue diffraction and LEED are required.

Energy scale and important excitations



3 eV

Mott Gap,
C-T Gap

1 eV

dd excitations,
Orbital Waves

Multiphonons/
Multimagnons/
pseudogaps

X

100 meV

Optical Phonons,
Magnons,
Local Spin -flips

0

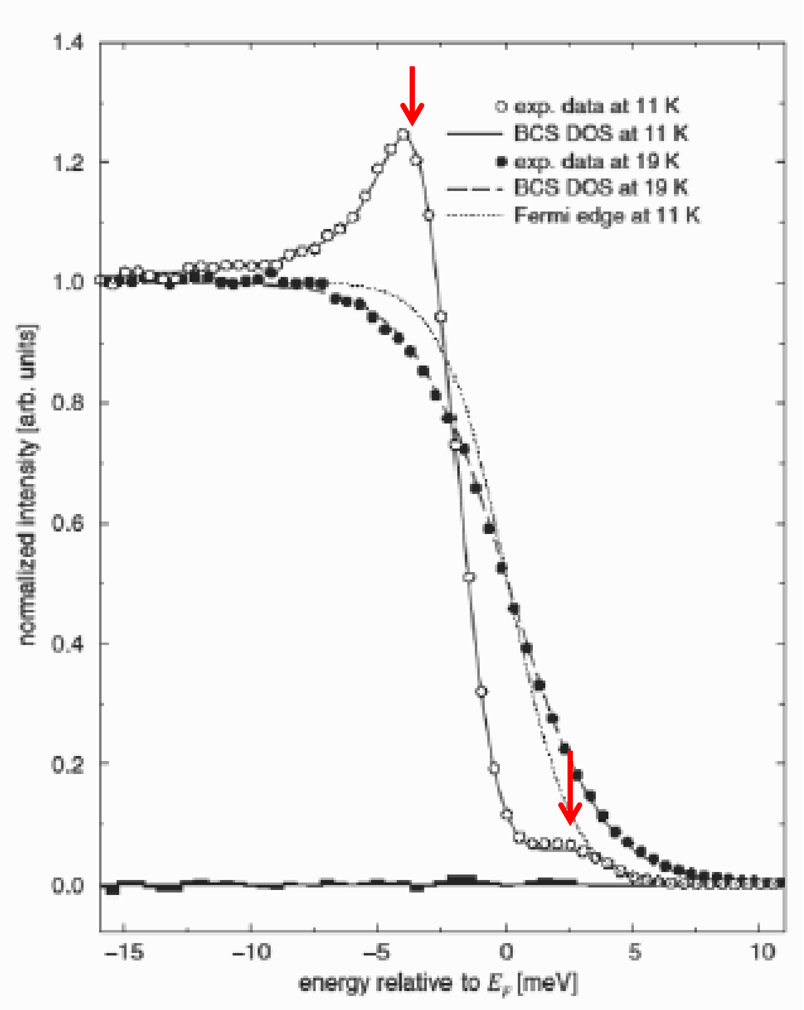
Superconducting gap

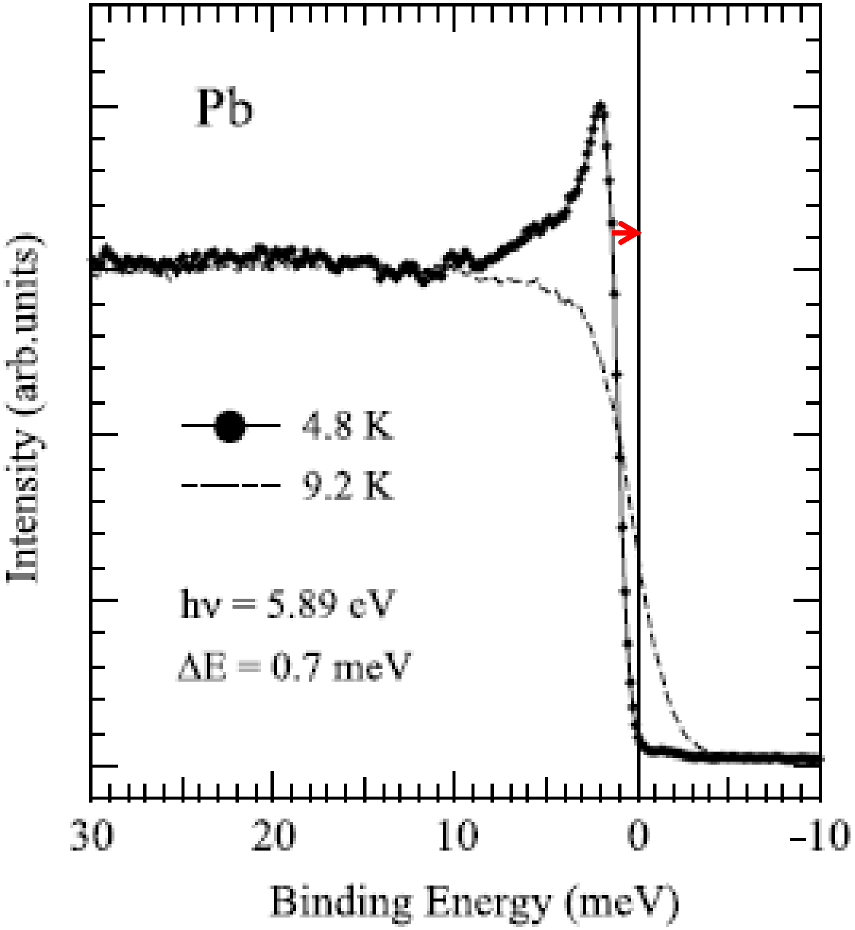
- ➢Superconducting gap ~ 1 – 100meV
- ➢Optical Phonons: ~ 40 - 200 meV
- ➢ Magnons: ~ 10 meV - 40 meV
- ➢ Pseudogap ~ 30-300 meV
- ➢Multiphonons and multimagnons ~ 50-500 meV
- ➢ Orbital fluctuations (originated from optically forbidden *d-d* excitations): ~ 100 meV - 1.5 eV

Requirement: High Energy Resolution with High Intensity

Z. Hussain, ALS summer school

Superconducting gap





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Hufner, Very high resolution photoelectron spectroscopy

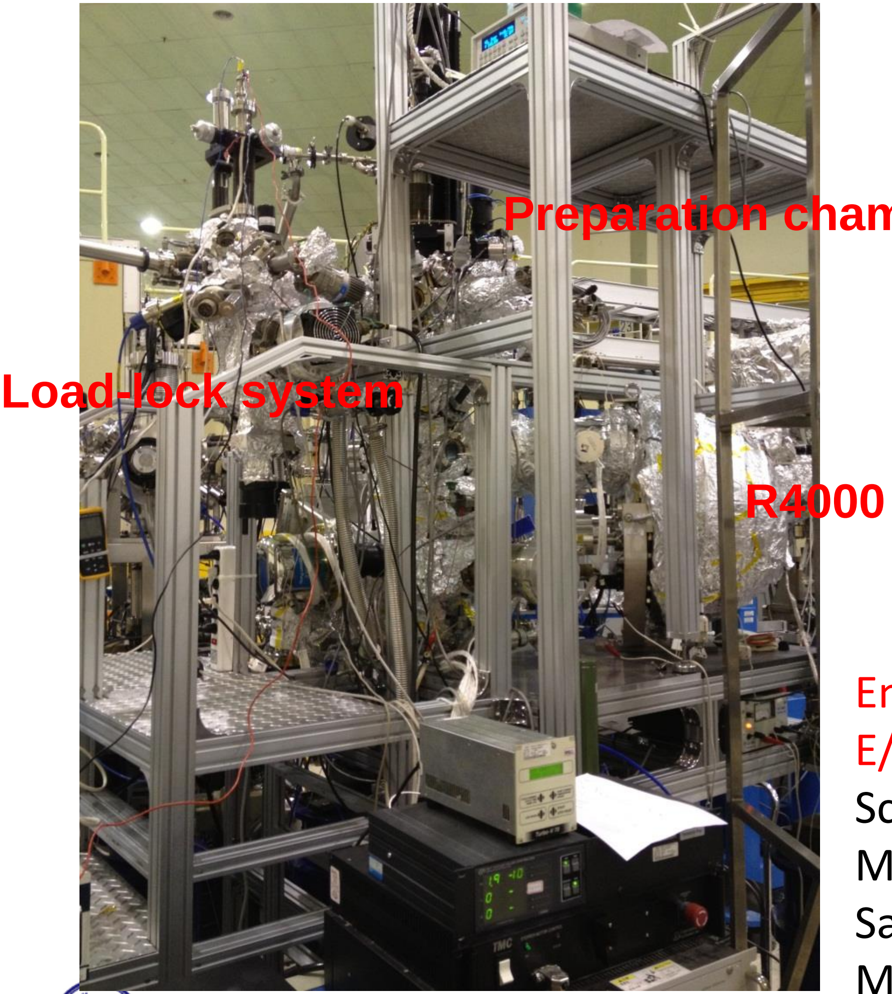
Light sources and terminology

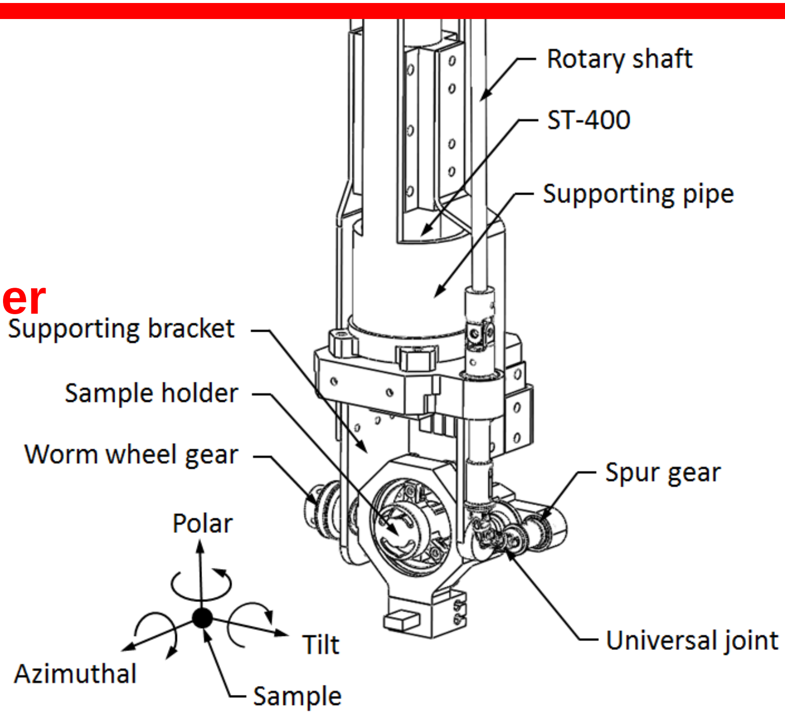
- **Ultraviolet Photoemission Spectroscopy (UPS)**
  - UV He lamp (21.2 eV, 40.8 eV)
  - Laser : 6 eV (BBO), 8 eV (KBBF), 11 eV (gas cell) or HHG (High harmonic generation)
  - Valence band PES, direct electronic state info.

- X-ray Photoemission Spectroscopy (XPS)
  (Electron Spectroscopy for Chemical Analysis) (ESCA)
  - X-ray gun (Al: 1486.6 eV, Mg: 1253.6 eV)
  - core level PE, indirect electronic state info
  - chemical analysis

- **Synchrotron radiation**
  - continuous tunable wavelength
  - valance band and core level

Current status of ARPES end station at TLS





Energy range : 5 eV~120 eV

E/ΔE: 100,000 at 16 eV and 64 eV

Scienta R4000 analyzer

Manipulator : 6-axis motorized manipulator

Sample Preparation: *in-situ* cleave, thin film growth

Measurement temperature range : 10 K~ 350 K

Base pressure : 4.5x10^{-11} torr

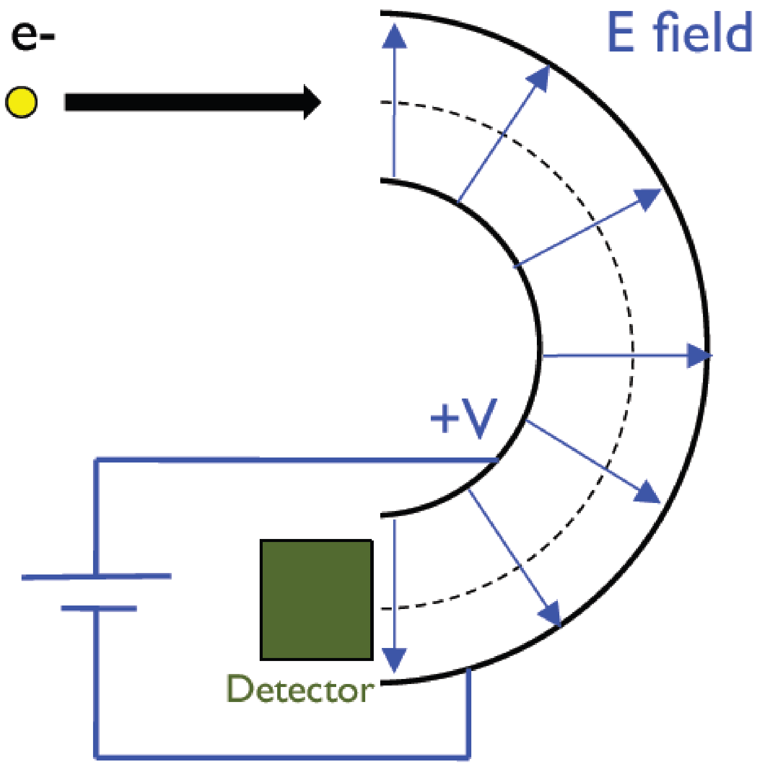
Basic principles of electron spectrometers / analyzers

- typical energy resolution ~ 0.1 to 0.01 eV. Best systems are ~ 0.001 eV.

- most electron analyzers operate using electrostatic optics (magnetic fields harder to control)

- detectors are typically channel plates (electron multipliers) with a CCD or current pulse output

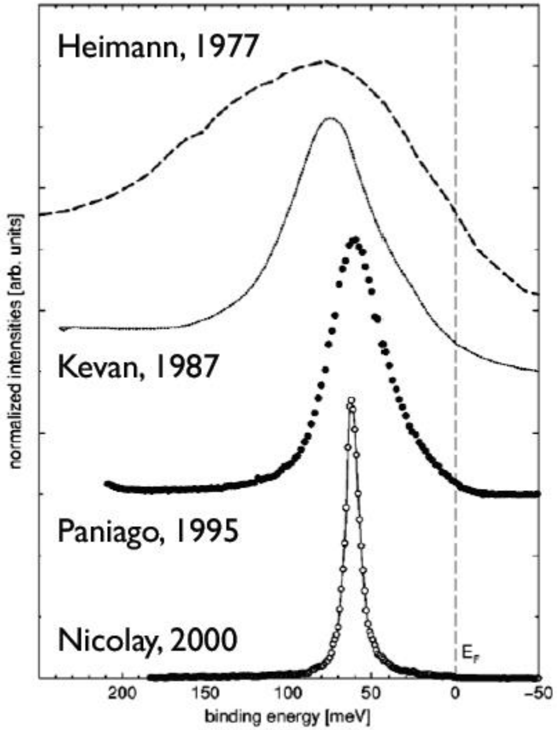
- detecting & manipulating electrons is relatively easy



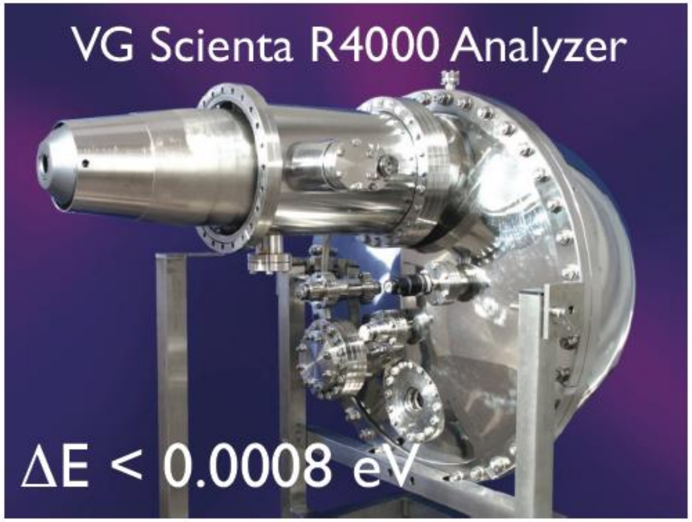
Kyle Shen, IGERT Lecture 2008

The state-of-the-art in electron spectroscopy

Evolution of instrumental resolution over time

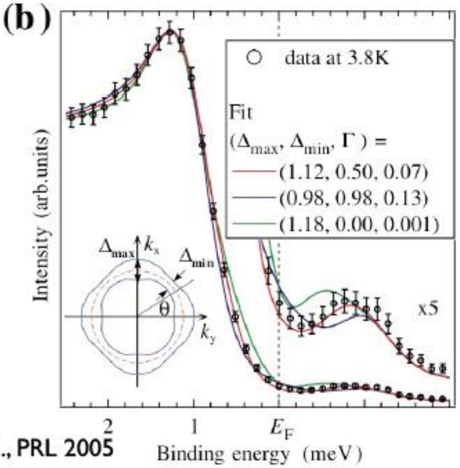


F. Reinert *et al.*, PRB (2001)



VG Scienta R4000 Analyzer

$\Delta E < 0.0008$ eV



T. Kiss et al., PRL 2005

National Synchrotron Radiation Research Center

Kyle Shen, IGERT Lecture 2008

Early ARPES experimental result

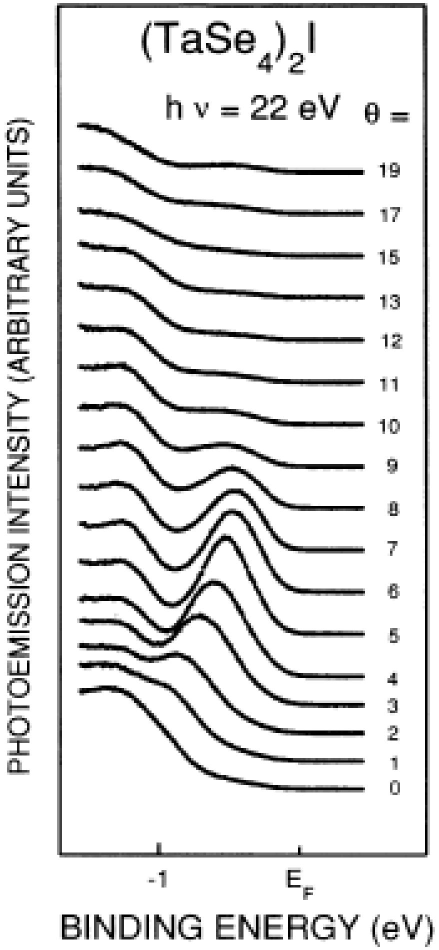


FIG. 1. A series of high-energy-resolution angle-resolved photoemission spectra, taken along the direction of the sample and for different values of the azimuthal angle.

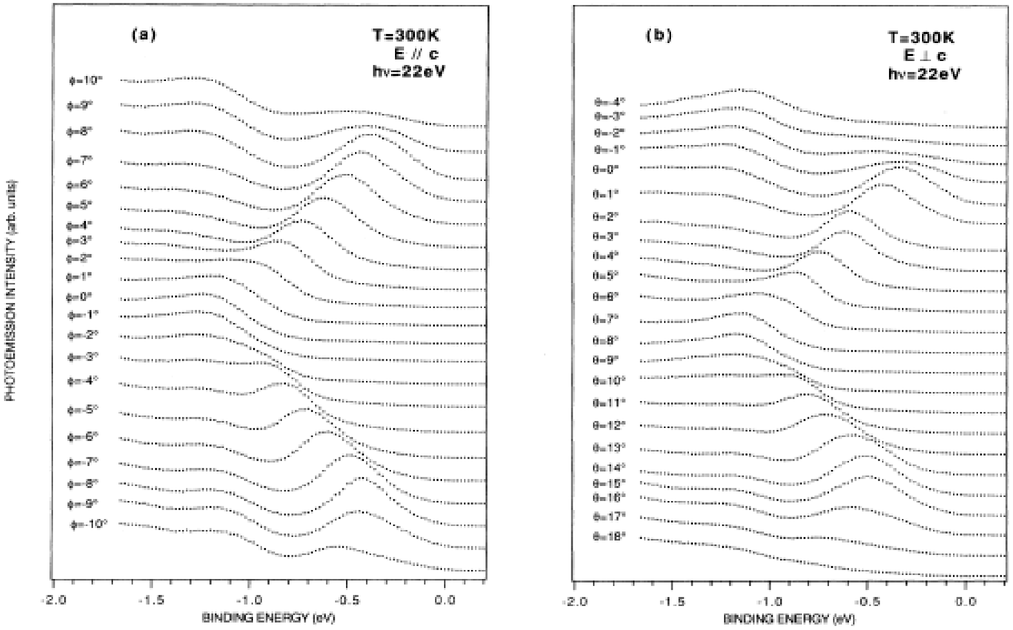
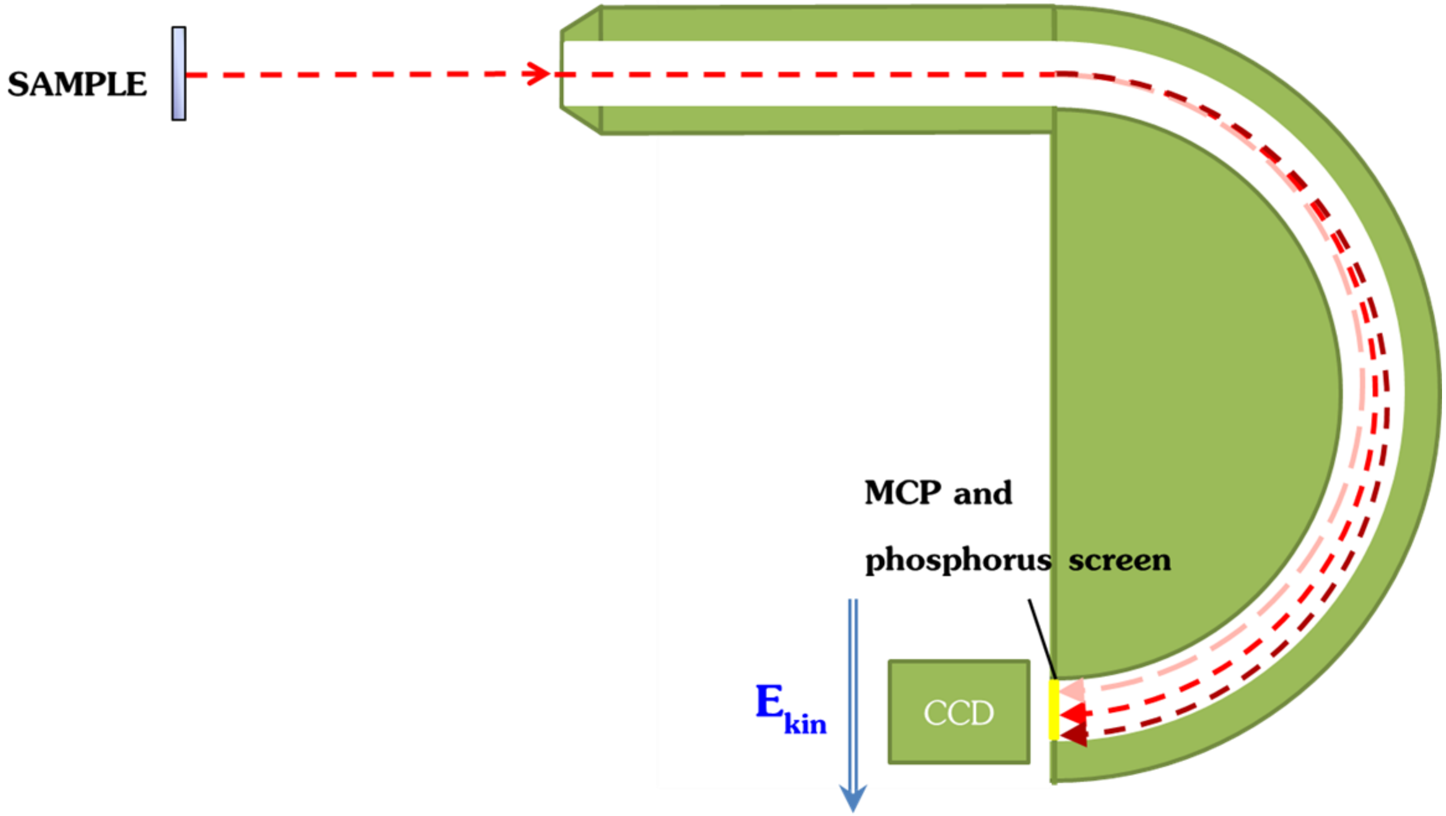
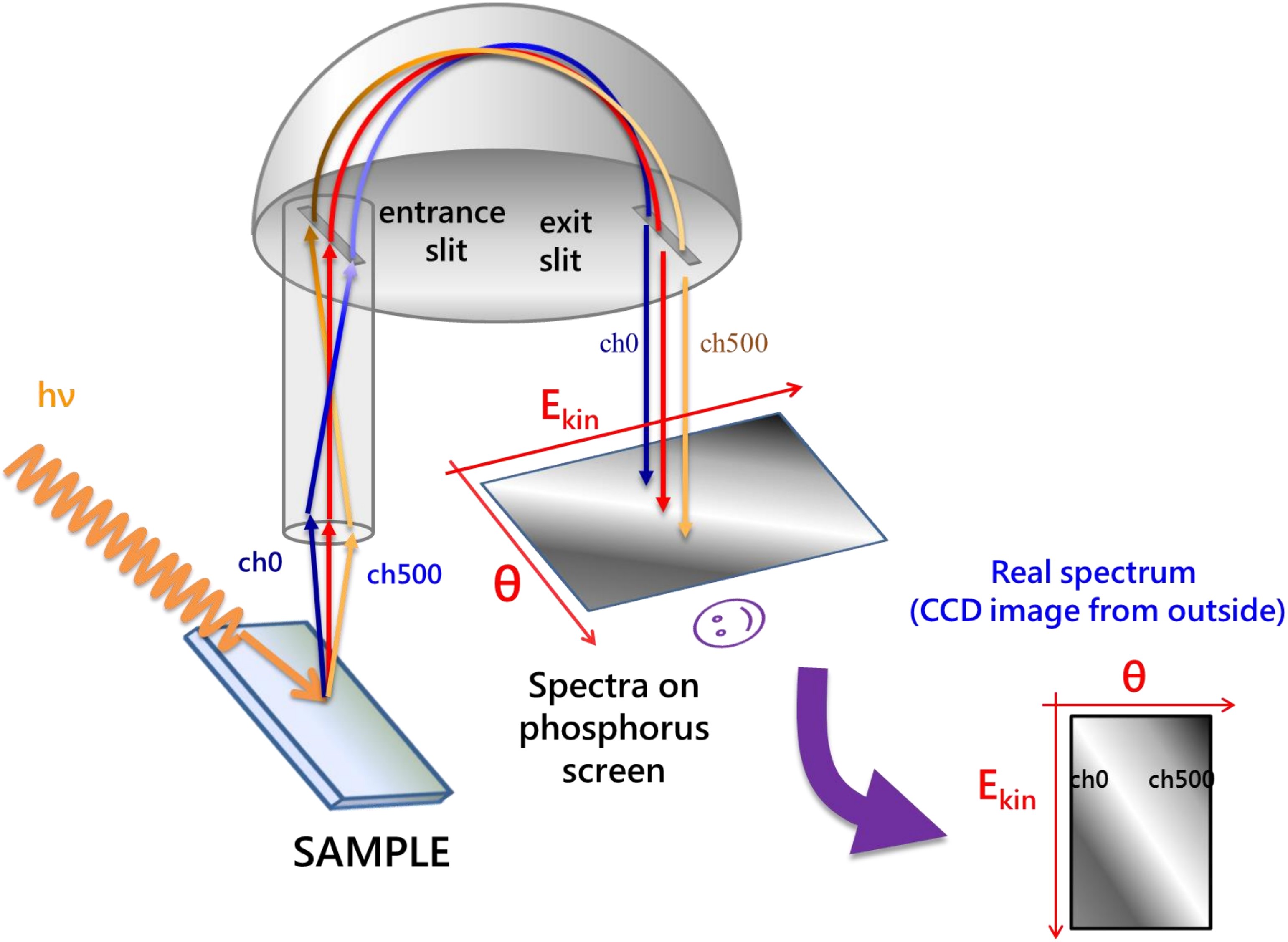


FIG. 1. Angle-resolved photoemission spectra taken using 22-eV photon energy, at room temperature, for photon electric field (a) parallel and (b) perpendicular to the conducting axis. The emission angle is along the conducting axis, with the surface normal defined as 0°.

Now a 2-D detector with ± 30° and 0.1° angular resolution can be obtained.

SCIENTA R4000 Side View



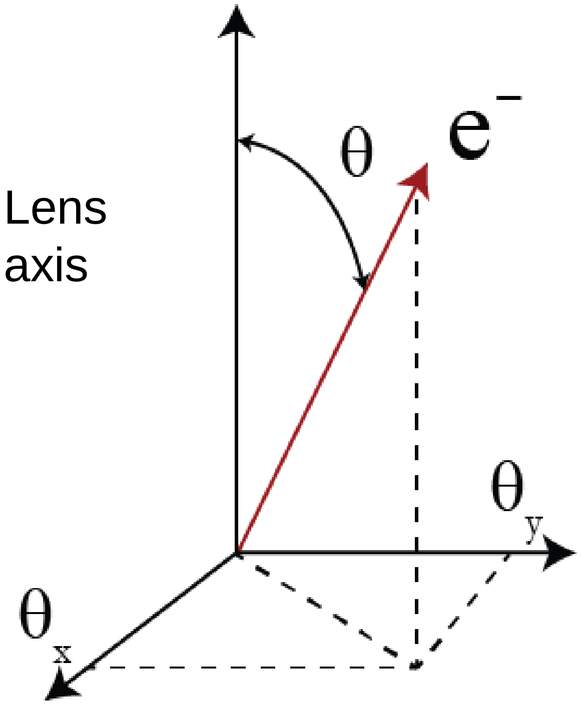


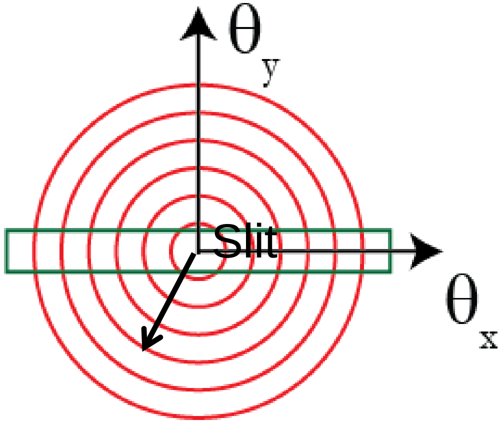
SAMPLE

Spectra on phosphorus screen

Real spectrum
(CCD image from outside)

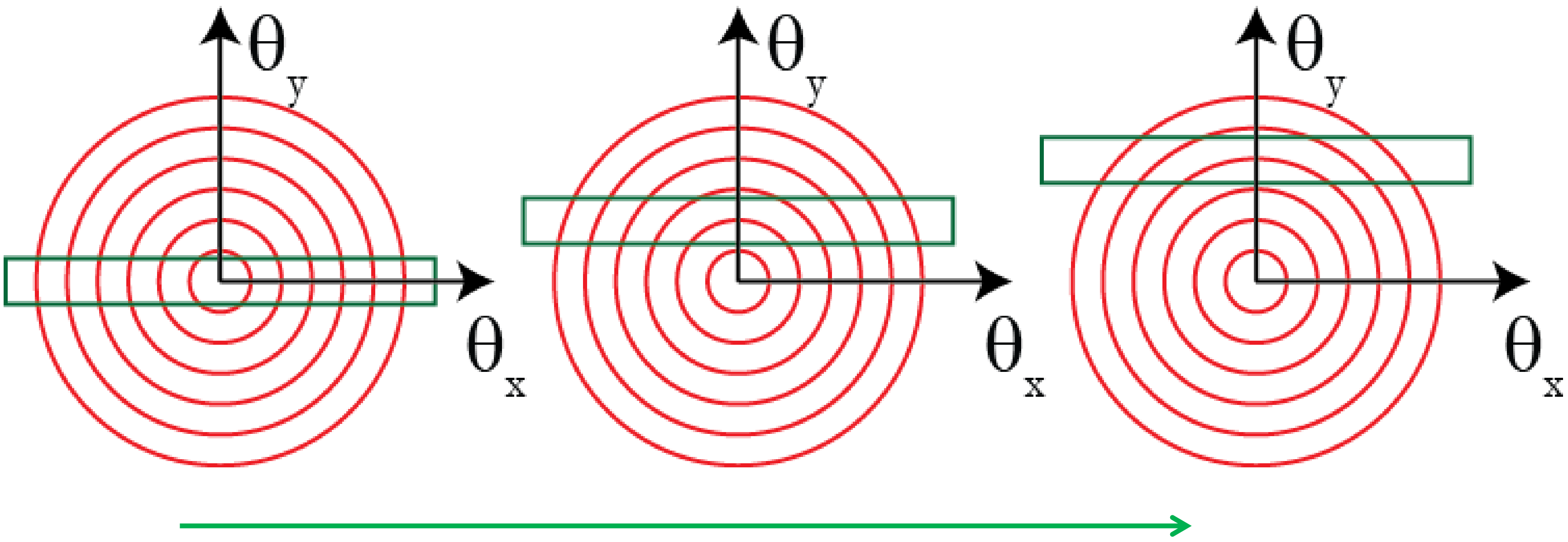
- Angle-resolved spectrometers collects electrons as a function of kinetic energy and emission angle
- Due to the slit, only angles along one axis (q_x) can be detected simultaneously





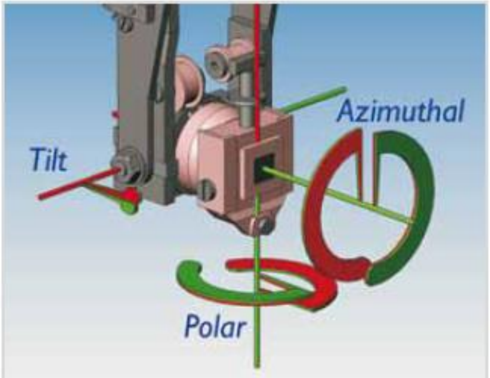
Constant energy mapping for ARPES Scan

- Deflection can also be done in θ_y
- This enables **full cone detection**, $0<\theta<15°$, **without sample rotation**



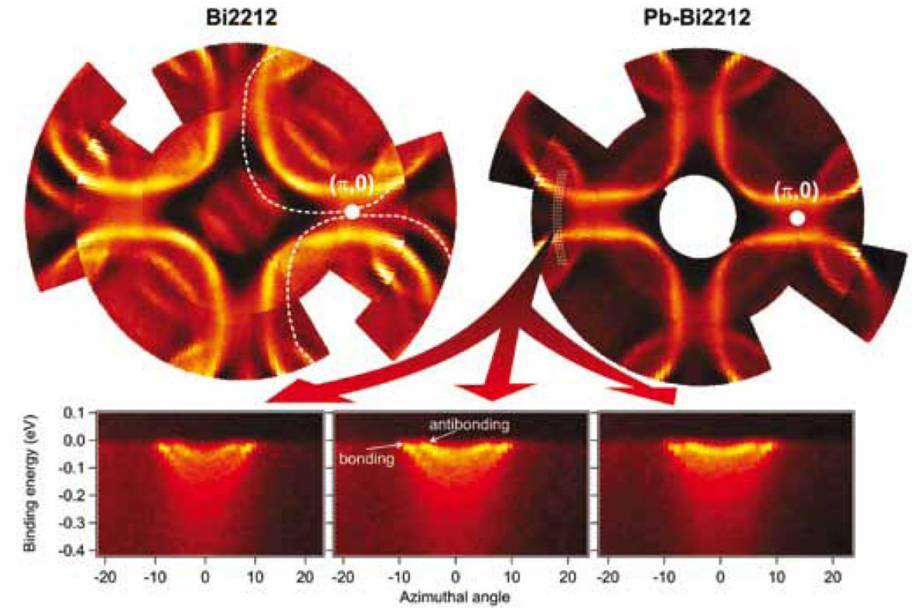
Increasing deflection in θ_y

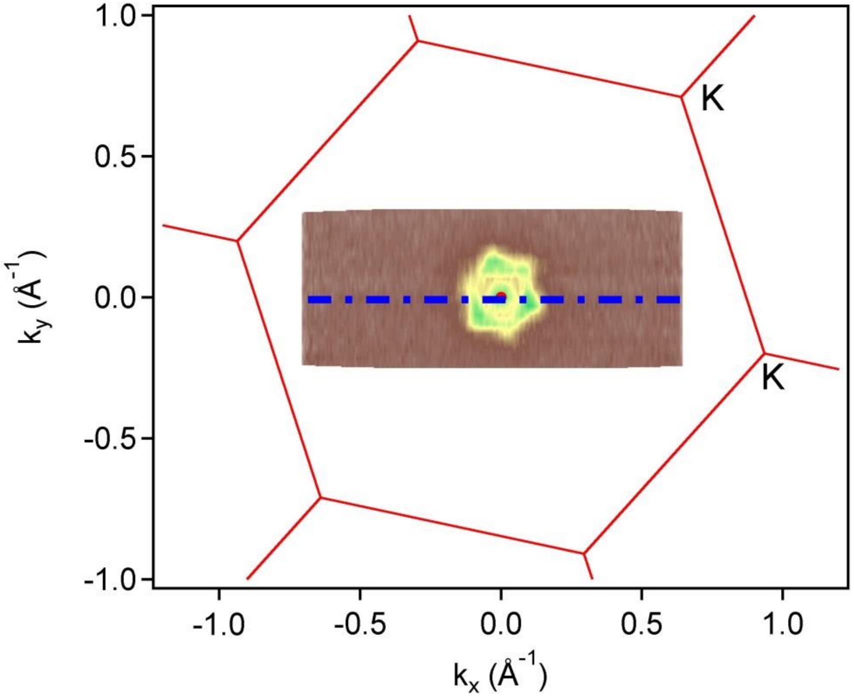
Angle is the soul of ARPES: Band mapping



Azimuthal angle scan

Tilt angle scan





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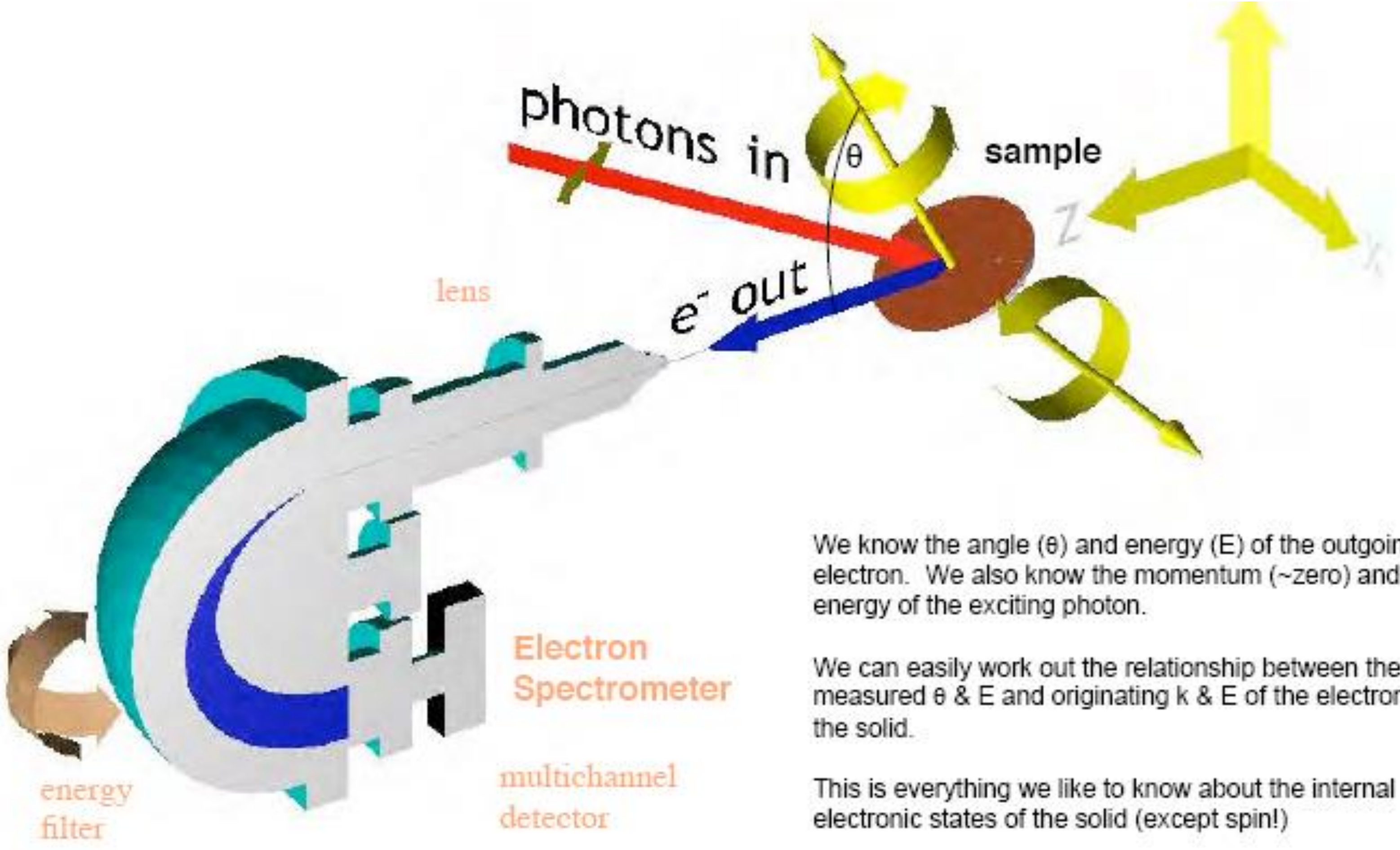
Experimental geometry



We know the angle (θ) and energy (E) of the outgoing electron. We also know the momentum (~zero) and the energy of the exciting photon.

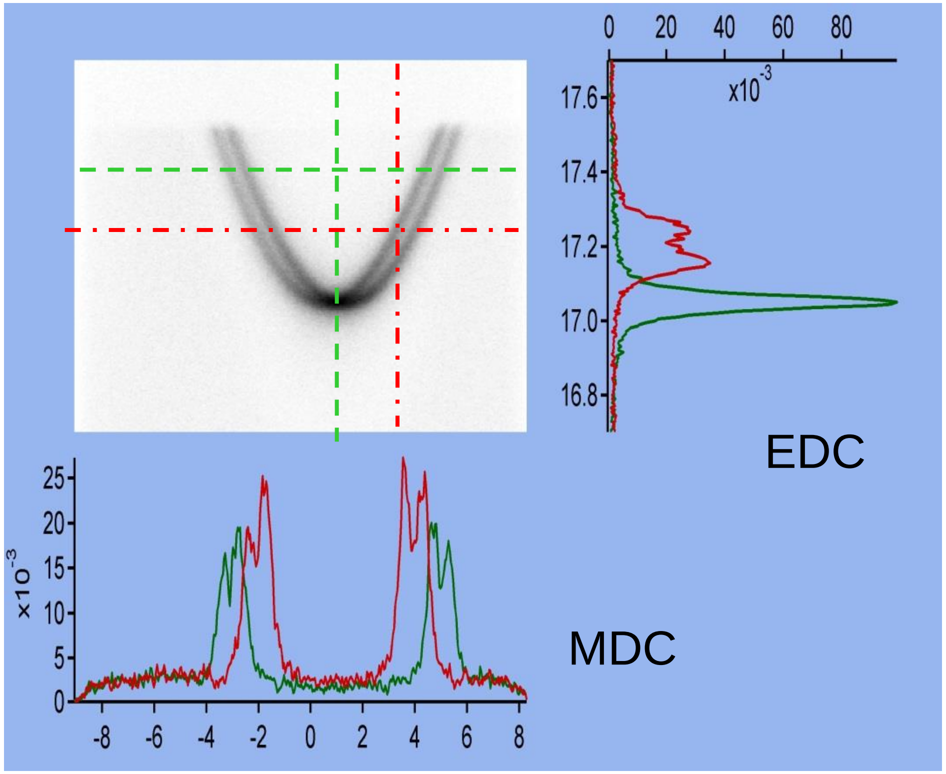
We can easily work out the relationship between the measured θ & E and originating k & E of the electrons in the solid.

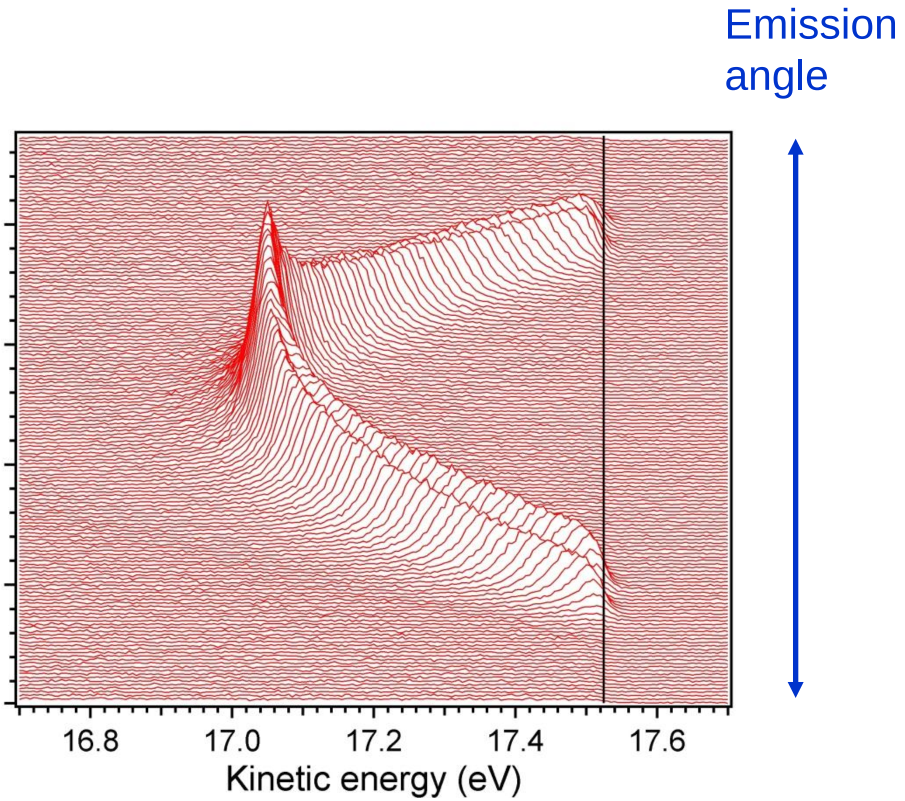
This is everything we like to know about the internal electronic states of the solid (except spin!)

