國家同步輻射研究中心
National Synchrotron Radiation Research Center

Angle-resolved photoemission spectroscopy (ARPES) for 2D layered structure : graphene and topological insulators

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NTHU, 2013/05/09

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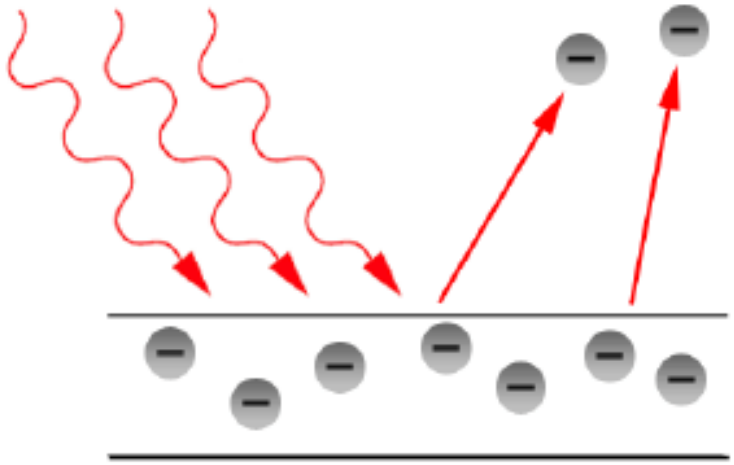
Outline

- Introduction to angle-resolved photoemission spectroscopy (ARPES)
  - The principle of ARPES
  - Synchrotron light source
  - Current status of ARPES beamline at NSRRC
  - Scientific cases
- The electronic structure of 2D layered structure
  - Surface states and quantum well states
  - Graphene (BLG)
  - Topological insulators (Tis)
- Summary

What is photoemission?

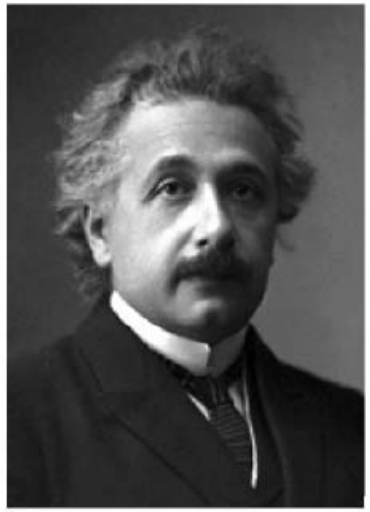


Photon in –> electron out (emission)

X-ray[1] Photoelectron spectroscopy, based on the photoelectric effect,[2,3] was developed in the mid-1960's as a practical technique by Kai Siegbahn and his research group at the University of Uppsala, Sweden.[4]

Wilhelm Conrad Röntgen

Heinrich Rudolf Hertz



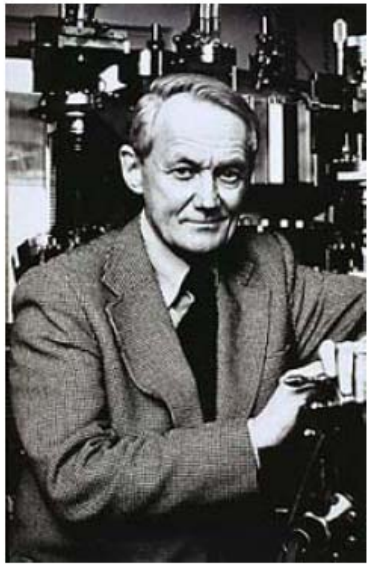
Albert Einstein

Kai M. Siegbahn

1. W. Röntgen, 1901 Nobel Prize in Physics "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him."
2. H. Hertz, *Ann. Physik* ***31,983 (1887).***
3. A. Einstein, *Ann. Physik* ***17,132 (1905). 1921 Nobel Prize in Physics "for his services to Theoretical Physics, and especially for his discovery of the*** law of the photoelectric effect."
4. K. Siegbahn, Et. Al.,*Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics "for his contribution to the development of* high resolution electron spectroscopy."

Kai Seigbahn: Development of X-ray Photoelectron Spectroscopy

C. Nordling E. Sokolowski and K. Siegbahn, *Phys. Rev.* **1957**, *105*, 1676.



Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

WE have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method

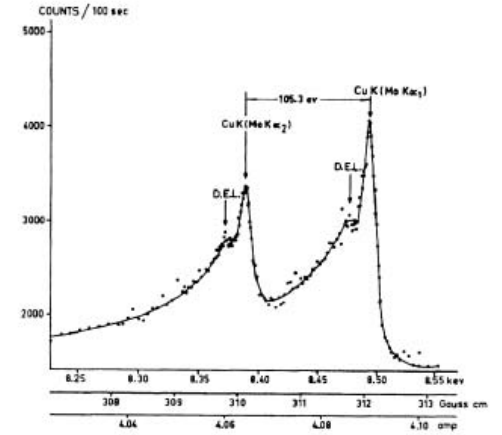
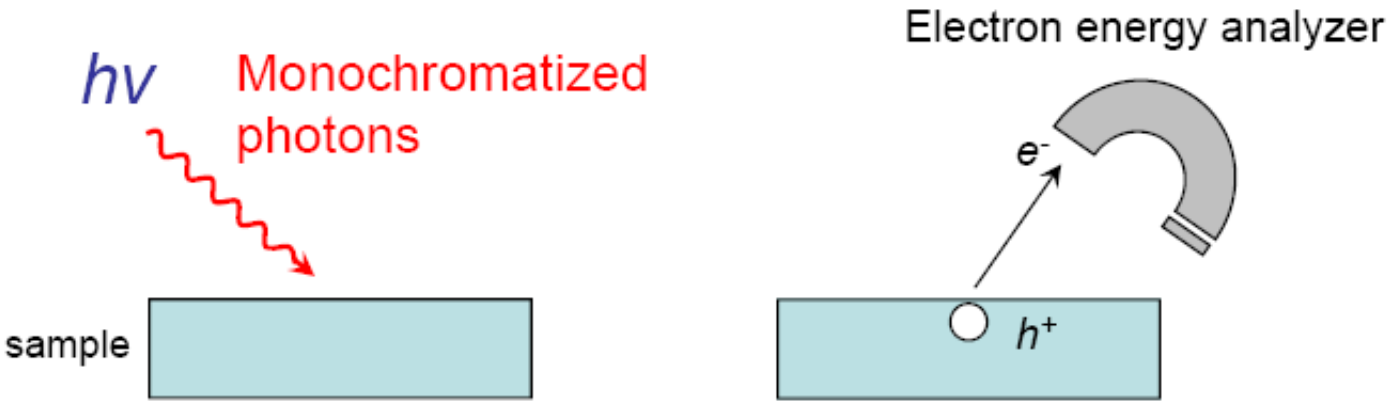


FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

Nobel Prize in Physics 1981
(His father, Manne Siegbahn, won the Nobel Prize in Physics in 1924 for the development of X-ray spectroscopy)

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)

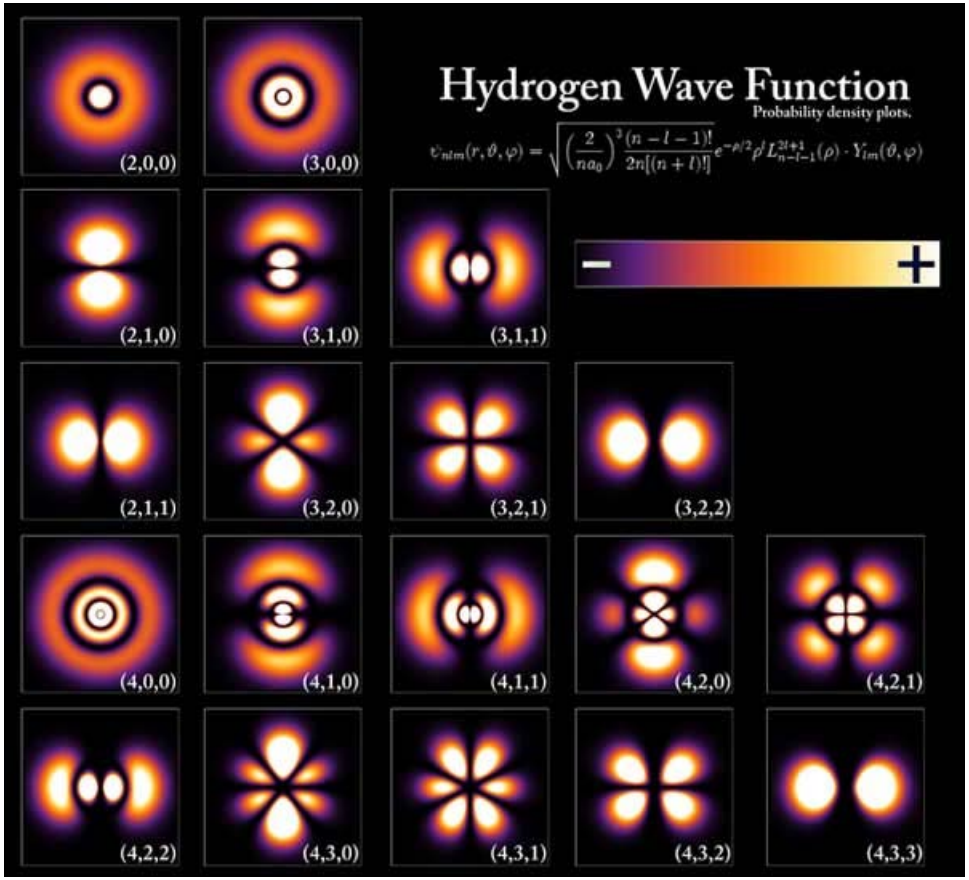
E_k : photoelectron kinetic energy
$E_i(N)$: total initial state system energy
$E_f(N\text{-}1)$: total final state system energy