Eli Rotenberg, ALS summer school

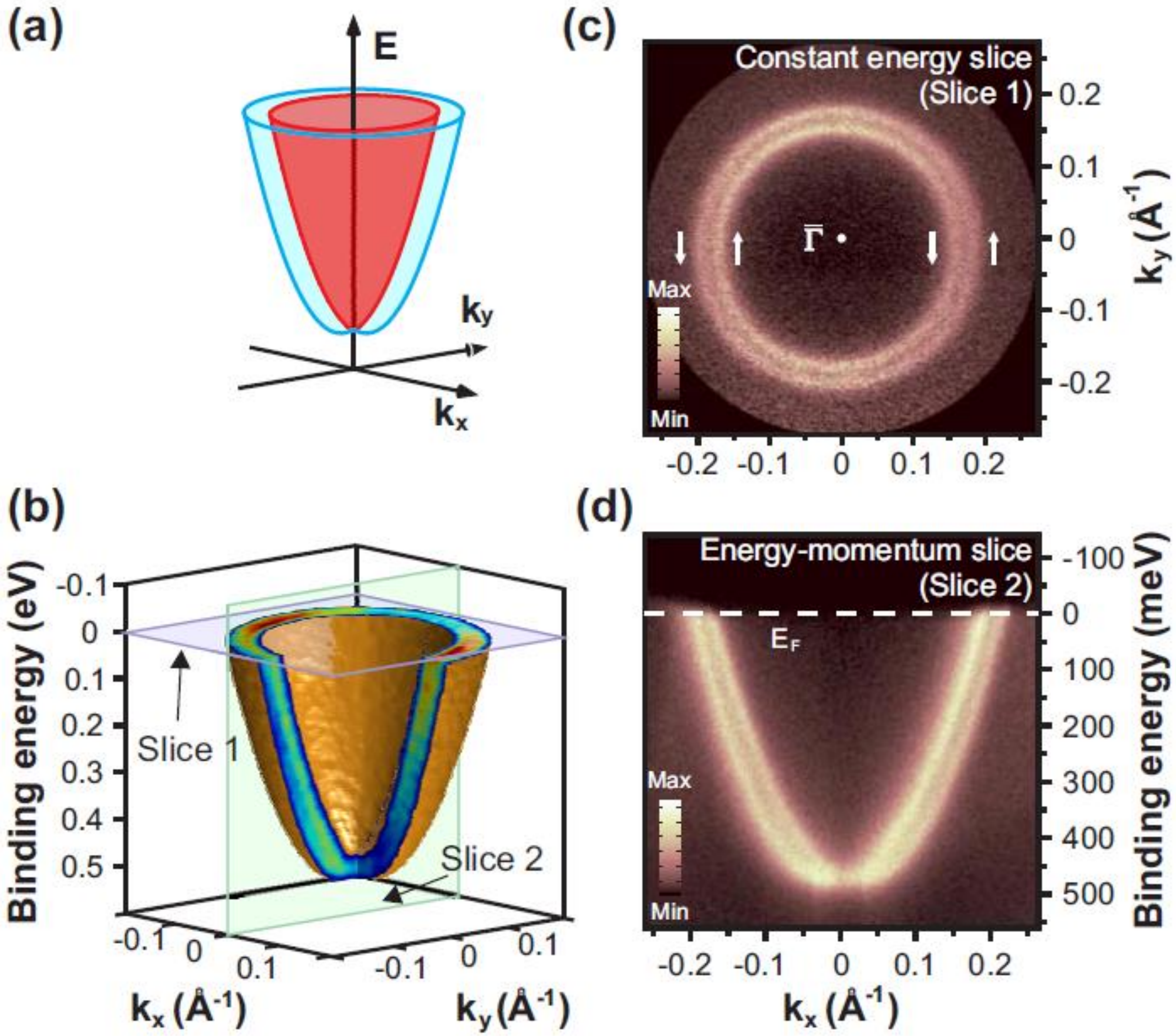
Typical Experimental Result

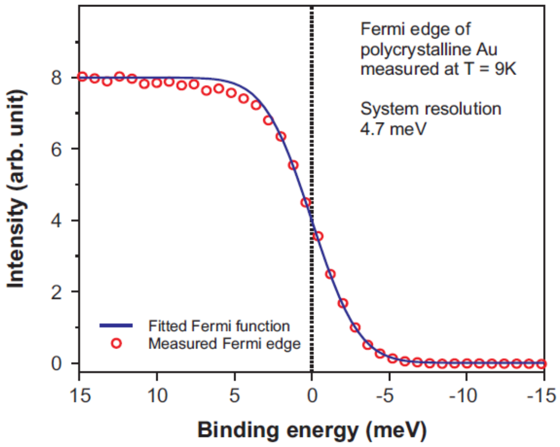
Accumulate spectra of Rashba effect on Au(111) as the angle is scanned





Surface state of Au(111)





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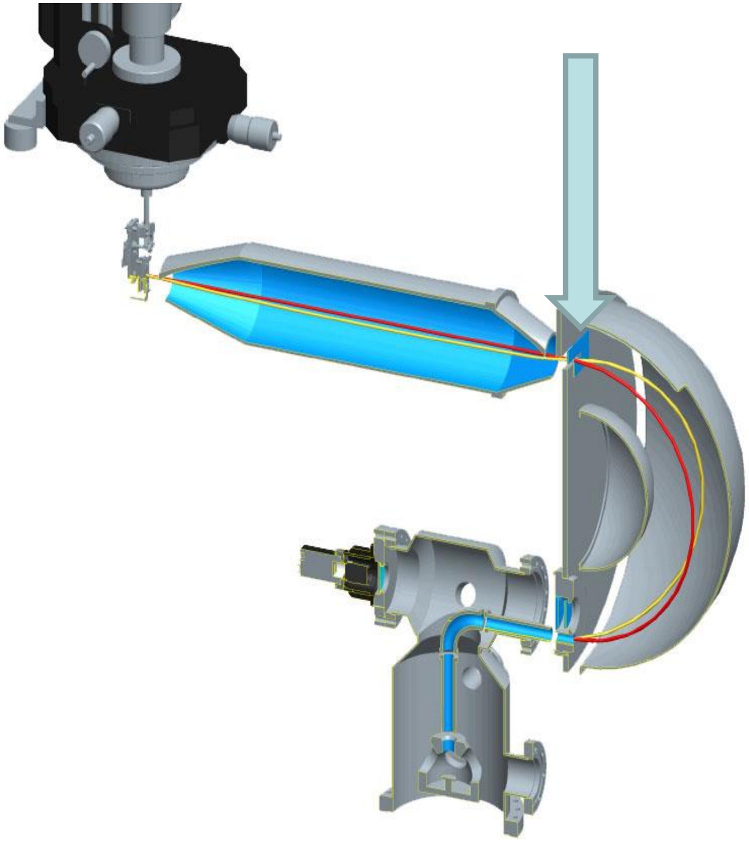
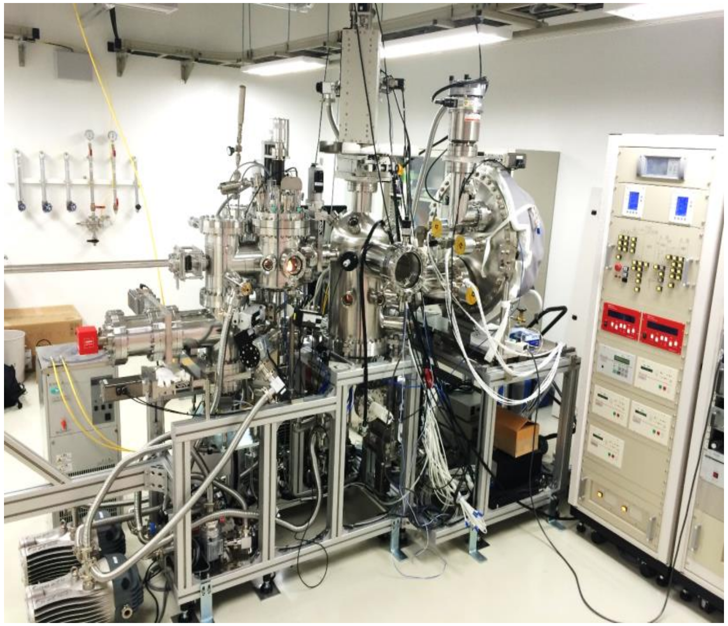
D. Malterre, CORPES05

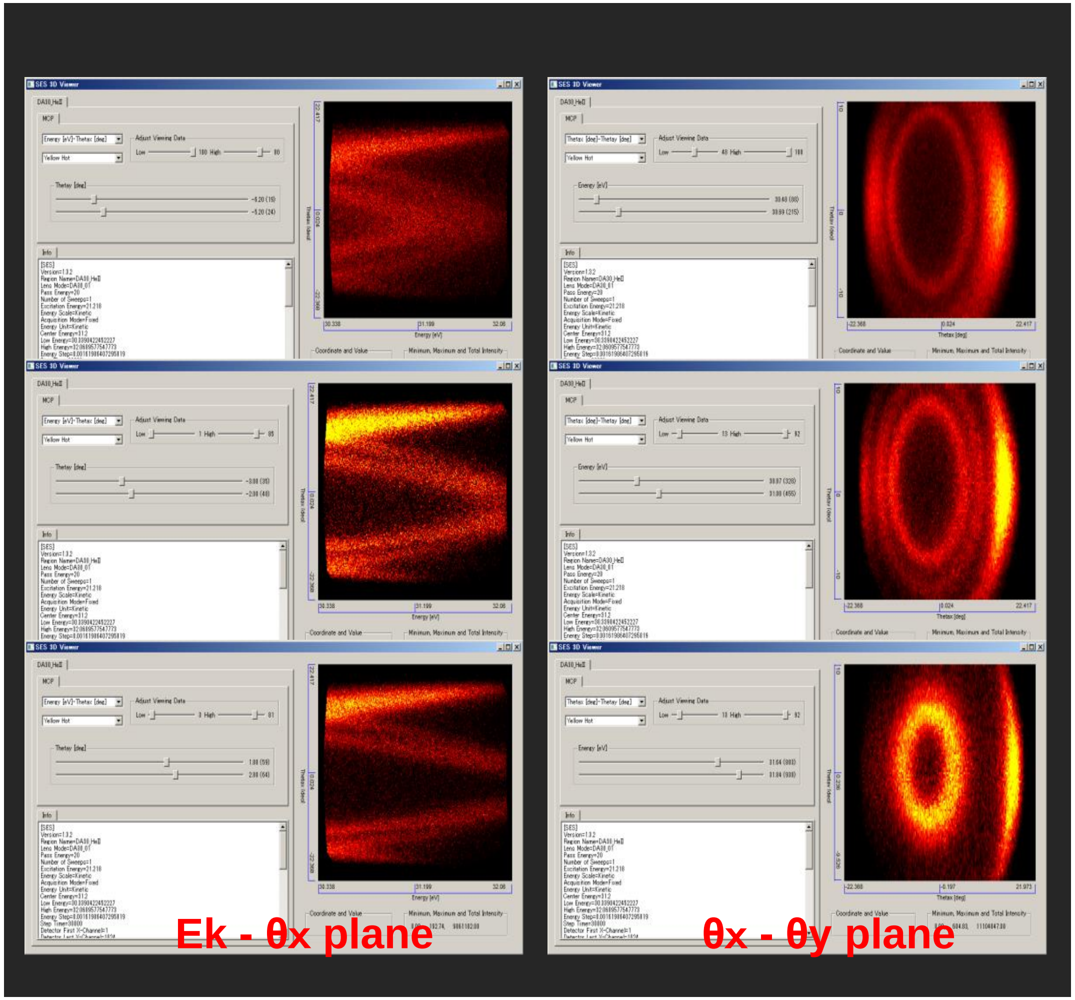
Deflector analyser

- With the deflector analyser, the electron trajectories can be deflected, to change the range of emission angles that reaches the detector
- Deflection can be done in q_x and in q_y.



Graphite





Data courtesy : Dr. Yamane, IMS

Electron Escape Depth : Surface Sensitivity

Why are electrons so useful as probes of surfaces?

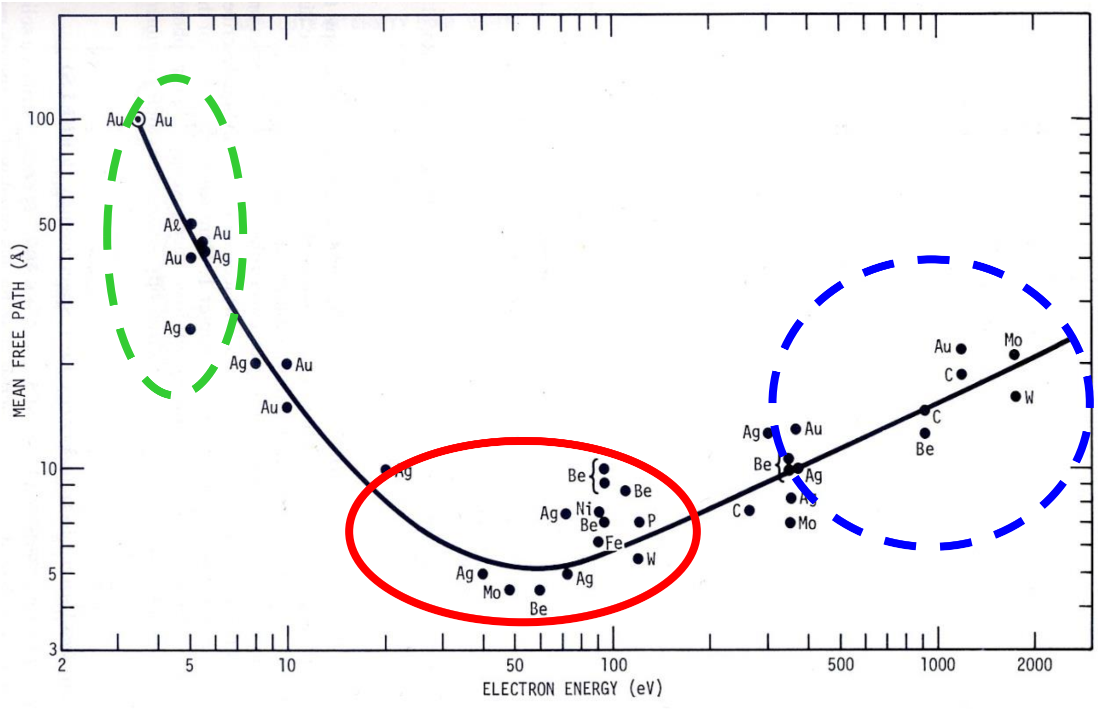
Or

Not so useful for studying bulk properties !!

Minimum due to electron-electron scattering, mainly plasmons

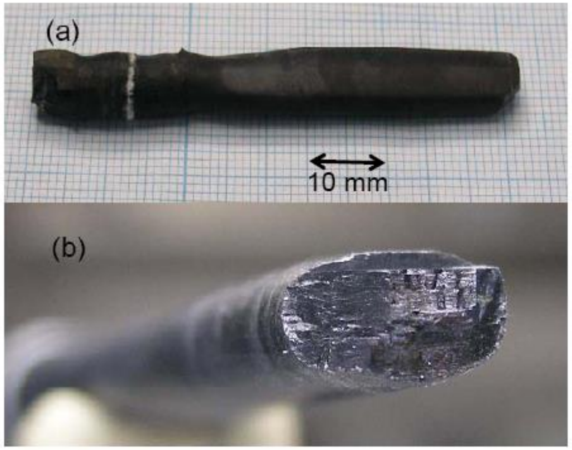
PES is a surface sensitive technique! (requires UHV)

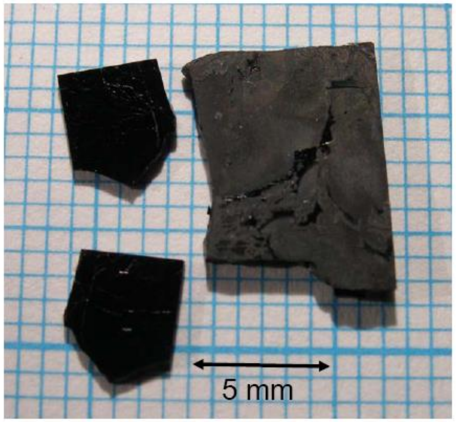
High energy photoemission: several keV to increase bulk sensitivity



The requirement of ARPES

- UHV environment : better than $1x10^{-10}$ Torr
- Single crystals or *in-situ* growth thin films
- Conductors or semiconductors
- Tunable photon energies





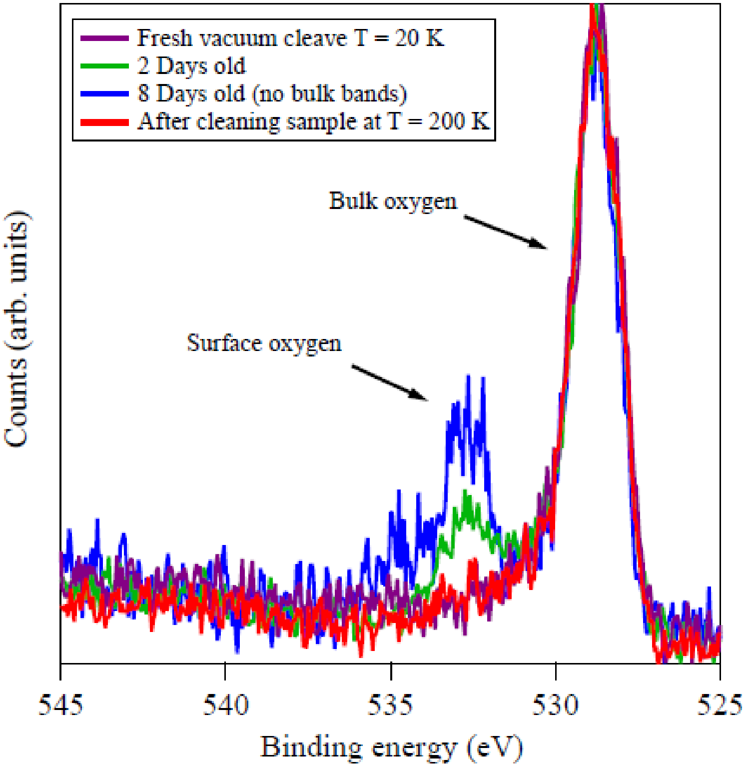
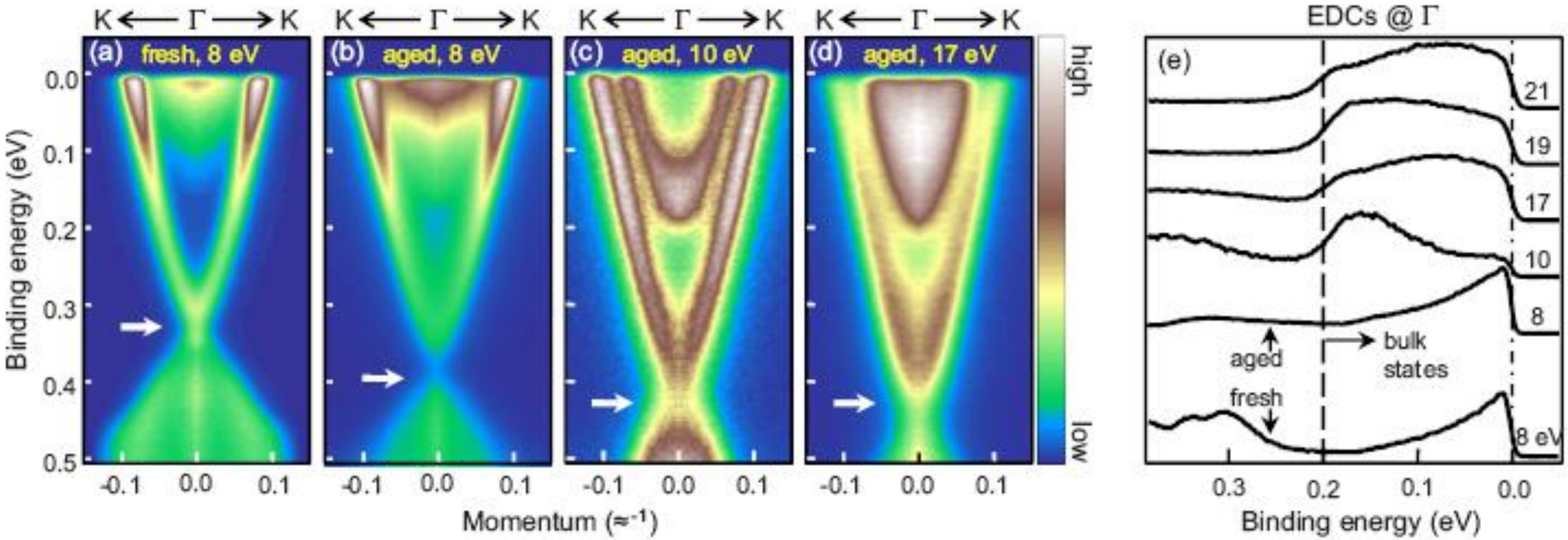


Figure 5.2: (color) The oxygen 1s peaks from Bi2212 at different times after the cleave. A constant background was subtracted from each spectrum to allow direct comparison. The peak derived from bulk oxygen is stable over time, while the surface oxygen peak grows as more oxygen sticks to the cold surface.

HC Hsu, Ph.D. Thesis NTNU(2010)
Koralek, U. Colorado Ph.D. Thesis (2007)

Single crystals or *in-situ* growth well-ordered thin films are favorable for ARPES measurement



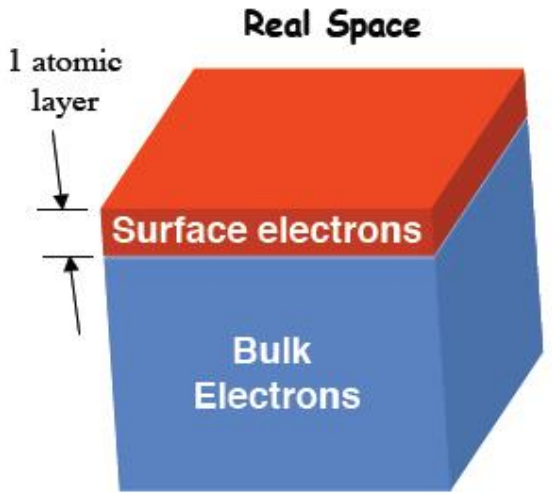
Base pressure : 1x10^{-10} Torr

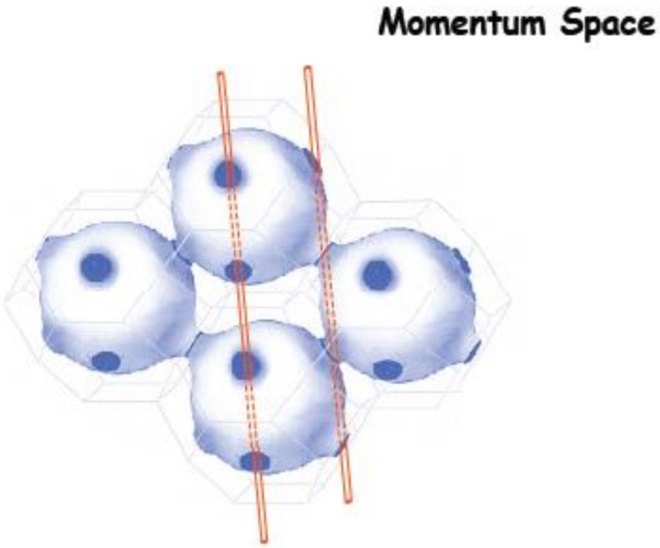
In-situ cleaved Bi_2Se_3 single crystal

Park et al., PRB (2010)

Using ARPES to study the electronic structure of 2D materials

Surface state





Surface states are highly localized in real space, therefore completely delocalized in k-space along *kz*.

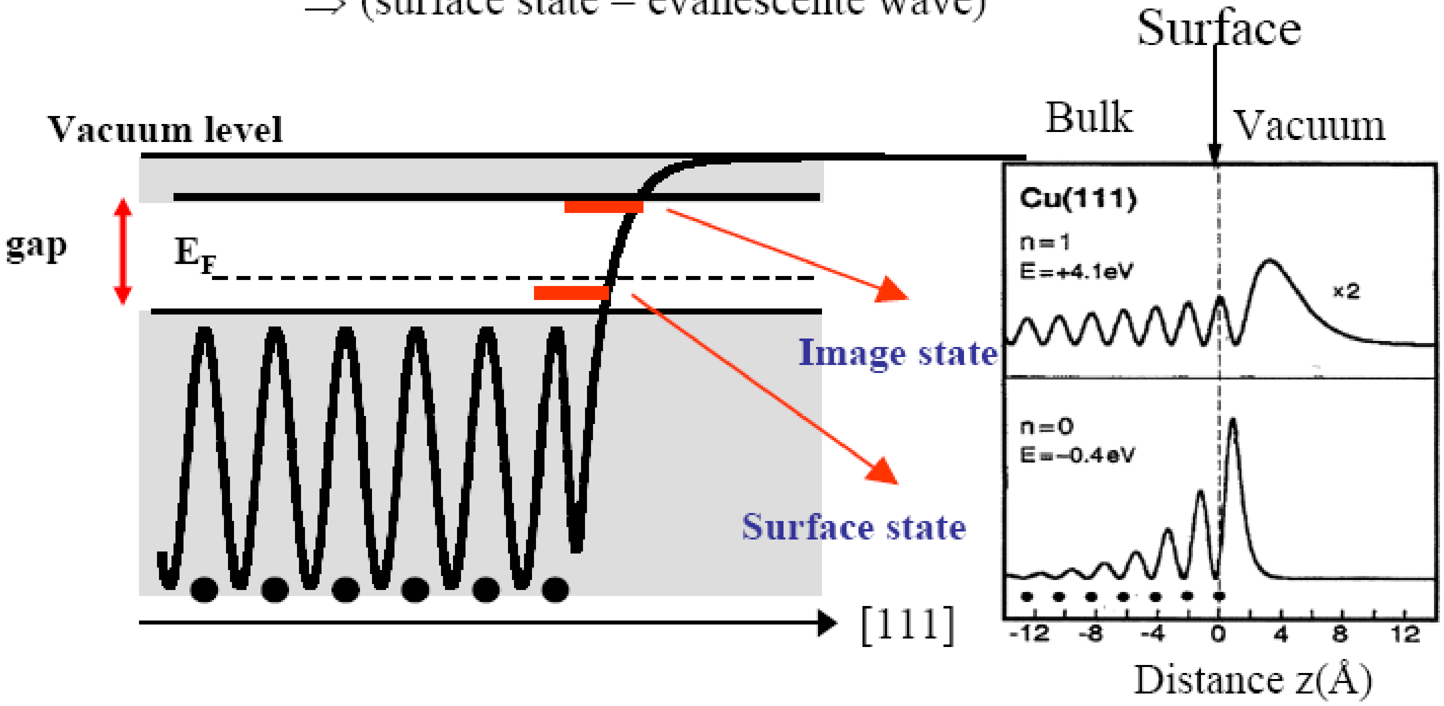
– NO DISPERSION OF SURFACE STATES in kz direction

Eli Rotenberg, ALS summer school

- Surface = Breakdown of the translational symmetry

⇒Peculiar solution in the gap with a complexe wave vector $k_{[111]}$

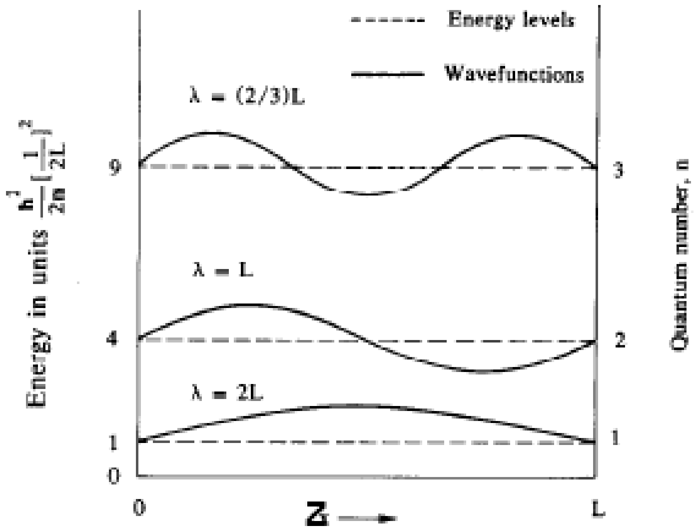
⇒ (surface state = evanescente wave)



→localisation of the electronic density at the surface

Surf. State is very sensitive to any structural modification

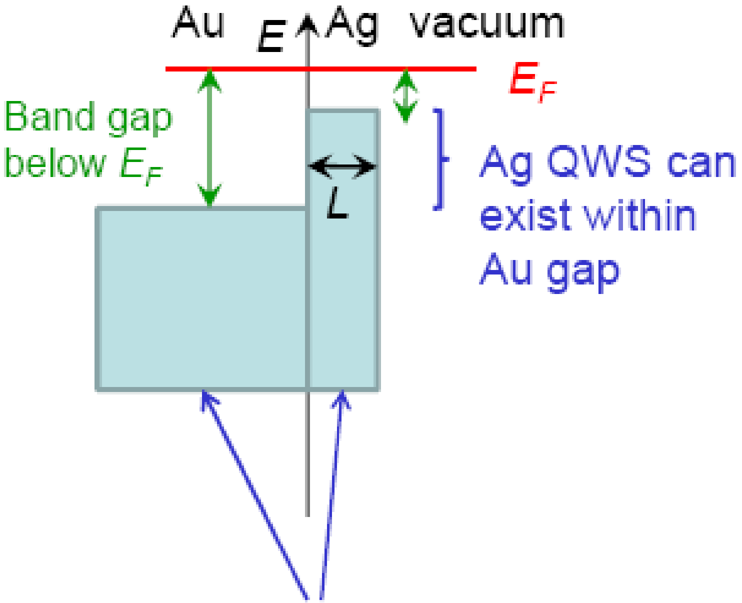
Quantum well states



Quantized discretely along z-direction
Energy levels depend on film thickness *L*

Nearly free electron like in xy-plane

Ag(111) thin films expitaxially grown on Au(111) substrate



Au *E* Ag vacuum

E_F

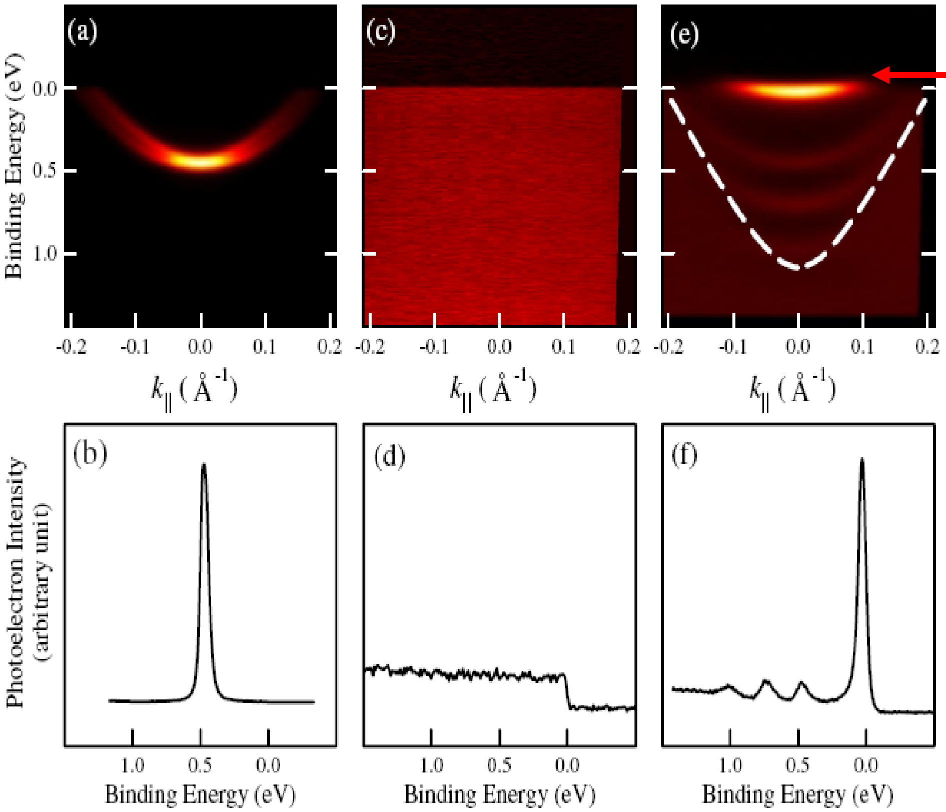
Band gap below E_F

L

Ag QWS can exist within Au gap

Bulk projected bands along ΓL of Au and Ag, respectively

Absolute coverage of thin films : Ag/Au(111) system



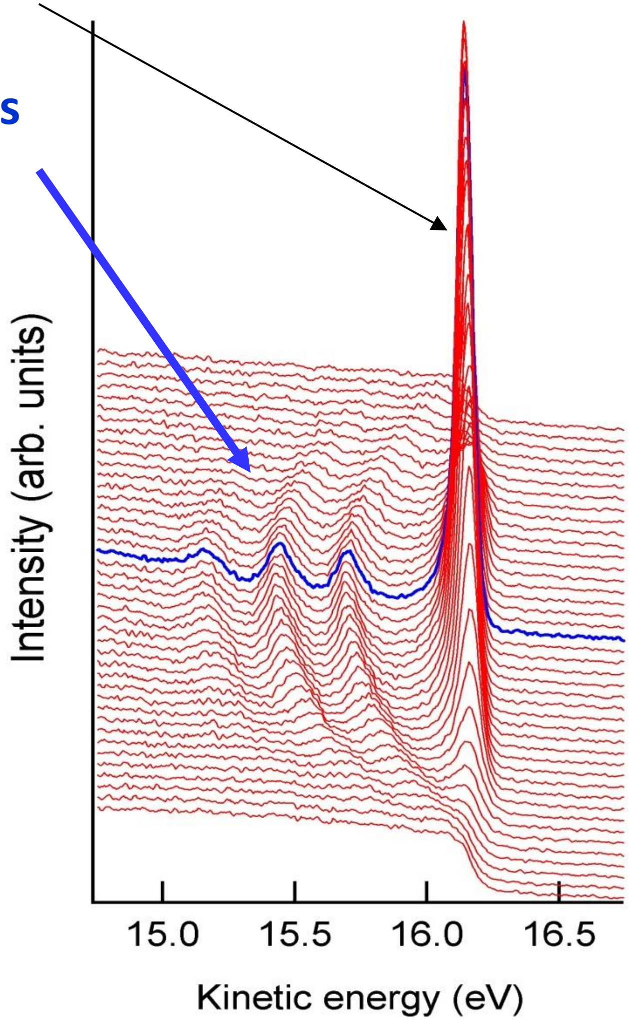
Clean Au(111)

LT deposited Ag/Au(111)

Anneal to near RT

Ag S.S

Ag QWs



$k_{||}$ = 0 normal emission EDCs

D. A. Luh et. al., PRL (2008)

Dynamically monitor the thin film growth mechanism

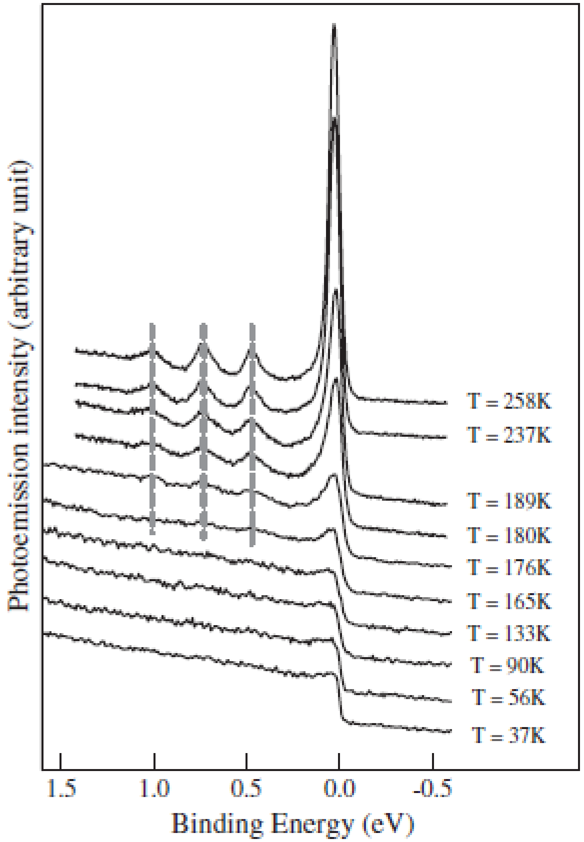
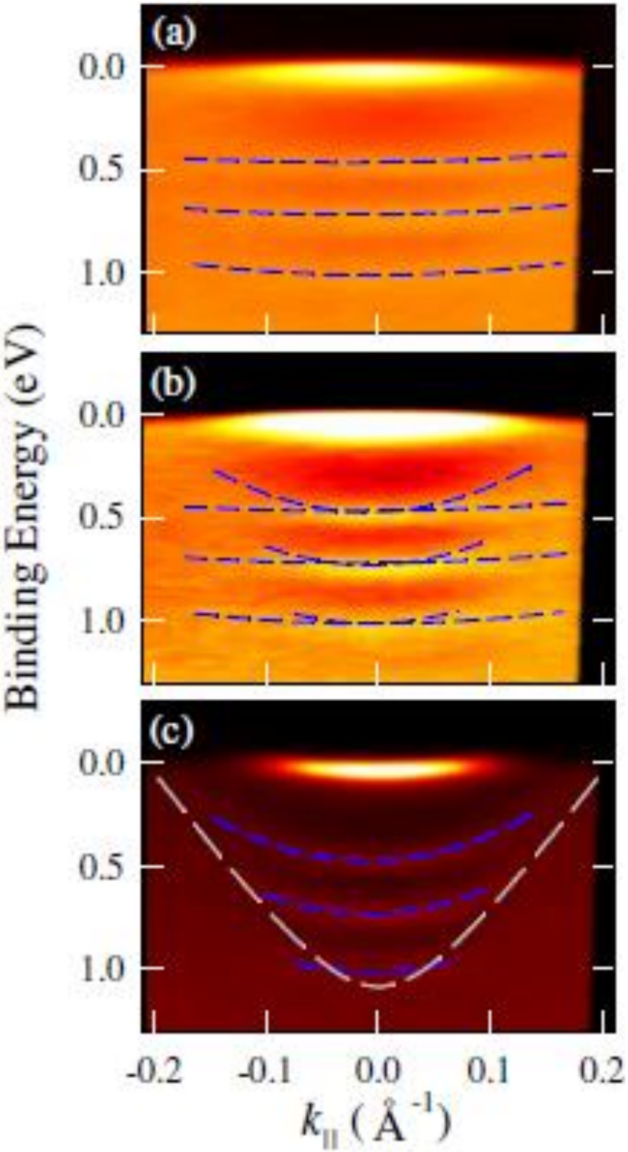
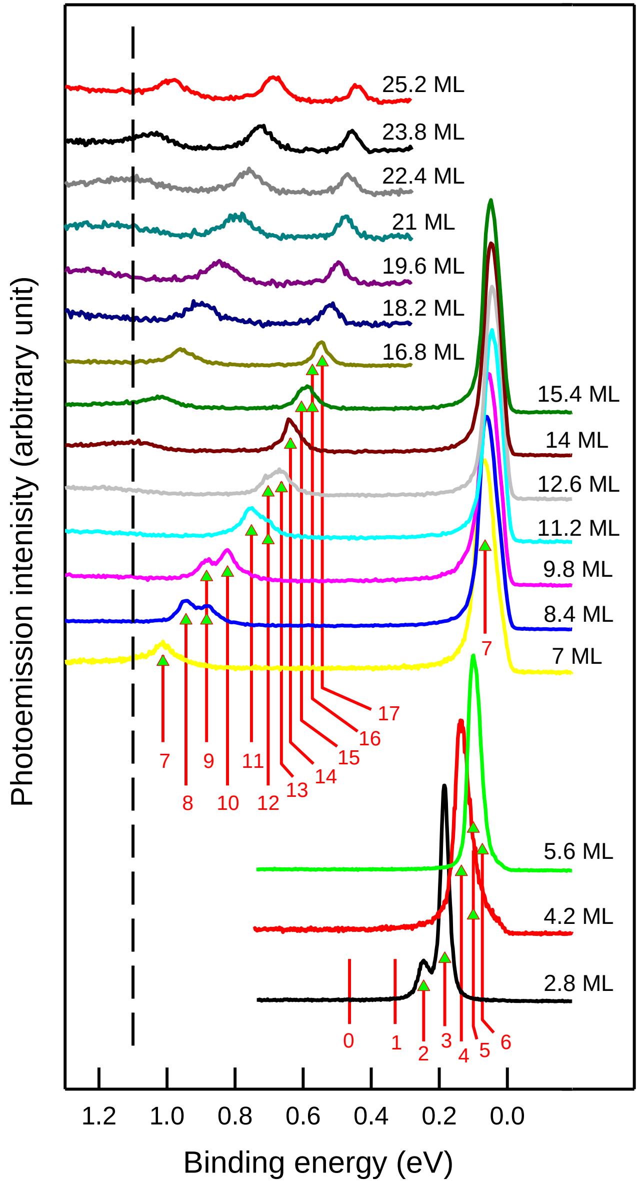
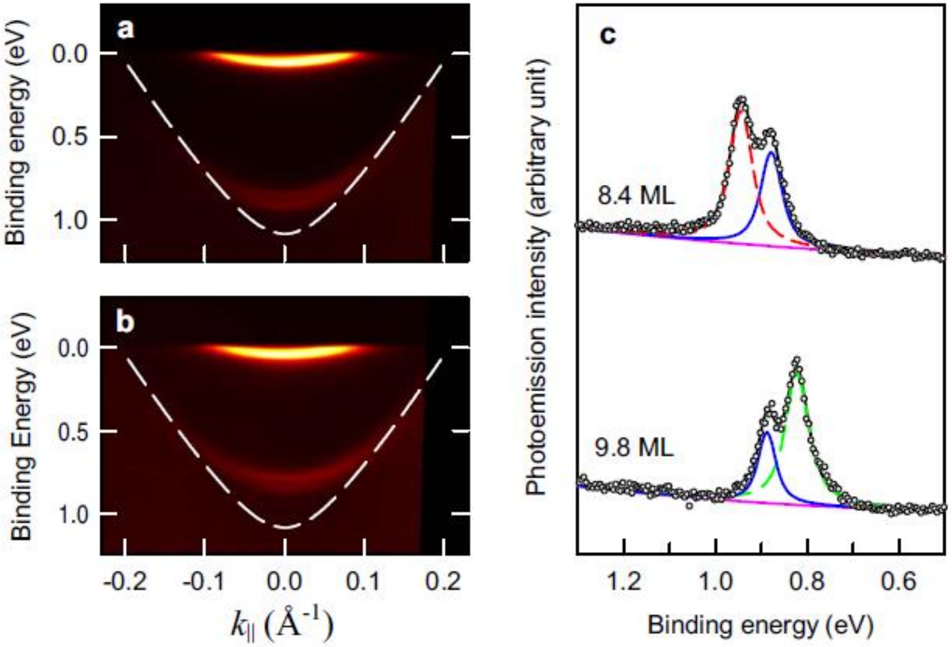
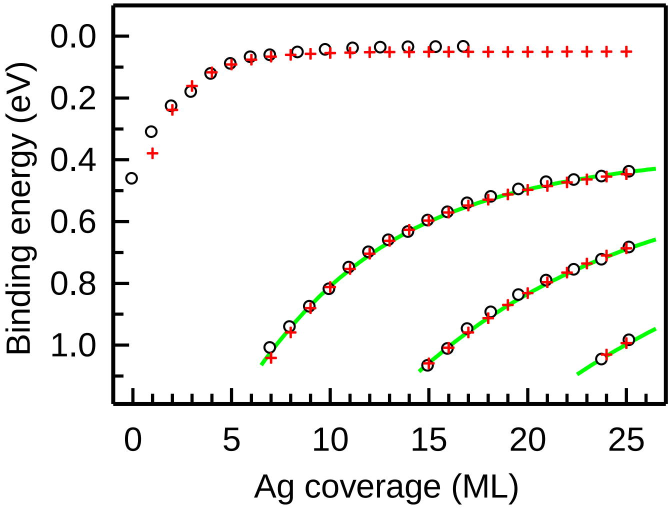


FIG. 2. Energy distribution curves of normal emission from Ag (22 ML) on Au(111) annealed at the indicated temperatures; intensities have been scaled variously for stacking presentation.









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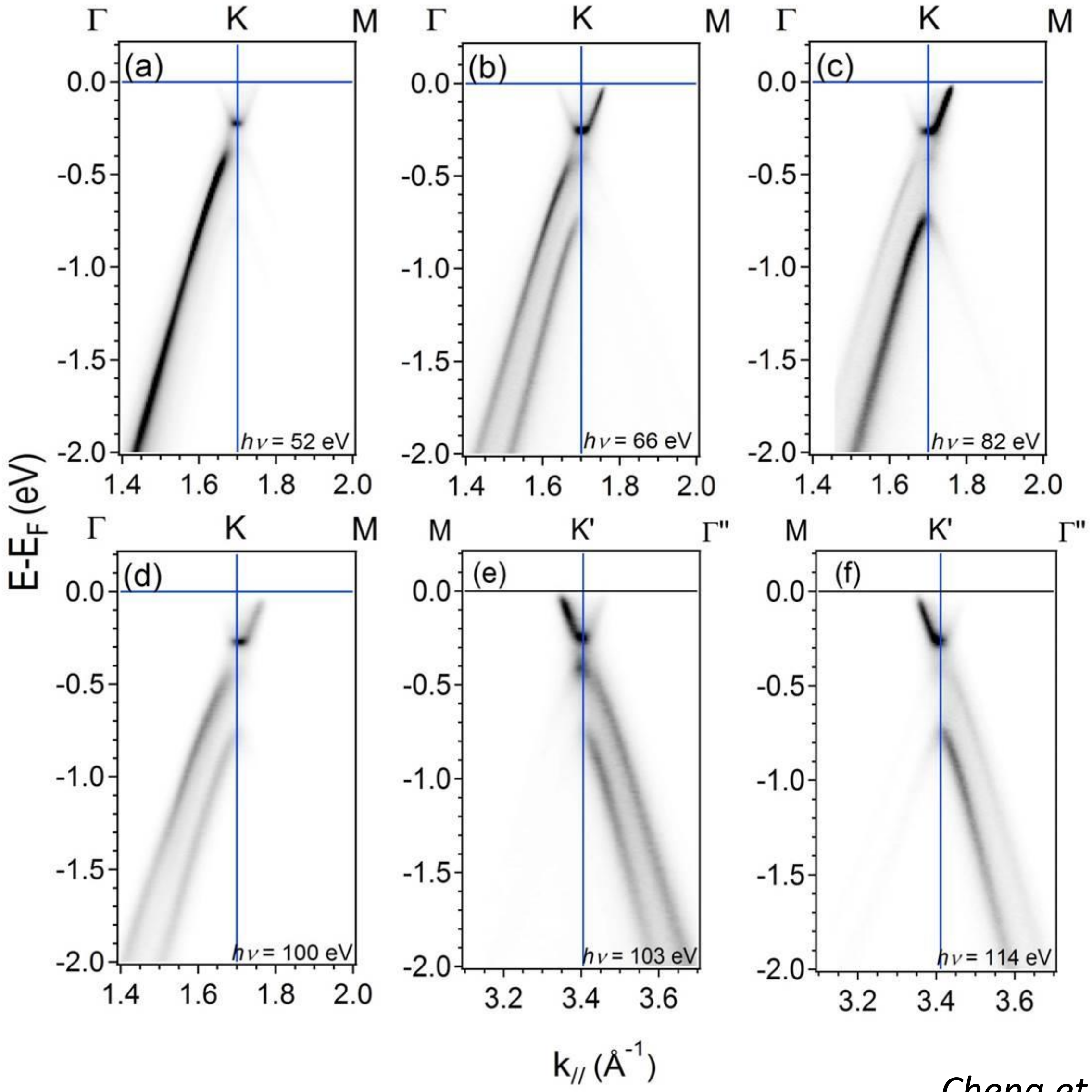
C.-M. Cheng et al., APL (2008)

C.-M. Cheng et al.,J. Phys. D: Appl. Phys. (2008)

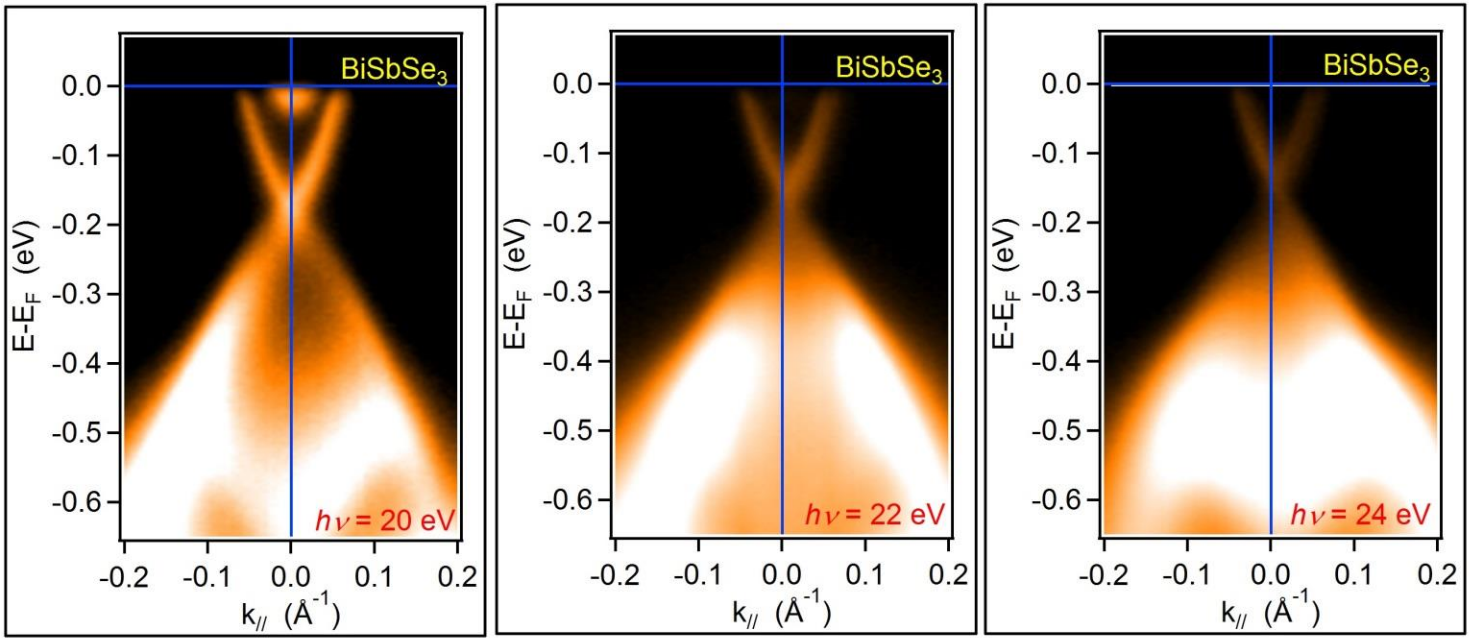
D.-A. Luh et al., PRB (2008)

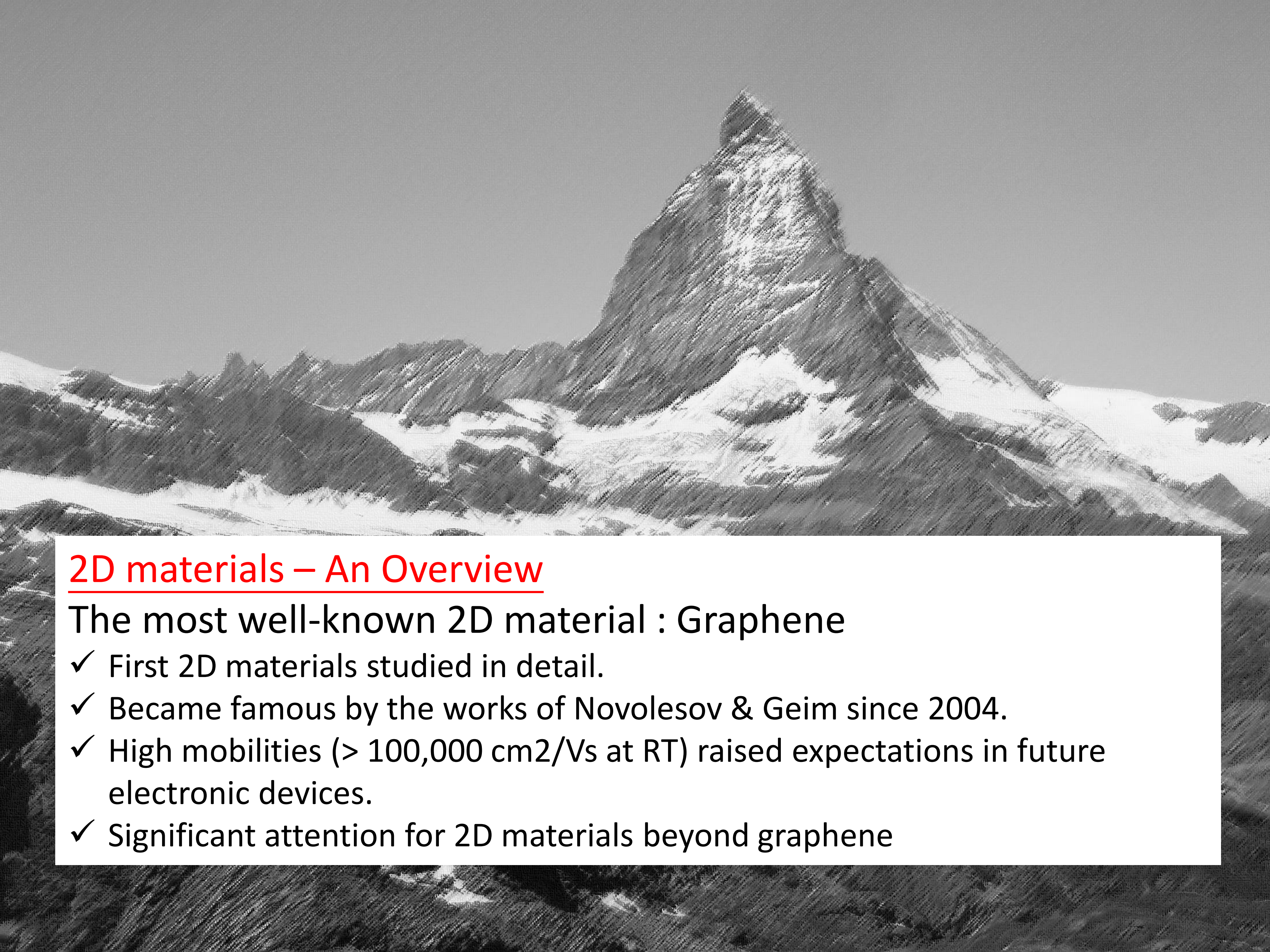
The examination of 2D behavior



Cheng et al., submitted

The examination of 2D behavior : tuning incident photon energy





2D materials – An Overview

The most well-known 2D material : Graphene

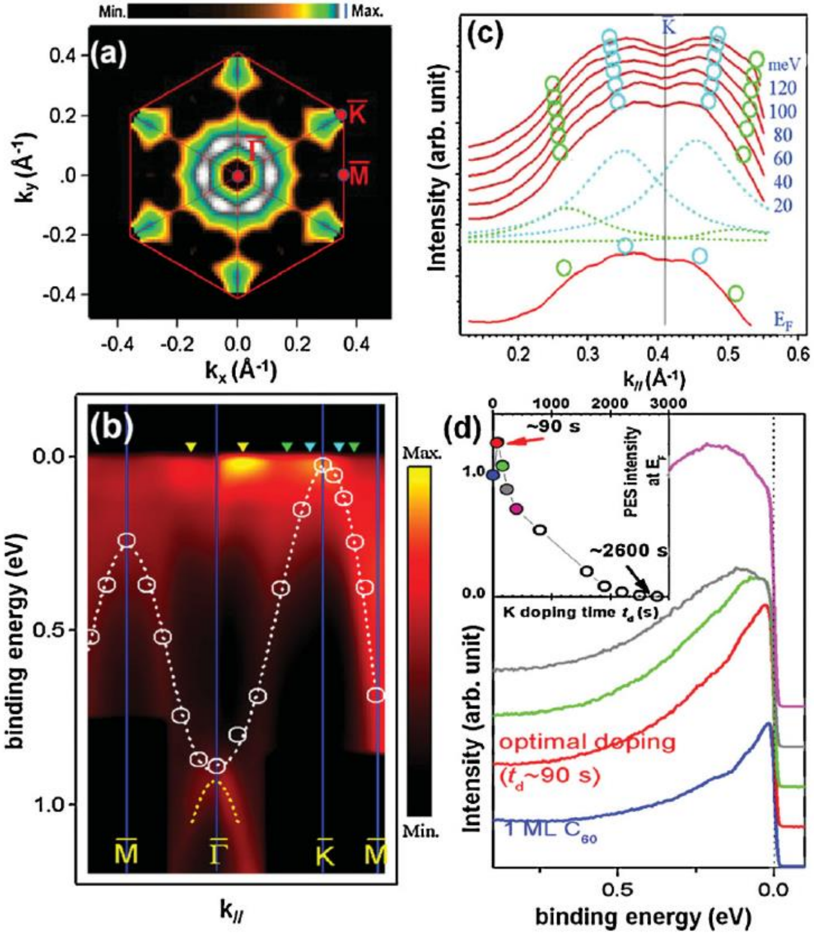
- ✓ First 2D materials studied in detail.
- ✓ Became famous by the works of Novolesov & Geim since 2004.
- ✓ High mobilities (> 100,000 cm2/Vs at RT) raised expectations in future electronic devices.
- ✓ Significant attention for 2D materials beyond graphene

The strictly two-dimensional material

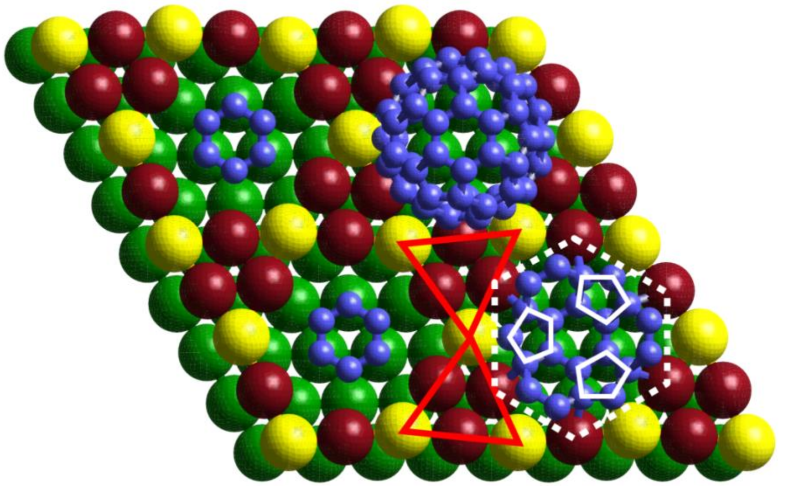
- 70 years ago, Landau argued that strictly 2D crystals were thermodynamically unstable and could not exist
- Before 2004, atomic monolayers only as integral part of 3D structure, grown epitaxially on top of monocrystal
- The discovery of graphene and other free-standing 2D atomic crystals (ex :single layer boron nitride and half-layer BSCCO)

New inroads into low-dimensional physics
New surprise to provide highly potential for application

Charge transfer process on ML C_{60}/Cu(111) system

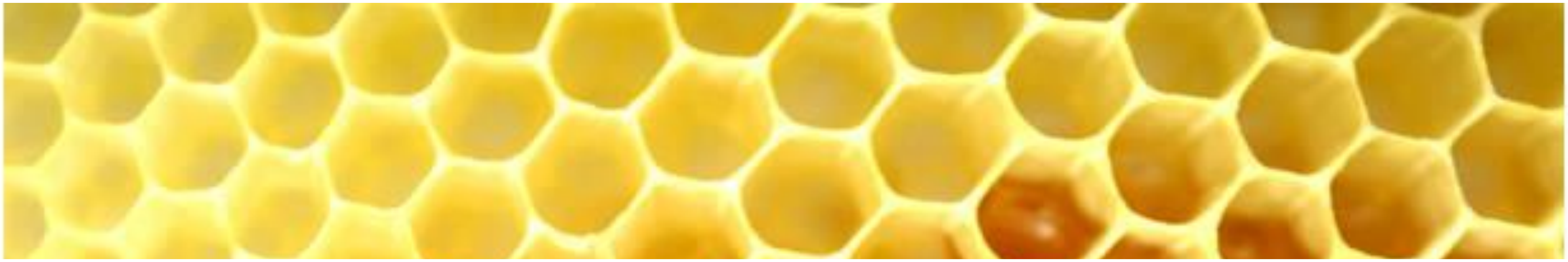


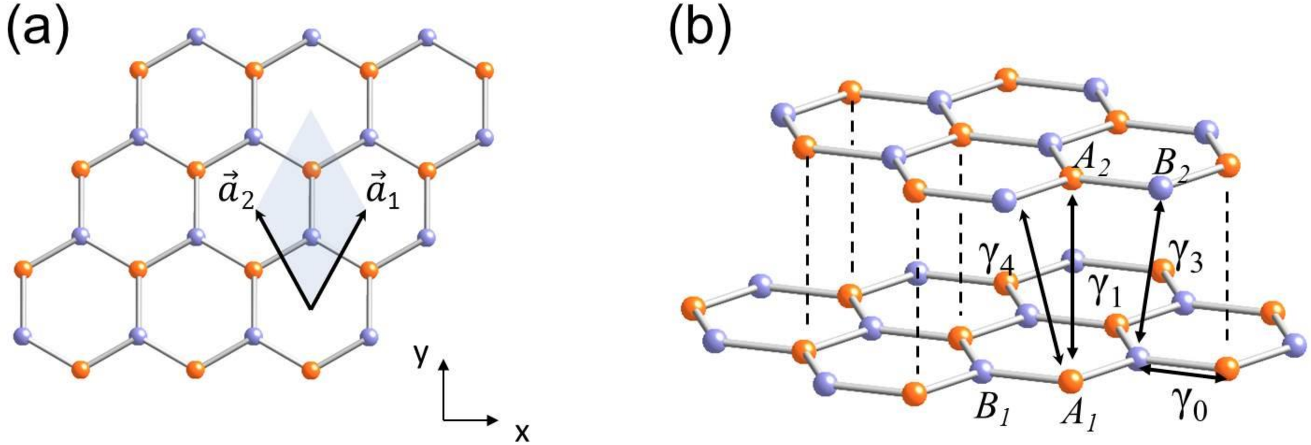
1. Large 7-atom vacancies.
2. Significant top Cu layer coherent distortion.
3. Nearly "optimal" C_{60}^{3-} doping purely by interface reconstruction.



Ref: W.W. Pai et al., PRL 104, 036103 (2010)

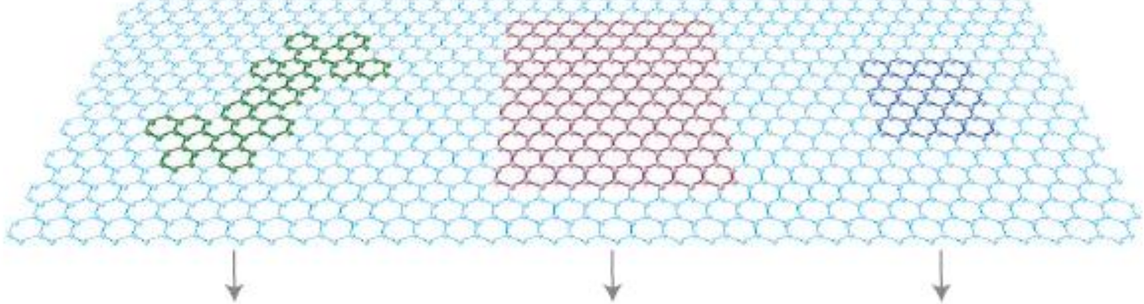
What Is Graphene



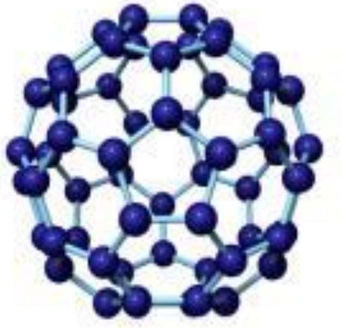


What is graphene

Very good conductors
Extremely thin and resistant



wrapped

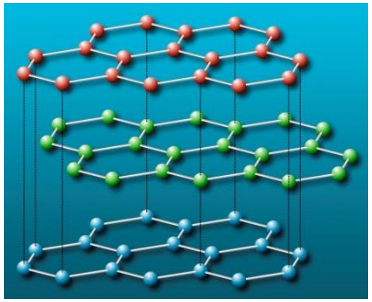


Zero dimensional: fullerenes

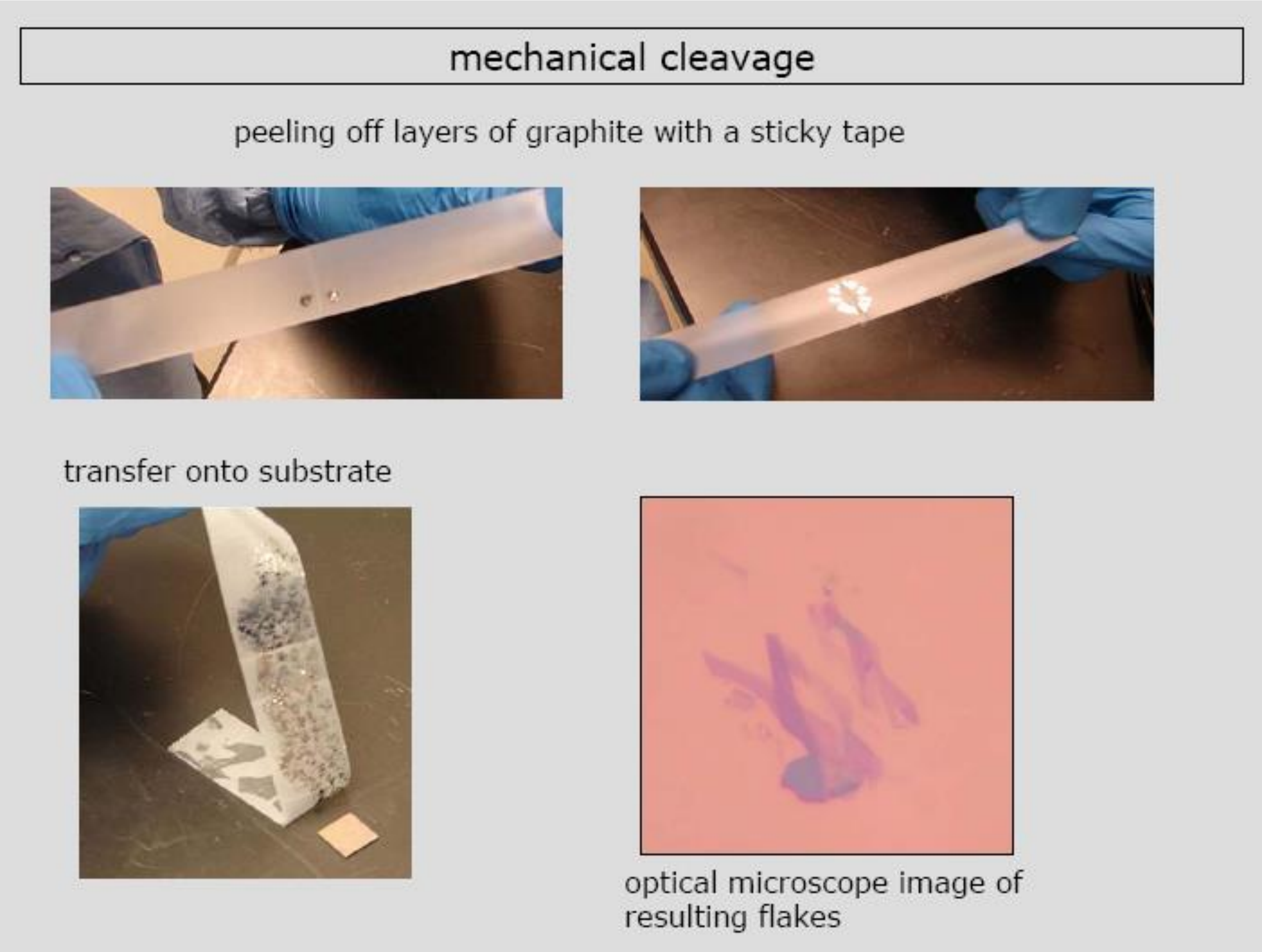
Rolled

One dimensional: carbon nanotubes

stacked



Three dimensional: graphite



mechanical cleavage

peeling off layers of graphite with a sticky tape

transfer onto substrate

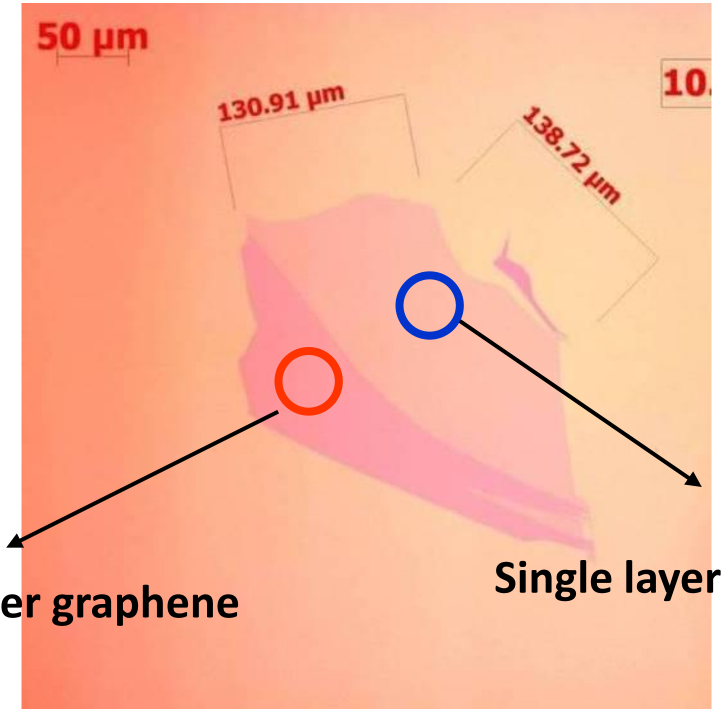
optical microscope image of resulting flakes

Novoselov et al., Nature (2005)

How to distinguish the thickness of graphene

SiO$_2$(200 nm)/Si

Optical microscopy

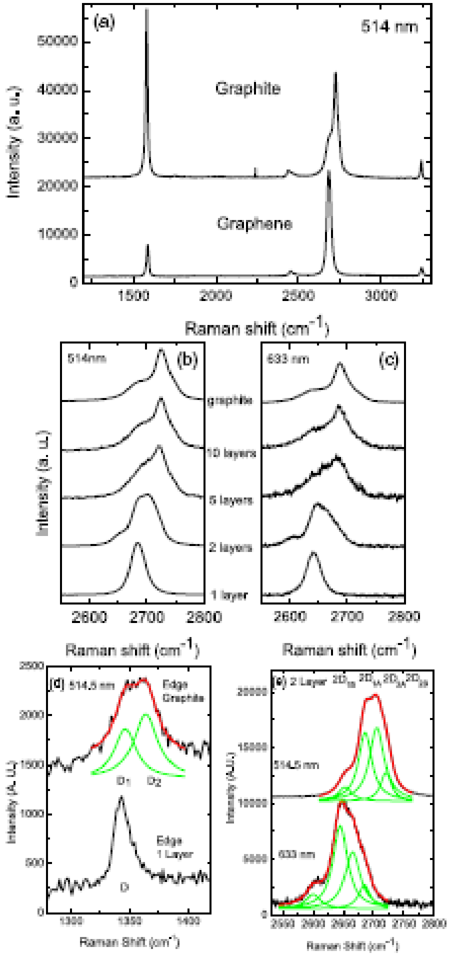


Bilayer graphene

Single layer graphene

B. özyilmaz , NUS, Singapore

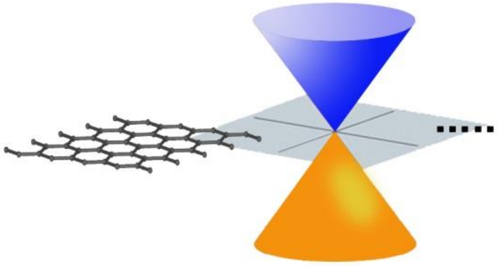
Raman spectroscopy



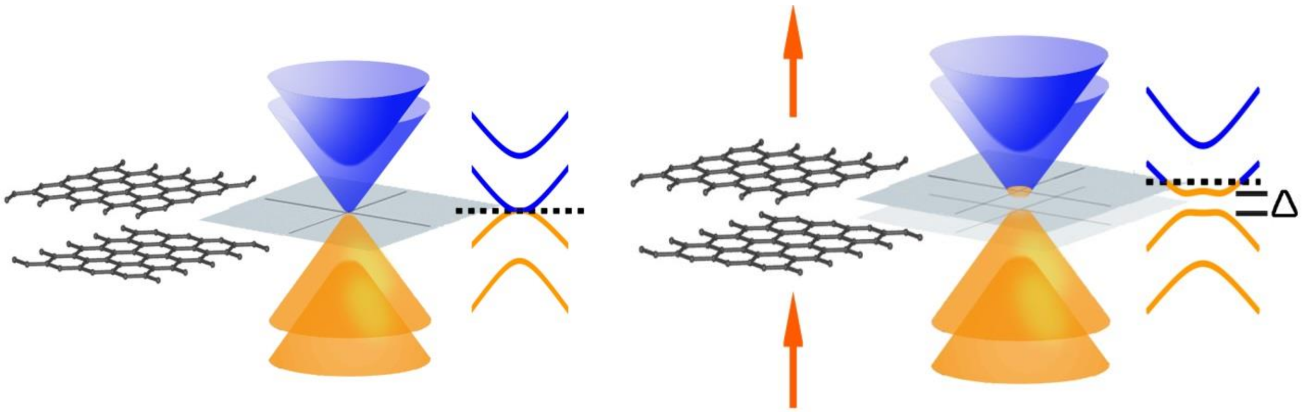
A. Ferrari , PRL 97,187401 (2006)

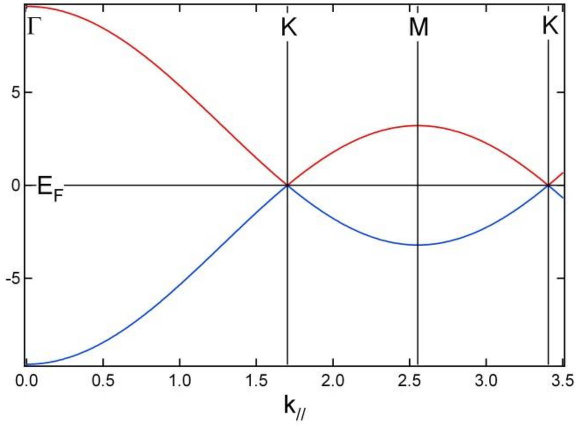
Single layer and bilayer graphene

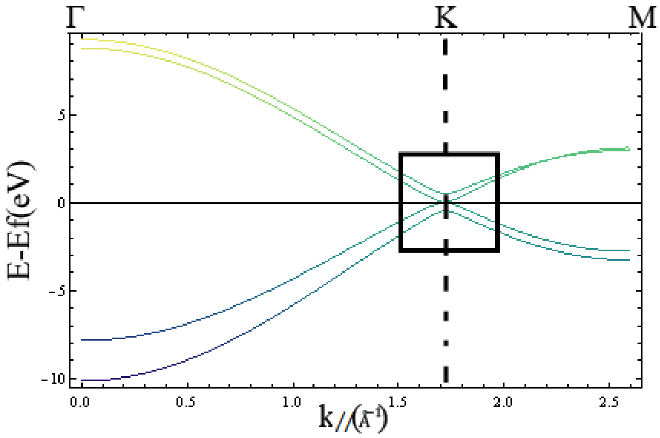
Single layer graphene



Bilayer graphene







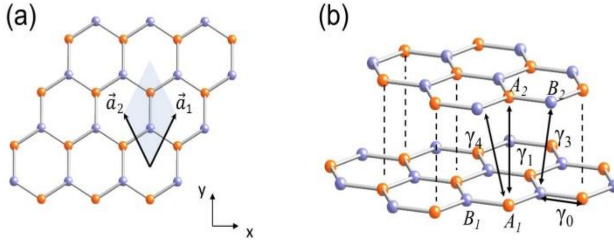
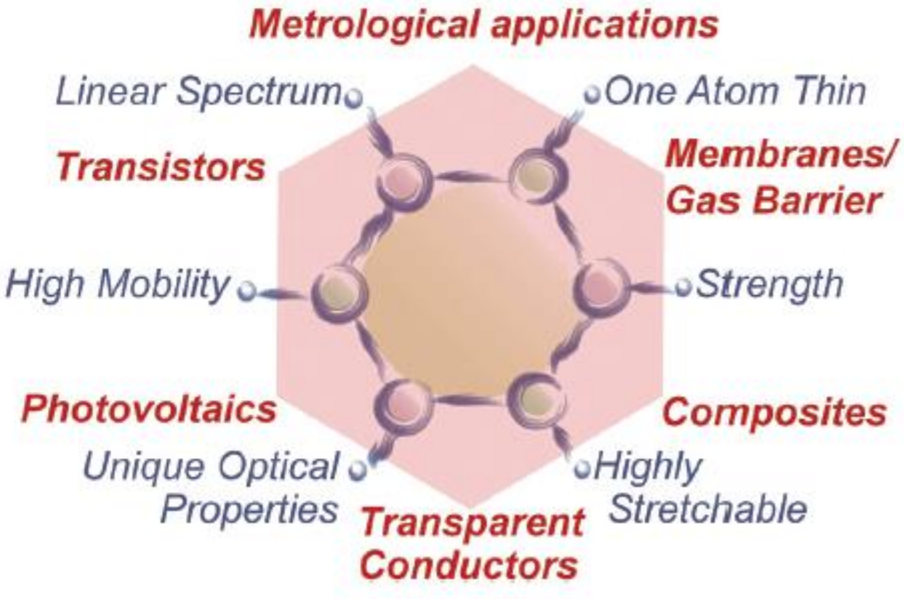
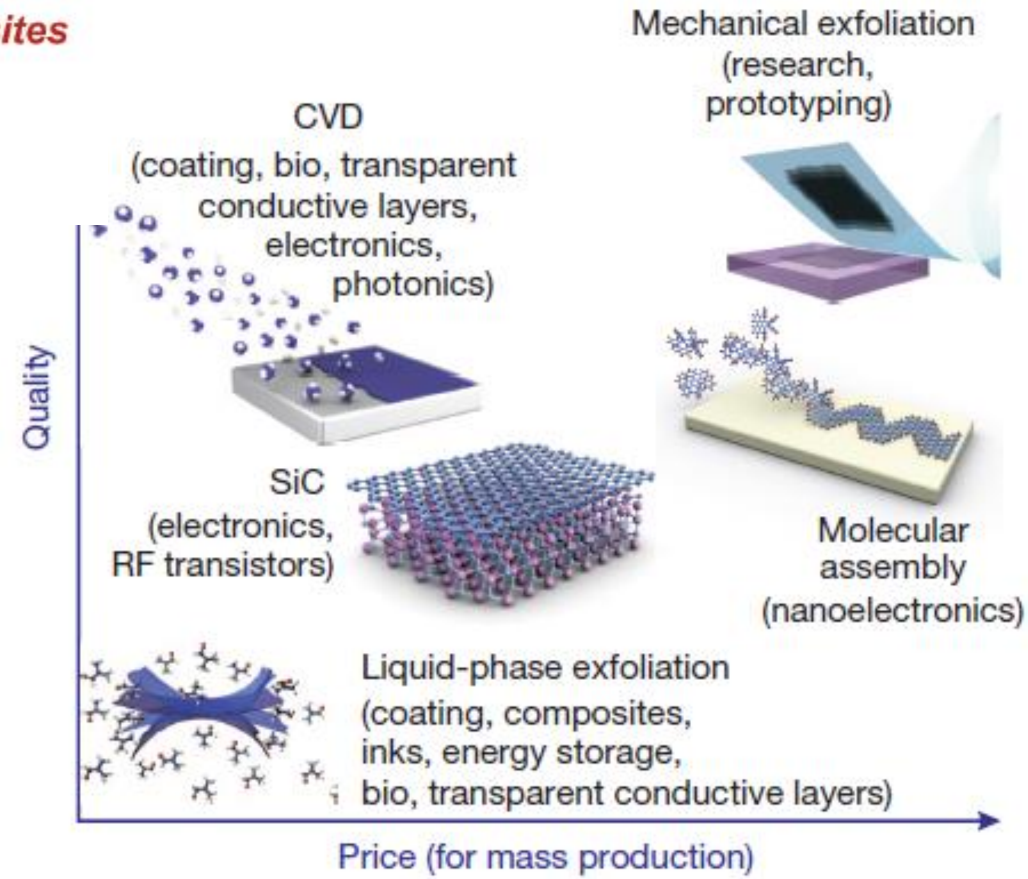


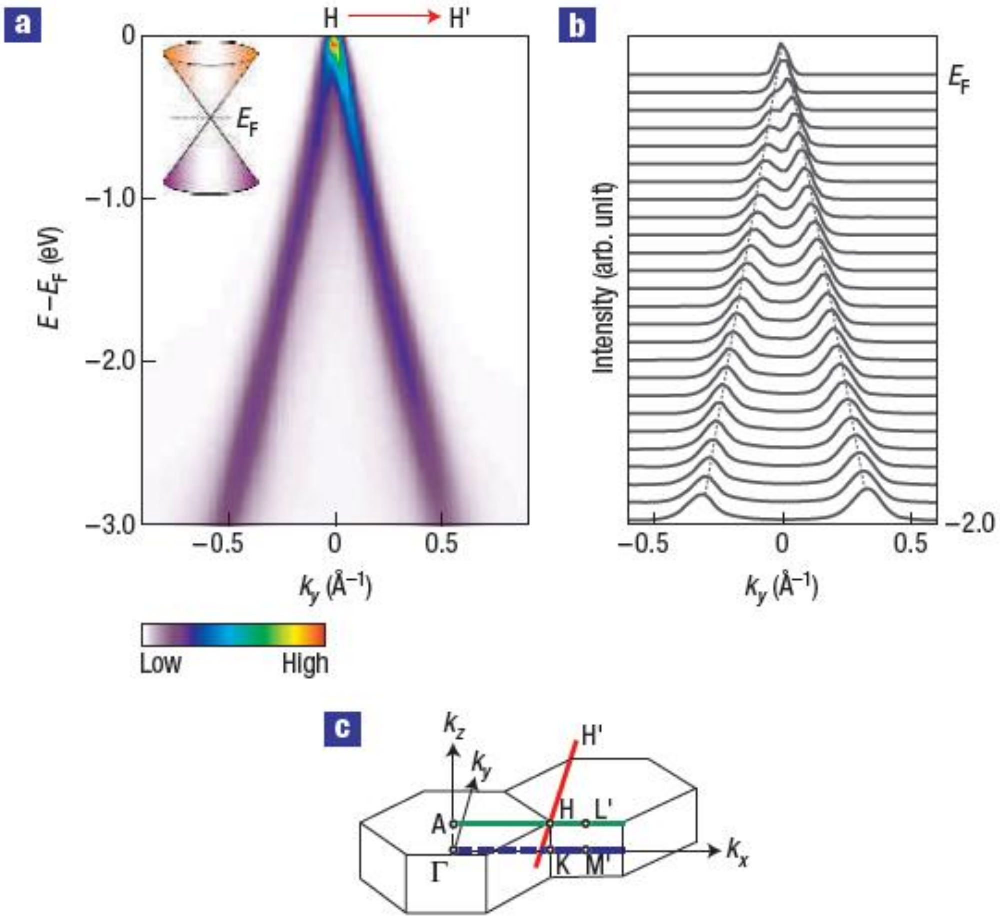
Image : http://infared.lbnl.gov.tw

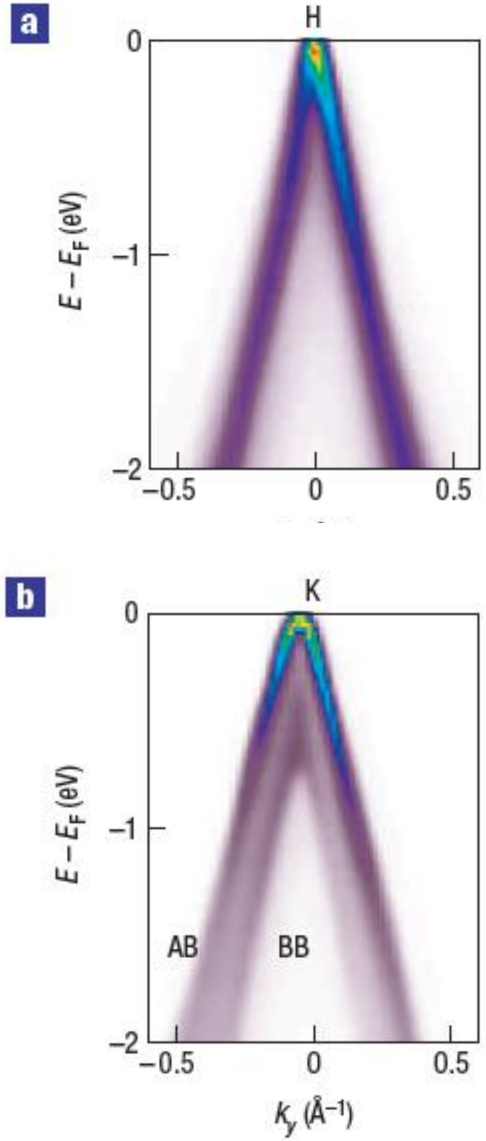




Novoselov et al., Nature (2012)

First treament: graphite

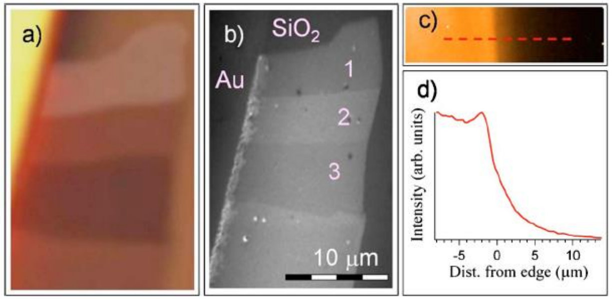




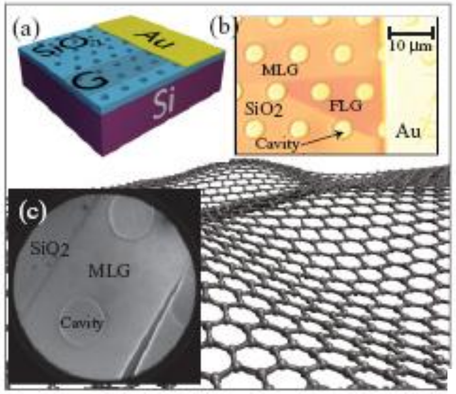
Zhou et al., Nature Physics 2, 595 (2006)

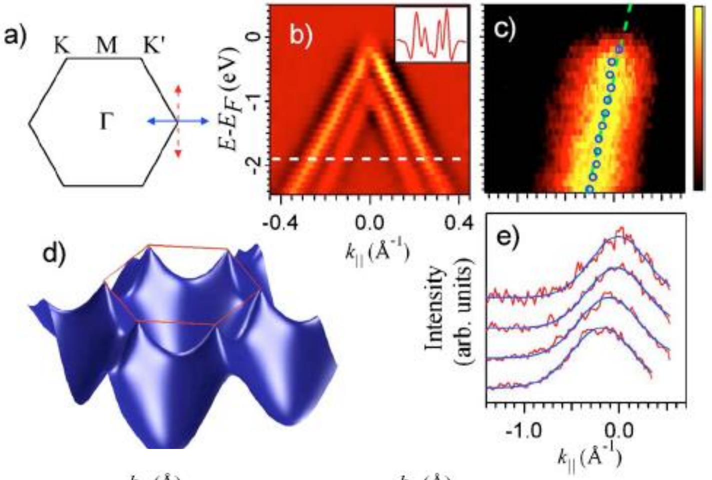
The experiments in graphene on SiO$_2$ (200nm) and suspended graphene

Graphene on SiO$_2$



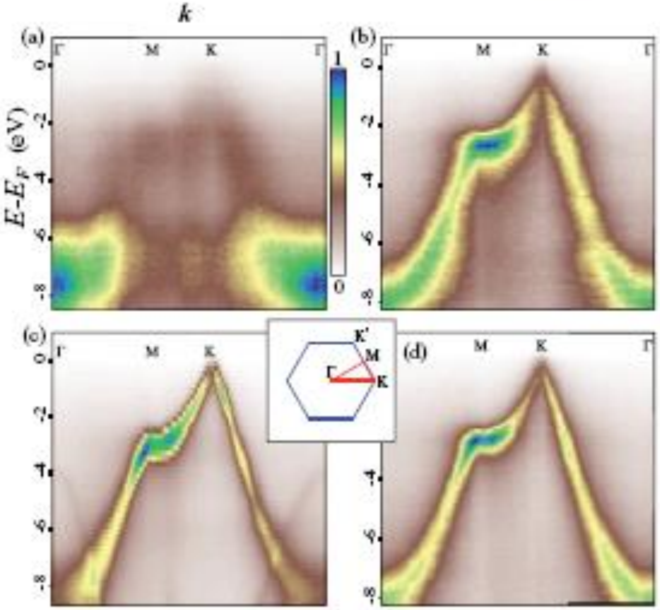
Suspended graphene



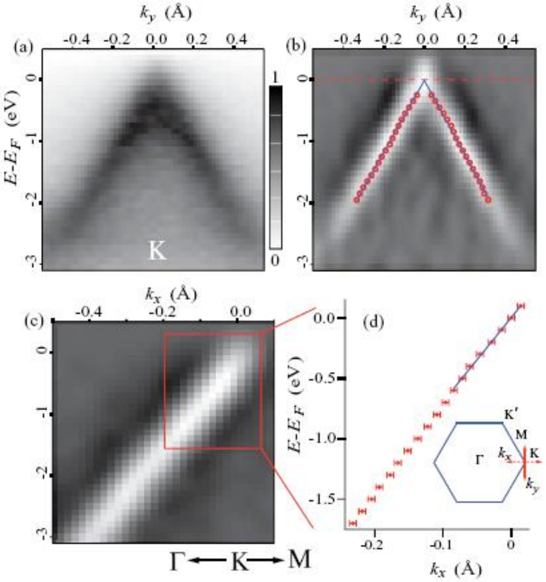


SLG/SiO2

graphite



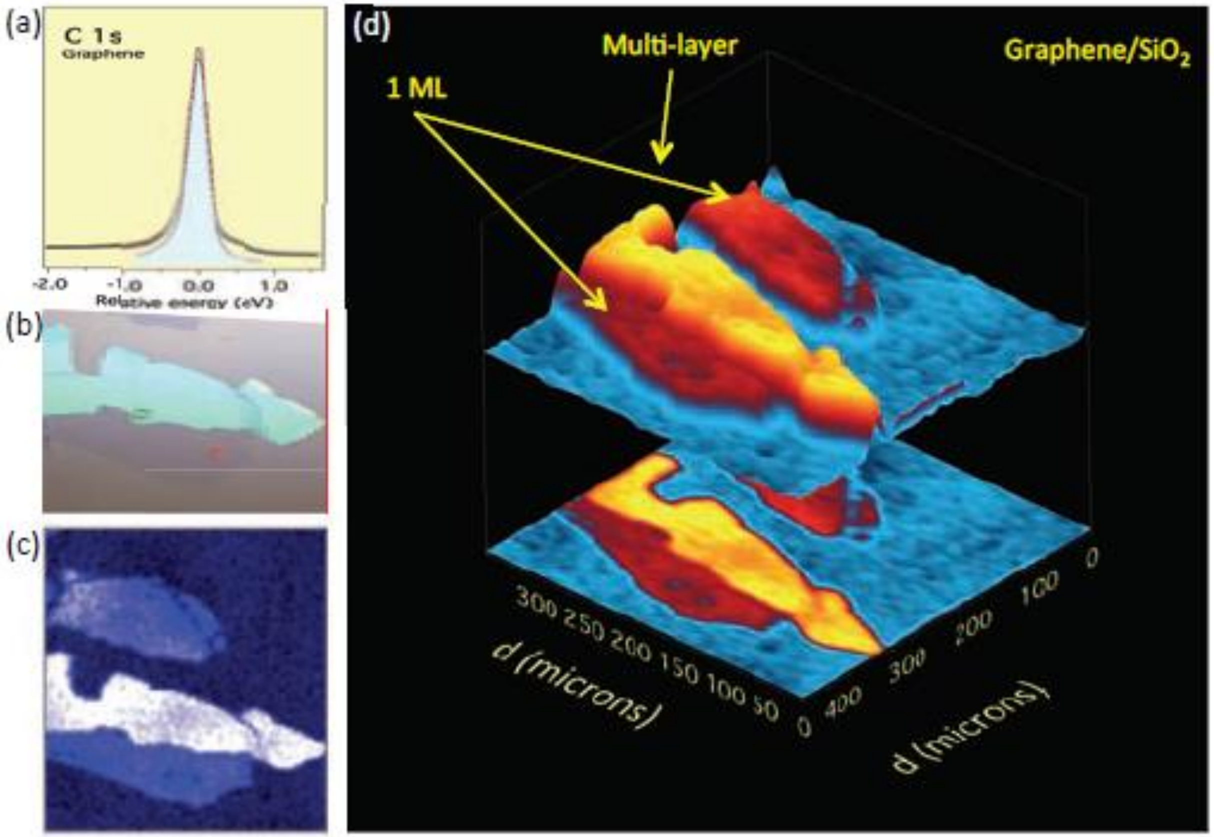
Suspended graphene



Knox et al., PRB 78, R201408 (2008)
PRB 84, 115401 (2011)

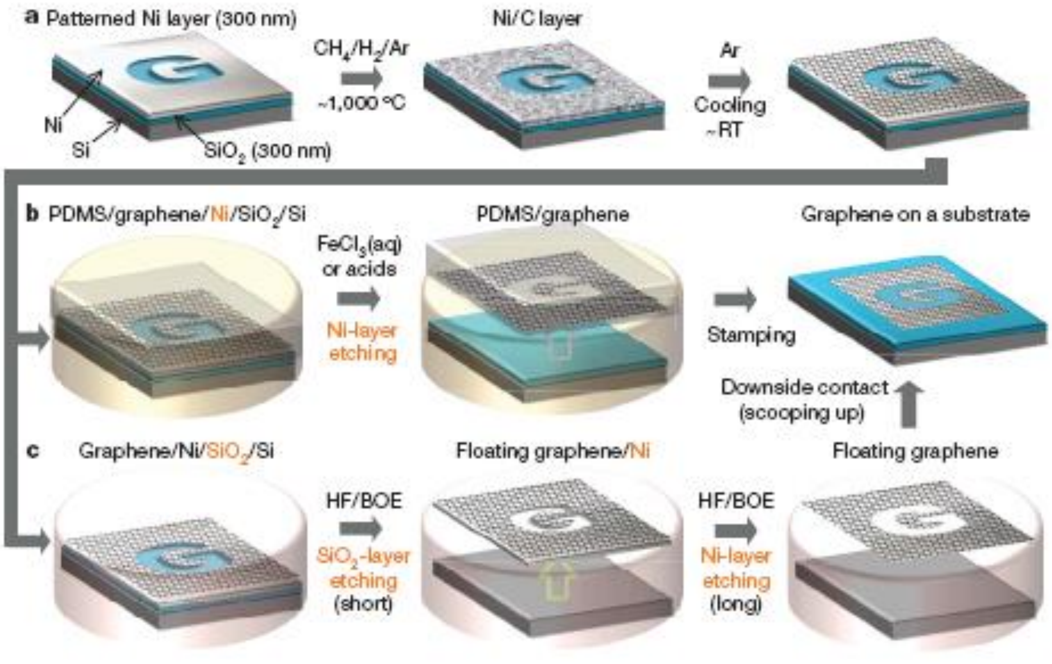
Multi-thickness domains in an exfoliated graphene

Nano-XPS results on exfoliated graphene samples on SiO_2 substrates at the ANTARES beamline, SOLEIL



Avila, Synchrotron Radiation News (2014)