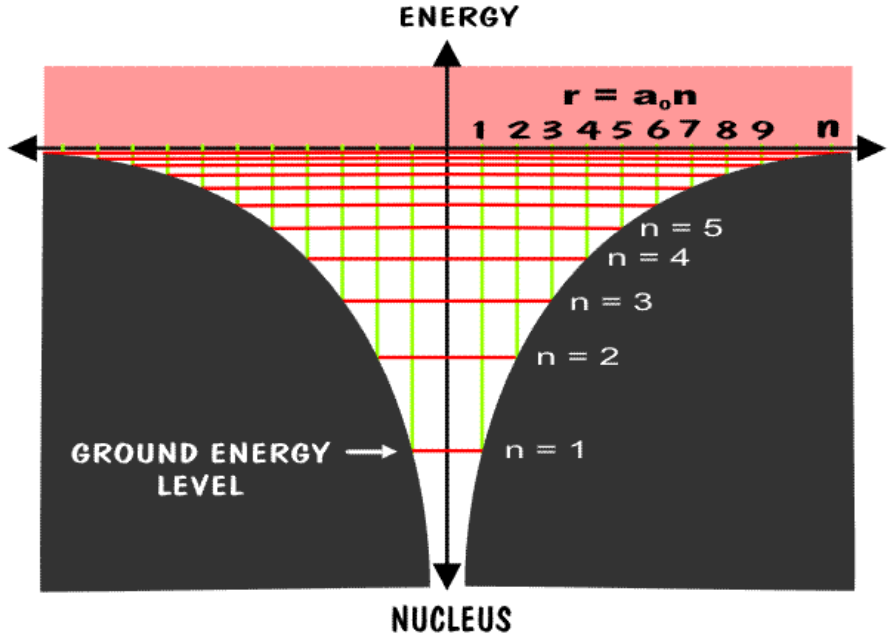
Energy Distribution Curve (EDC) (Spectrum)

What are the samples and probed states?

- Atoms — atomic orbitals (states)
- Molecules — molecular orbitals
  core level states (atomic like)
- Nanoprticles — valence bands/states
  core level states (atomic like)
- Solids — valence bands
  core level states (atomic like)