CVD for large scale graphene film



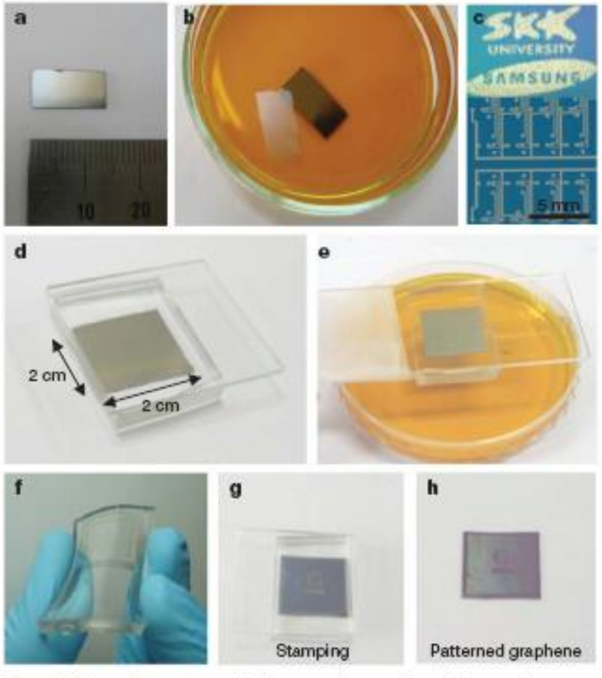
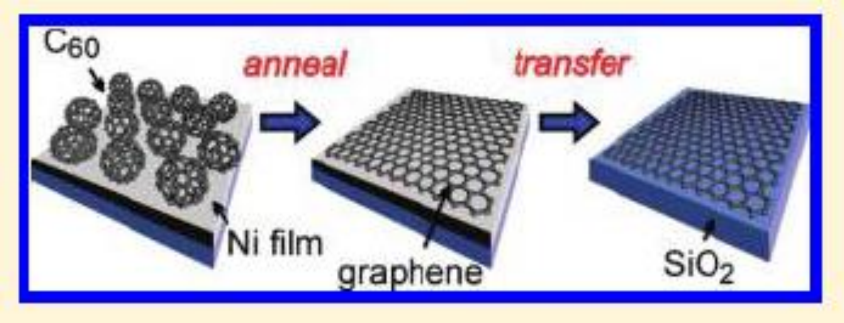
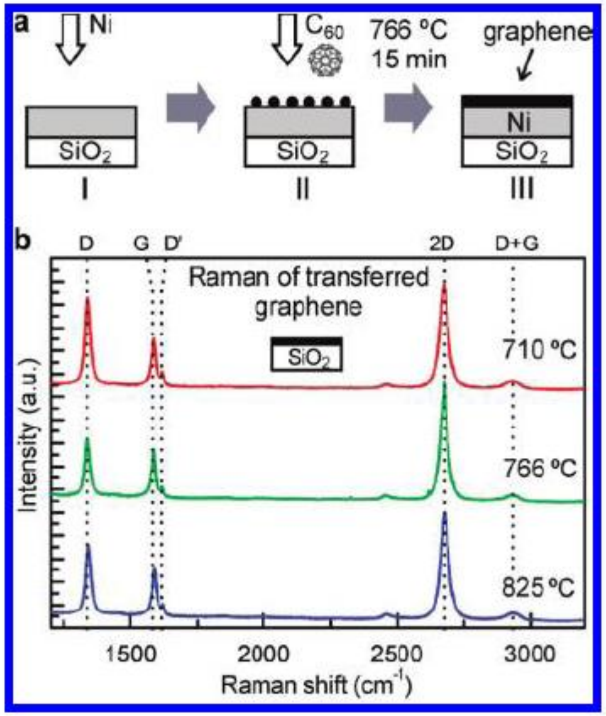


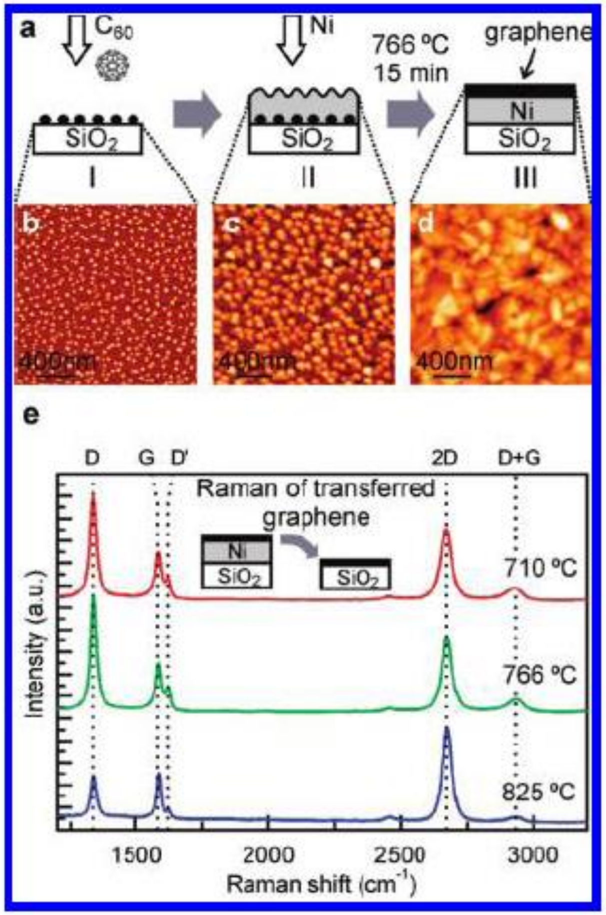
Figure 3 | Transfer processes for large-scale graphene films. a, A

Kim et al., Nature (2009)

Graphene formation by decomposition of C_{60}

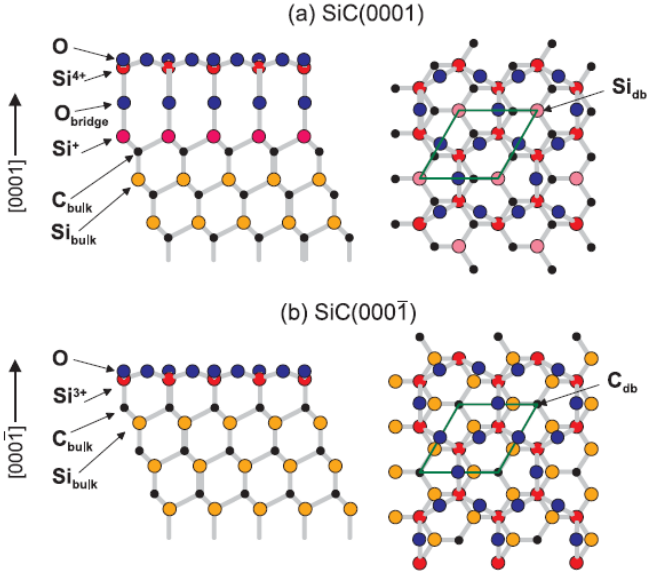


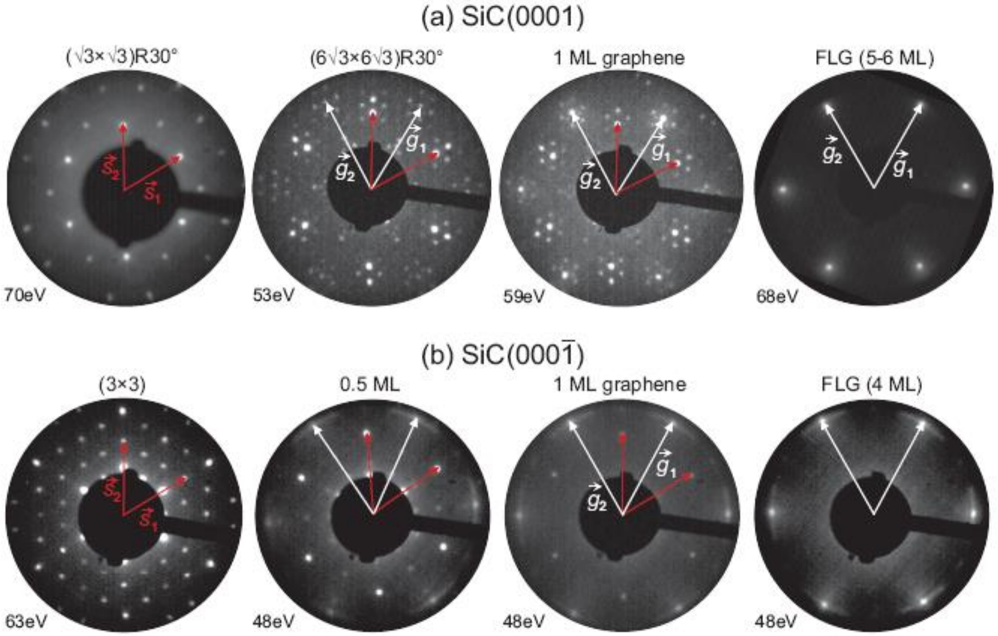


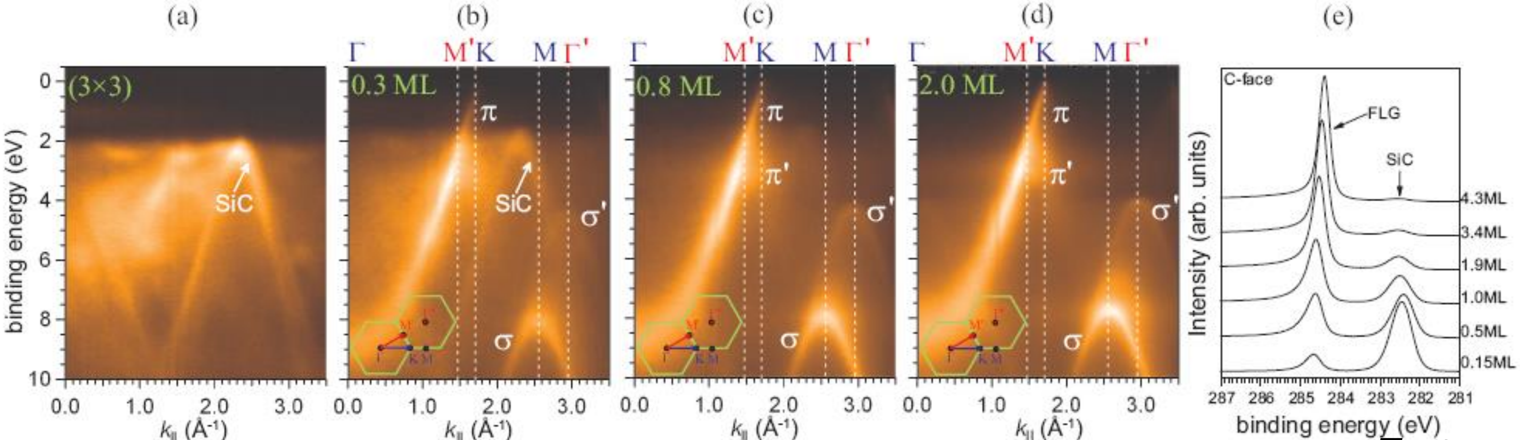


Perdigao et al., J. Physical Chemistry C (2011)

Epitaxial growth graphene on SiC



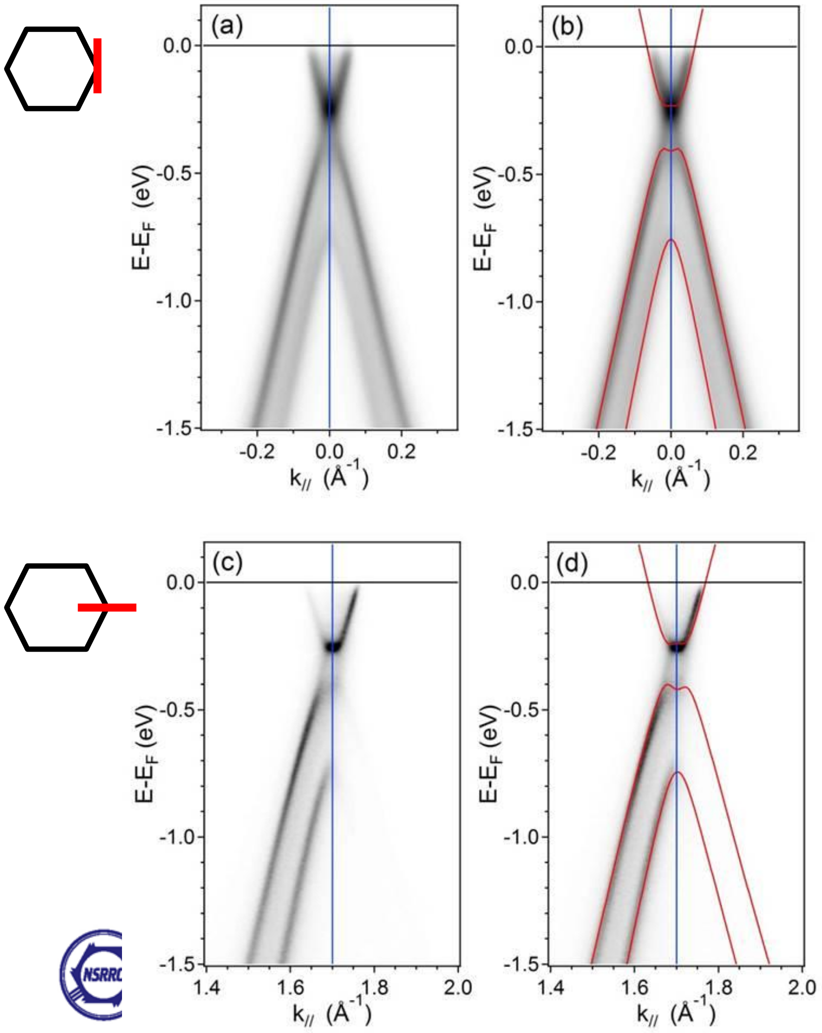




Emtsev et al., PRB (2008)

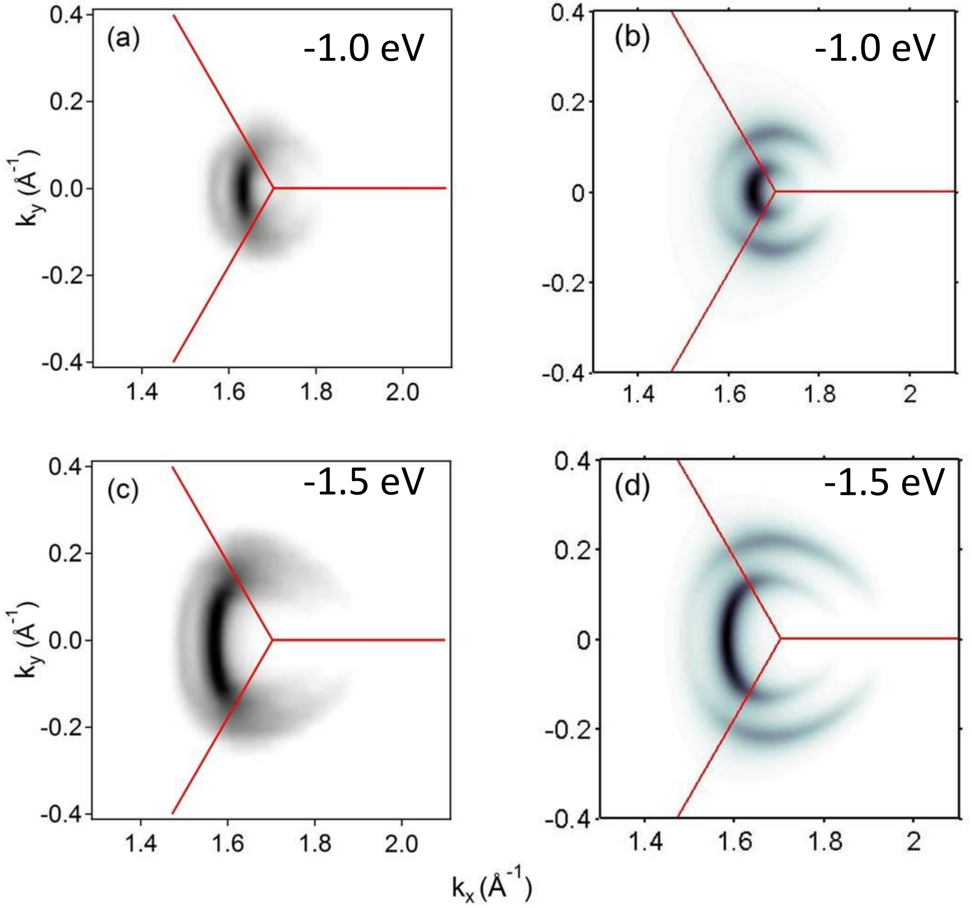
The electronic structure of bilayer graphene on SiC substrate

Data taken at 40 eV



Exp. at 82 eV

TB simulated



Cheng et al., submitted

A intrinsic gap exists or not ?

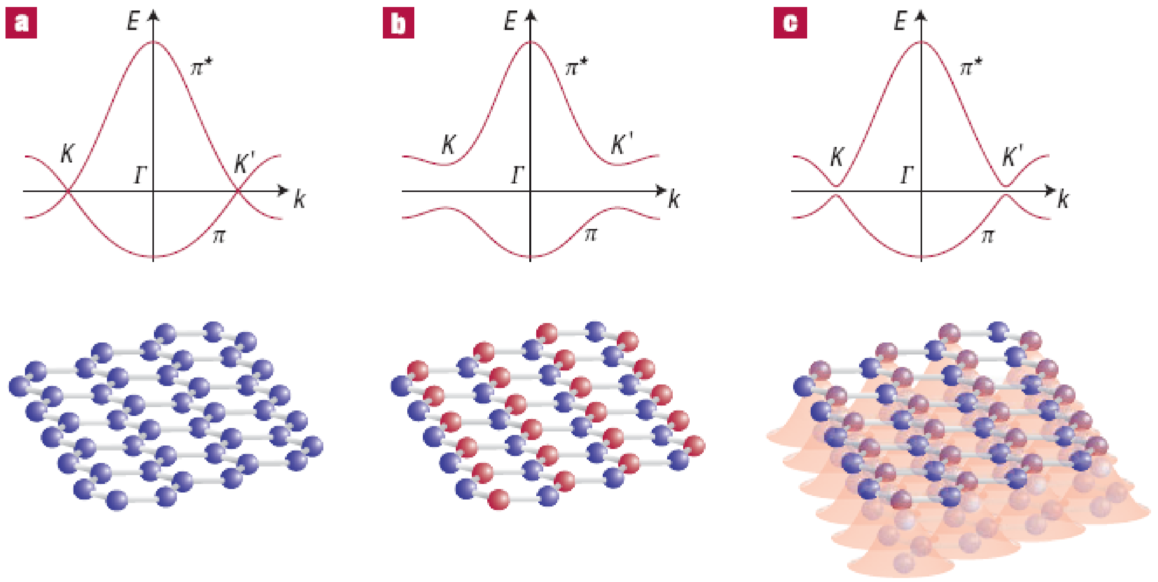
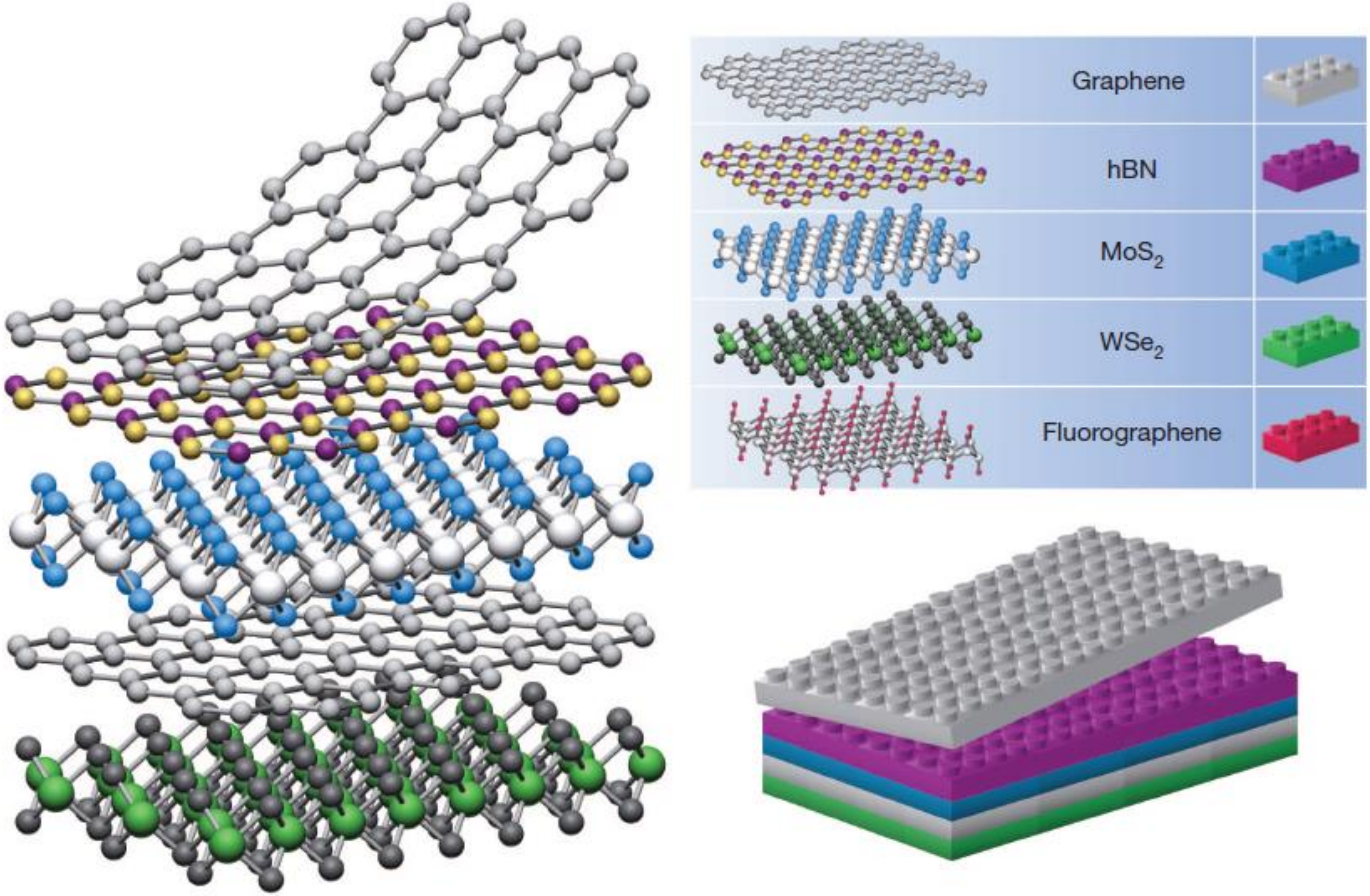


Figure 1 Schematic representation of crystal and electronic band structures (only π-bands are shown). **a**, Free-standing graphene. **b**, Boron-nitride. **c**, Epitaxial graphene. Symmetry between the sublattices in graphene guarantees gapless spectra around *K* points. This symmetry is broken in boron-nitride (one sublattice consists of boron atoms, another of nitrogen), which immediately opens a gap. In epitaxial graphene, the commensurate underlying potential gives rise to different on-site energies for the two sublattices, which opens a small gap around *K* points.

Novoselov, Nature Mat. (2007)

A crucial problem to understand the electronic of exfoliated graphene

Van der Waals heterostructures



Geim, Nature (2013)

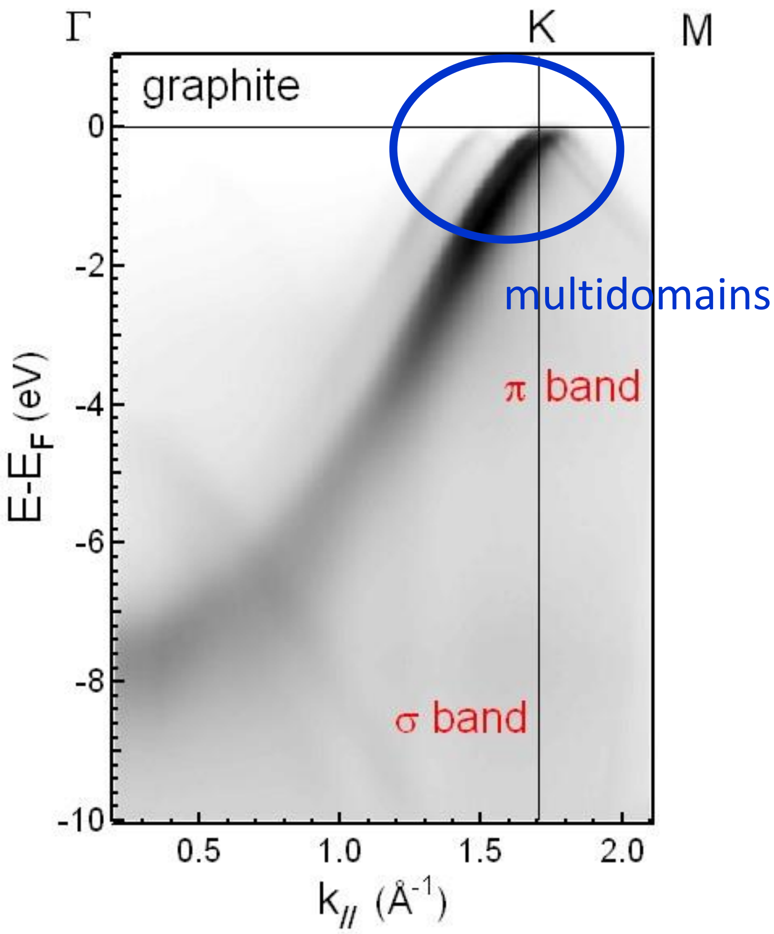
The difficulties for studying the electronic structure of exfoliated graphene

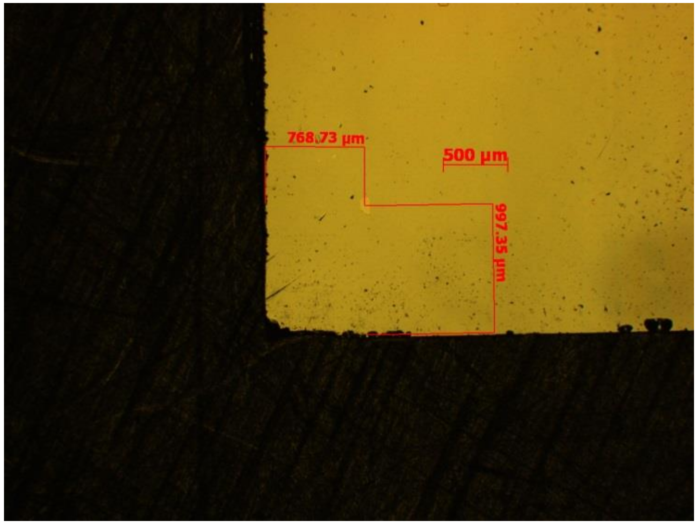
- Insulating substrate induces the strong charging effect.

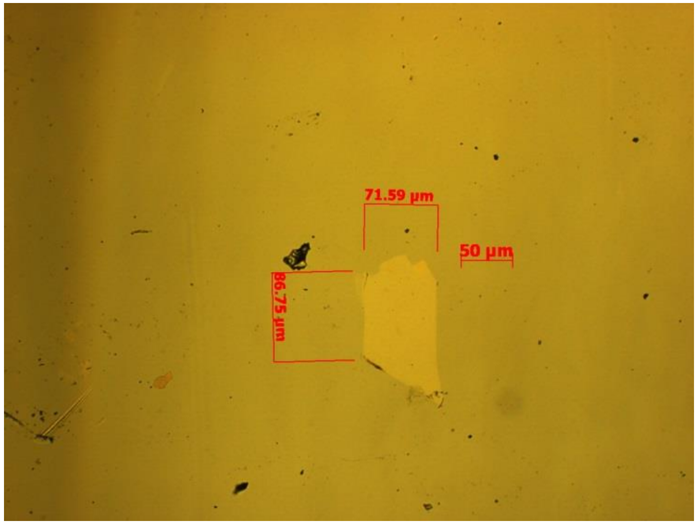
- Sample size : only several tens microns sample is obtained, but this sample size is quite small for current ARPES beam spot (> 100 μm) in VUV region. Nano-ARPES provides an advantage to study the electronic structure of exfoliated graphene, but the used photon energy is above 100 eV due to the short focal length of zone plate. It is difficult to make line shape analysis for the many body effect due the poor momentum resolution in high photon energy and the matrix element effect.

- *ex-situ* sample preparation is not favorable for ARPES experiments.

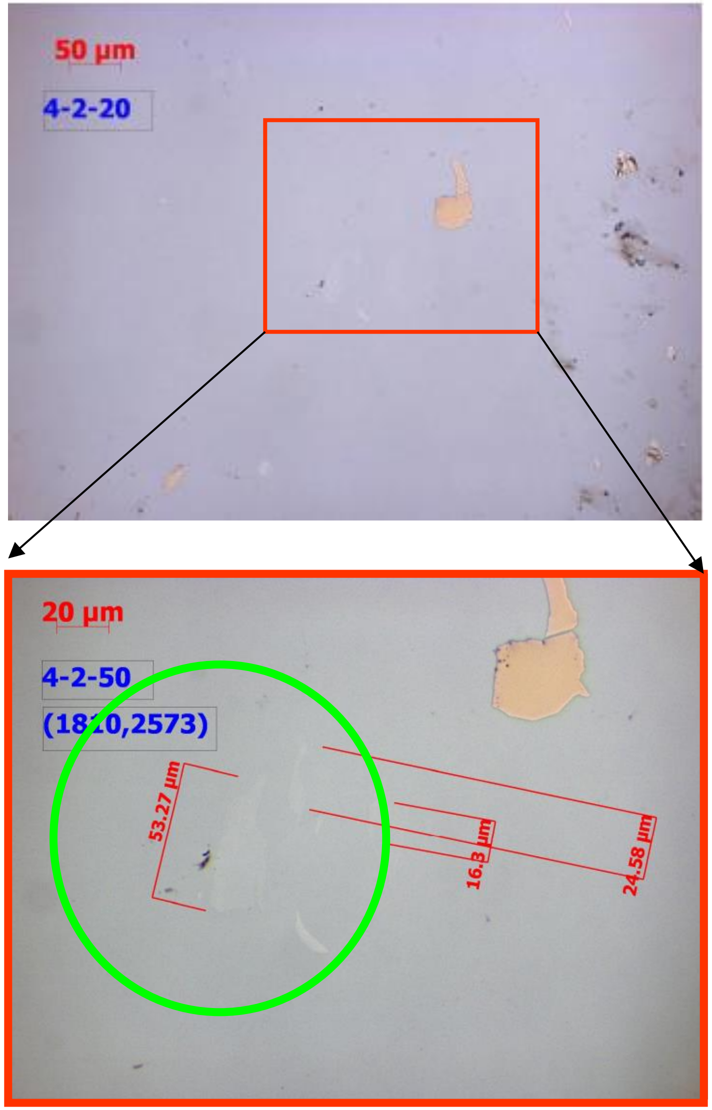
The band mapping result of Kish graphite

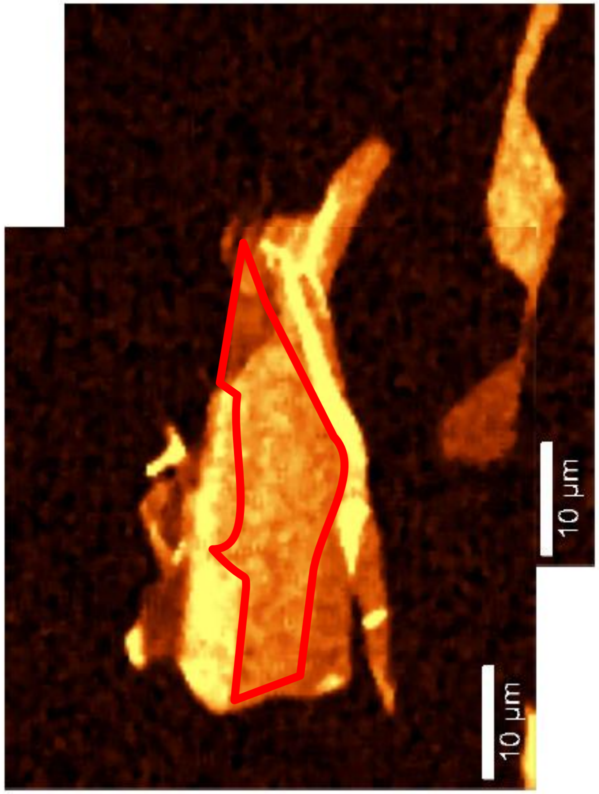






Bilayer graphene / Highly doped Si substrate

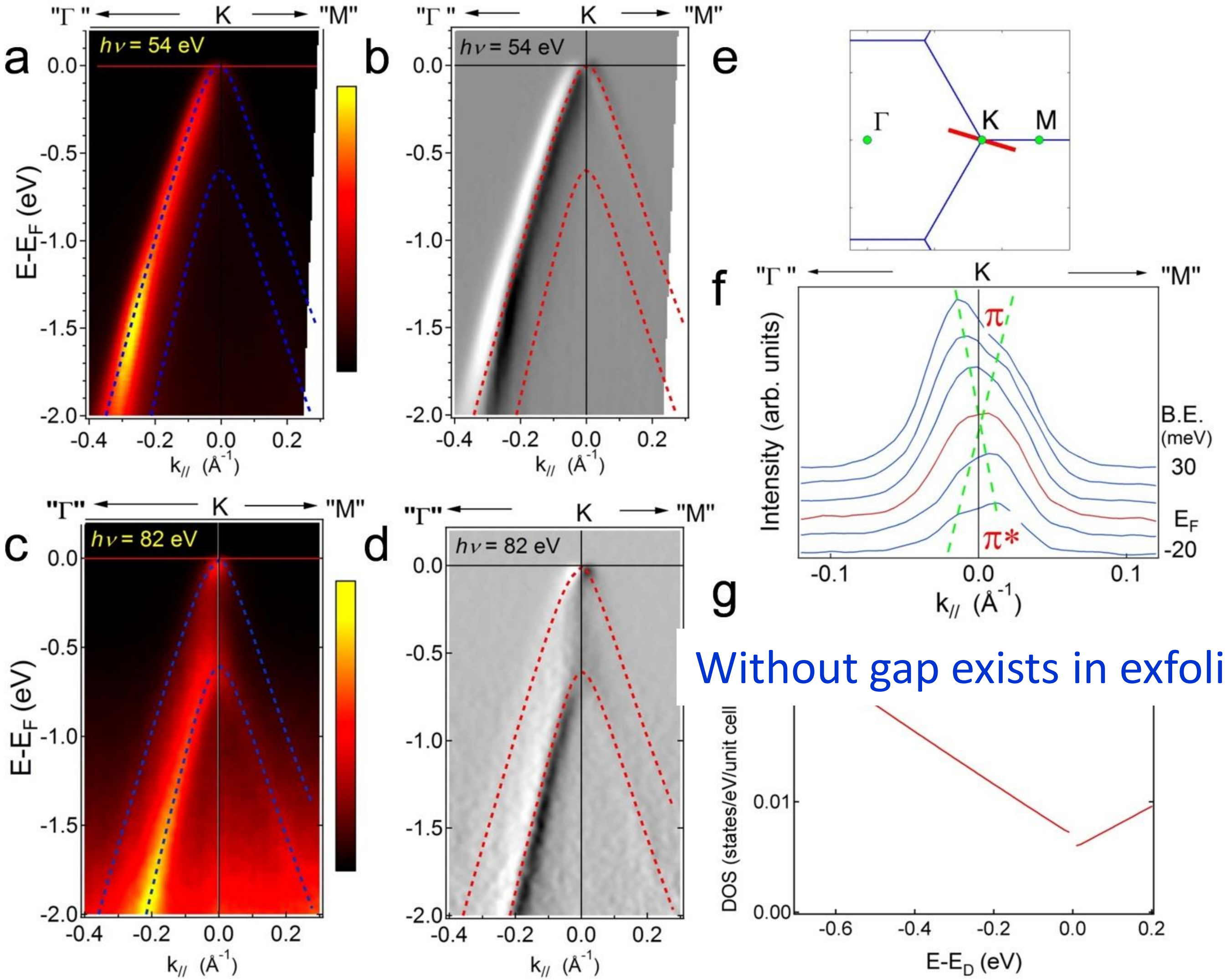




Intensity of G band (overlap of 2 scans showing flake 1 and 3)

Raman result : BLG is the area marked with red color.

The electronic structure of bilayer graphene



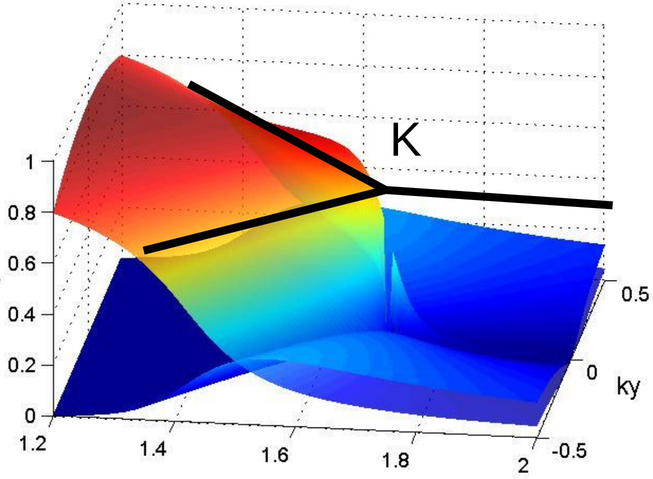
Without gap exists in exfoliated BLG

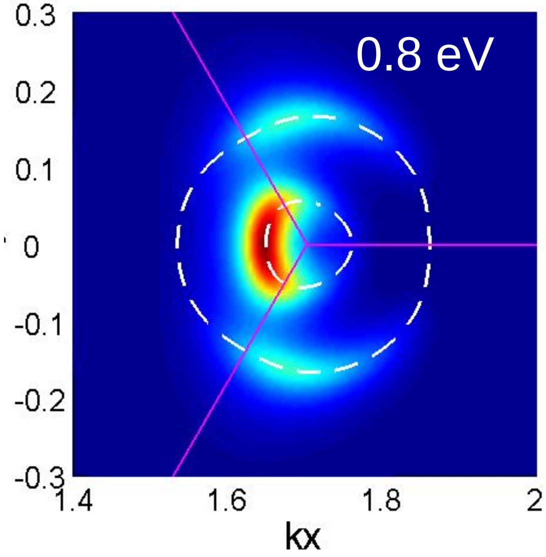
Cheng et al., Scientific Report (2015)

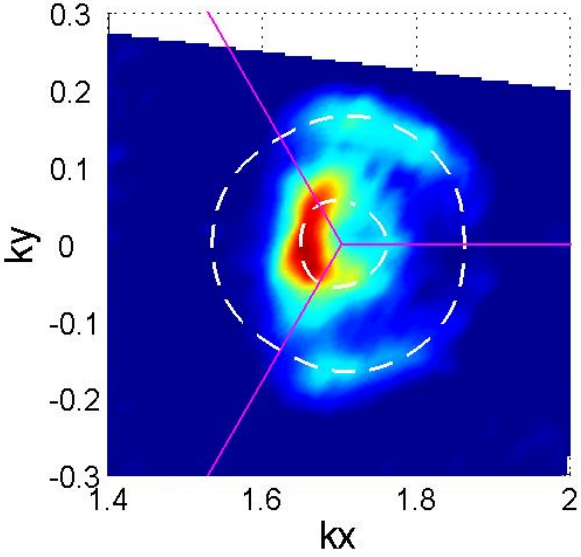
82 eV ME effect

Simulated result

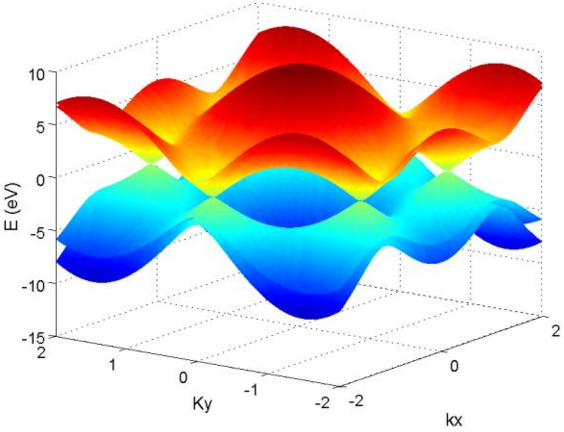
Experimental result

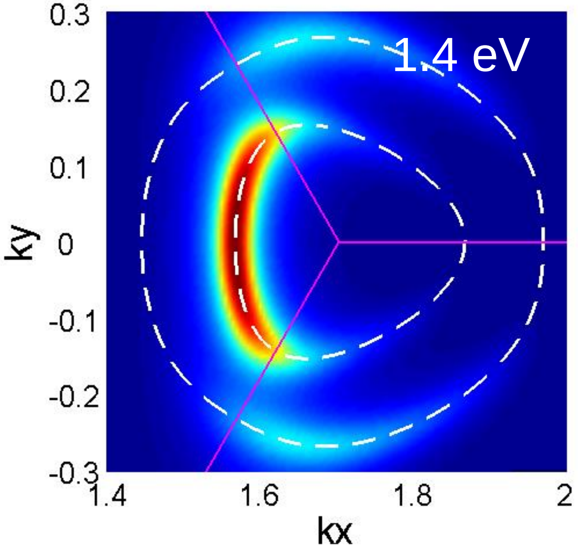


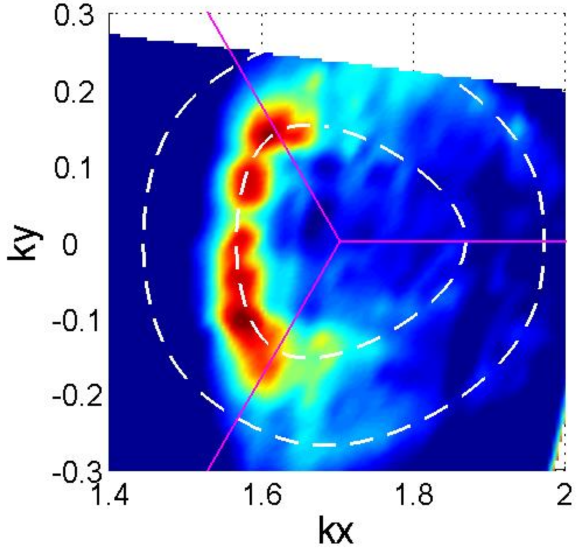




Electronic structure of BLG







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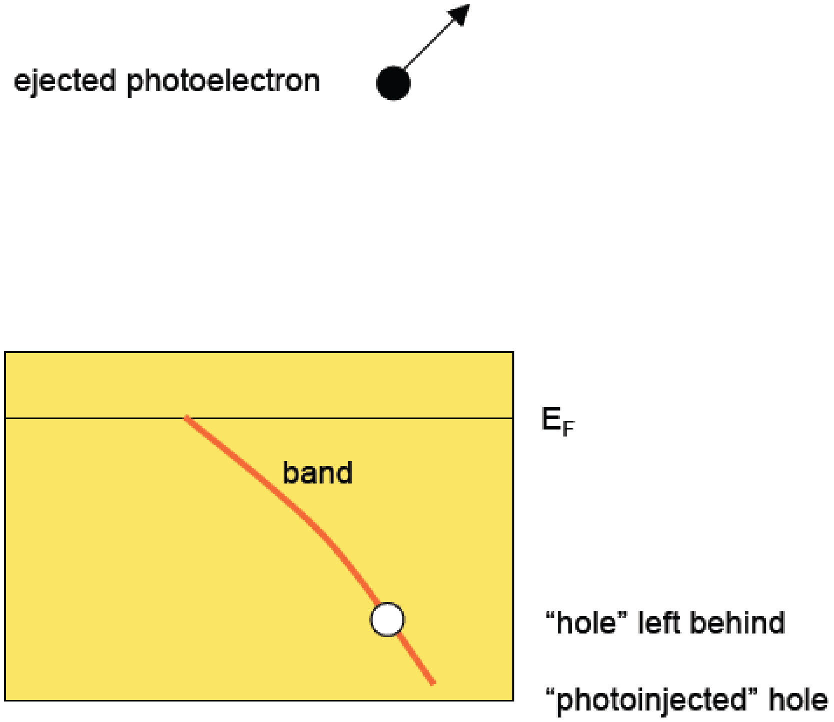
What does ARPES measure

$$I \propto \sum_{f,i,\mathbf{k}} \left| \langle \phi_f | H_{\text{int}} | \phi_i \rangle \right|^2 A(\mathbf{k}, E)$$

Matrix element

Spectra function



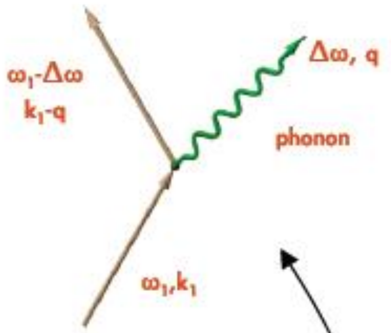
we believe the properties of the photoelectron reflect the properties of the injected hole

namely,

we can learn about the scattering and lifetime of the injected hole

Eli Rotenberg, ALS summer school

The carriers have a finite lifetime due to absorption and emission of phonons and other excitations



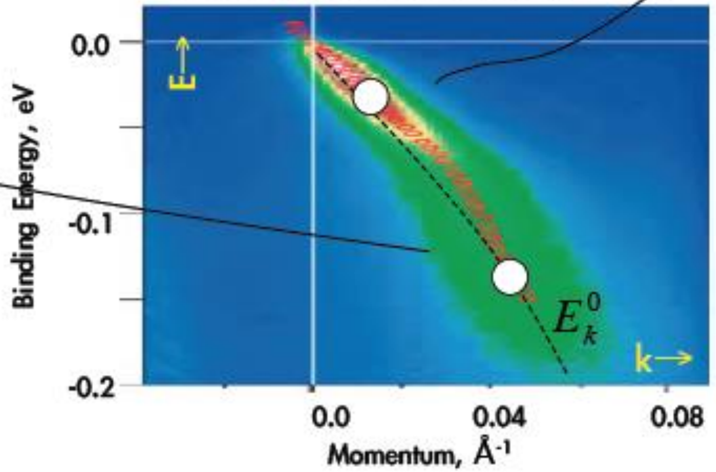
electron emits a phonon : change of energy **ω** and momentum *k*

The measured state is broader in momentum and energy

electron emits and reabsorbs a phonon :Change of mass and slope

The mass of carrier is increased

BSCCO Superconductor Results [1]



there is no direct way to probe these processes except through ARPES measurments

Self energy in photoemission spectra

The quantity determined in ARPES experiments is the single-particle spectral function

$$G(k,\omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(k,\omega)}$$

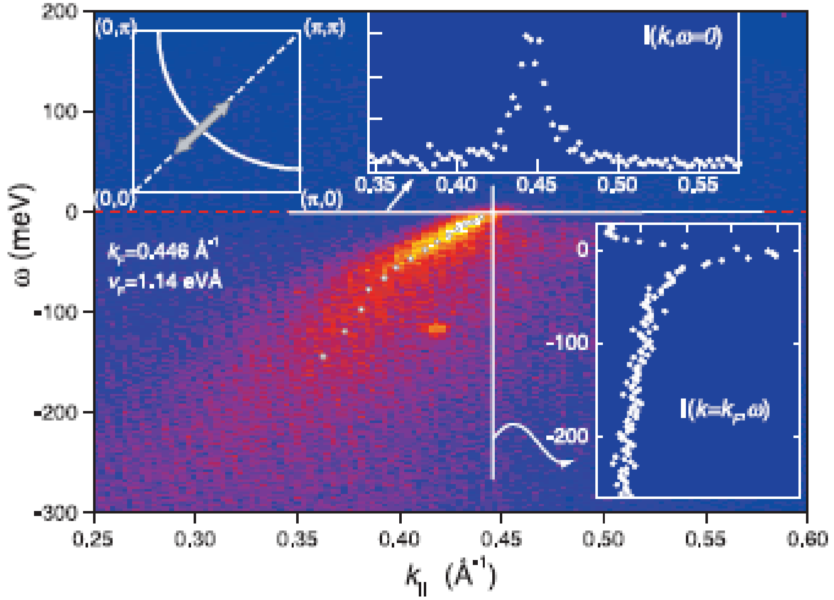
$$A(k,\omega) = \frac{\mathrm{Im}\,\Sigma(k,\omega)}{[\omega - \varepsilon_k - \mathrm{Re}\,\Sigma(k,\omega)]^2 + [\mathrm{Im}\,\Sigma(k,\omega)]^2}$$

$$\Sigma = \mathrm{Re}\,\Sigma + i\,\mathrm{Im}\,\Sigma$$

Dispersion:
E-k Relation (Velocity;
Effective mass etc.)

Scattering rate
(Lifetime)

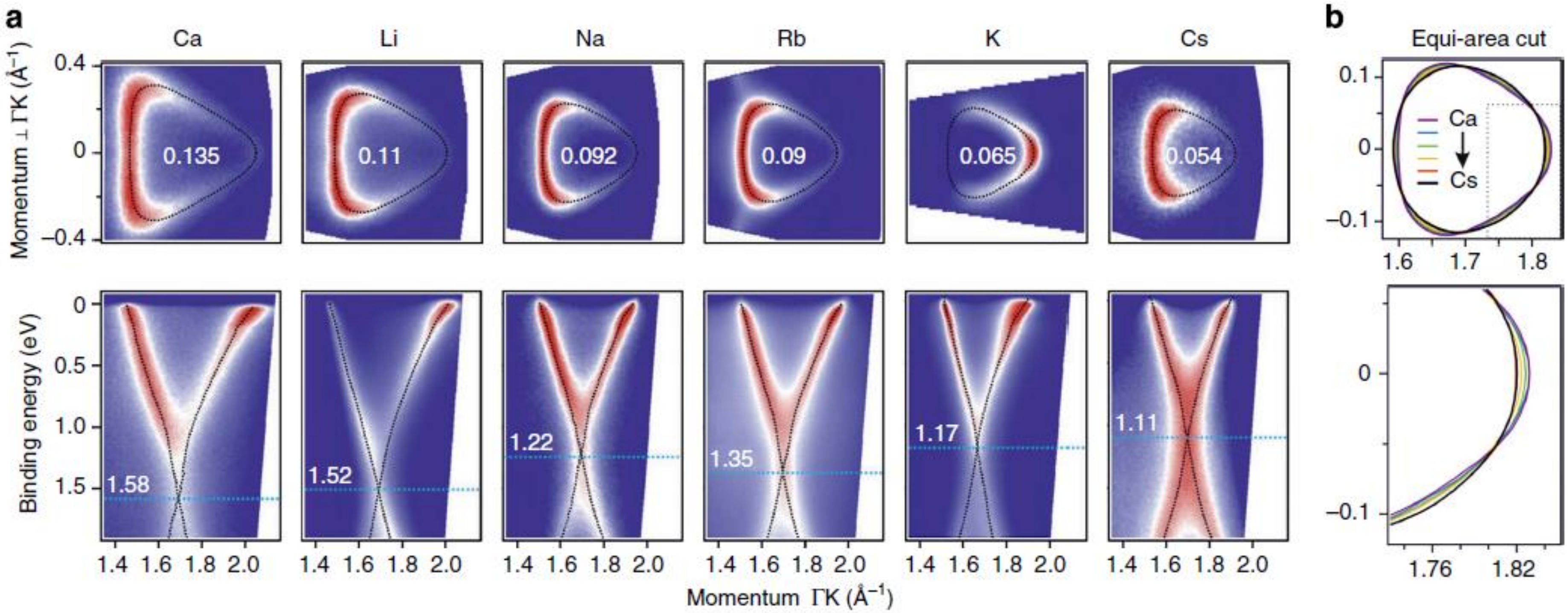
Optimally doped Bi-2212 cuprate



$$\hbar v_k \Delta k = \frac{\hbar v_k}{l} = \left|2\,\mathrm{Im}\,\Sigma(k,\omega)\right|$$

T. Valla et al., Science 285, 2110 (2000)

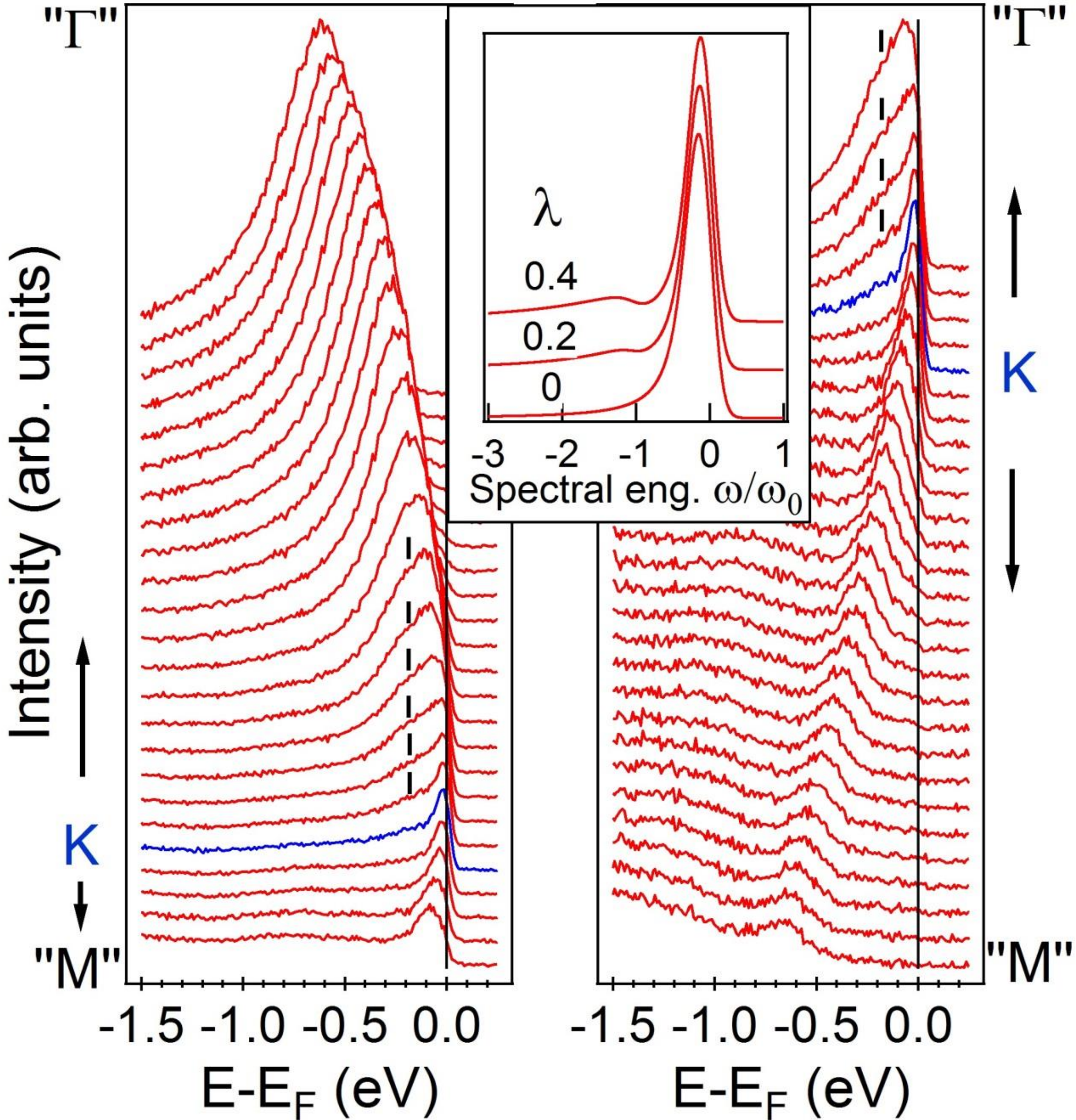
Electron-phonon interaction in doped graphene



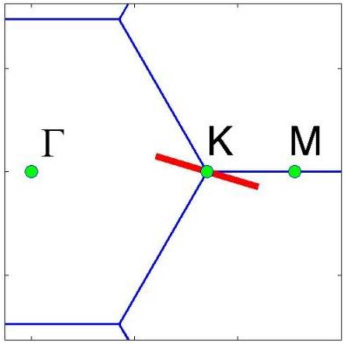
国家同步辐射研究中心
National Synchrotron Radiation Research Center

Fedorov, Nat. Comm. (2014)

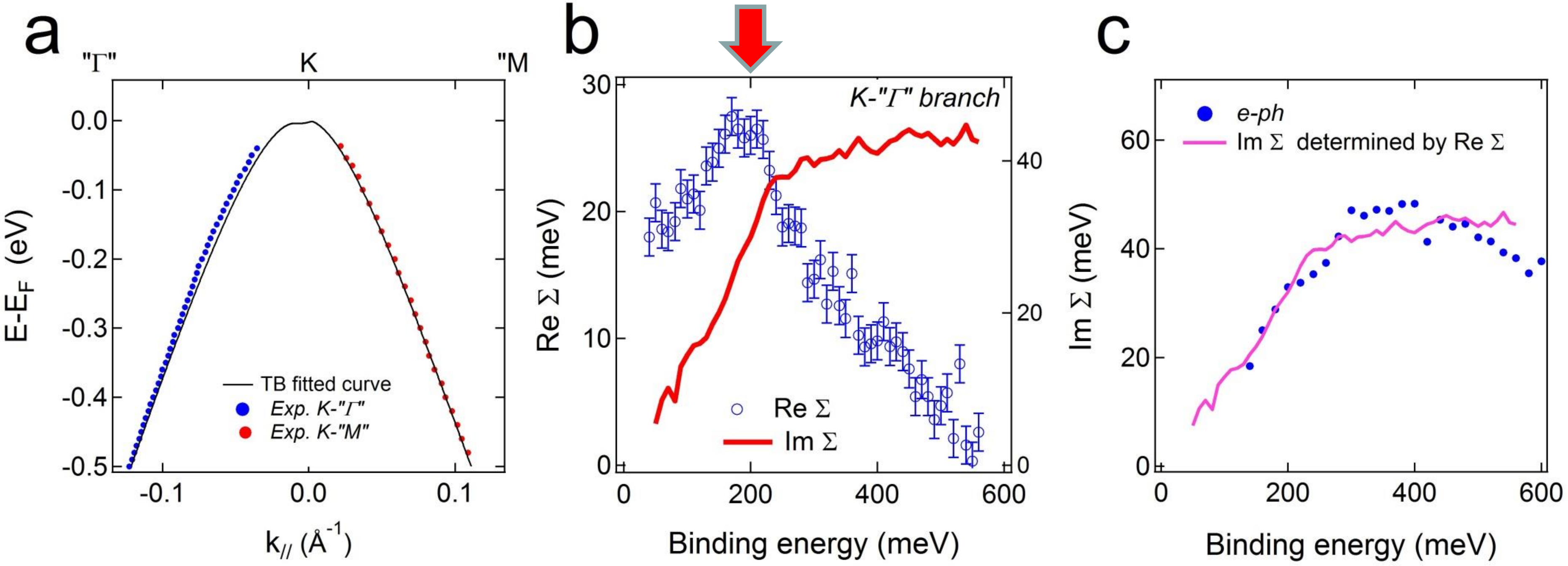
Anisotropic *e-ph* interaction property on K-Γ and K-M branches



A bump appears at 200 meV due to the optical phonon

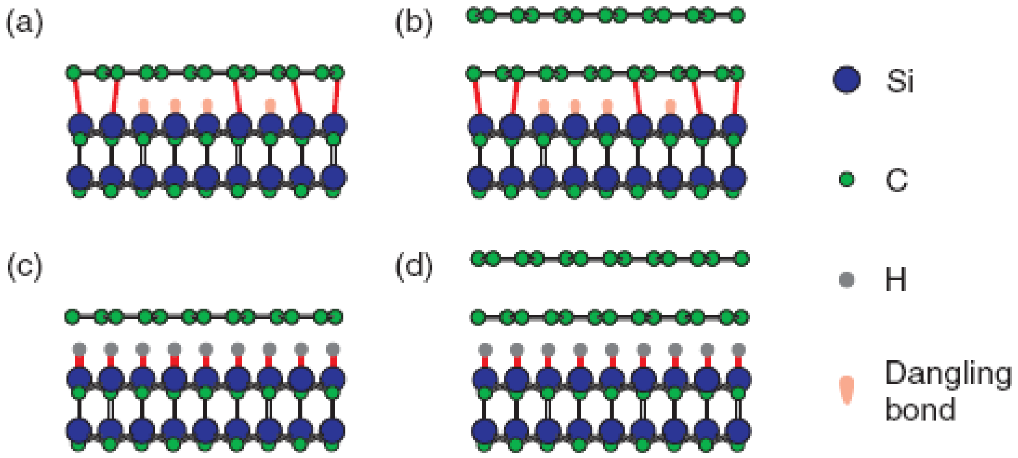


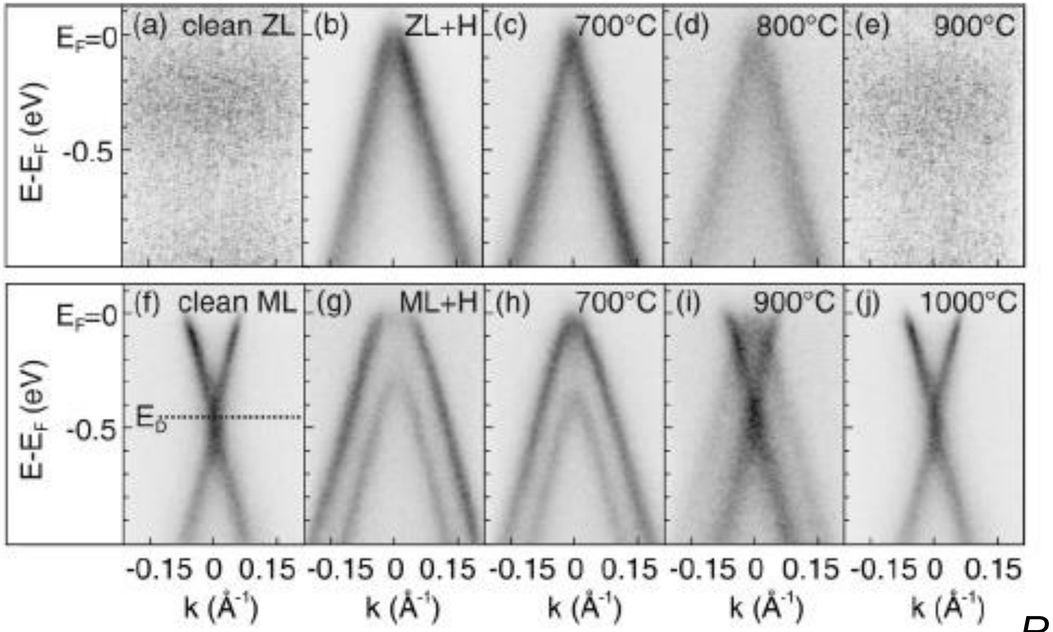
The KK transformation between Re Σ and Im Σ



Im Σ extracted from the width of line shape analysis is consistent with Im Σ determined by Re Σ

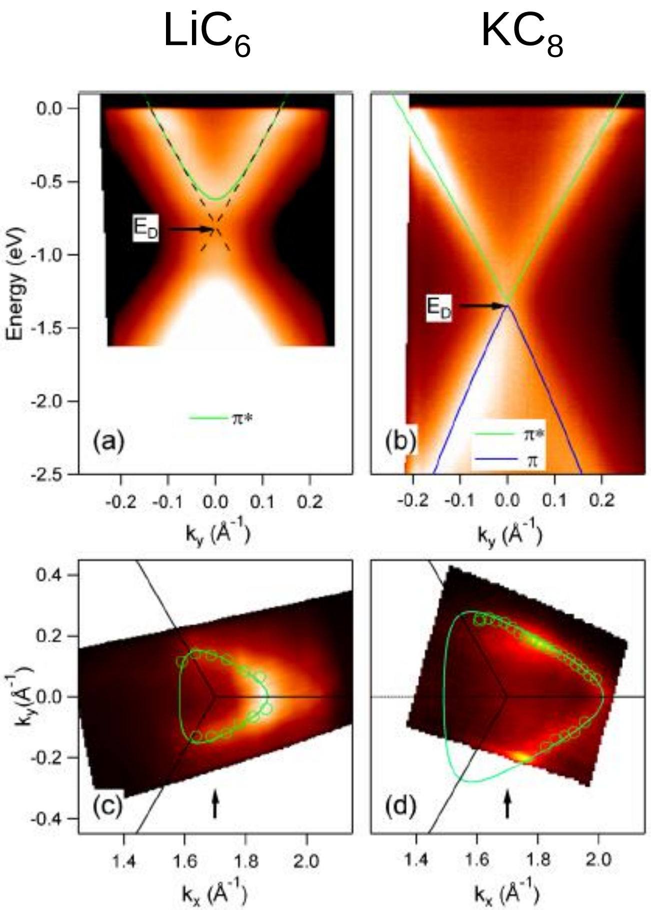
Hydrogen intercalated graphene/SiC

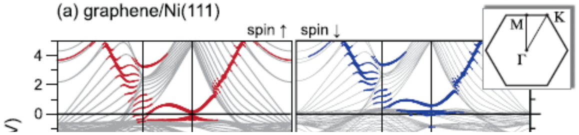


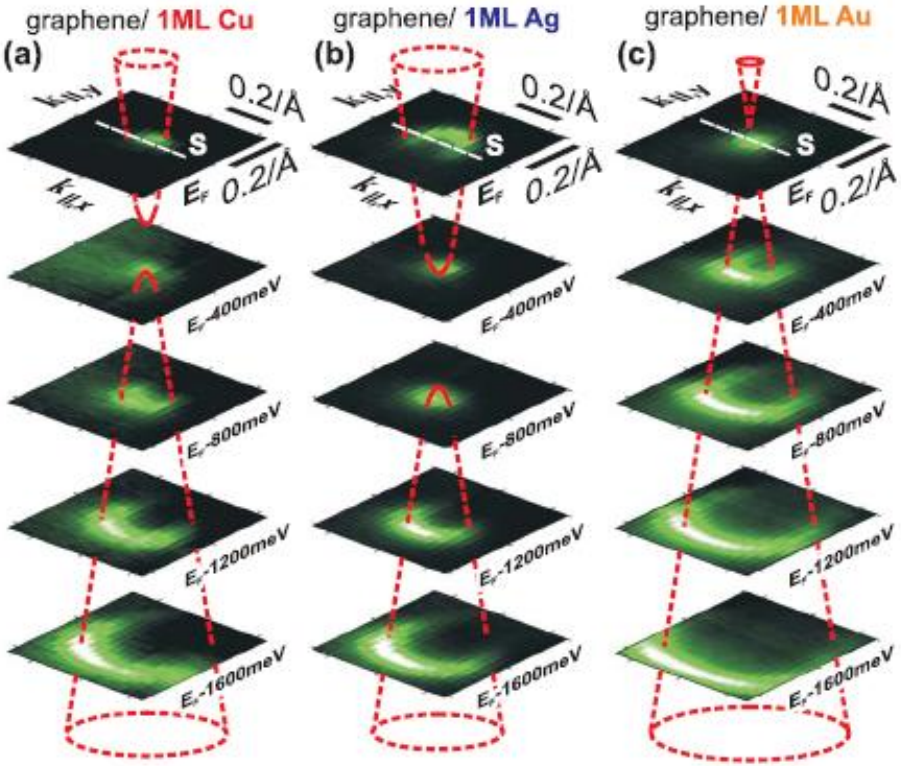


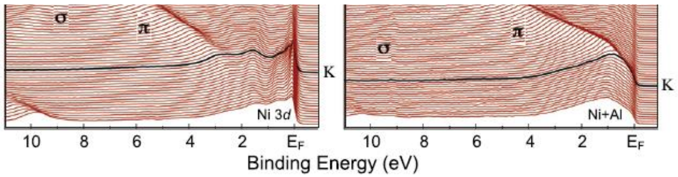
Riedl et al., PRL (2009)

Graphene intercalated compounds (GICs)









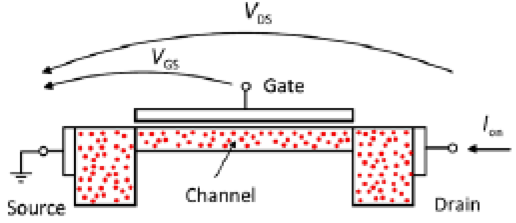
Pan et al., PRL (2011)

Voloshina et al., NJP (2011)

Varykhalov et al., PRB (2010)

Beyond Graphene :
Graphene nanoribbons (GNRs), transition metal dichalcogenides (TMDs), black phosphorus (BP), stanene and van der Waals heterstructure

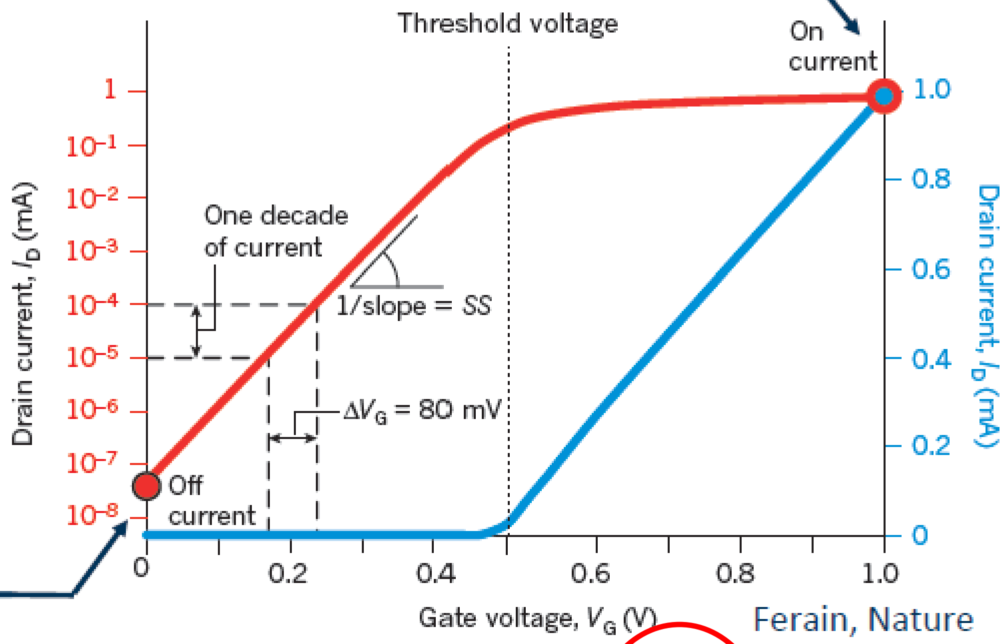
FET Basics – Digital CMOS



On-state

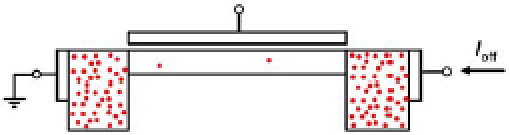
Requirements for logic

- High on-off ratio I_{on}/I_{off} $10^4 \ldots 10^7$.
- High I_{on} (high speed).
- Low I_{off} (low static power).
- Steep slope in sub-threshold, i.e., small *SS*.



Ferain, Nature 479, 310 (2011).

Off-state

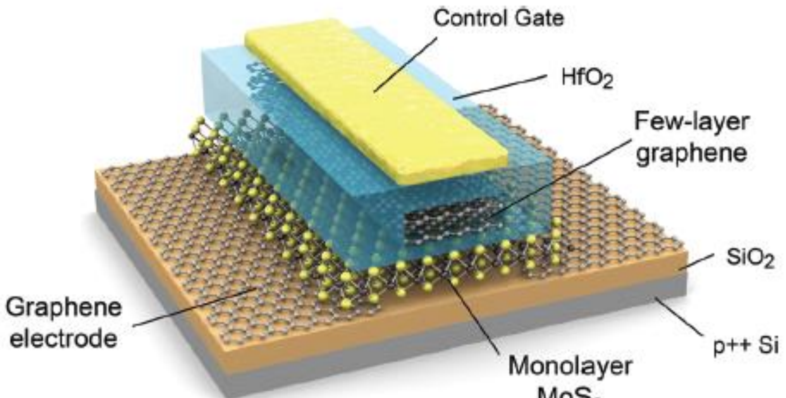


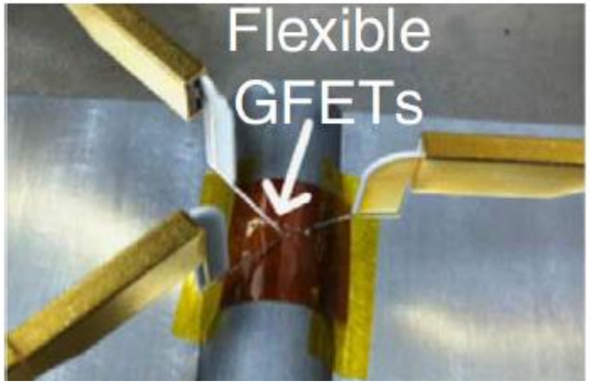
Long channels: $I_{\text{off}} \propto \exp \dfrac{-E_G}{m\, k_B\, T}$

A sizeable gap is mandatory!

Frank Schwierz, Nanoscale (2015)

2D materials :potential candidates for future applications





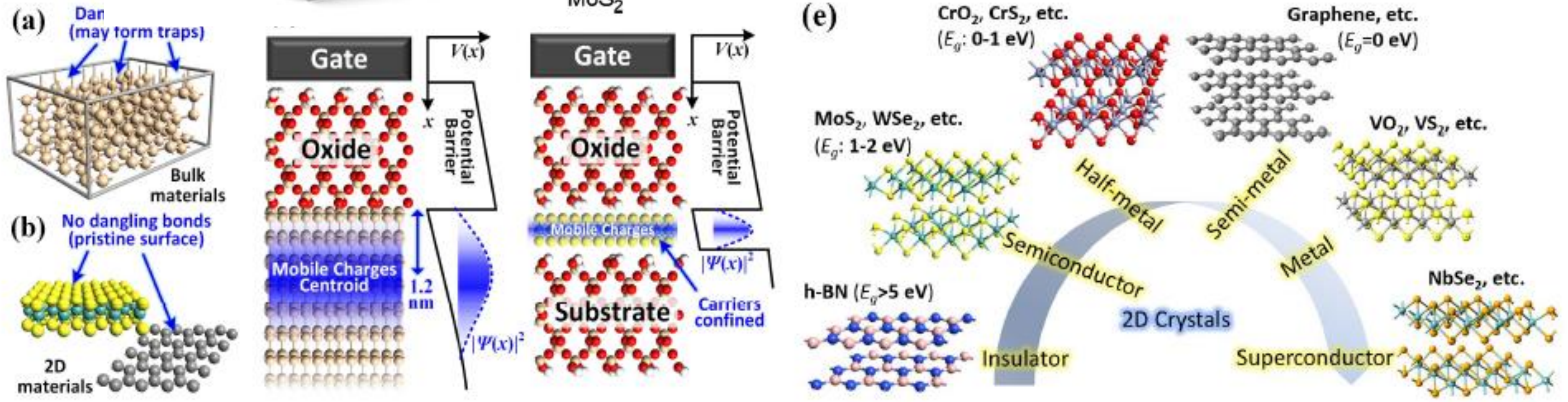


Figure 1. Schematic illustrating advantages of 2D materials: surfaces of **(a)** 3D and **(b)** 2D materials. The pristine interfaces (without out-of-plane dangling bonds) of 2D materials help reduce the interface traps. Mobile charge distribution in **(c)** 3D and **(d)** 2D crystals used as channel materials. The carrier confinement effect in 2D materials leads to excellent gate electrostatics. **(e)** Various types of 2D materials from insulator to superconductor. E_g denotes the band gap.

Kang et al., Proc. SPIE (2014)

Graphene family

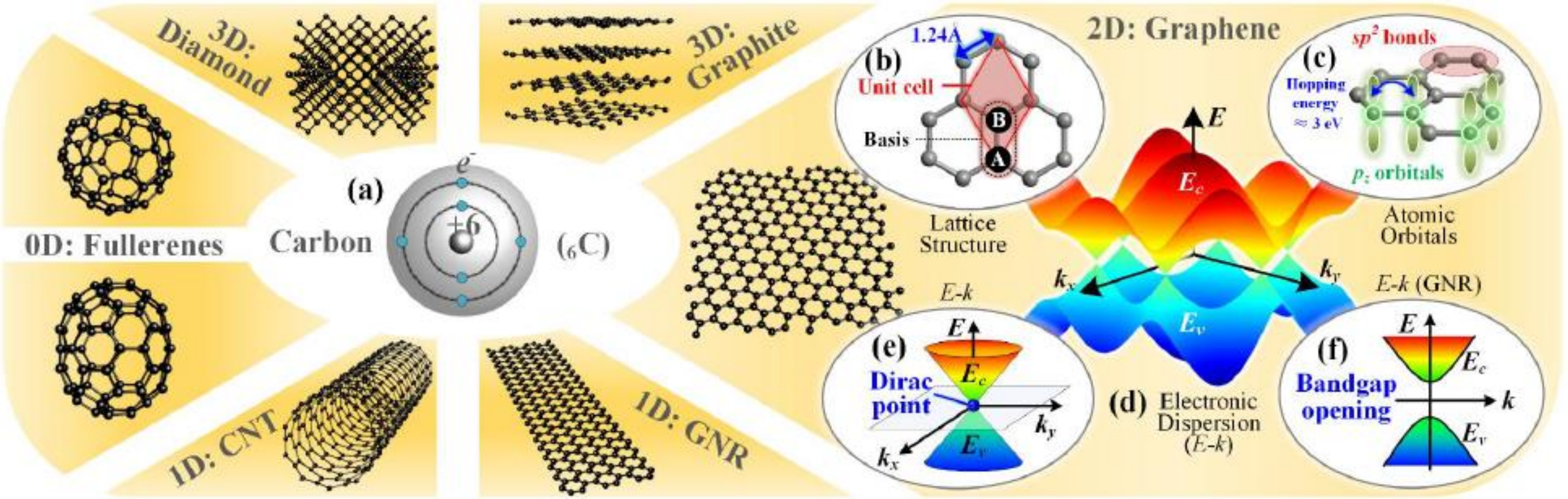
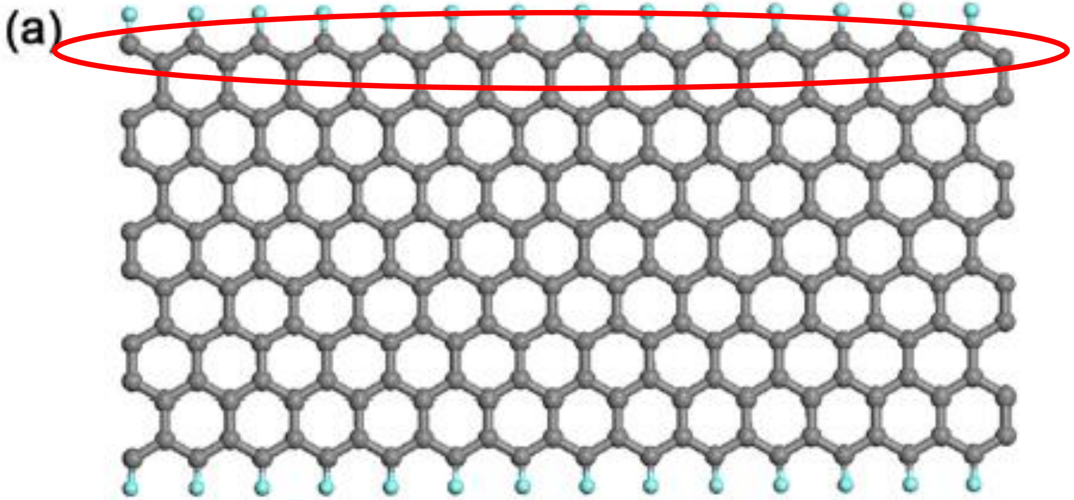


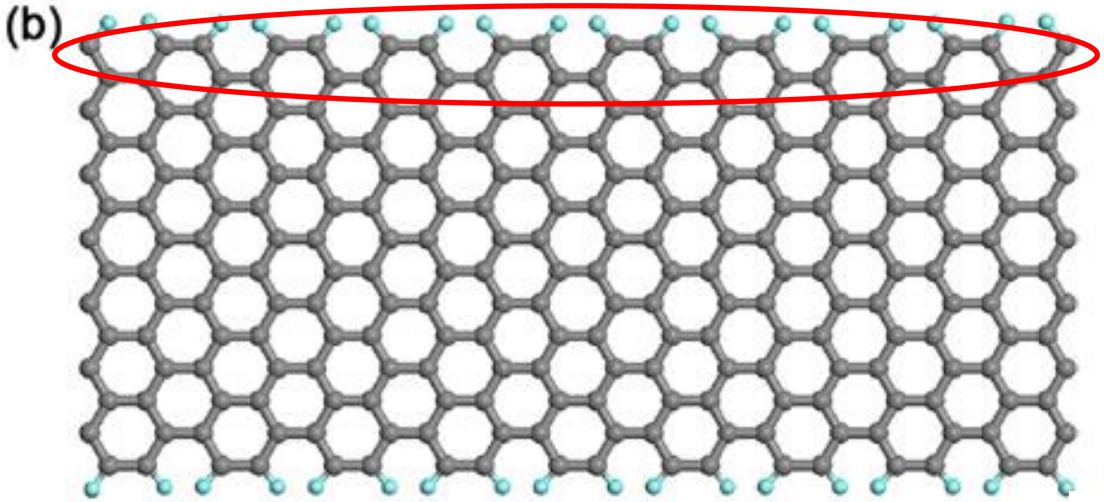
Figure 2. **(a)** Schematic of carbon atom and carbon allotropes, from 0D to 3D; **(b)** unit cell, basis and bond length of graphene; **(c)** atomic orbitals of graphene; **(d, e)** energy dispersion of graphene, where the energy dispersion is linear for low energies near the six corners (Dirac points) of the two-dimensional hexagonal Brillouin zone. **(f)** Energy dispersion of a semiconducting GNR, where a bandgap can be engineered by varying the width.

Kang et al., Proc. SPIE (2014)

Crystal structure of GNRs

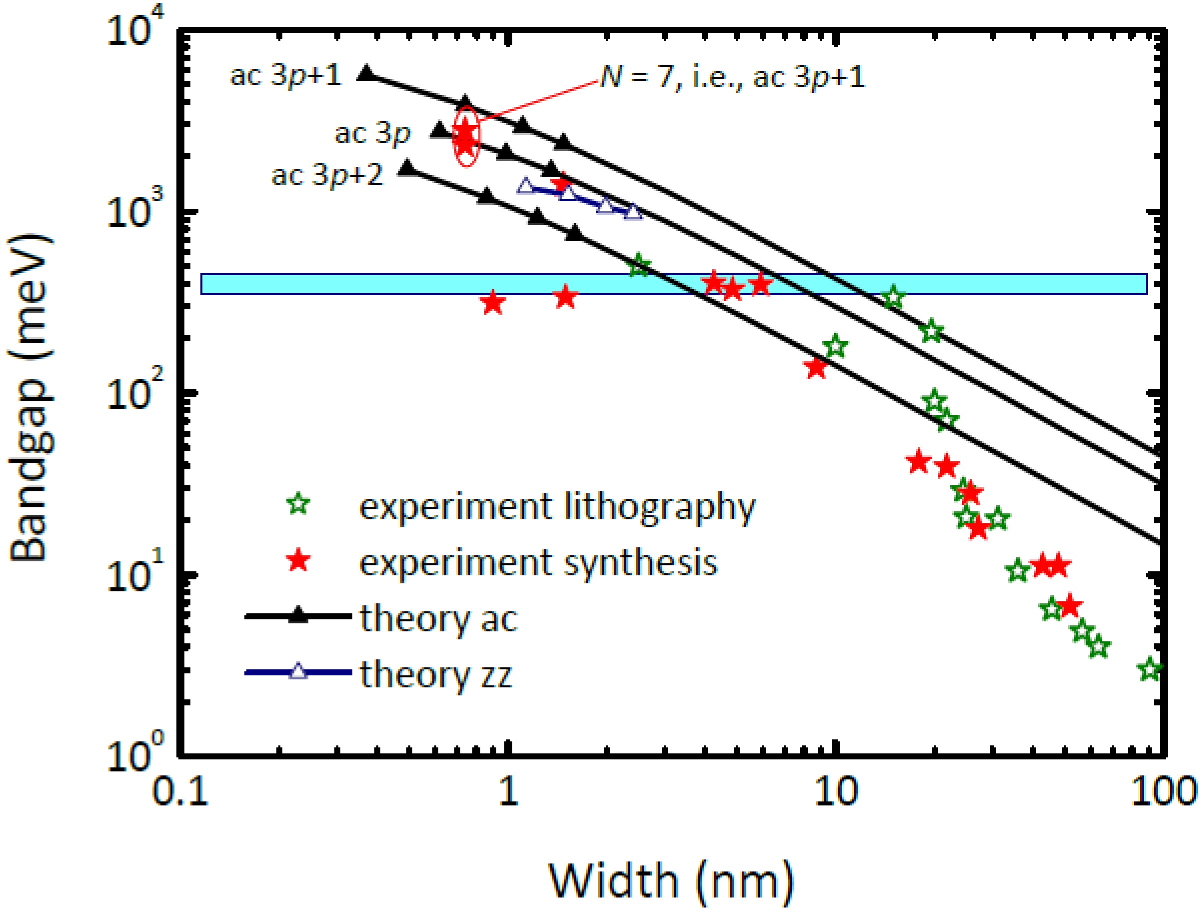


Armchair Graphene Nanoribbons (AGNRs)
TB simulation : semiconducting or metallic depending on the width of AGNRs



Zigzag Graphene Nanoribbons (ZGNRs)
TB simulation : metallic for all ZGNRs

H. Terrones et al., Rep. Prog. Phys. (2012)



GNR bandgap vs width.

FS, Pezoldt, Granzner, Nanoscale 2015.

The bandgap of GNRs depends strongly on the ribbon width and the edge configuration!

國家同步輻射研究中心
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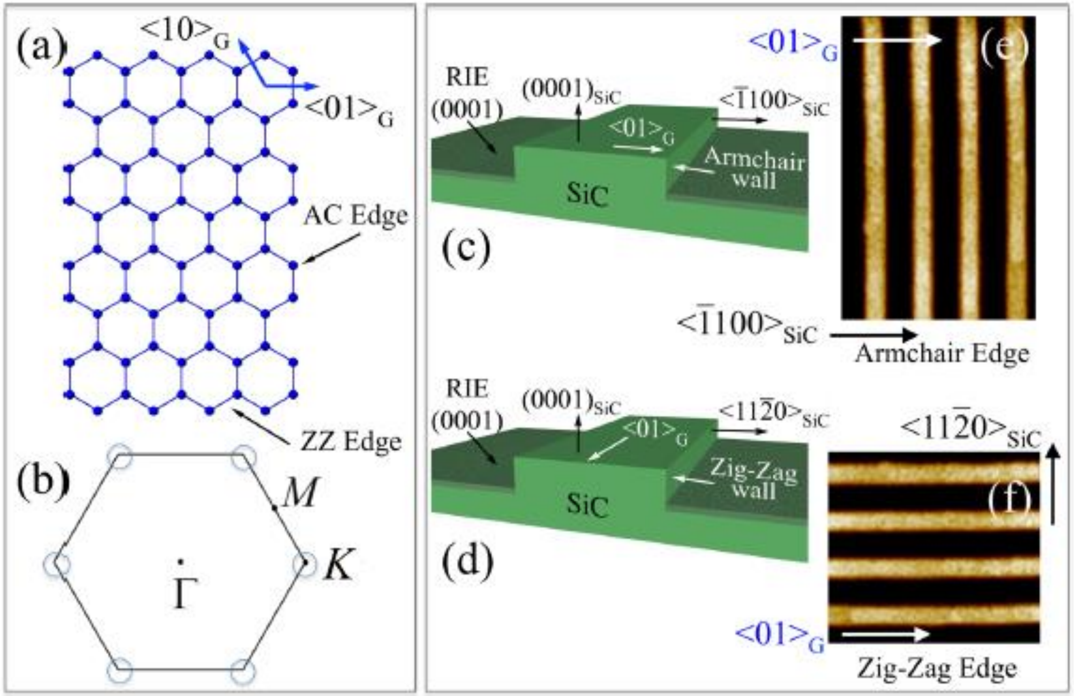
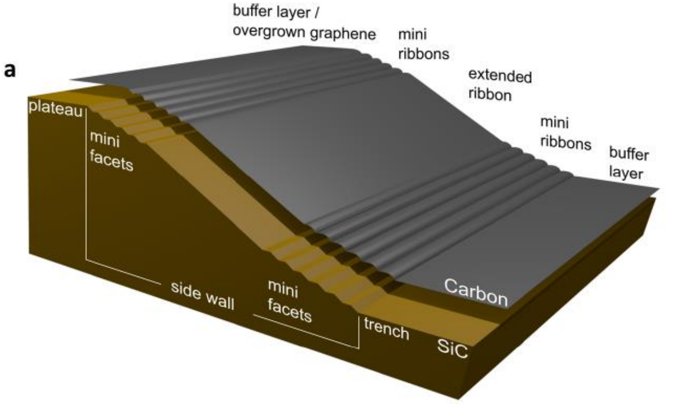
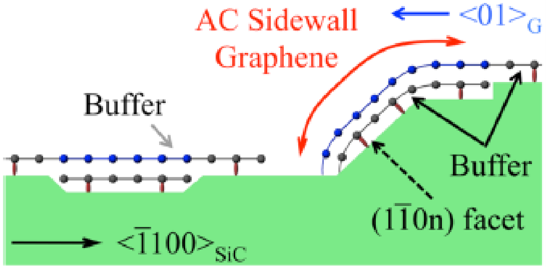
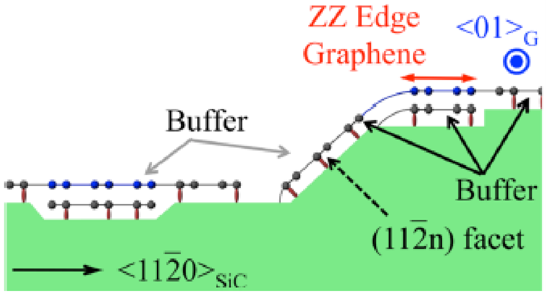
Frank Schwierz, Nanoscale (2015)

Sample preparation for GNRs





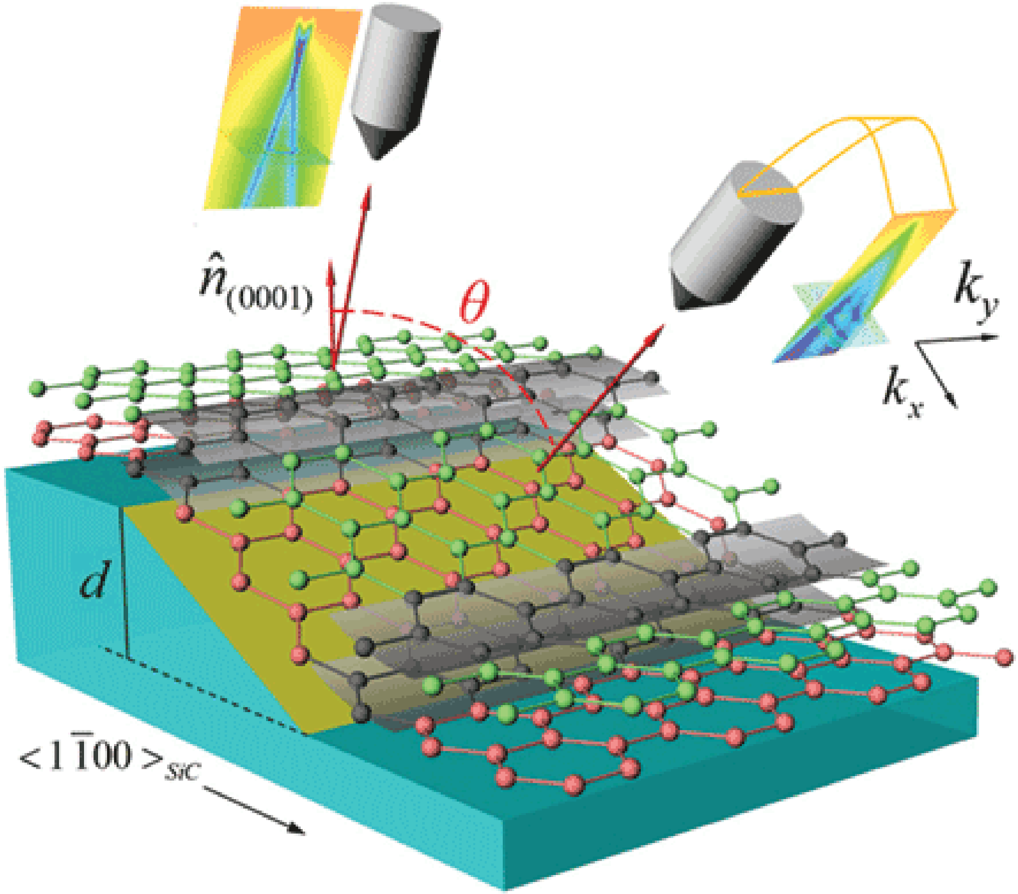


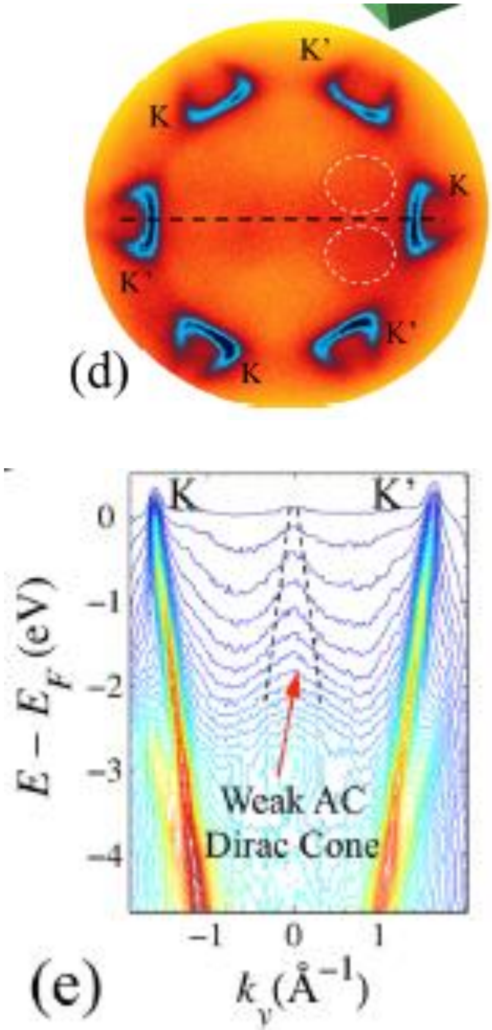


Nevius et al., Nano Lett. (2014)

Palacio et al., Nano Lett. (2014)

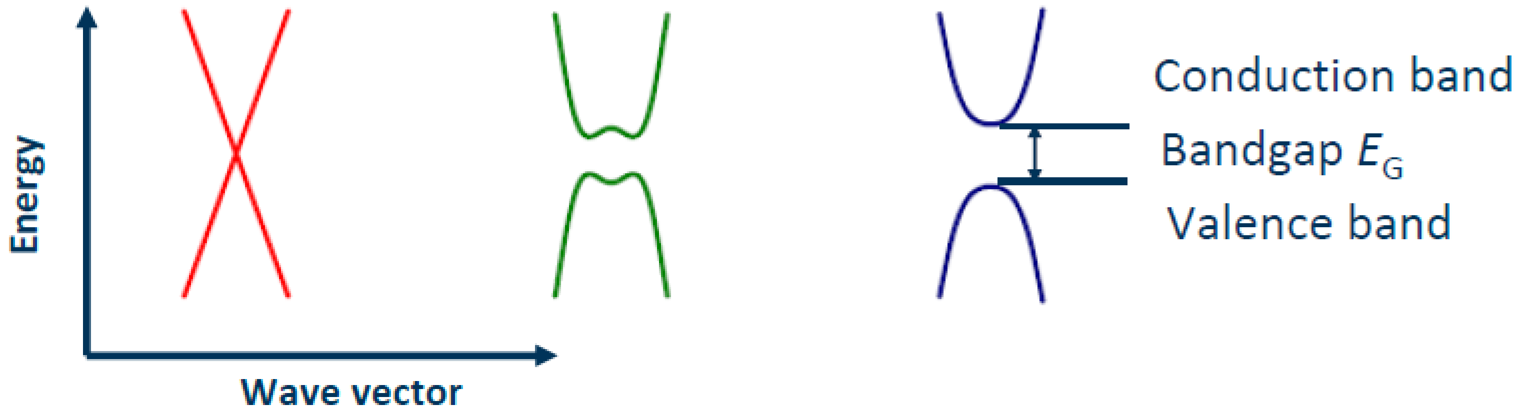
Using ARPES to probe GNRs/SiC





Nevius et al., Nano Lett. (2014)

2D Materials – An (Incomplete) Overview



X-enes
- Graphene
- Silicene
- Germanene

No gap, $E_G = 0$! This is really a pitty, since the missing gap causes serious problems for transistors.