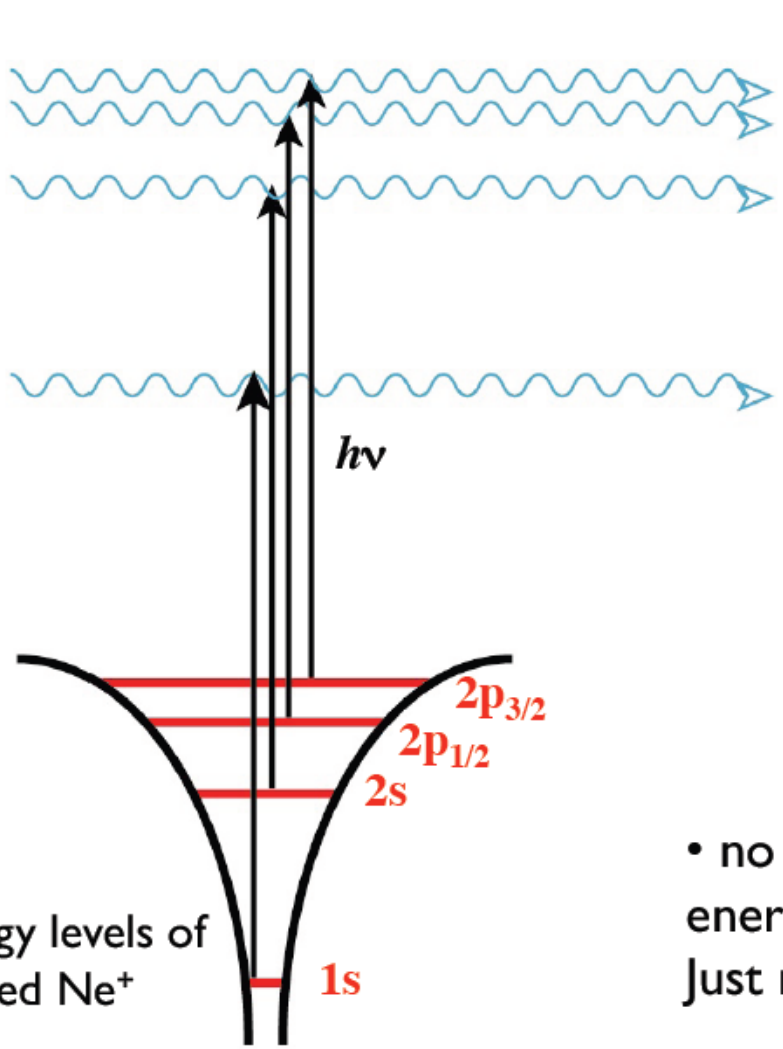
The energy level of hydrogen atom



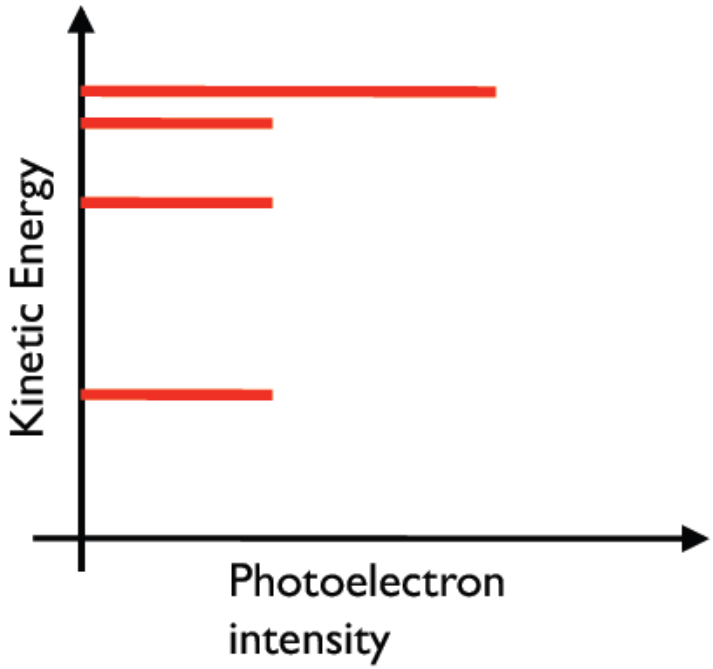


Electron ionization levels are formed from *discrete levels* in an atom

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!