BLG

$E_G \leq 130$ meV Too narrow for logic transistors.

X-enes
- Phosphorene
- Stanene
- GNRs

X-anes
- Graphane
- Silicane
- Germanane

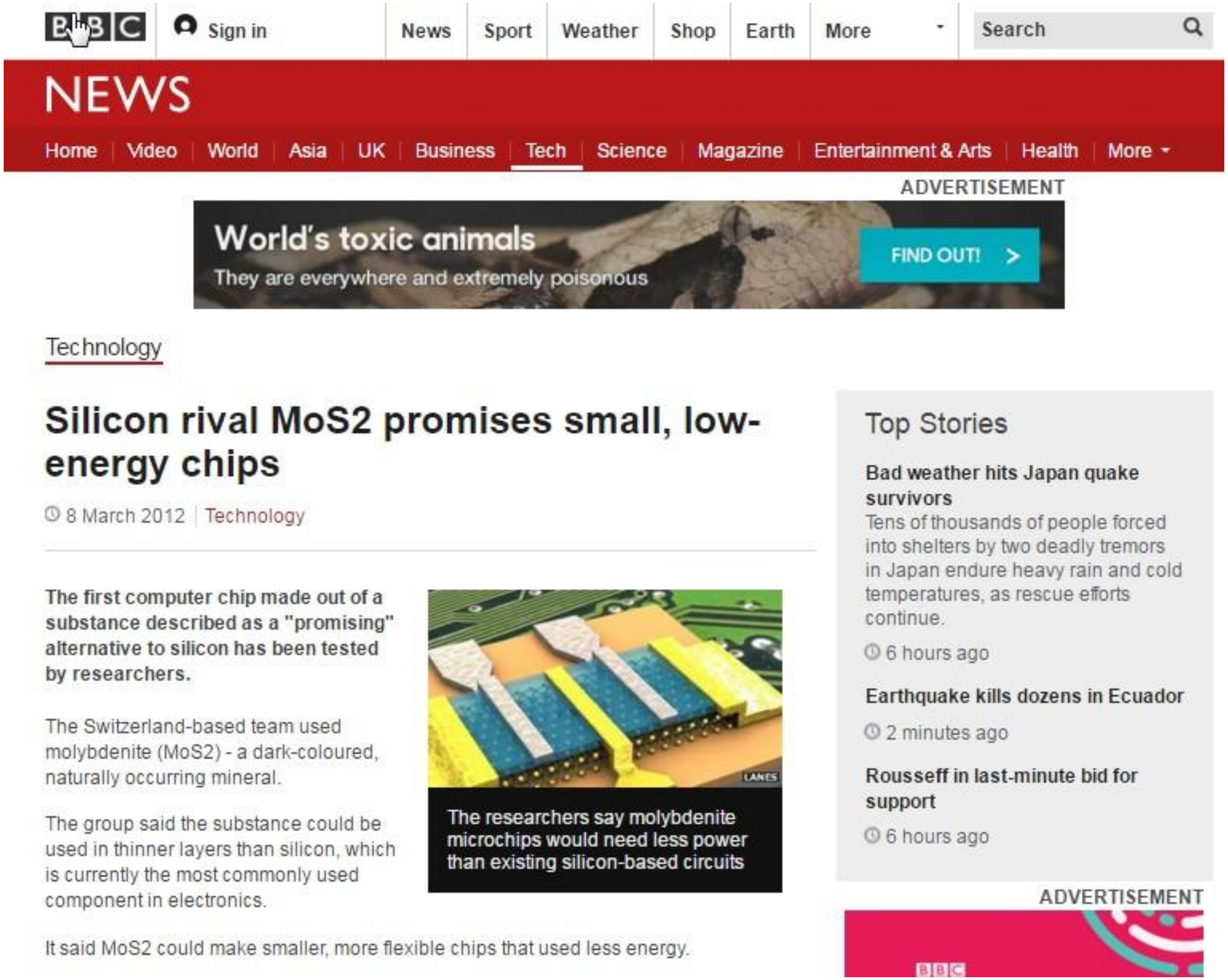
MX-enes
- Sc_2CF_2
- $TiCO_2$

2D TMDs
- MoS_2, $MoSe_2$, $MoTe_2$
- WS_2, WSe_2, WTe_2

etc., etc.

Many of these materials have a gap $E_G = 0.5... 2.5$ eV, perfect for transistors.

Frank Schwierz, Nanoscale (2015)



Technology

Silicon rival MoS2 promises small, low-energy chips

8 March 2012 | Technology

The first computer chip made out of a substance described as a "promising" alternative to silicon has been tested by researchers.

The Switzerland-based team used molybdenite (MoS2) - a dark-coloured, naturally occurring mineral.

The group said the substance could be used in thinner layers than silicon, which is currently the most commonly used component in electronics.

It said MoS2 could make smaller, more flexible chips that used less energy.

The researchers say molybdenite microchips would need less power than existing silicon-based circuits

Top Stories

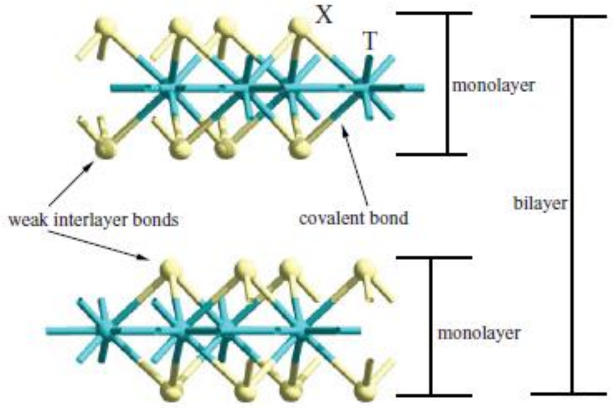
Bad weather hits Japan quake survivors
Tens of thousands of people forced into shelters by two deadly tremors in Japan endure heavy rain and cold temperatures, as rescue efforts continue.
6 hours ago

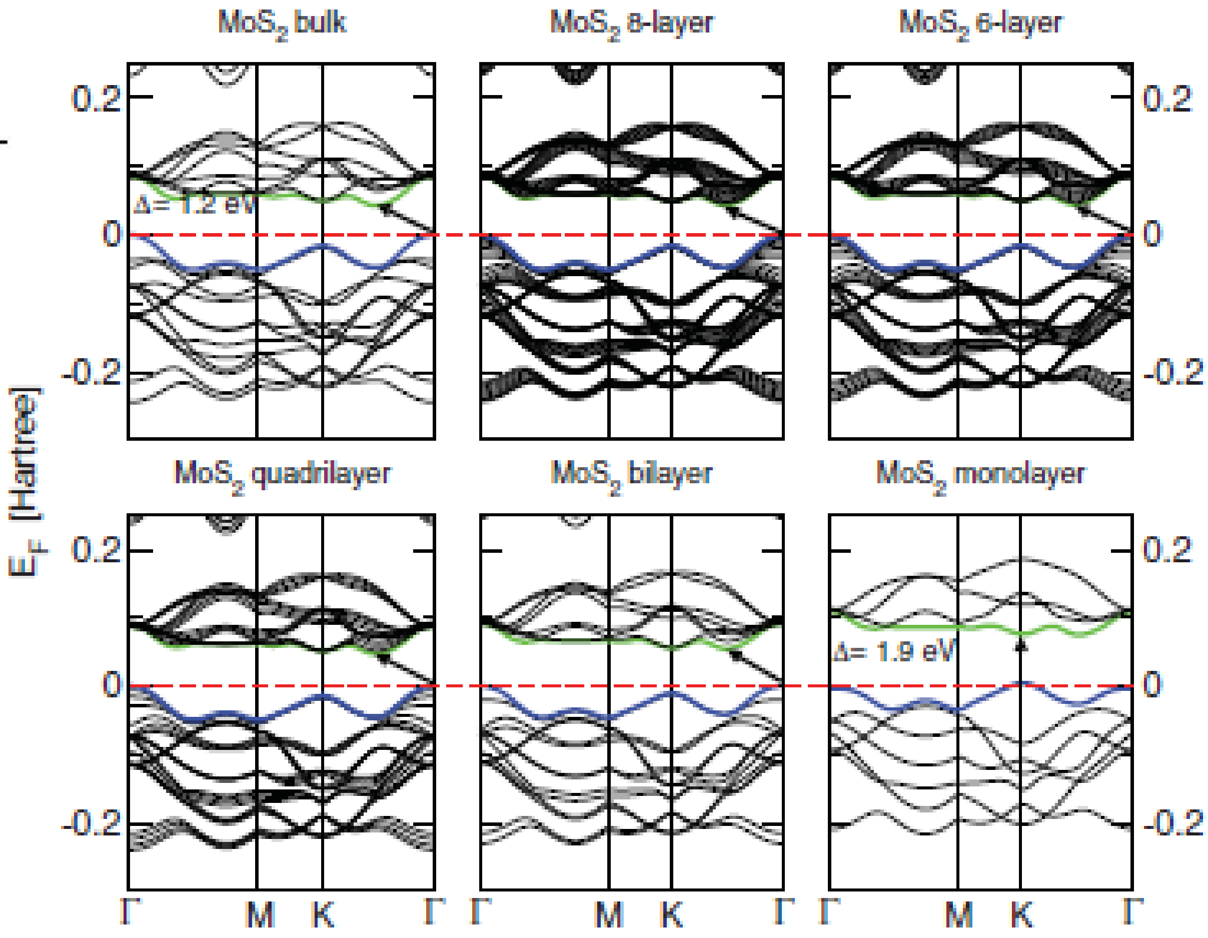
Earthquake kills dozens in Ecuador
2 minutes ago

Rousseff in last-minute bid for support
6 hours ago

A demonstration of electric transistor fabricated with monolayer MoS_2 shows high current on/off ratios of > 10^8 . Even the mobility ~ 200 $cm^2V^{-1}s^{-1}$ is much lower than that in graphene. The large current on/off ratio originates from sizeable band gap in MoS_2.

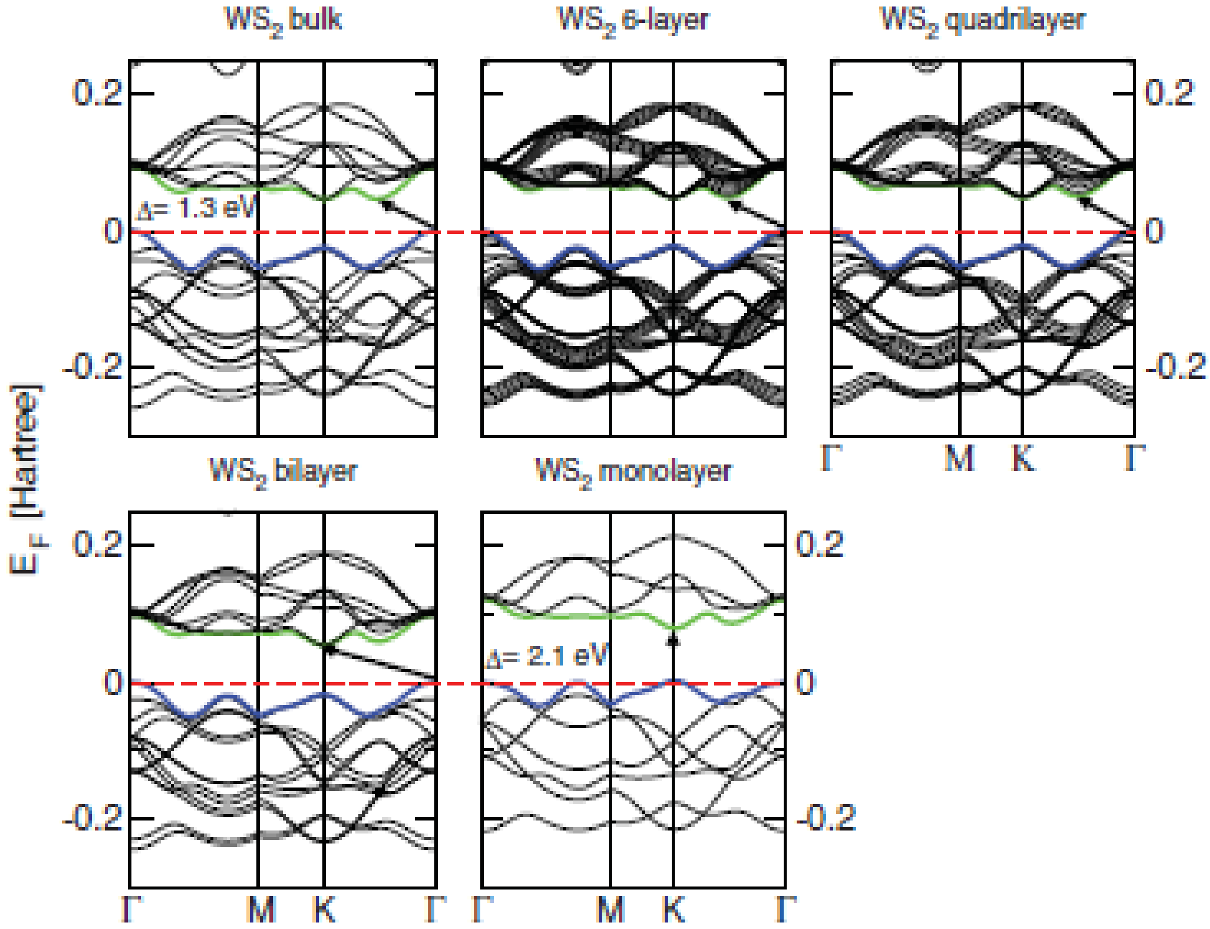
The band structure of MoS_2





Kuc et. al., PRB (2011)

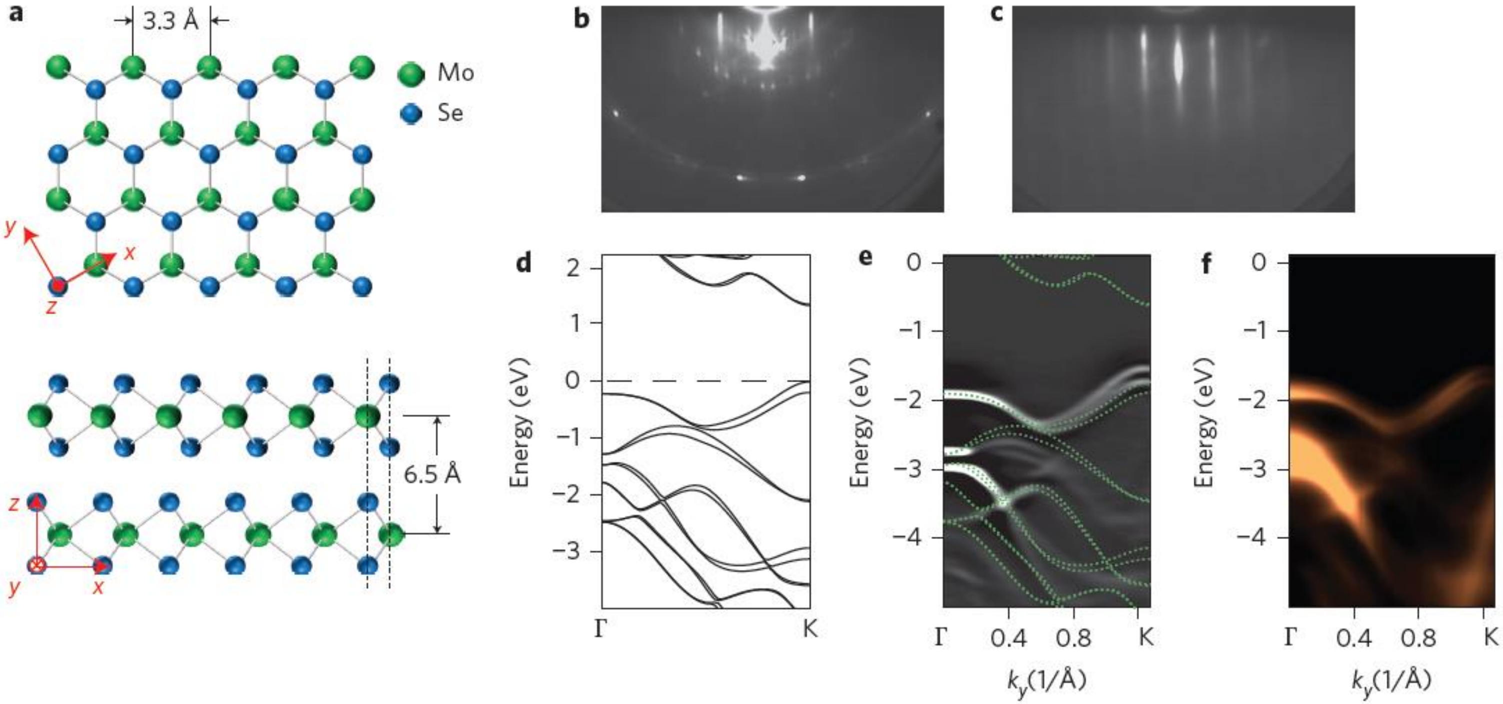
The band structure of WS_2



National Synchrotron Radiation Research Center

Kuc et. al., PRB (2011)

The electronic structure of $MoSe_2$



國家同步輻射研究中心
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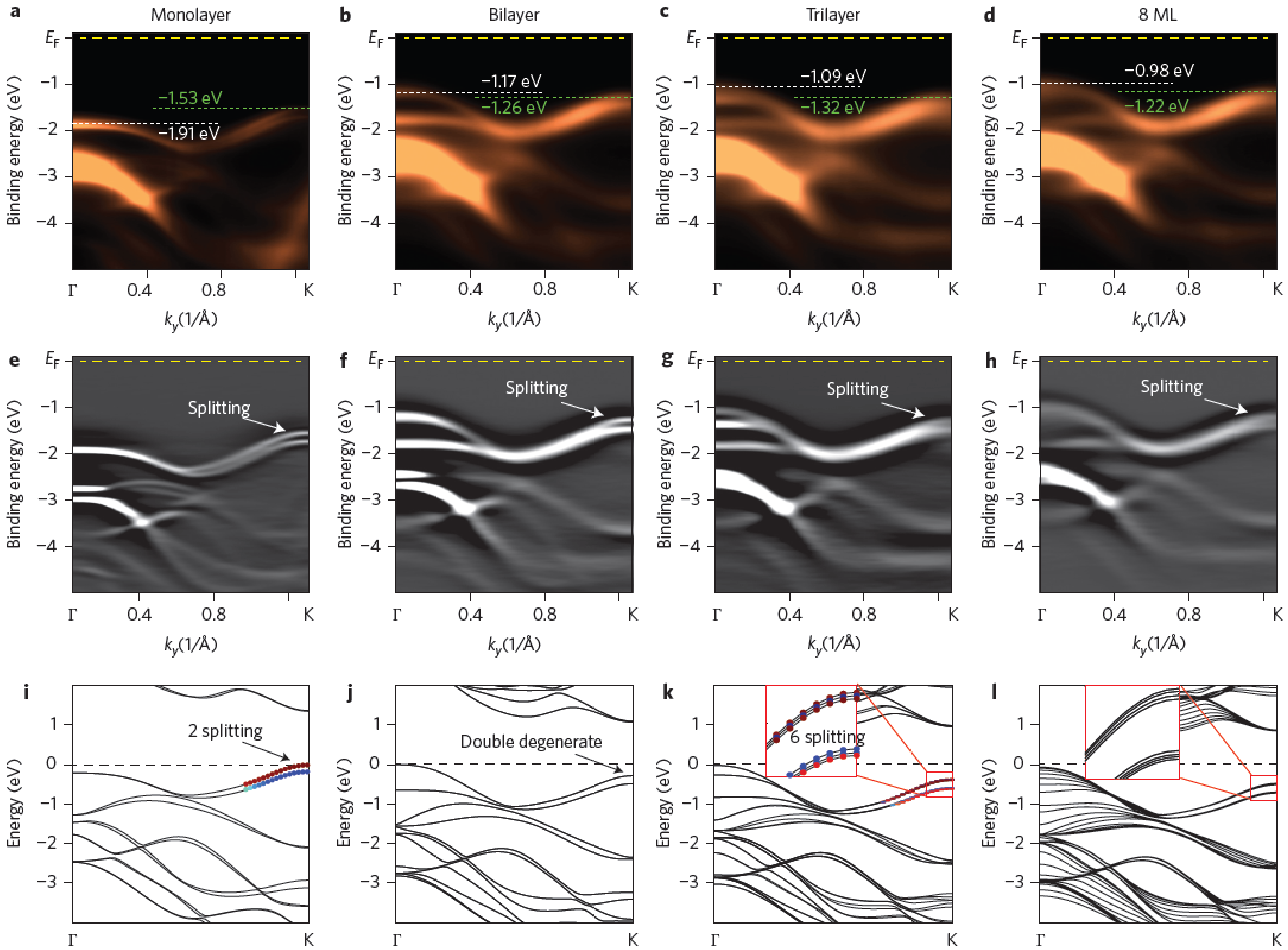
Zhang et al., Nat. Nano. (2013)



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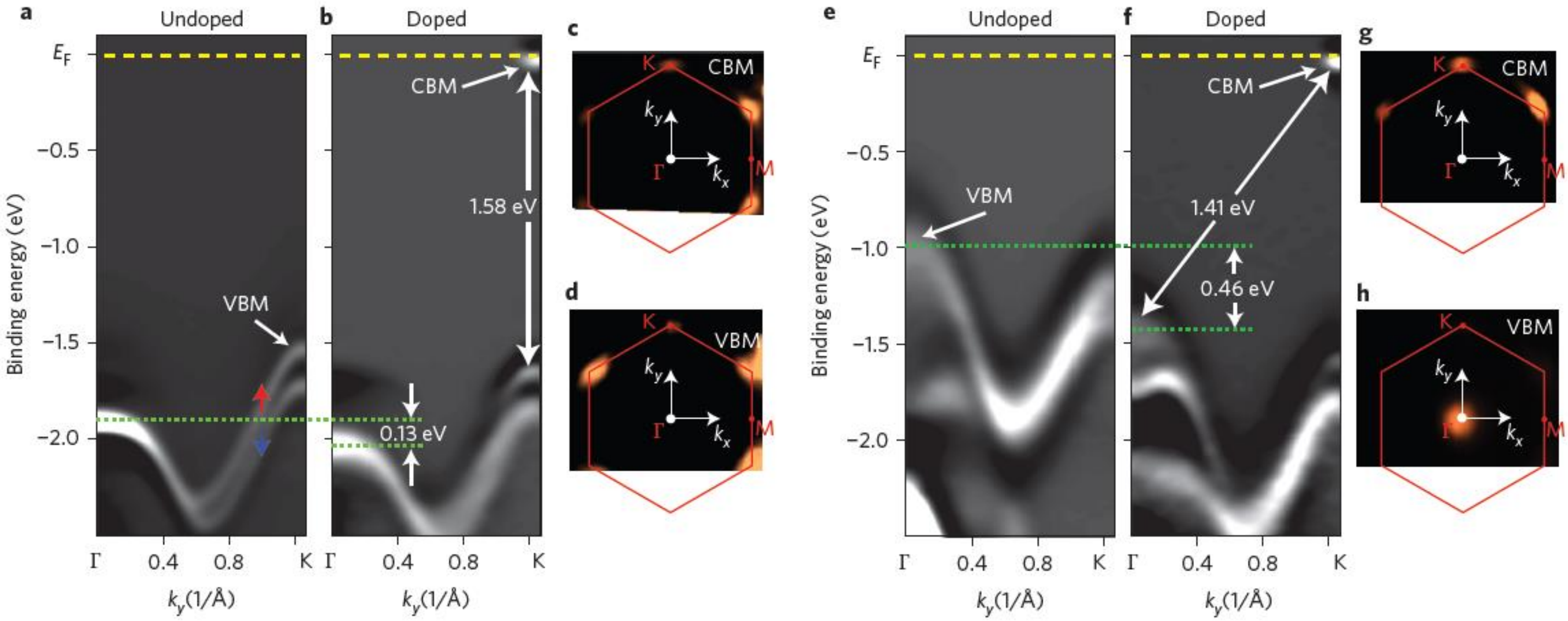
Zhang et al., Nat. Nano. (2013)

Alkali metal doped $MoSe_2$



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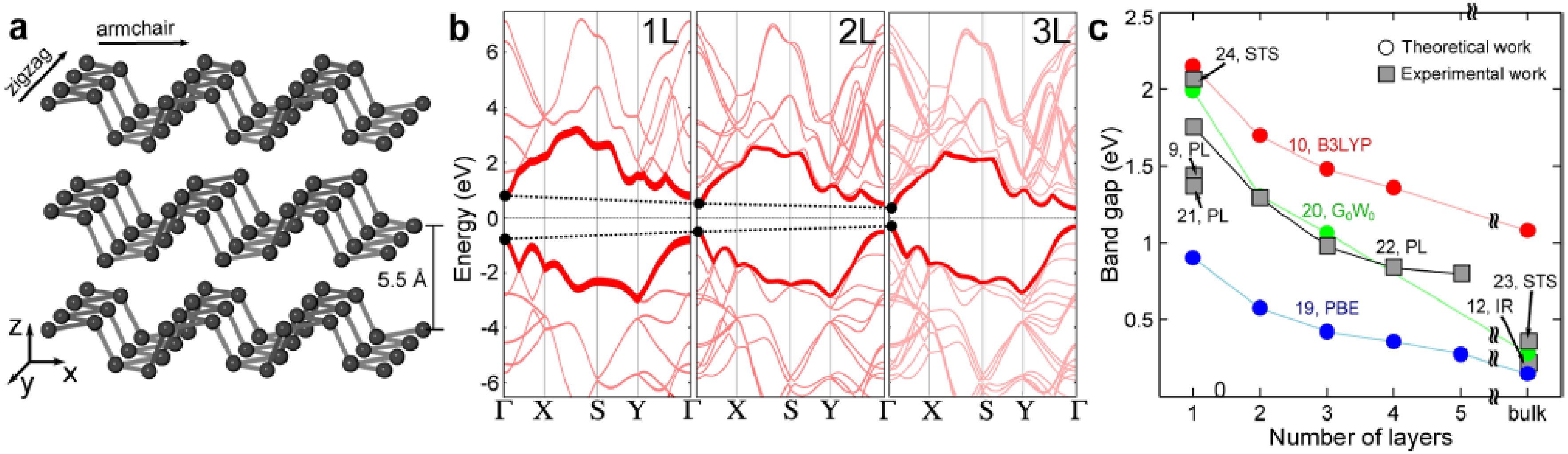
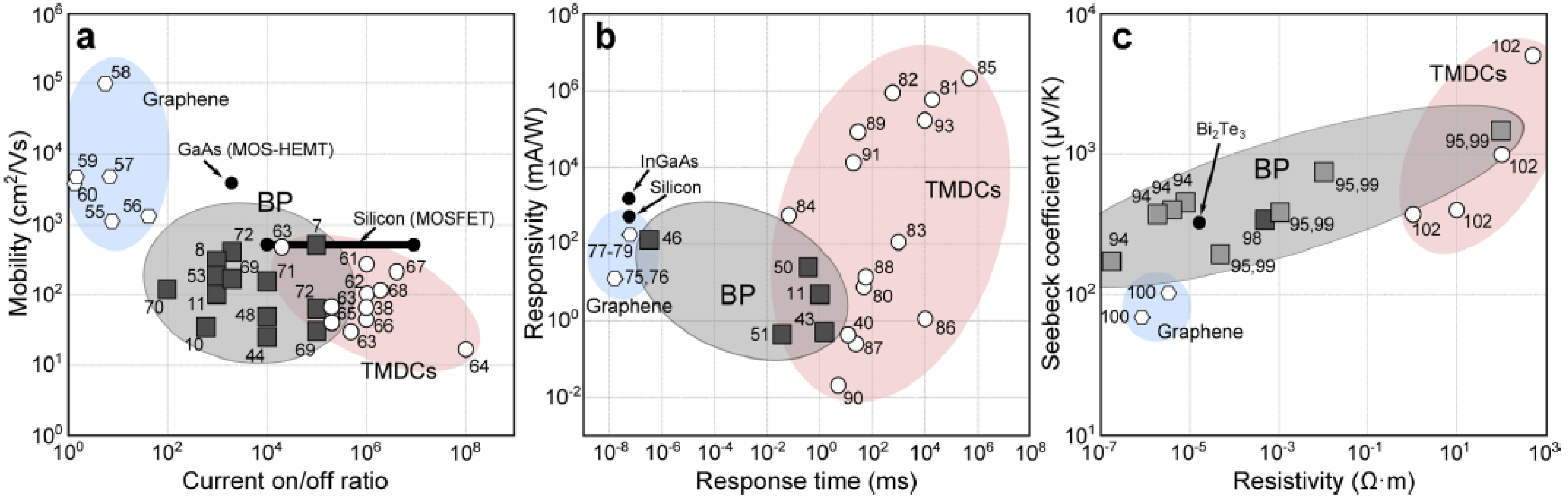
Zhang et al., Nat. Nano. (2013)

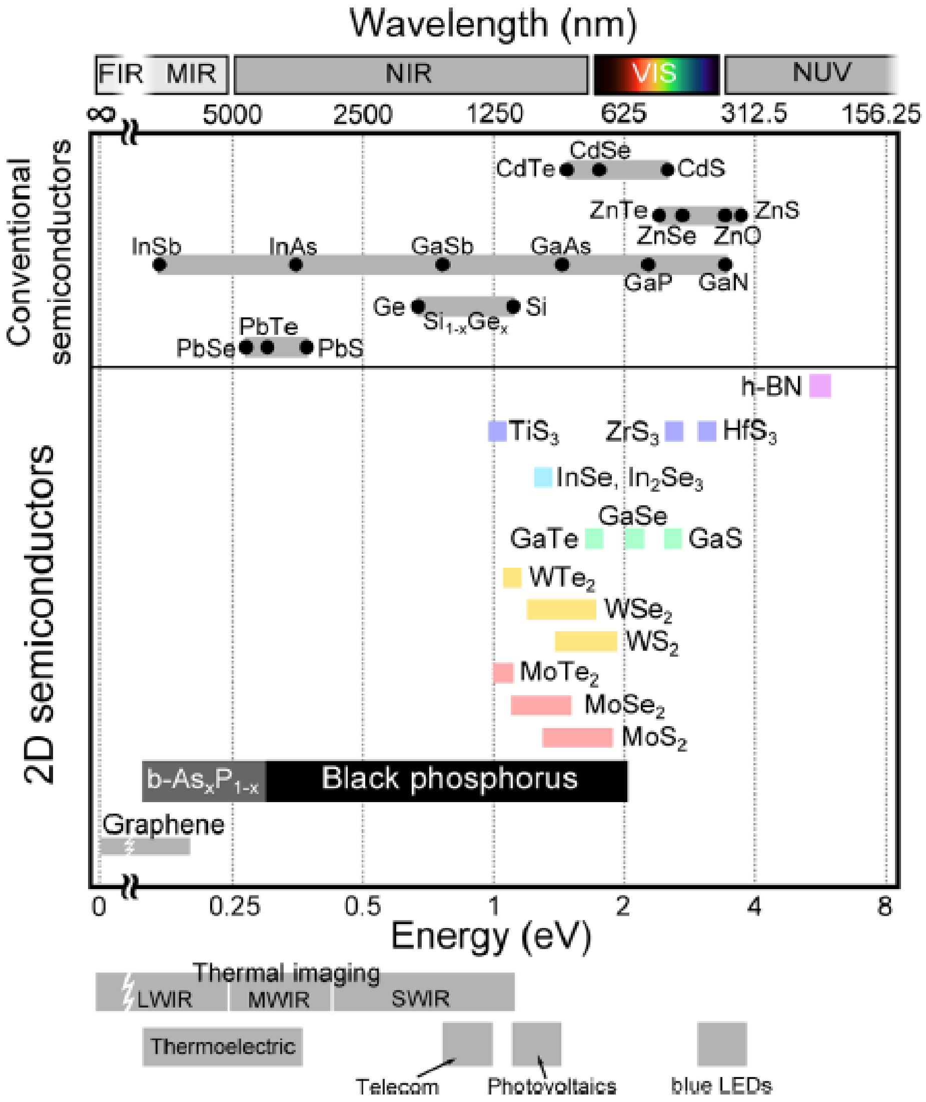
Black phosphorus (BP)

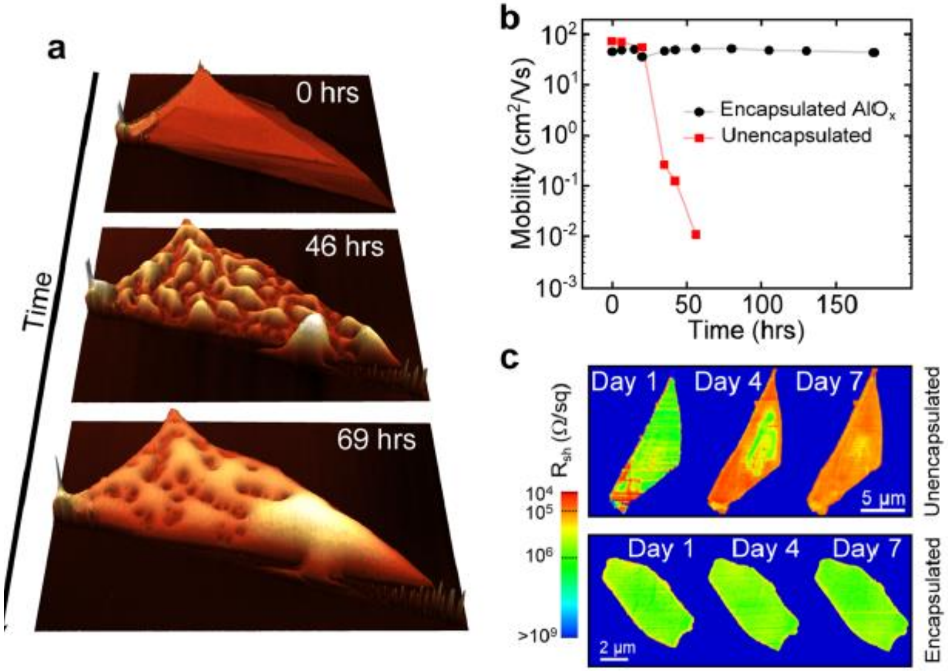




Catellanoas-Gomez, J. Phys. Chem. Lett. (2015)

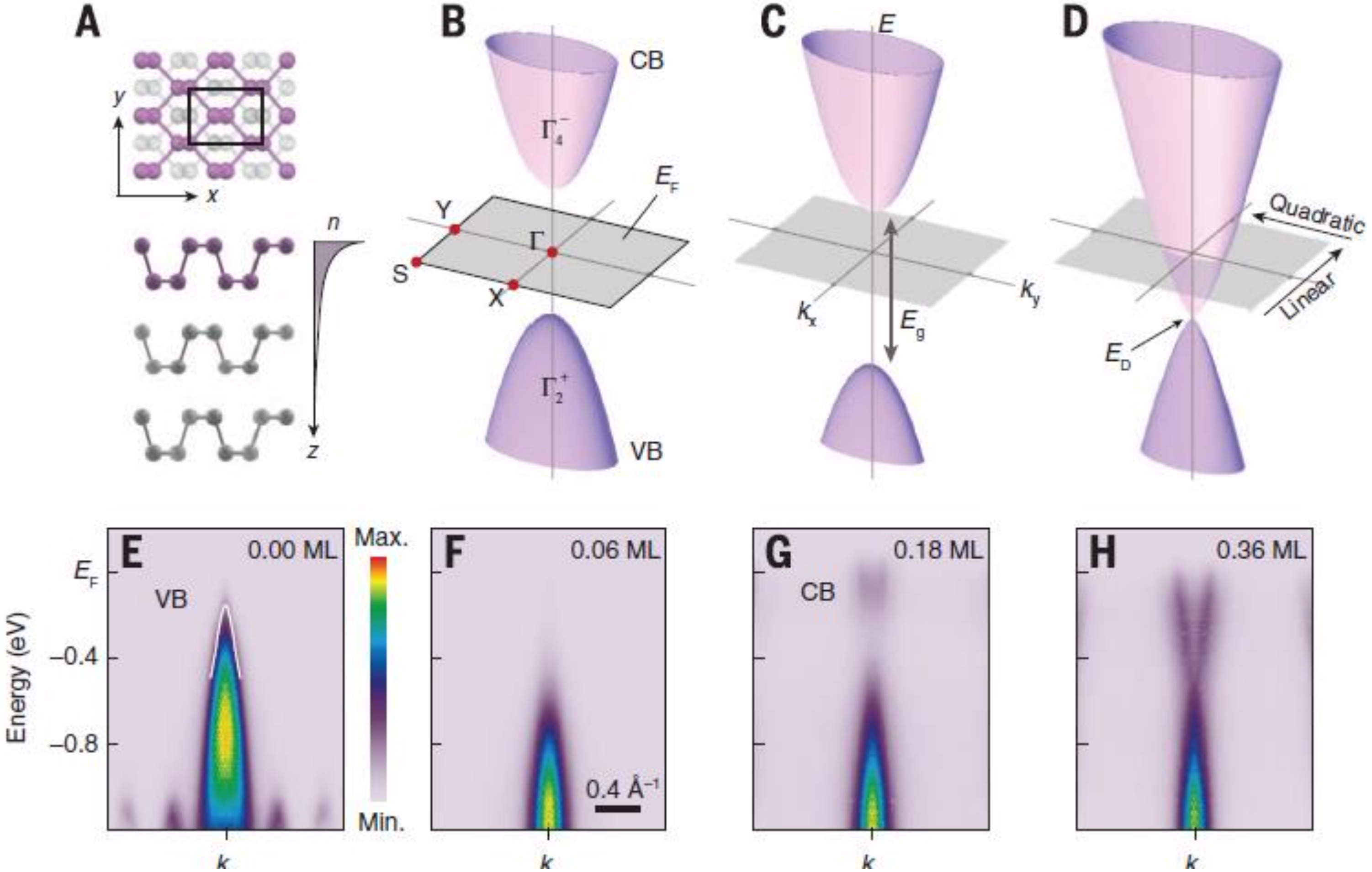
The degradation of black phosphorus (BP)





Catellanoas-Gomez, J. Phys. Chem. Lett. (2015)

Anisotropic Dirac semimetal state in BP



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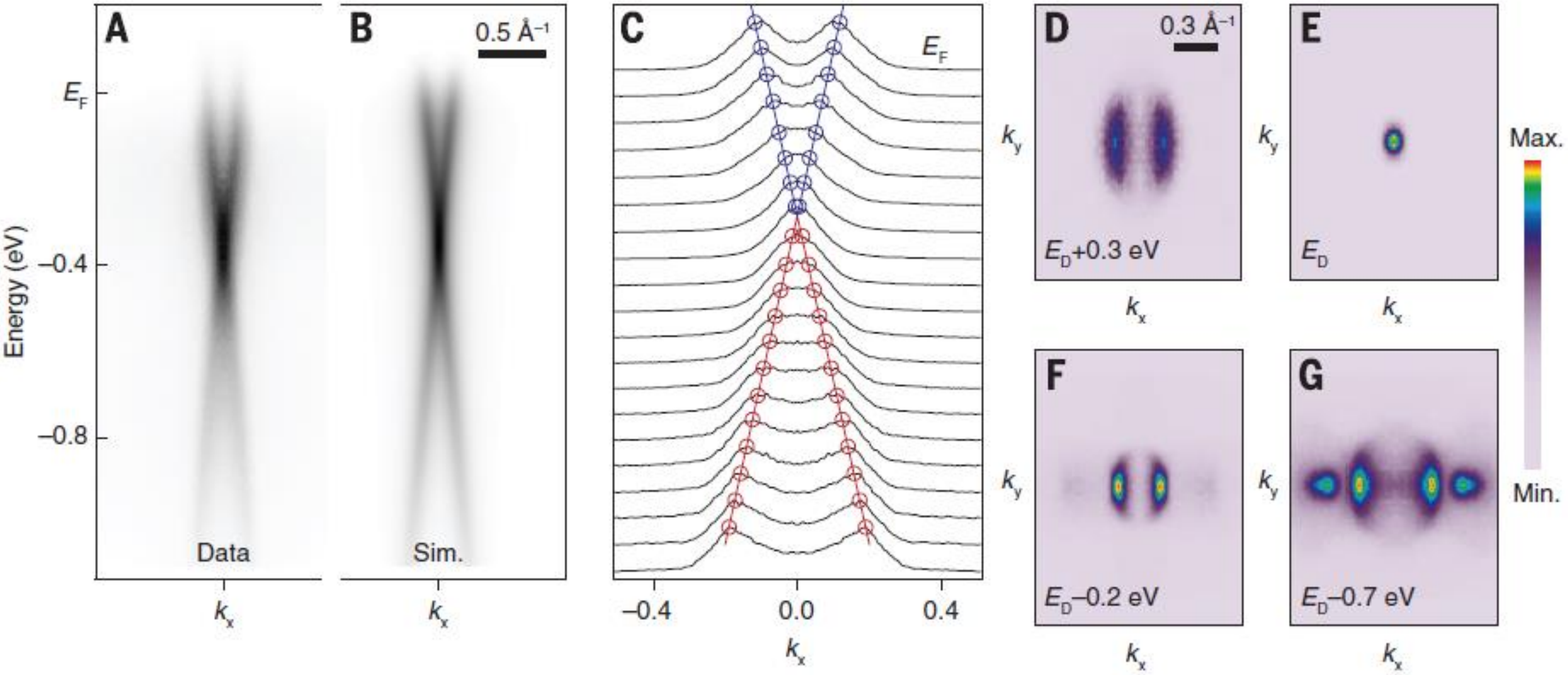
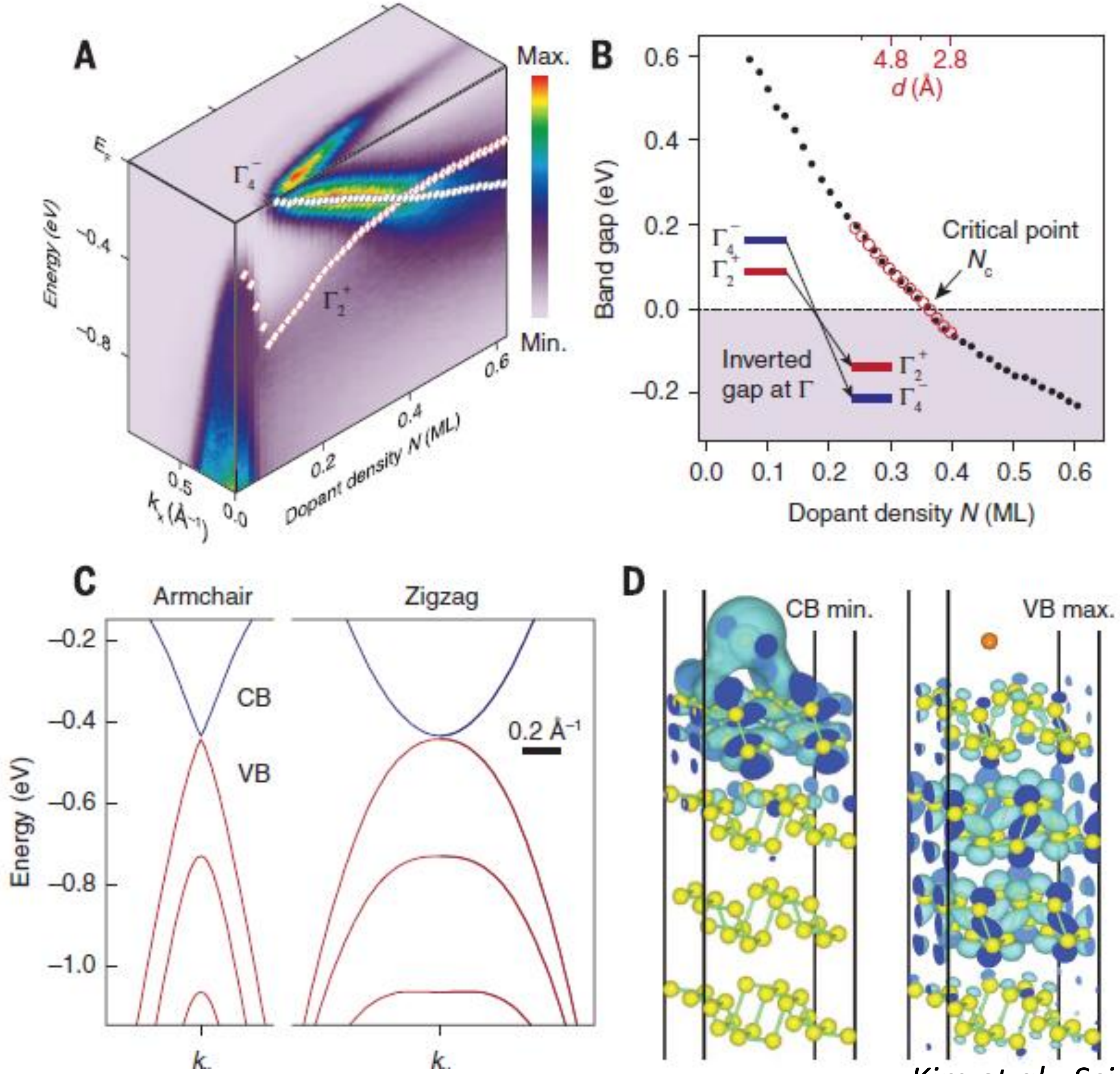
Kim et al., Science (2015)

Anisotropic Dirac semimetal state in BP



Kim et al., Science (2015)