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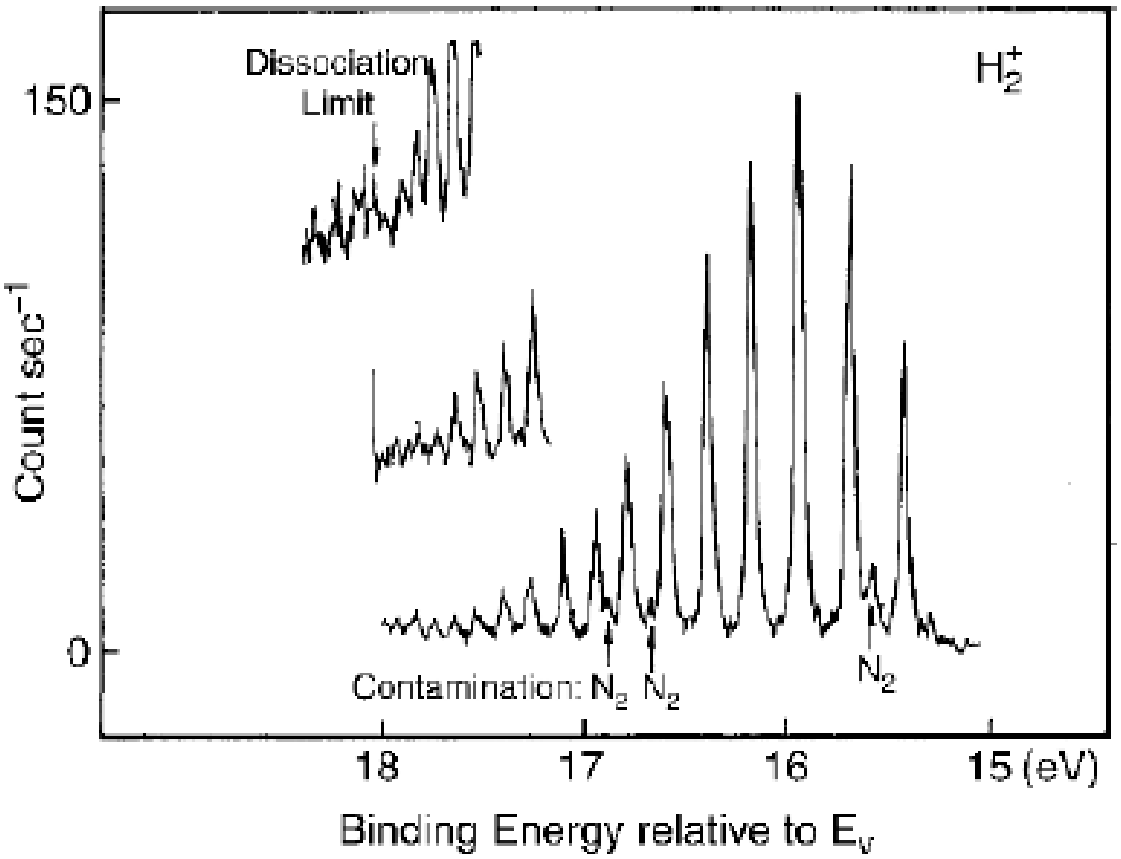
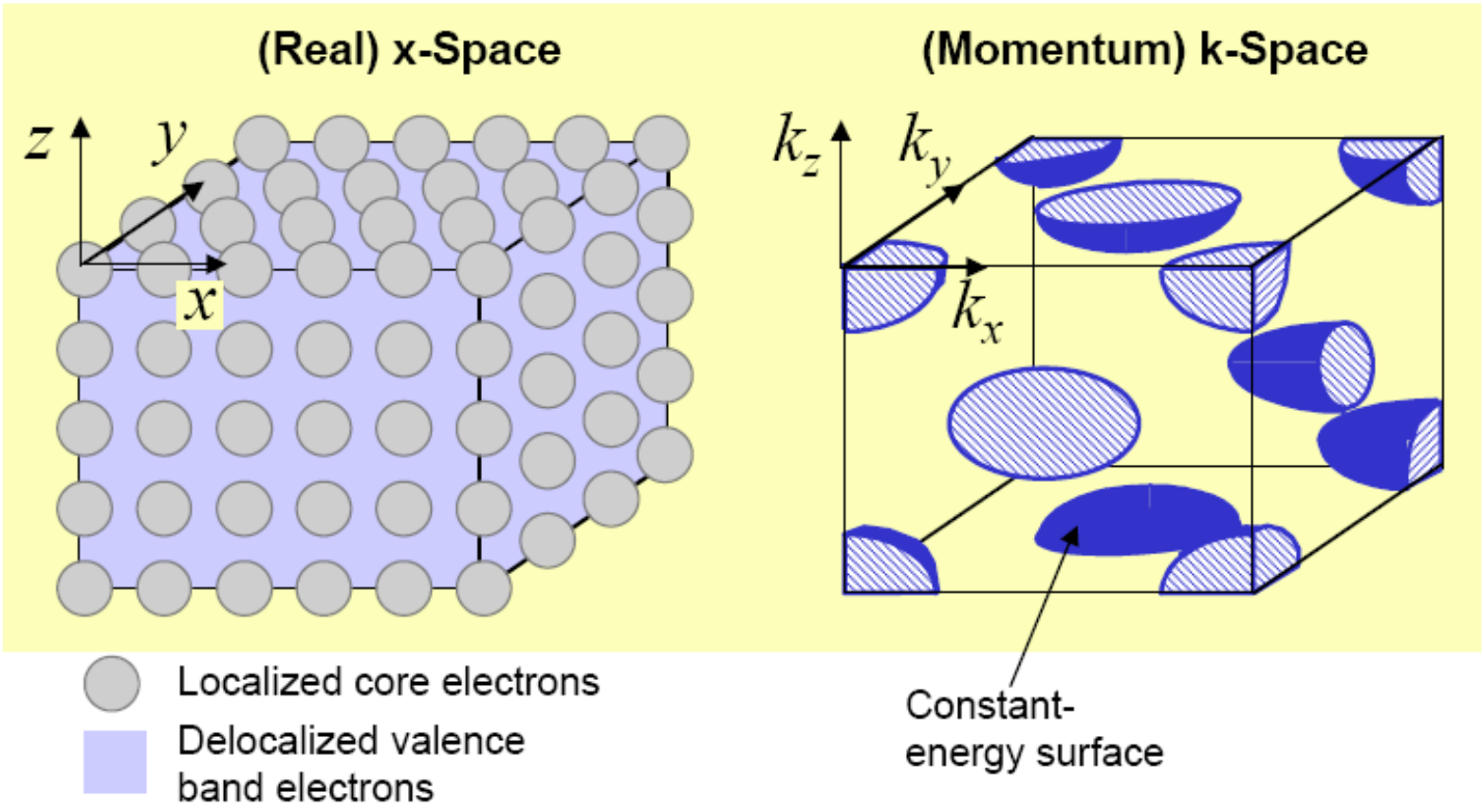
Kyle Shen, IGERT Lecture 2008

Xeon gas phase test

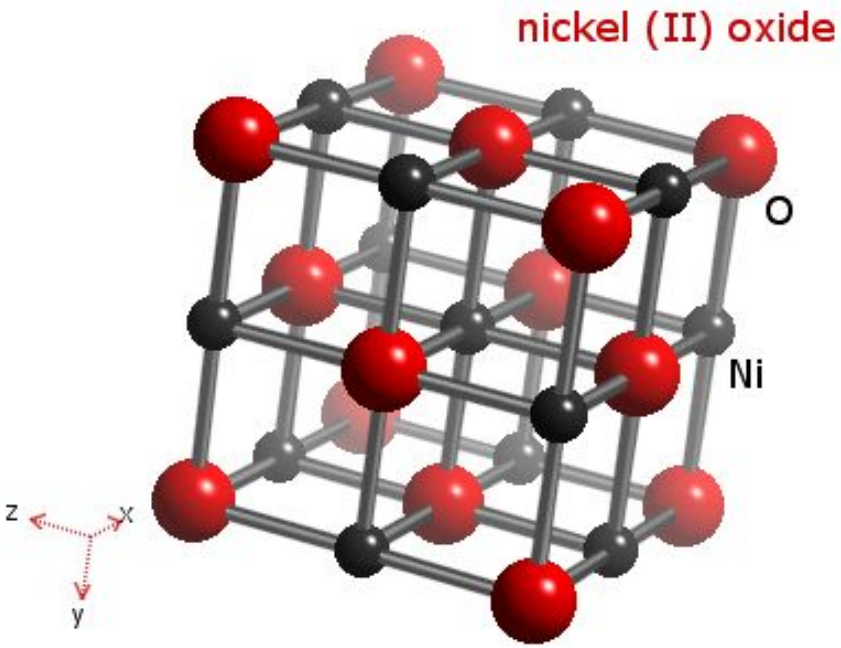


ect
t: R4000-4MS278
Scienta
1/27/2011
gy: 2 eV
Scienta
e: 59000 ms
1
t Resolution: 3.8 meV
t Resolution: 1.7 meV

The crystal structure and momentum space



Z. Hussain, ALS summer school



primitive vectors $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$

reciprocal lattice vector $\mathbf{b_1}$,$\mathbf{b_2}$,$\mathbf{b_3}$

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

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

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

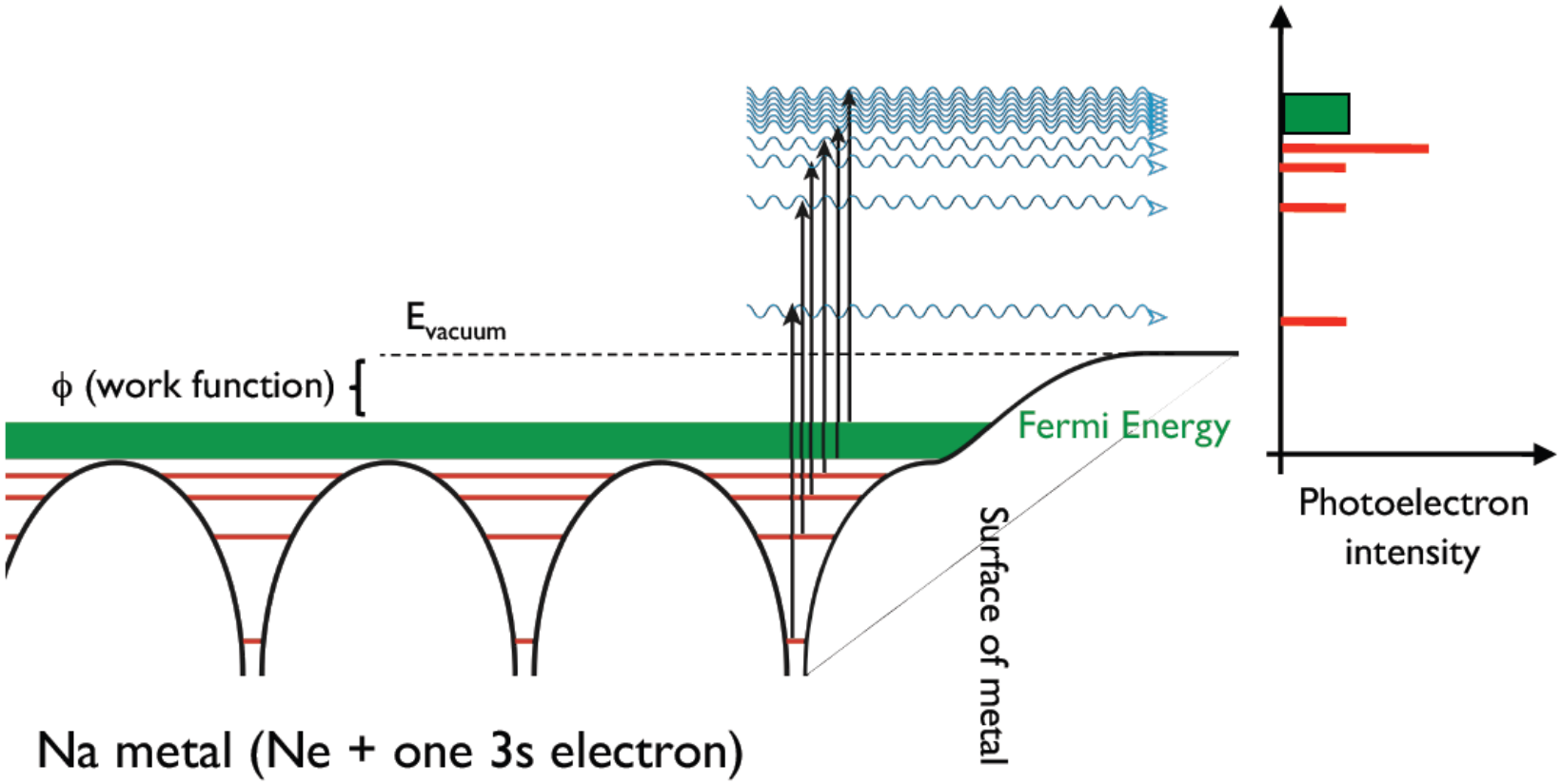
$$V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$$

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*"



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.