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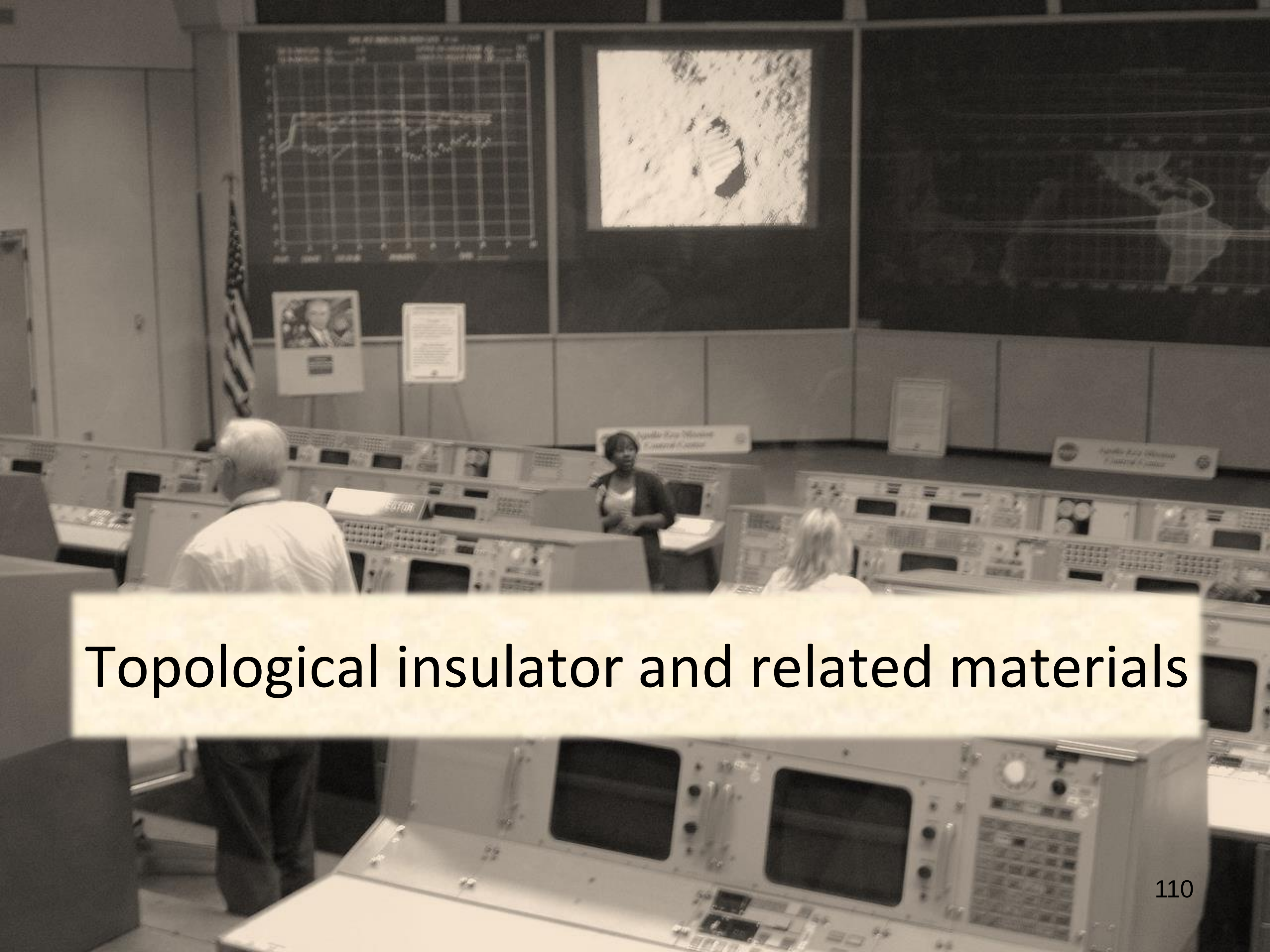
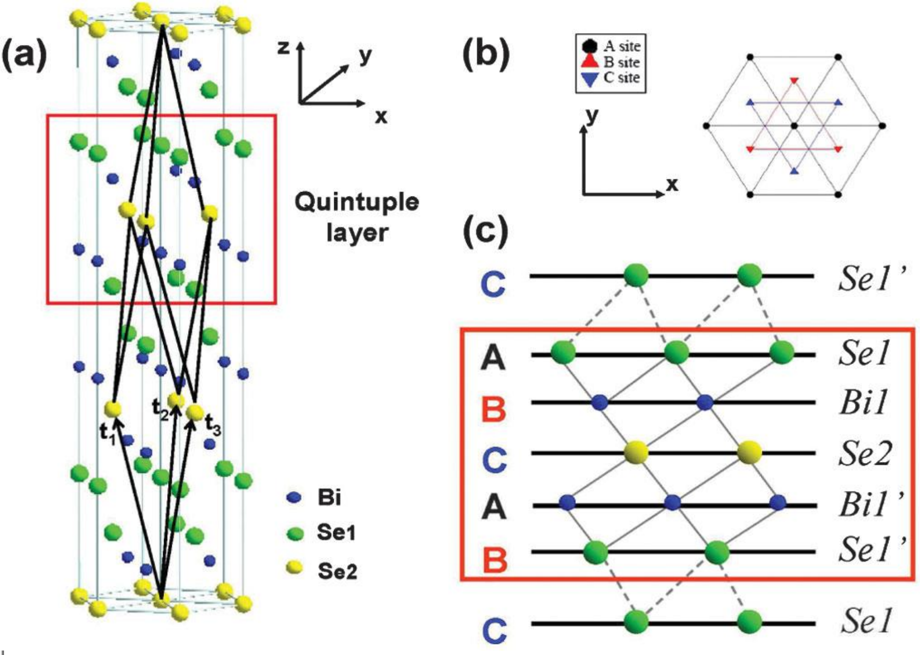
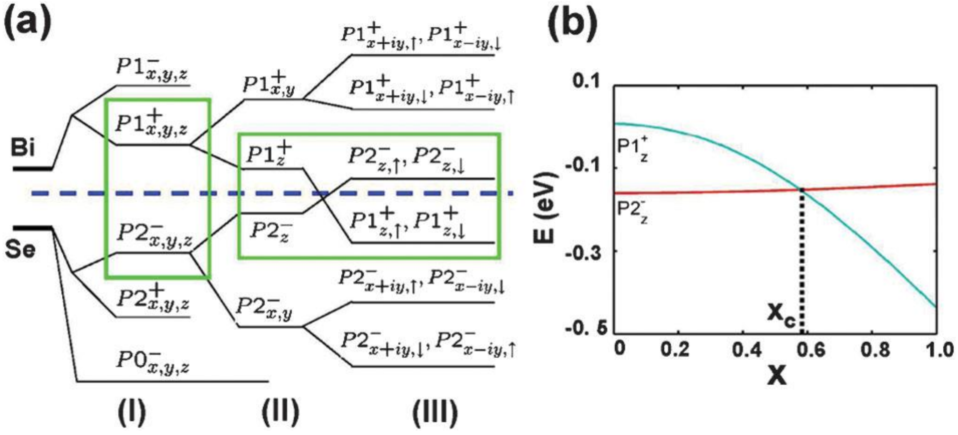
Kim et al., Science (2015)



Topological insulator and related materials

3D topological insulators

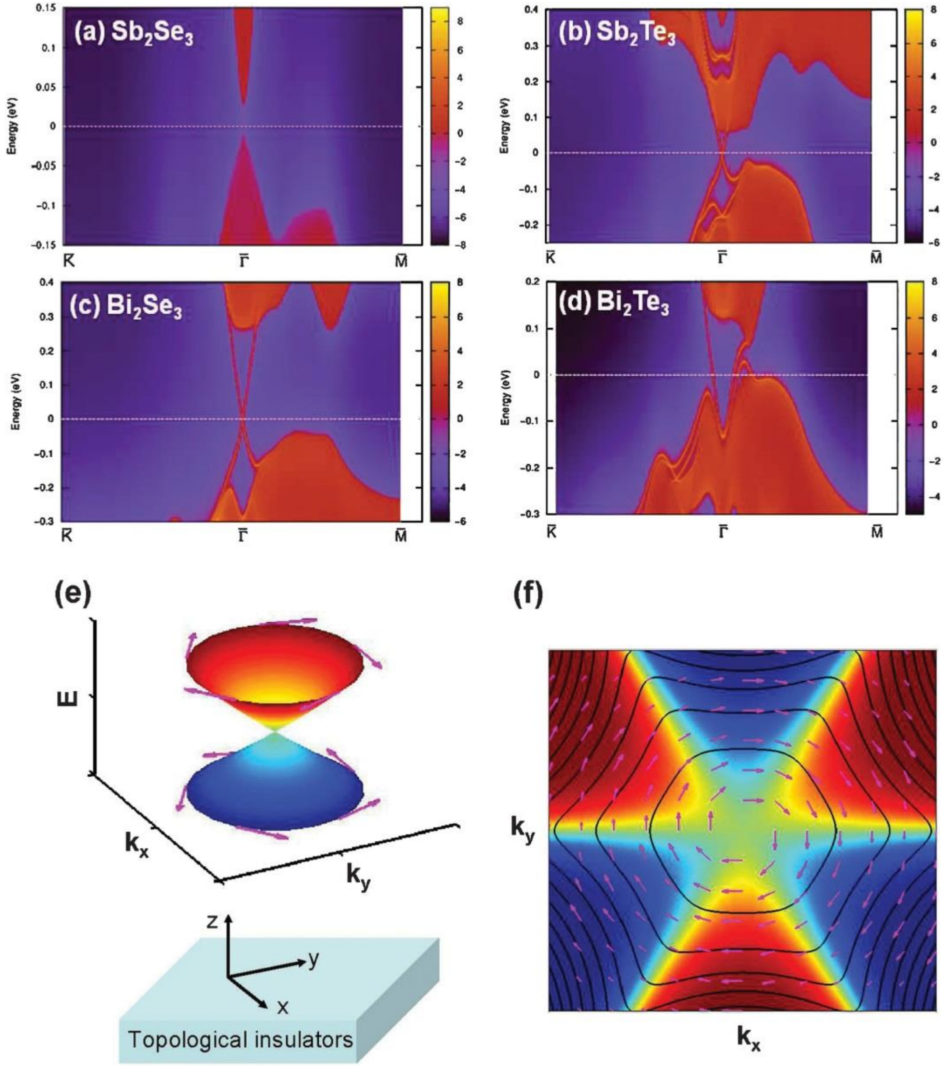




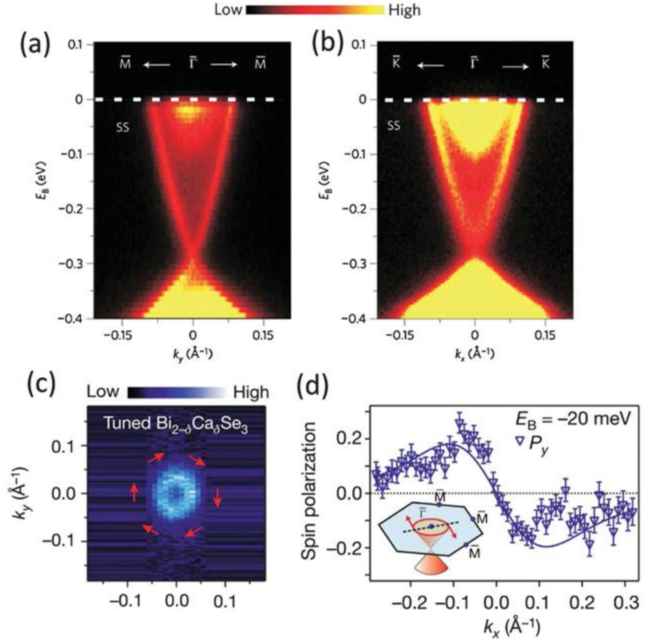
Strong spin-orbit coupling
Induce the band inversion

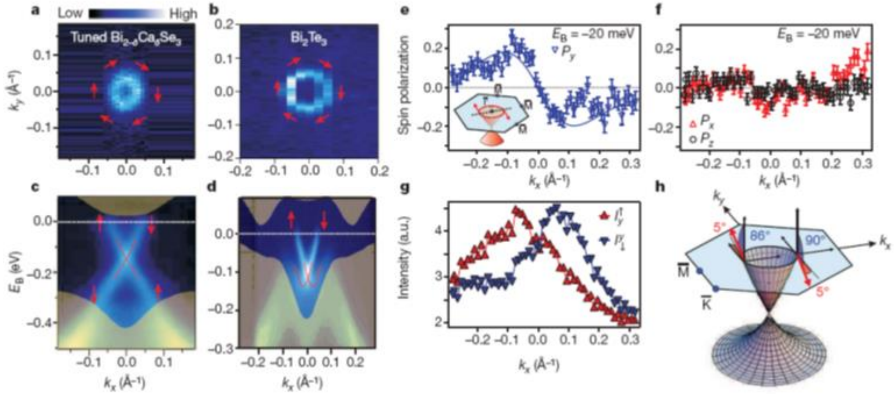
Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

Predictions of 3D topological insulators



Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

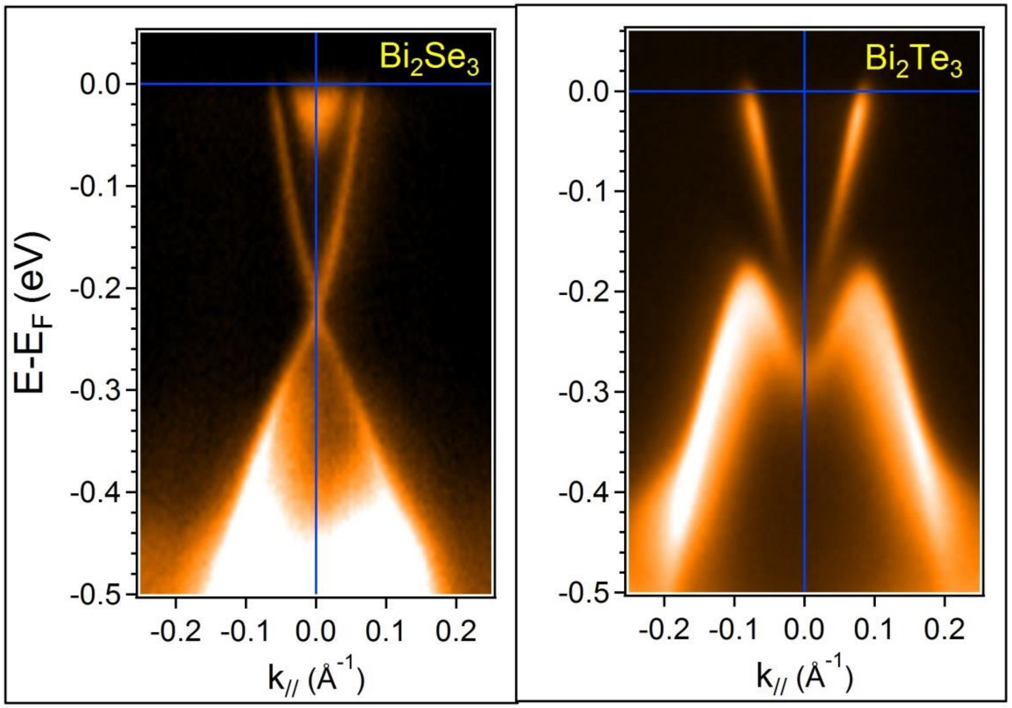




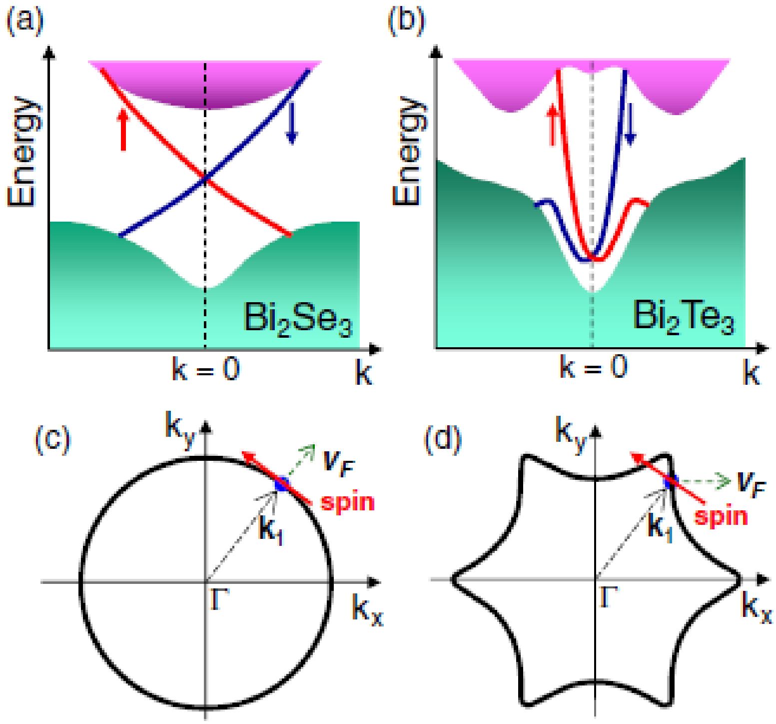
Xia et al., Nature Physics (2009)
Hsieh et al., Nature (2009)

Chen et al, Science (2009)

Predictions of 3D topological insulators



Spectra taken at BL21B1, NSRRC



Y. Ando, J. Phys. Soc. Japan (2013)

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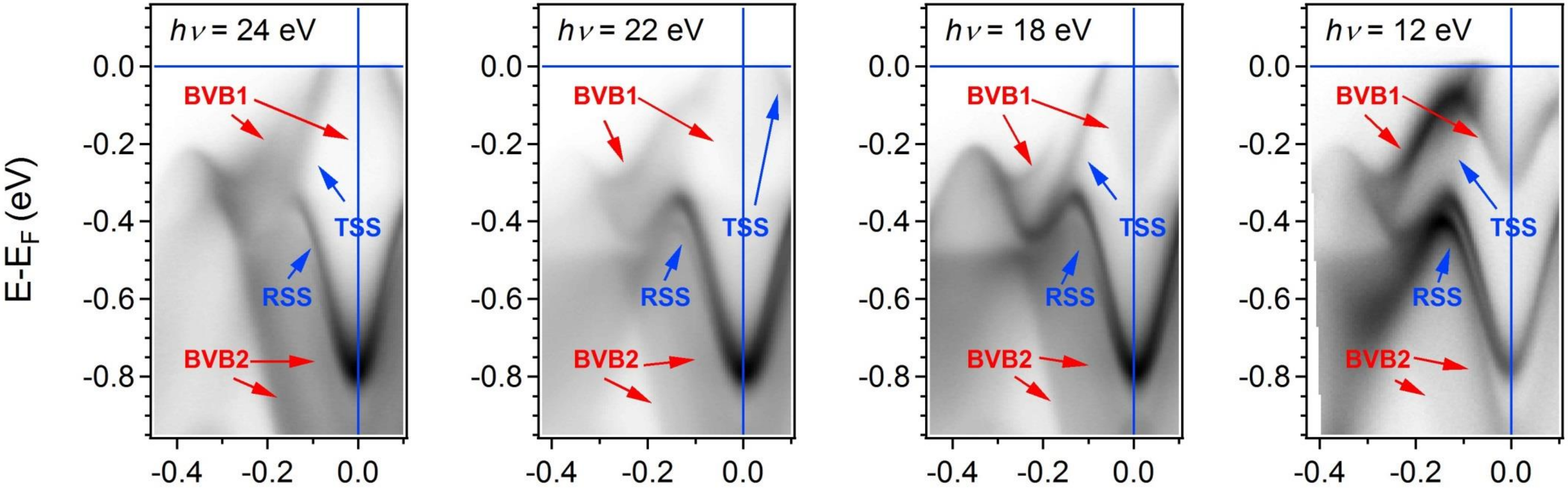
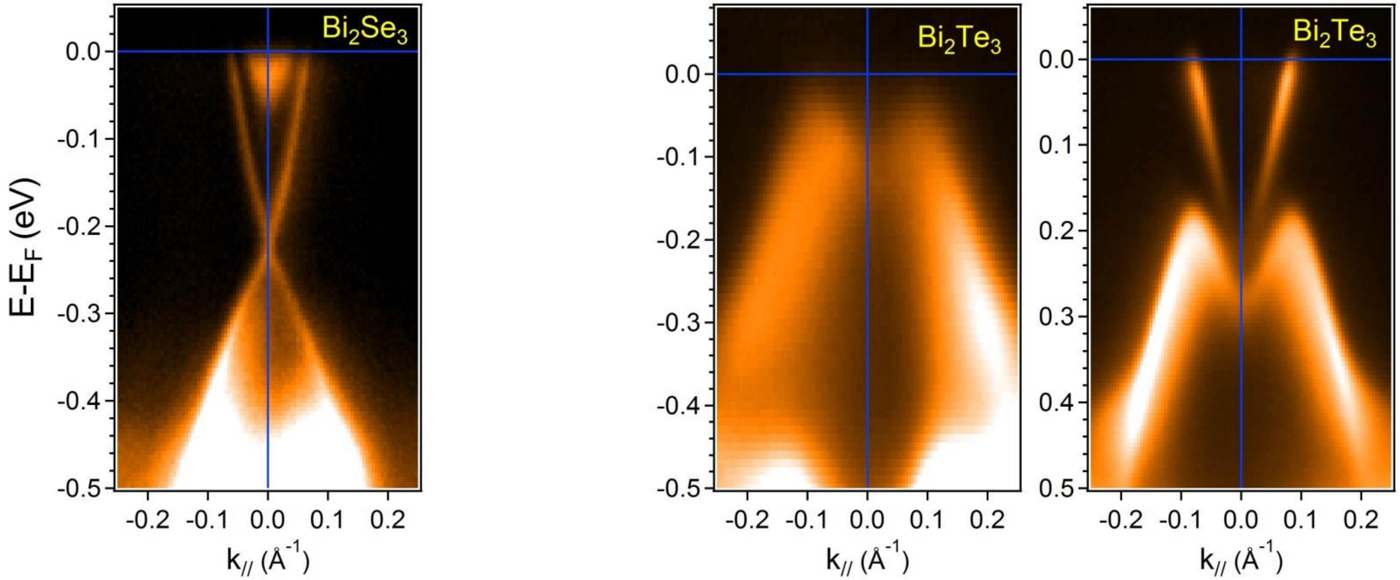
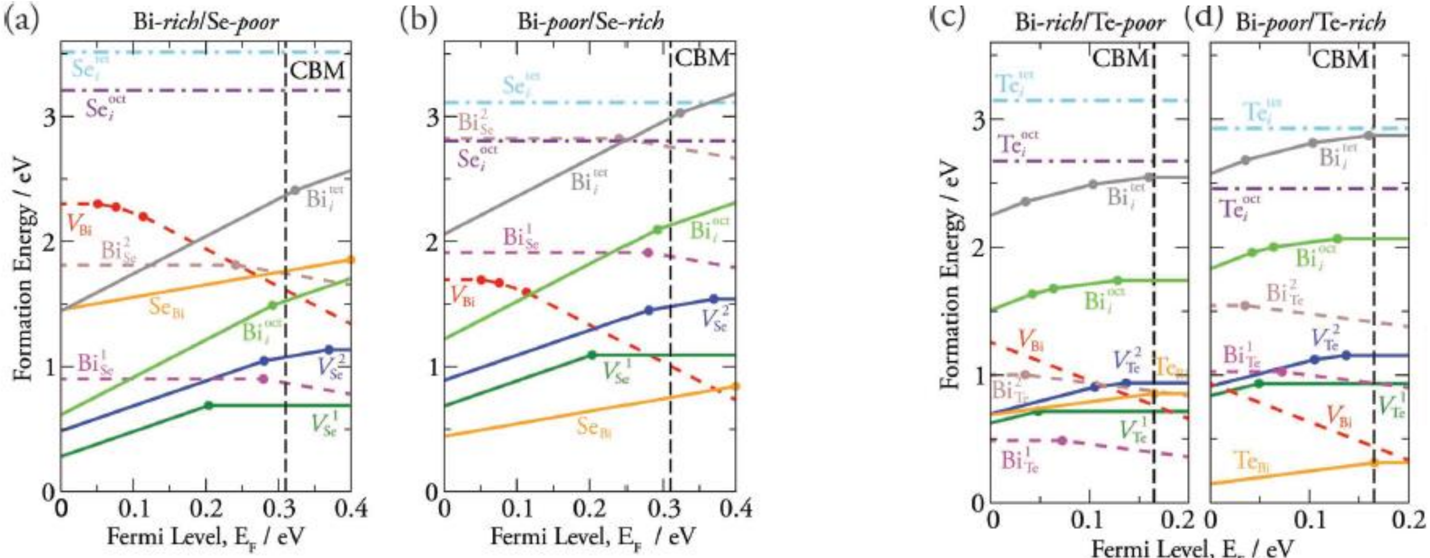
The electronic structure of Sb_2Te_3 insulators



Cheng et al., submitted to Sci. Rep.

Initial growth condition of Bi family TIs





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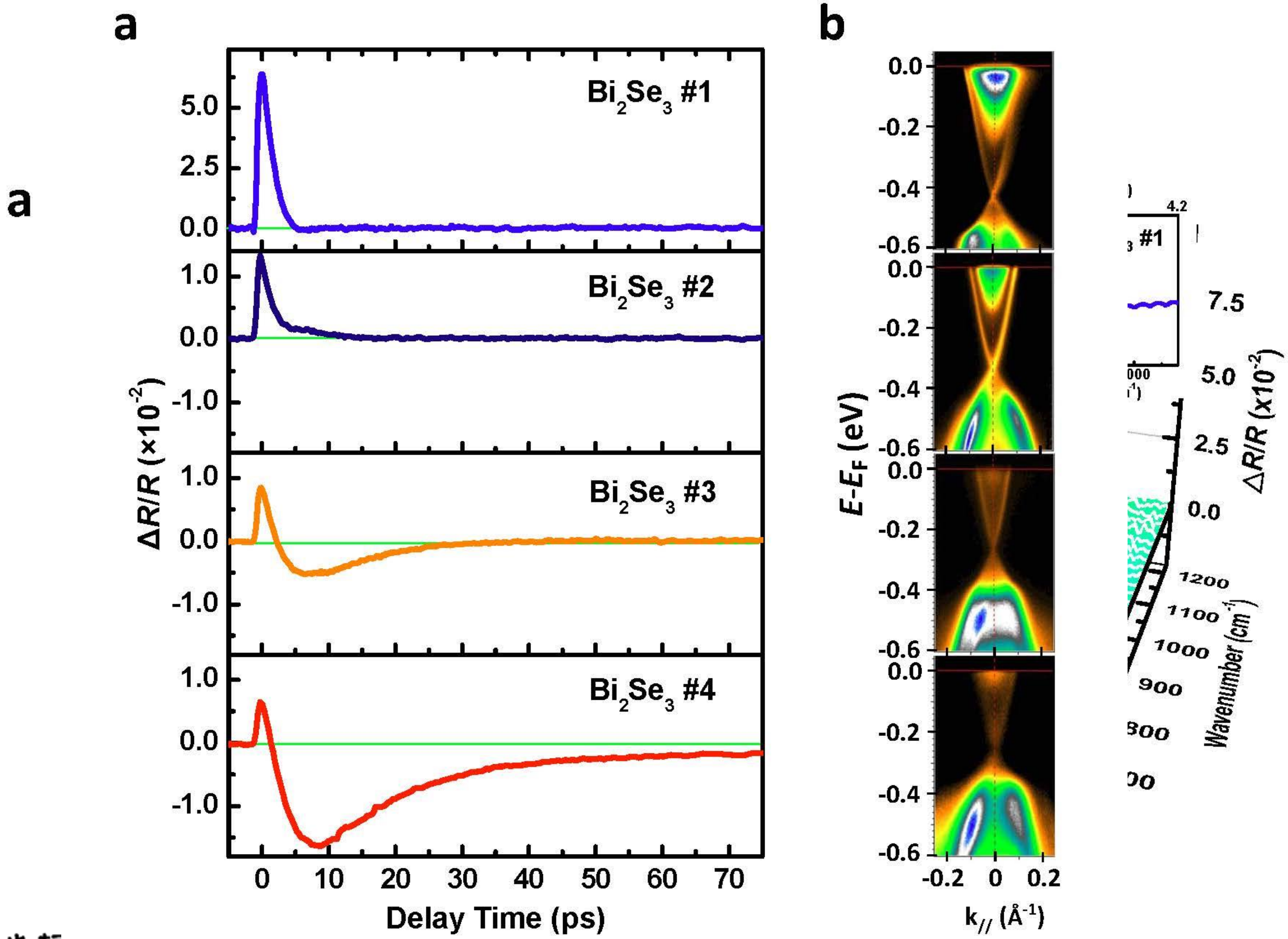
D.O. Scanlon, Adv. Mat. (2012)

Ultrafast Dynamics of Dirac Fermion in Topological Insulators



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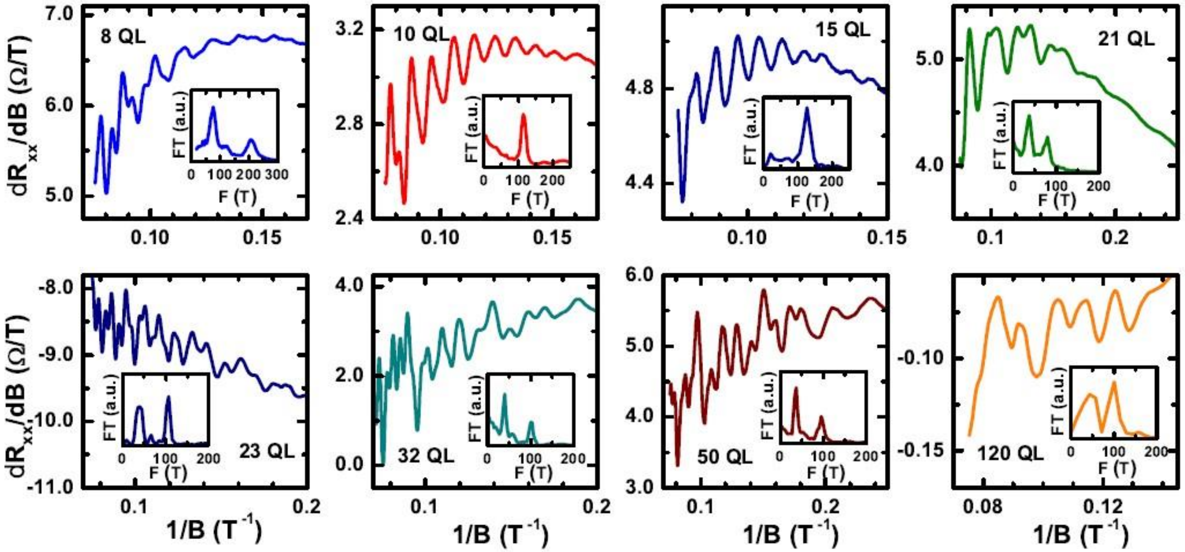
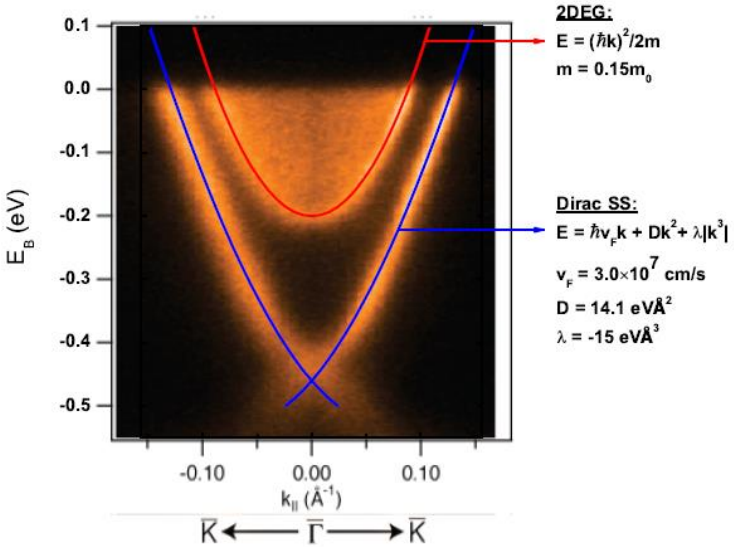
Luo et al., Nano Lett. (2013)

Estimate the surface charge carrier density : *SdH* oscillations ($n_s = \frac{{k_F}^2}{4\pi}$)



Estimate the surface charge carrier density : ARPES



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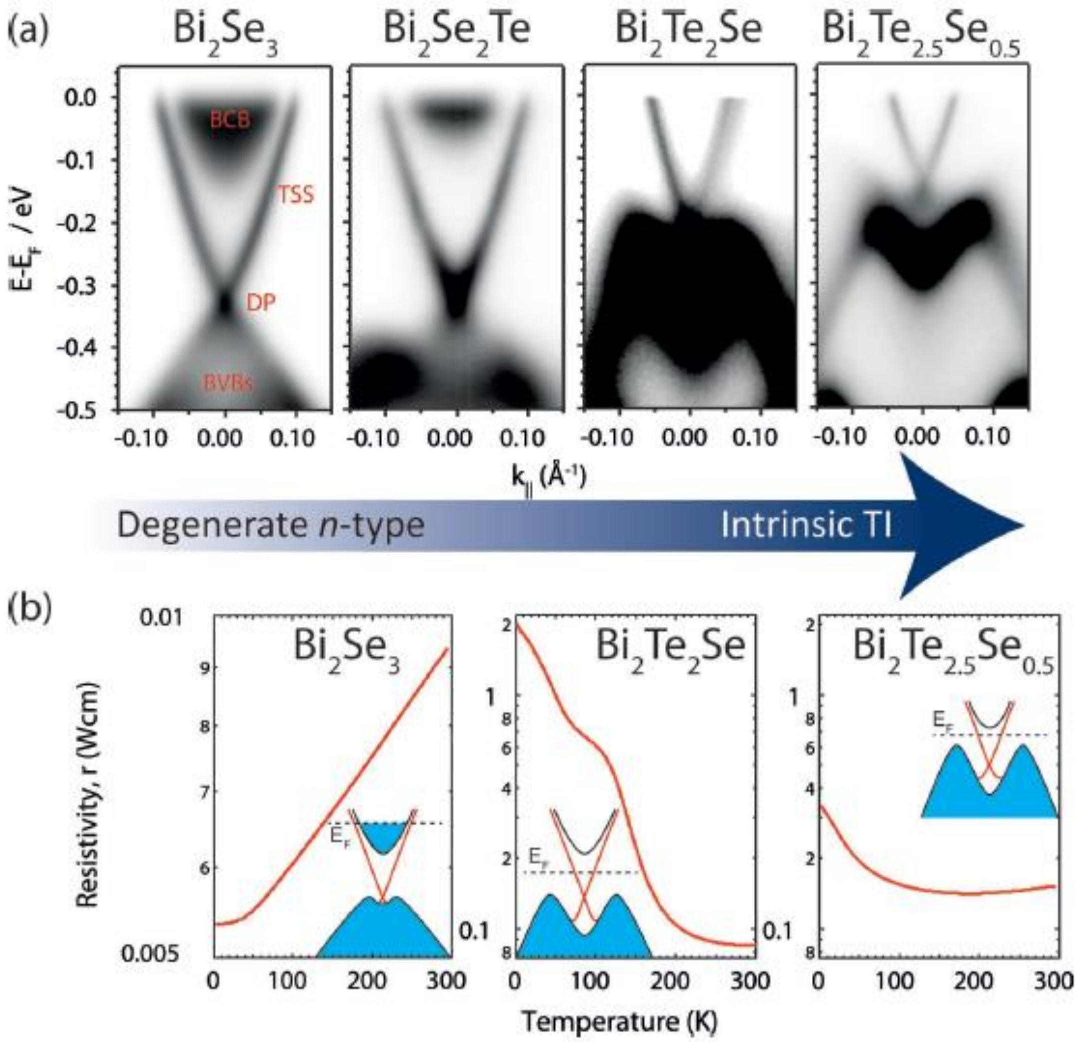
Tuning the position of the Dirac point in ternary topological insulators



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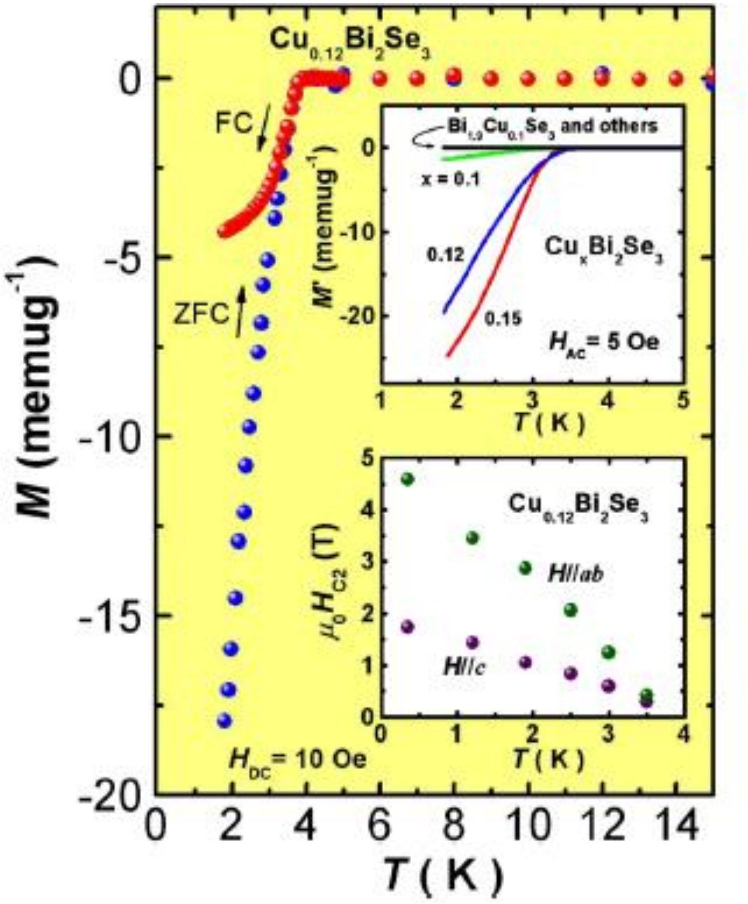
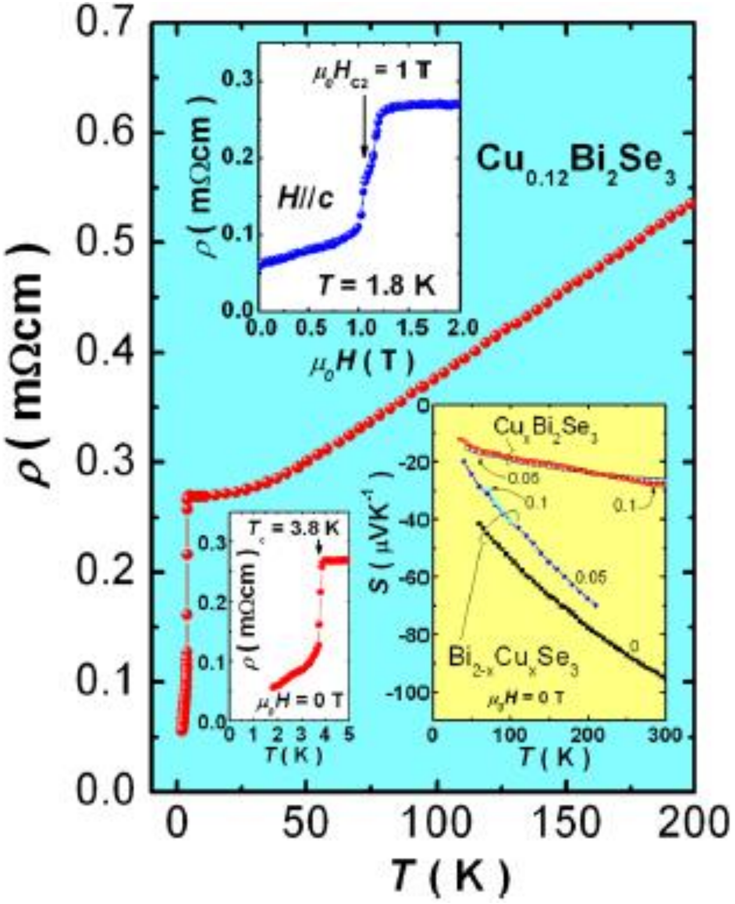
Another way is to dope topological insulators : Cu, Mn, Ca, C….

Superconductivity in Cu doped Bi_2Se_3 compound

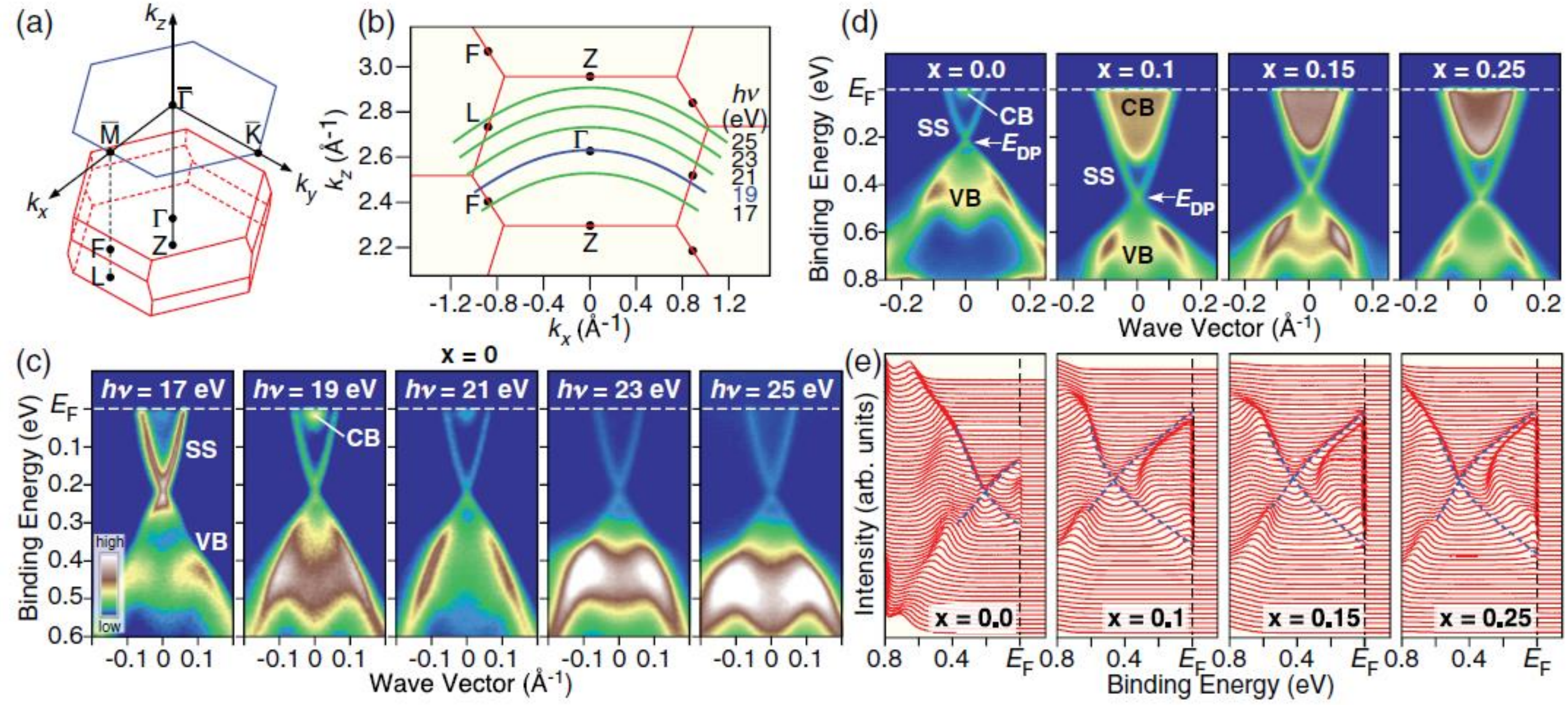




Hor et al., PRL (2010)

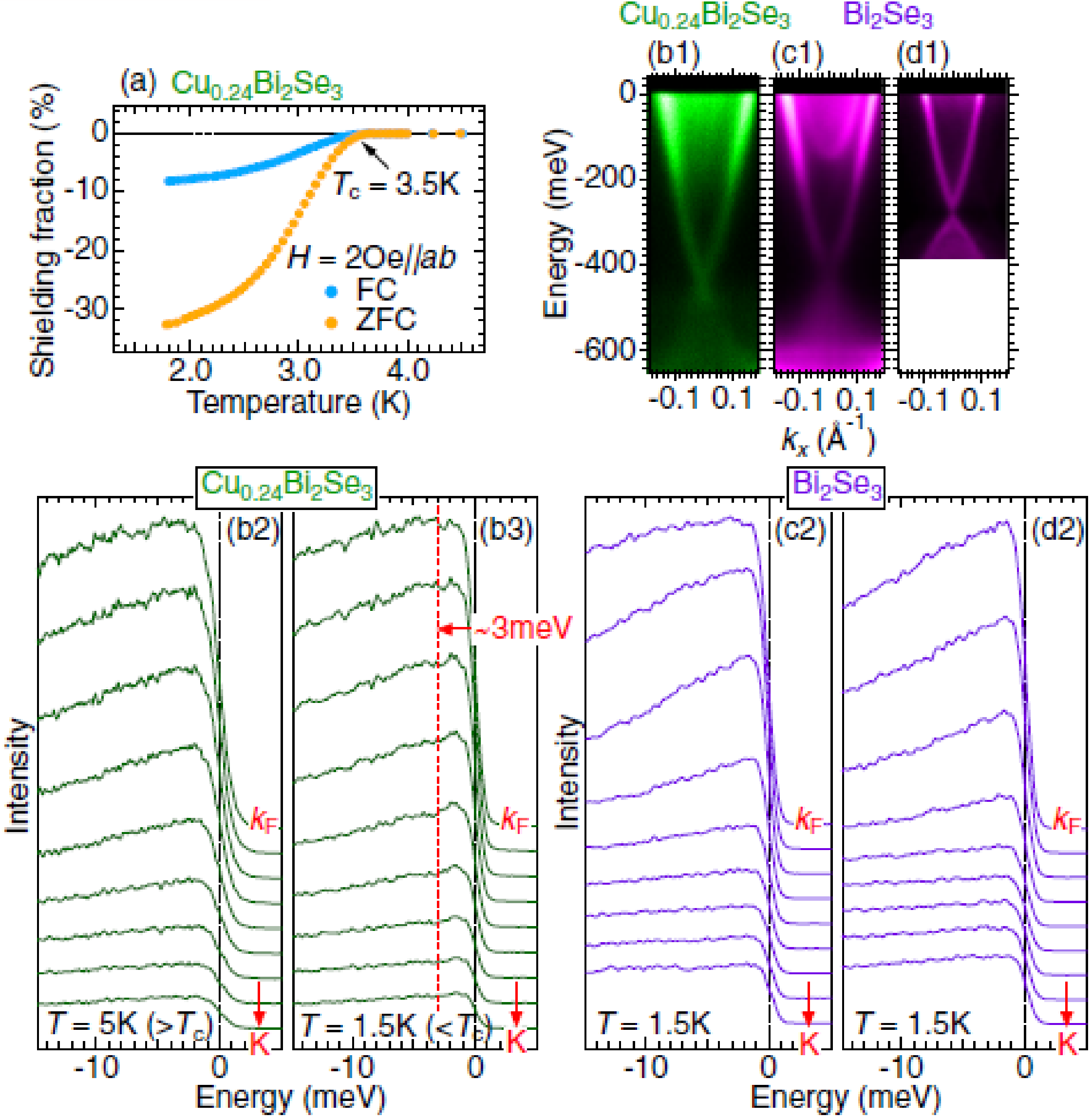
$Cu_xBi_2Se_3$ for $0.1<x<0.15$

Superconductivity in Cu doped Bi_2Se_3 compound



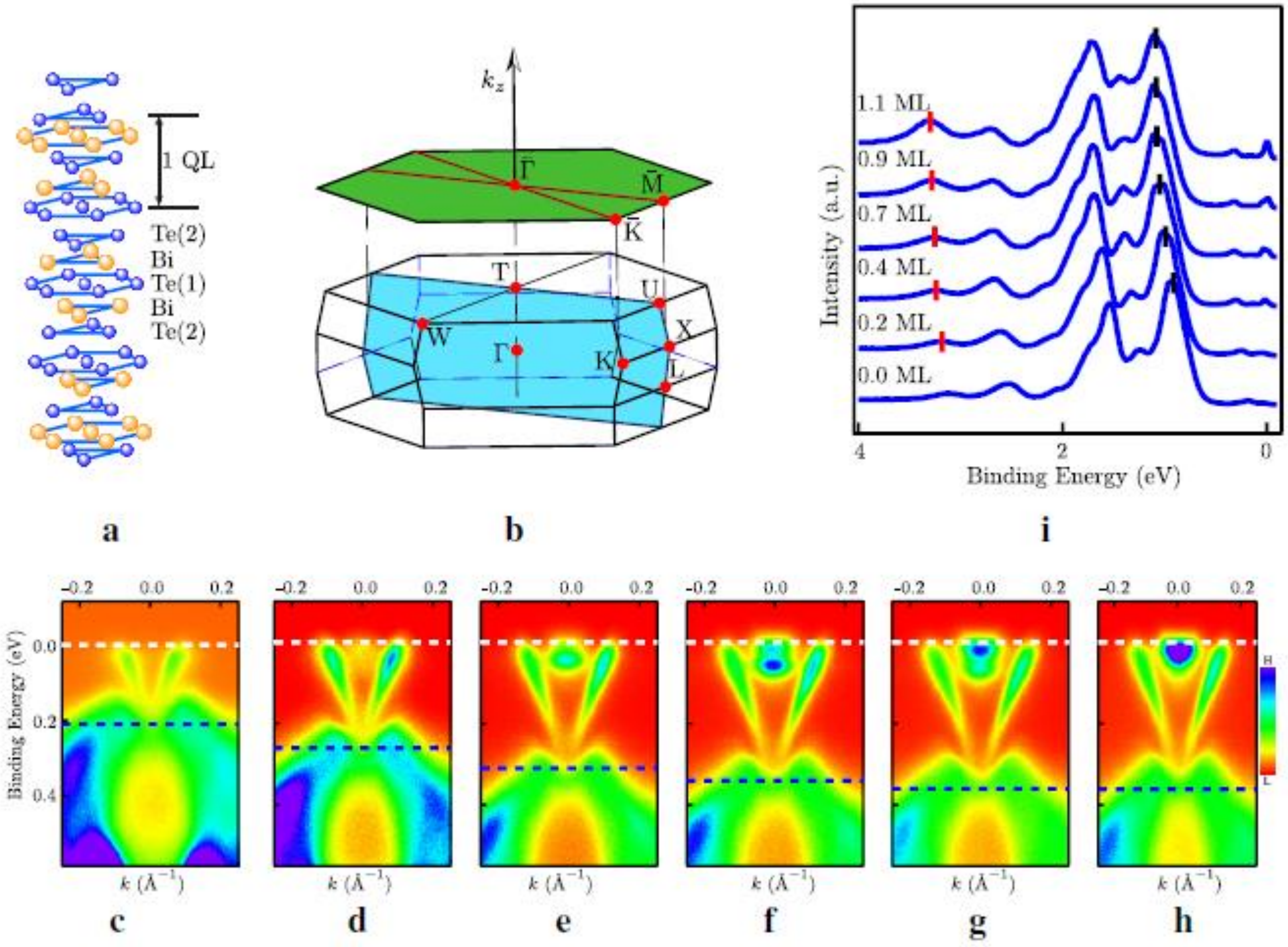
Tanaka et al., PRB (2012)