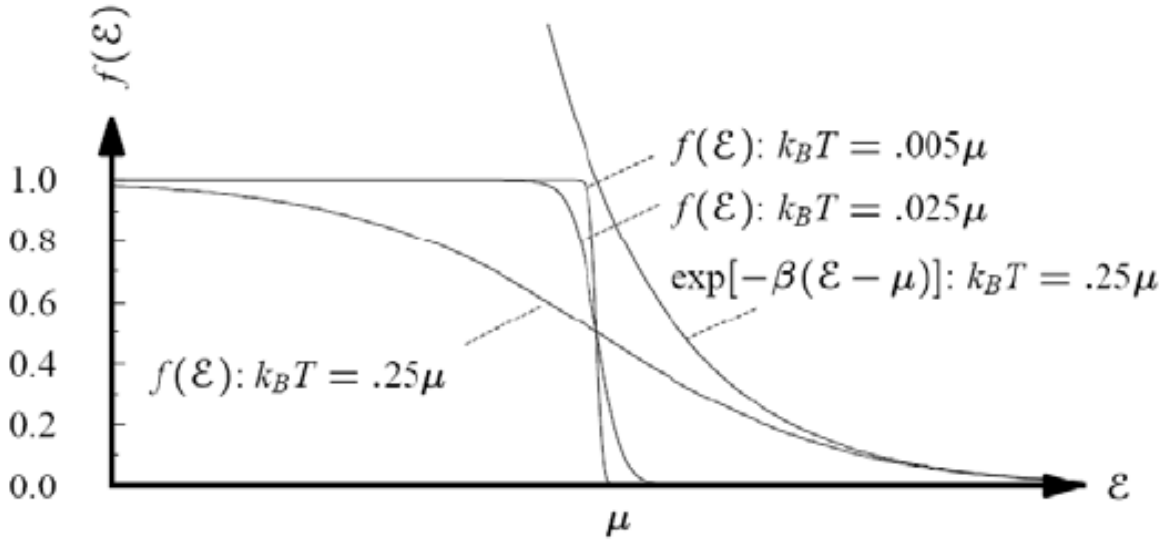
Fermi-Dirac Distribution

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

Thermal Properties of Free Electron Gas:

Fermi function (Fermi-Dirac distribution)

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



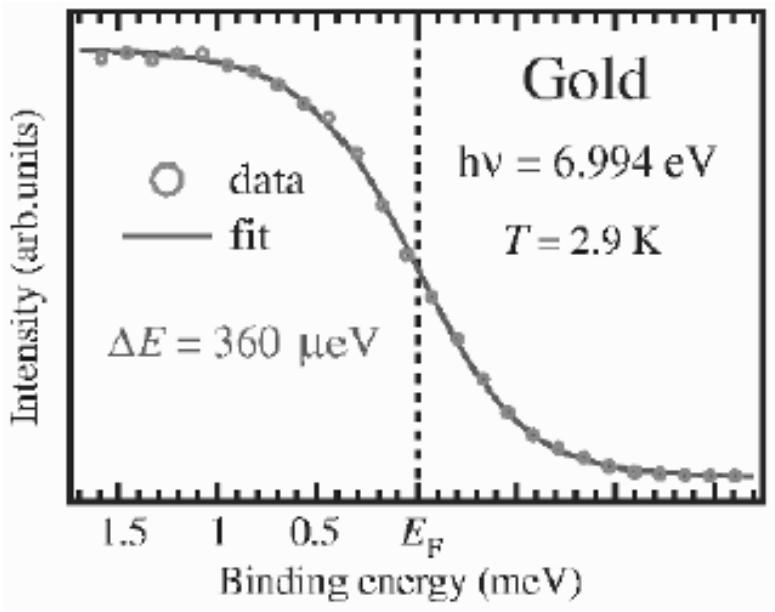
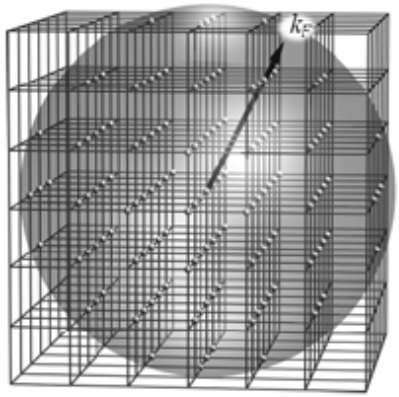


Fig. 2.3. Ultra-high resolution photoemission spectrum on a polycrystalline gold sample (evaporated Au film) for the determination of the energy resolution. The Fermi edge was measured at $T = 2.9\,\mathrm{K}$ using a frequency tripled ($KBe_2BO_3F_2$ crystal, KBBF) YVO_3 laser for the photoexcitation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

Hufner, very high resolution photoelectron spectroscopy

Density of State



In building up the ground state of very large N electrons, the ground state corresponds to setting the occupation number f_k =1 for $k \le k_F$ and f_k =0 for others; k_F is called the Fermi vector.