Superconductivity in Cu doped Bi_2Se_3 compound



Kondo et al., PRL (2013)

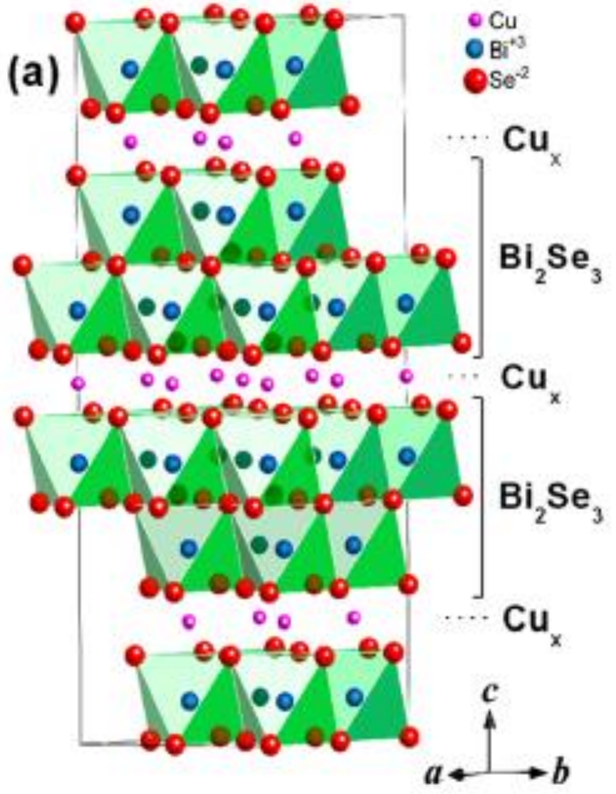
Cu doped epitaxial Bi_2Te_3 thin films



Zhu et al., Surf. Sci. (2013)

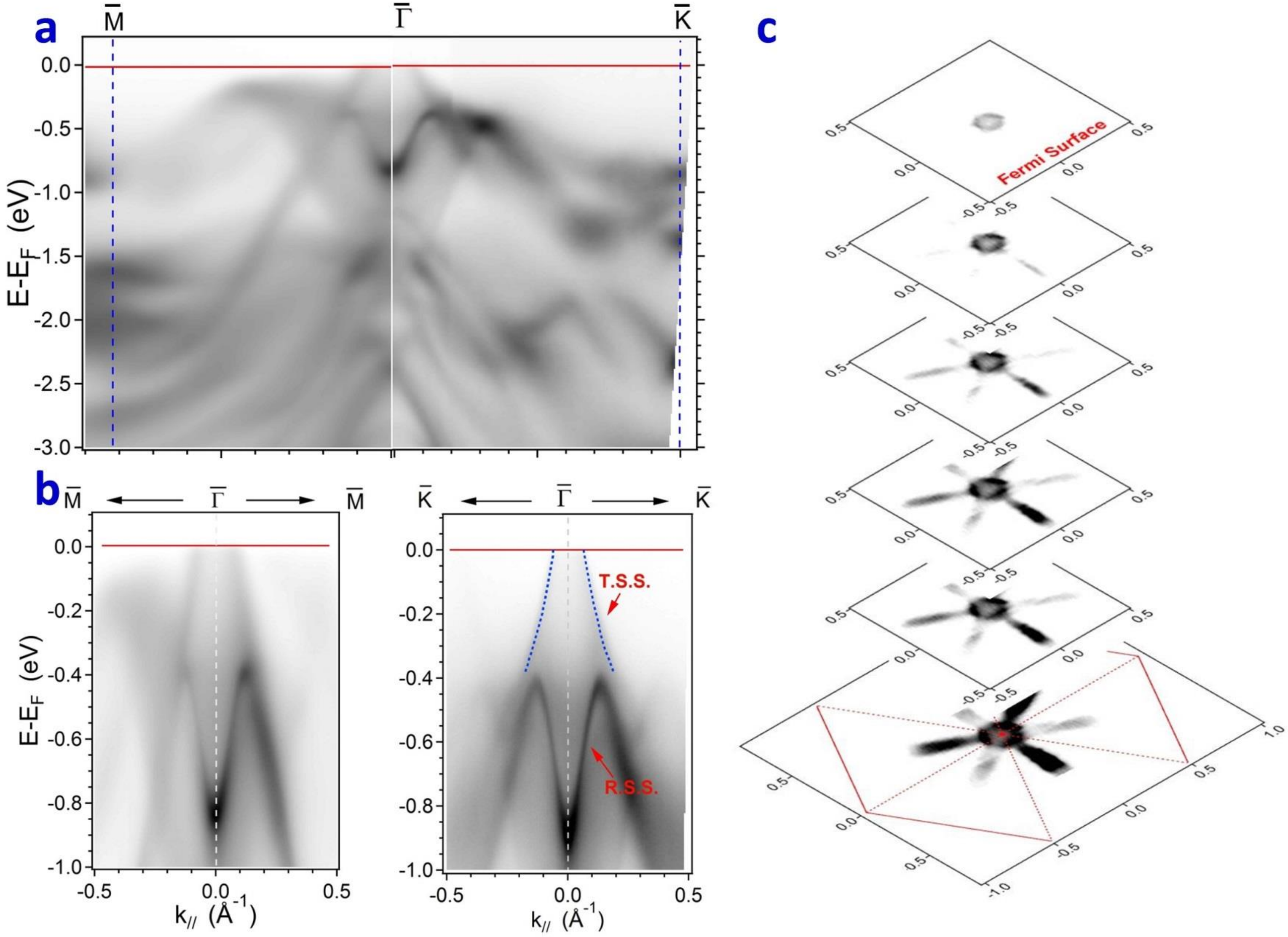
The role of Cu atoms in Cu doped Bi_2Se_3 and Bi_2Te_3 topological insulators

$Cu_xBi_2Se_3$ or $Bi_{2-x}Cu_xSe_3$?

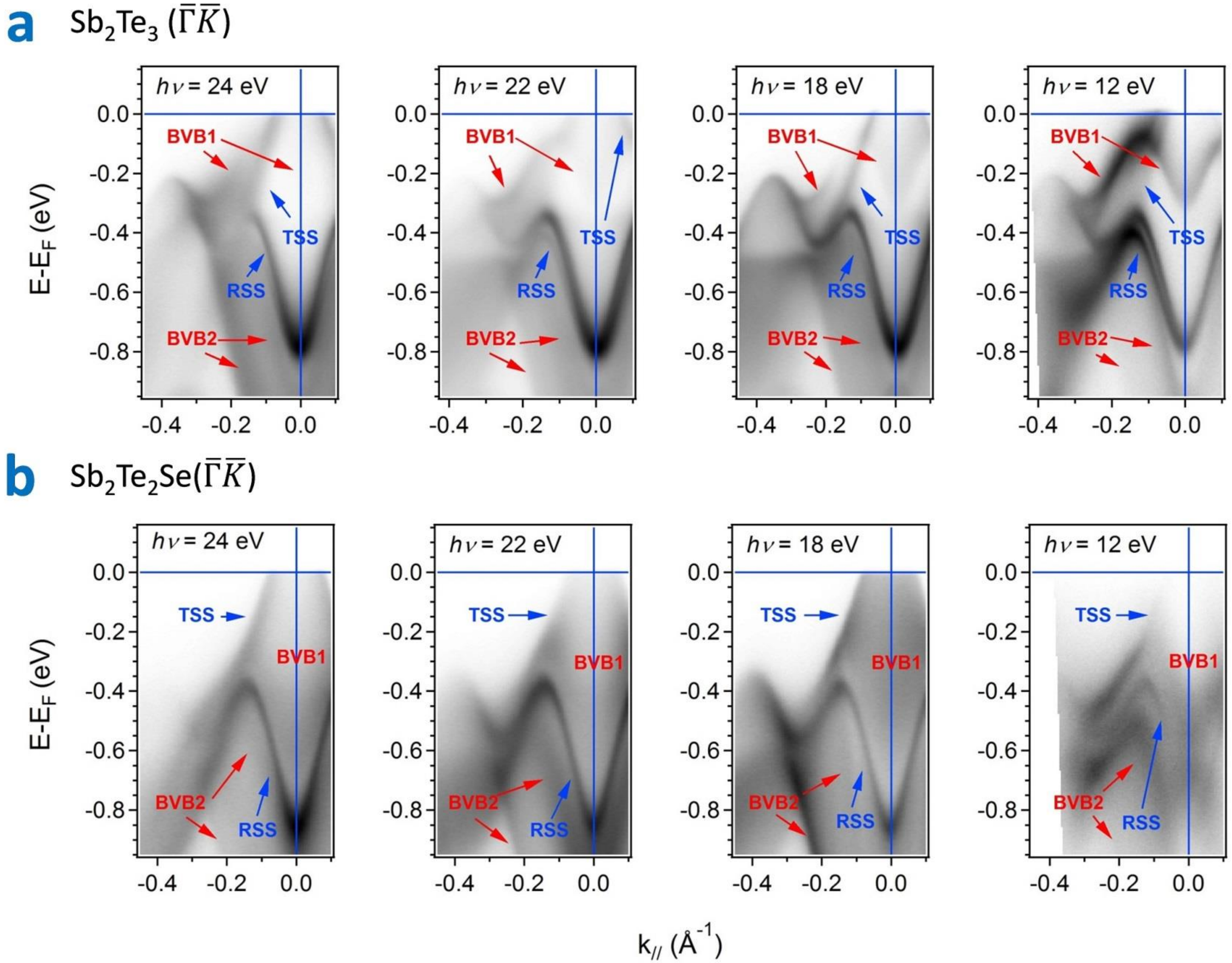


Hor et al., PRL (2010)

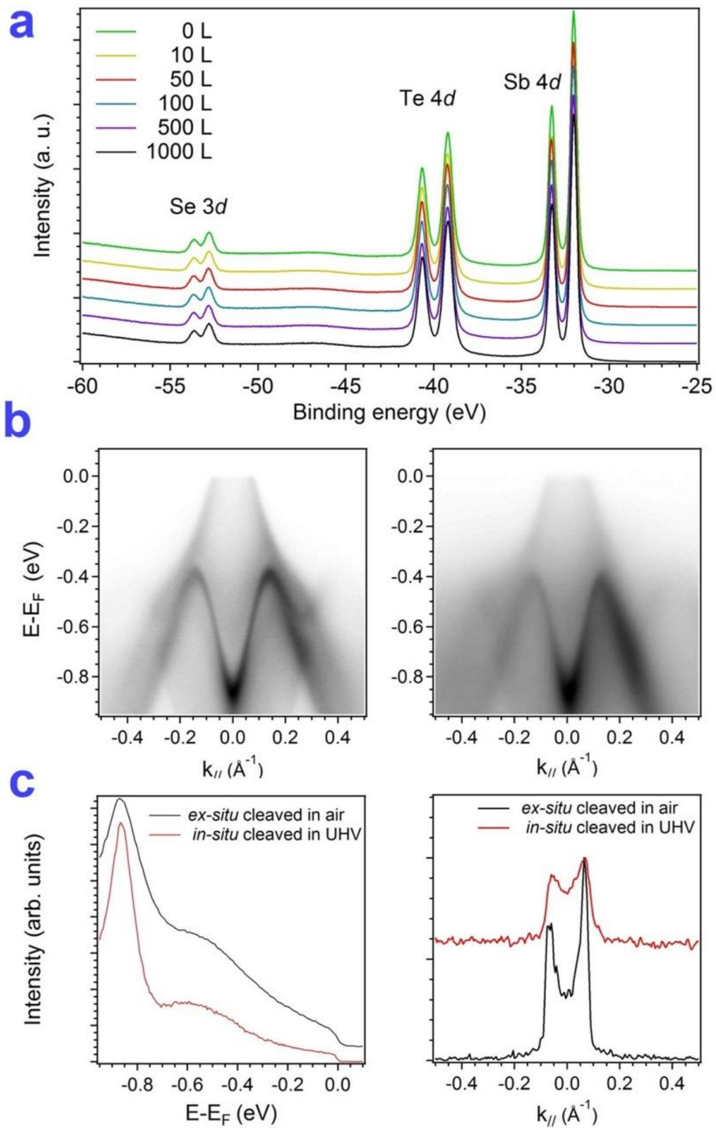
The electronic structure of Sb_2Te_2Se

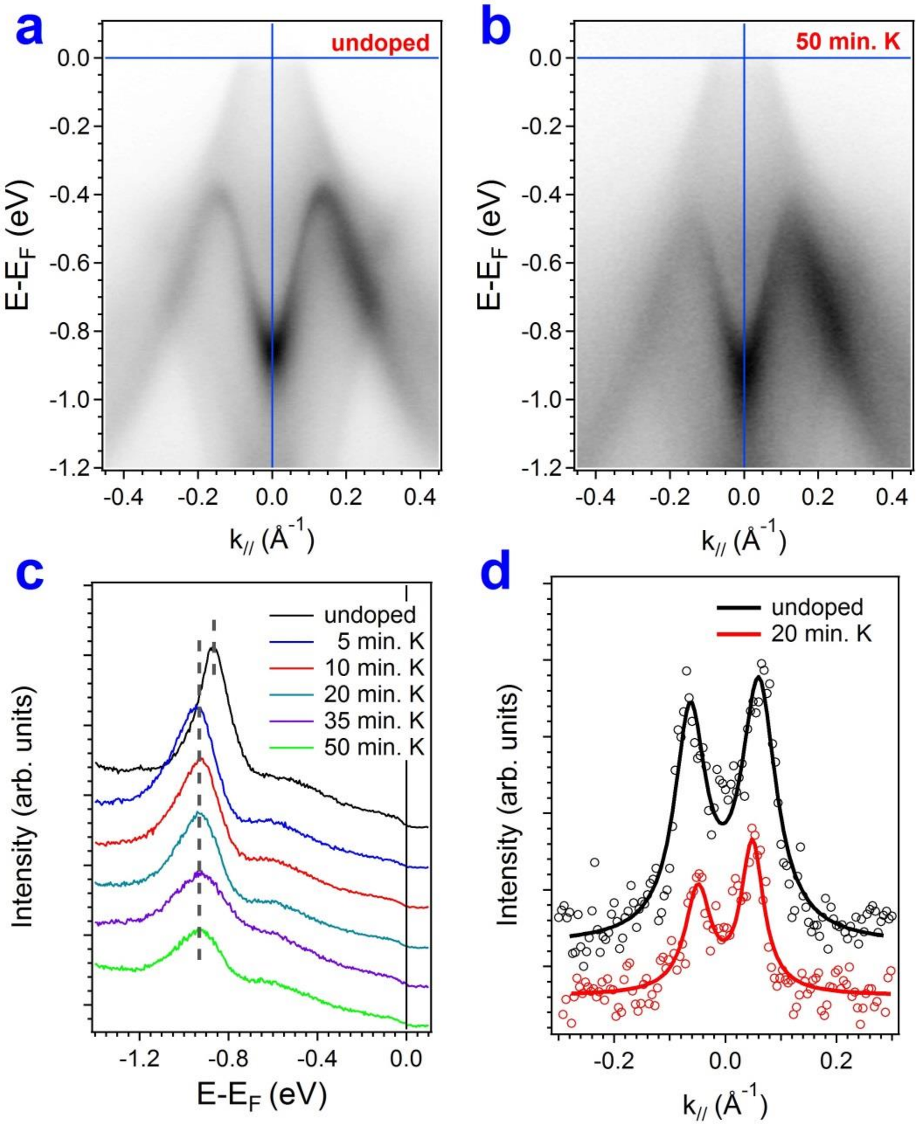


Comparison of Sb_2Te_3 and a Sb_2Te_2Se



Robustness of a Topologically Protected Surface State in a Sb_2Te_2Se Single Crystal

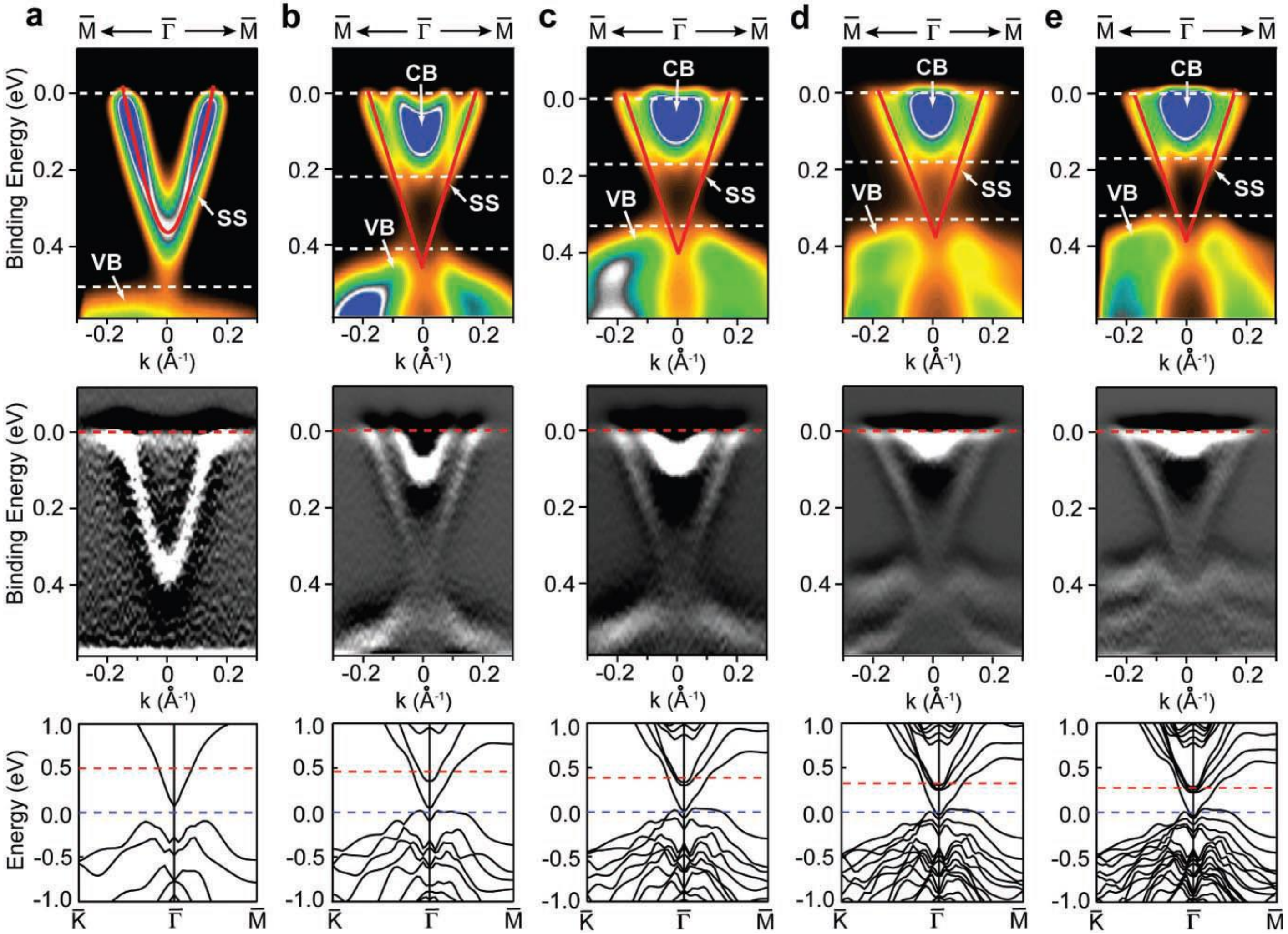




Toward future electronic devices

MBE growth topological insulators (Bi_2Te_3)

Bi_2Te_3/Si



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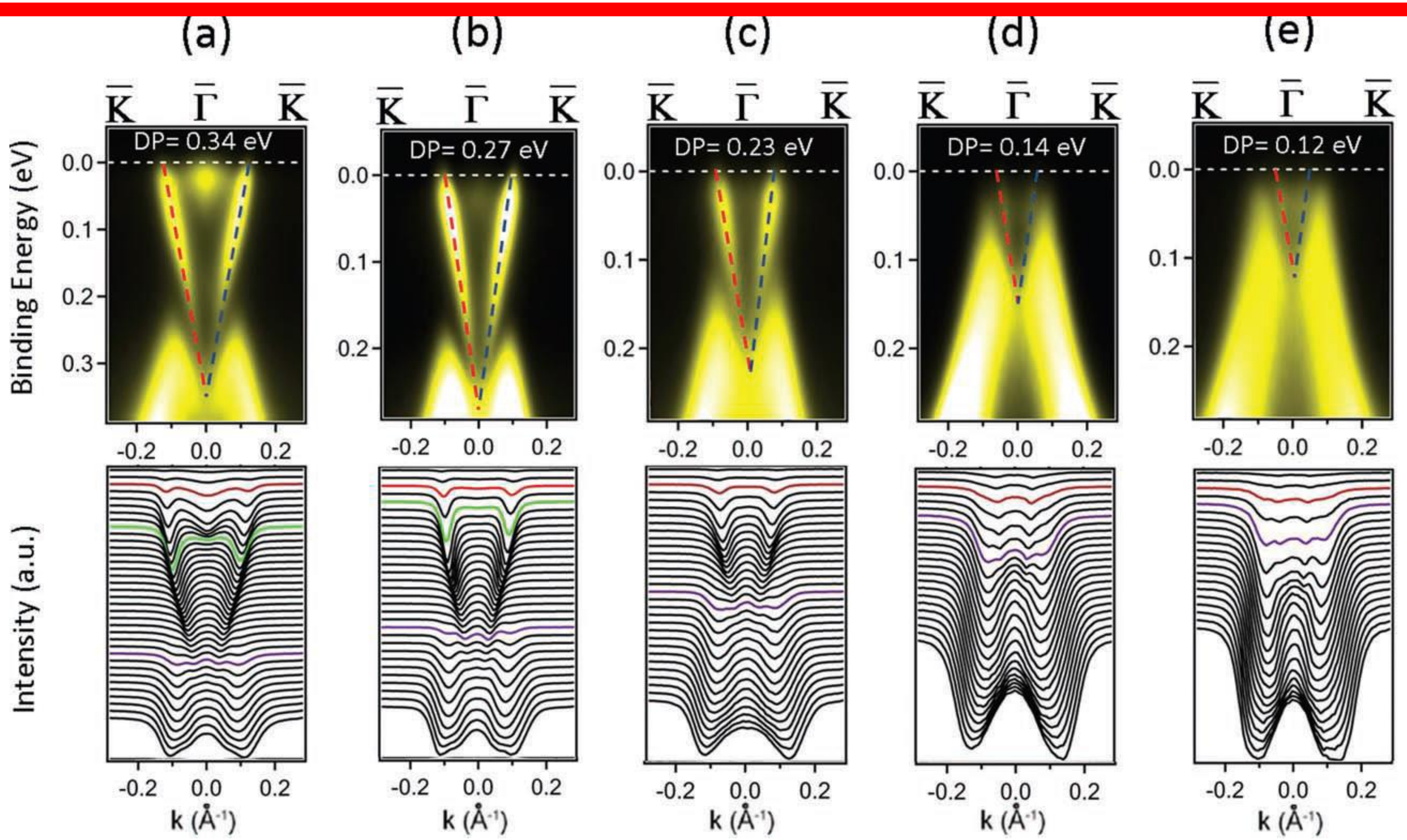
Li et al., Adv. Mat. (2010)

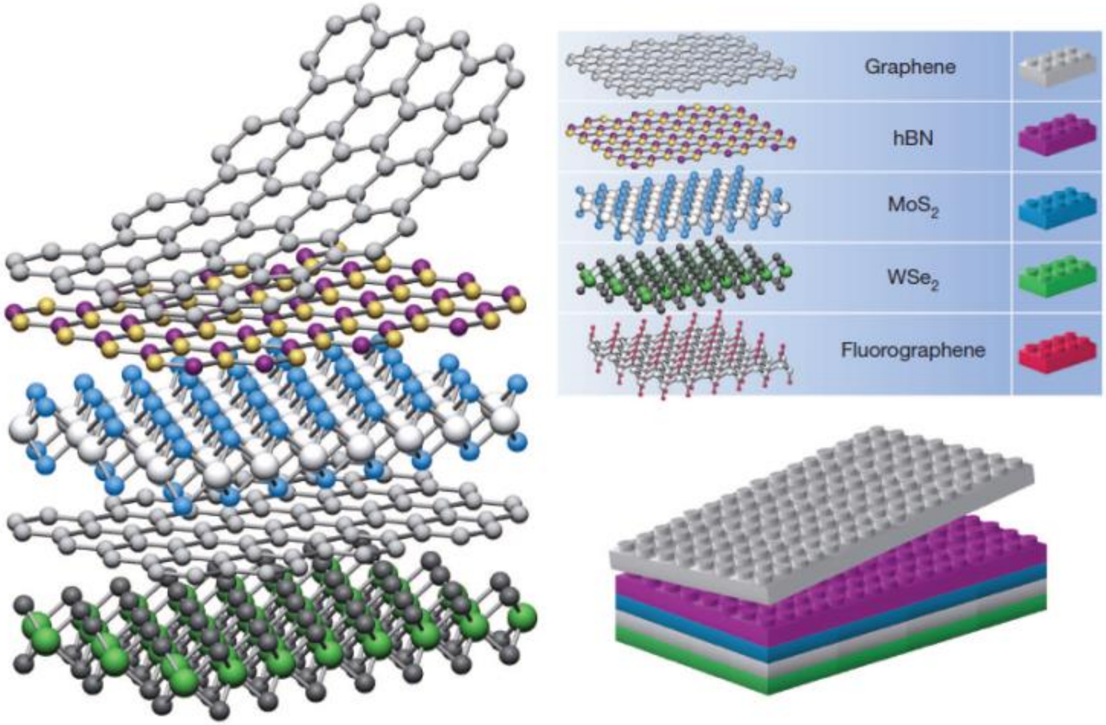
Temperature effect on MBE growth TIs

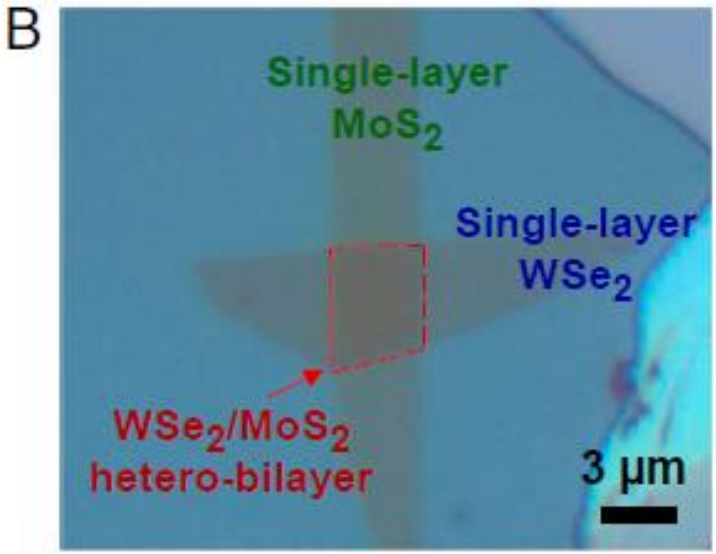


560 K 580 K 600 K 625 K 630 K

Wang *et al.*, Adv. Mat. (2011)

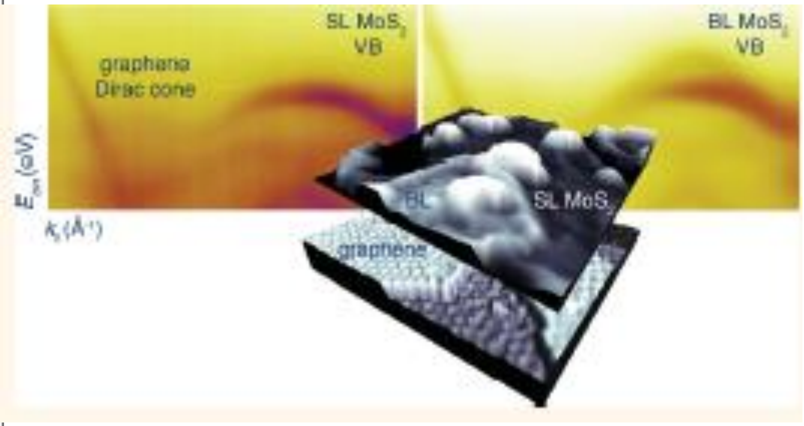
Van der Waals heterostructure

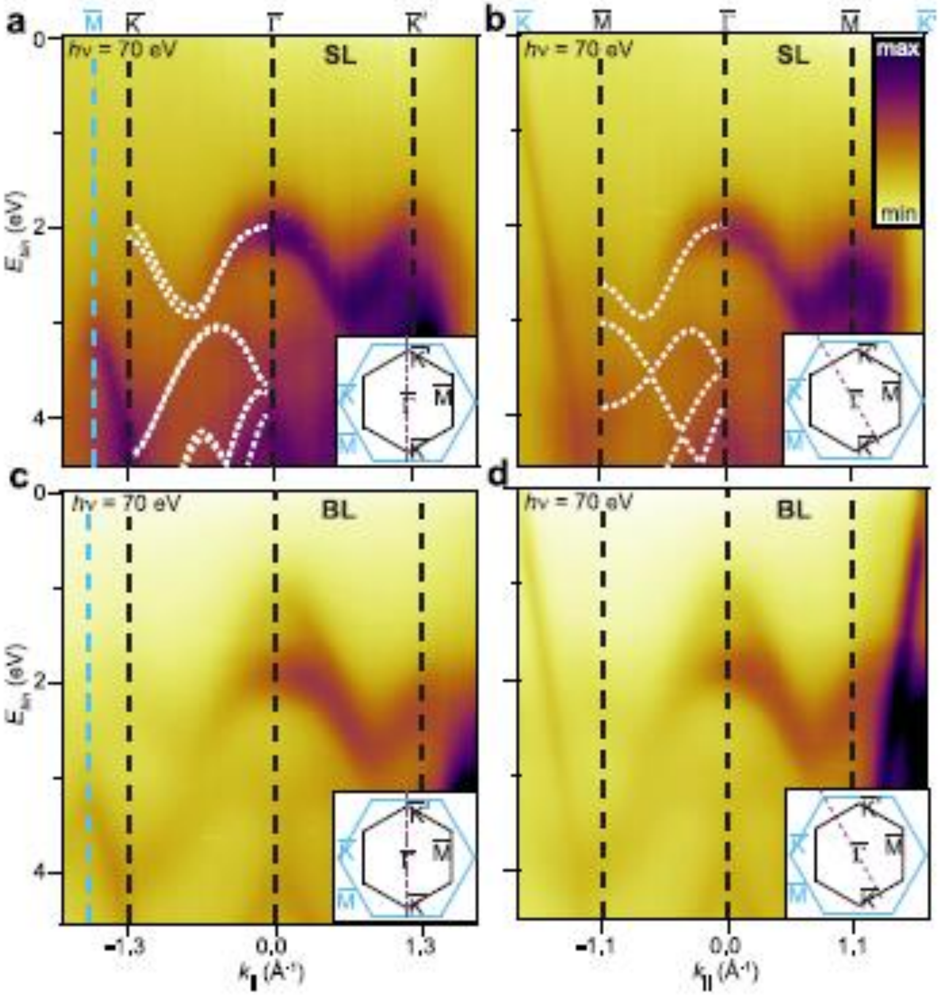




Ref : Geim, Nature (2013)

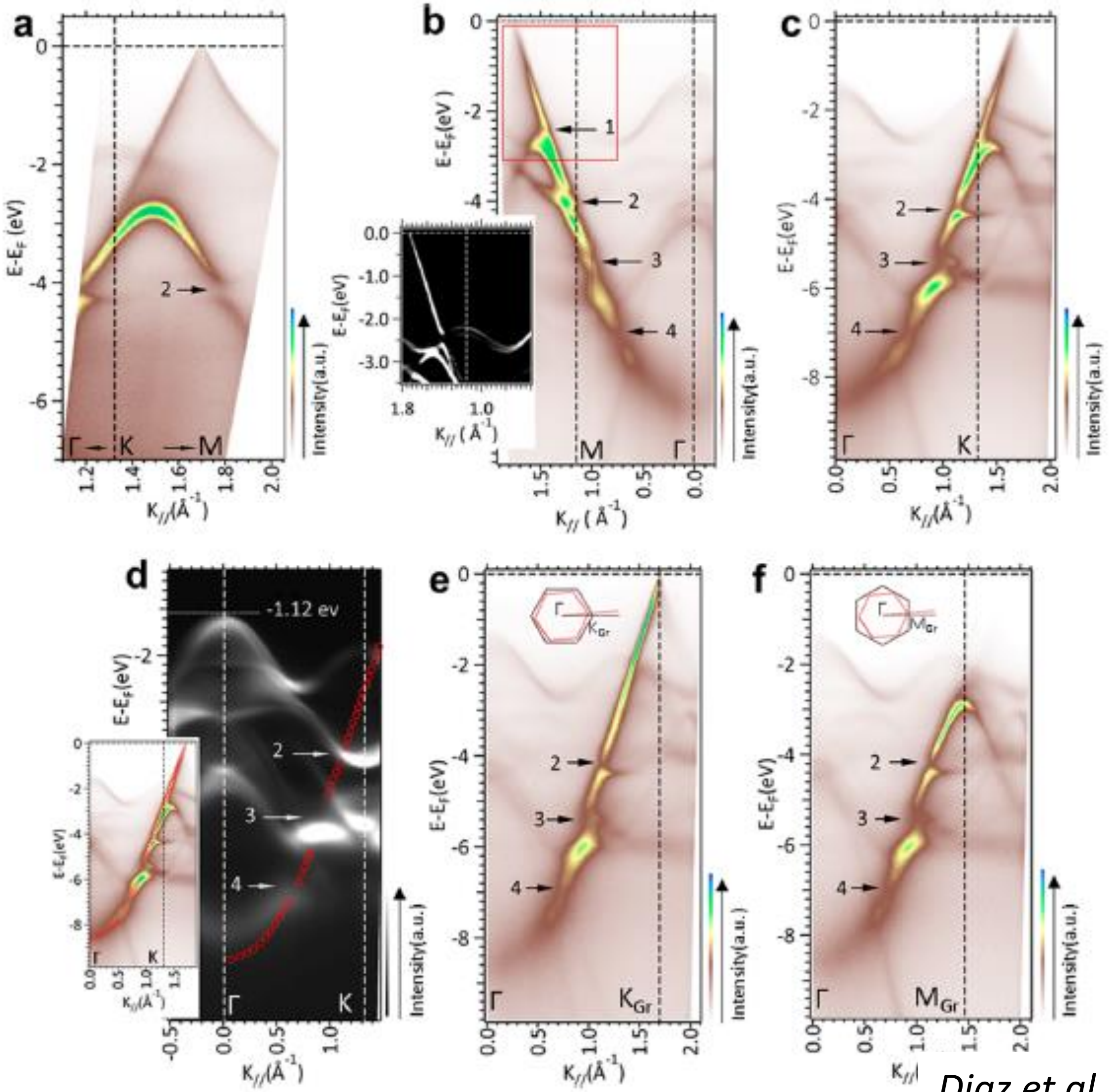
Van der Waals heterostructure : MoS_2/graphene





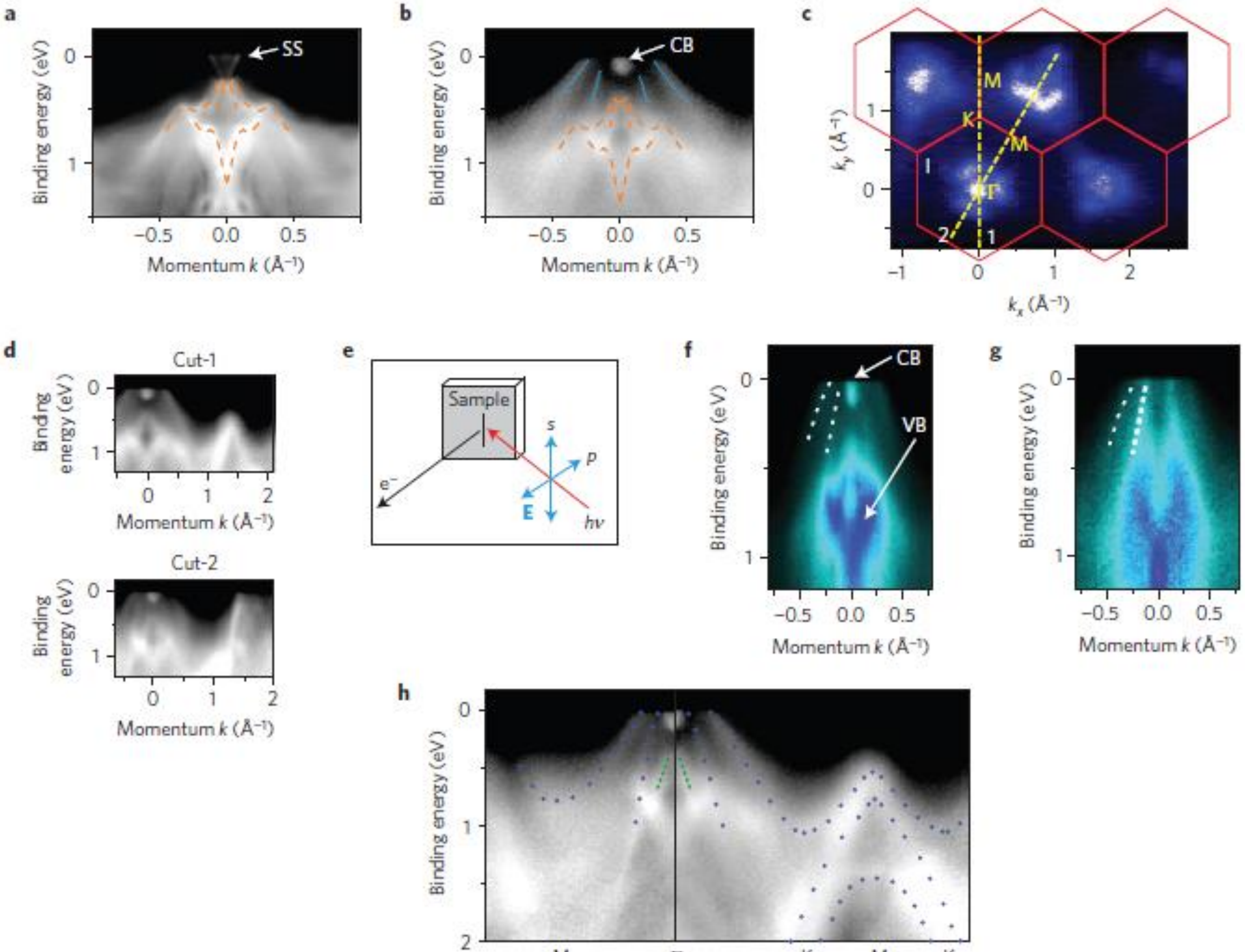
Miwa et al., ACS Nano (2015)

Van der Waals heterostructure : Graphene/MoS_2



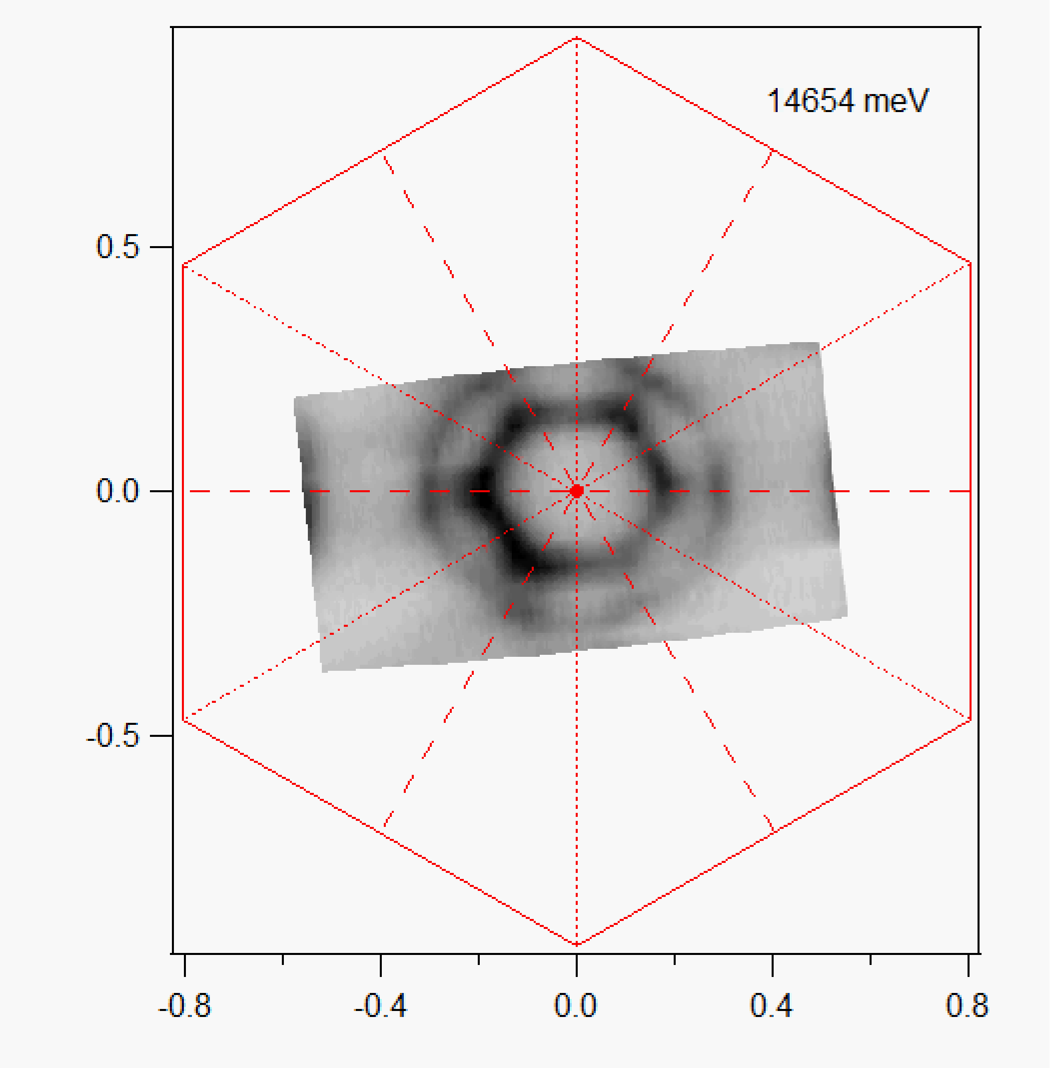
Diaz et al., Nano Lett. 2015

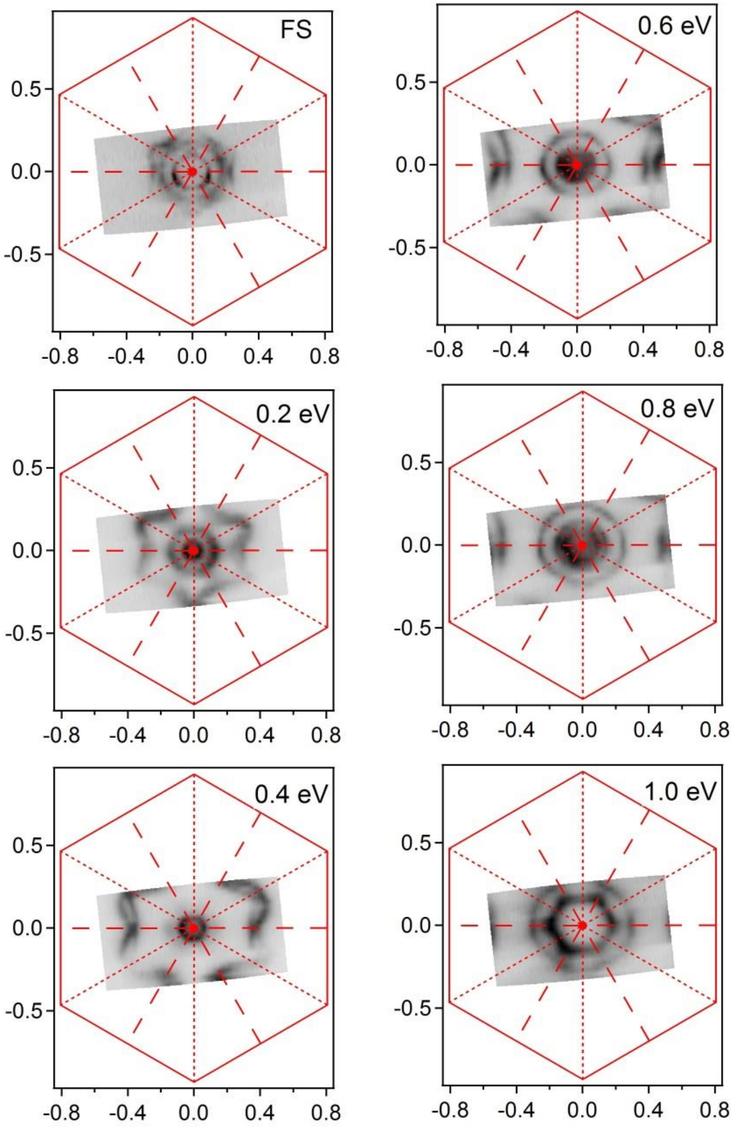
Hybrid nanostructure : Stanene/Bi_2Te_3



Zhu et al., Nat. Mater. (2015)

Single Bi bilayer/Bi_2Se_3





Summary

- ARPES can provide a deeper insight for the understanding of electronic property in 2D materials.

- A combination with other tools, such as XPS, XAS, STM, pump-probe experiment …etc., can establish better model to explain novel phenomena in emergent materials

- A cooperation with theorists is necessary for ARPES guys.

- Hungry for high quality single crystal or thin film

Thanks for your attention