The volume of the Fermi sphere is $\frac{4\pi k_F^3}{3}$.

Electronic density $n = \frac{N}{\mathcal{V}} = (\frac{4\pi k_F^3}{3}) D_{\vec{k}} = (\frac{4\pi k_F^3}{3}) \frac{2}{(2\pi)^3} = \frac{k_F^3}{3\pi^2}$

For an energy $\mathcal{E}$, total numbers of states:

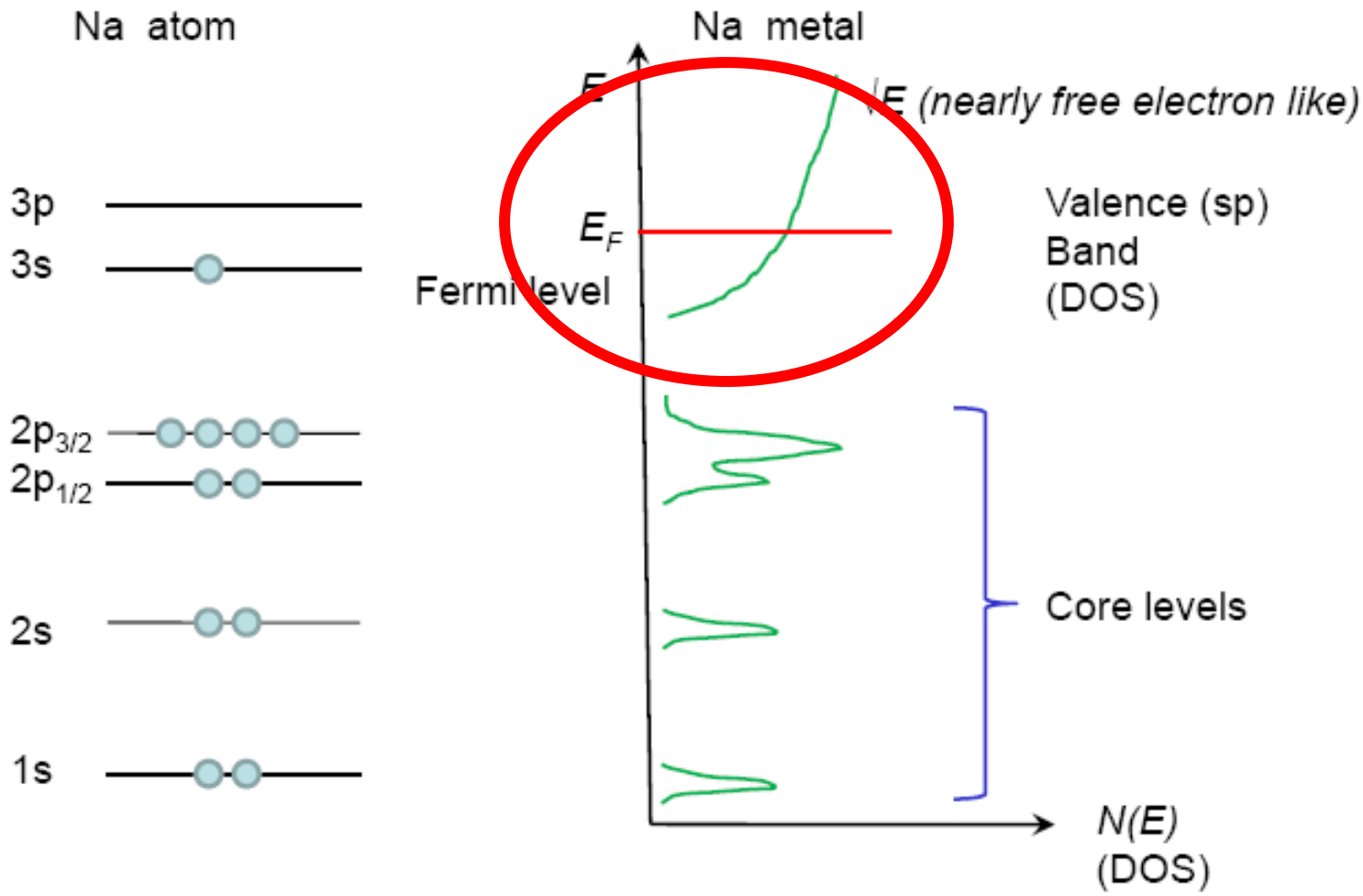
$$N = \mathcal{V} \frac{k^3}{3\pi^2} = V \frac{(2m\mathcal{E})^{3/2}}{3\pi^2\hbar^3} \qquad \because \ \mathcal{E} = \frac{\hbar^2 k^2}{2m} \quad k = \frac{\sqrt{2m\mathcal{E}}}{\hbar}$$

Energy density of states $D(\mathcal{E}) \equiv \frac{1}{\mathcal{V}} \frac{dN}{d\mathcal{E}}$

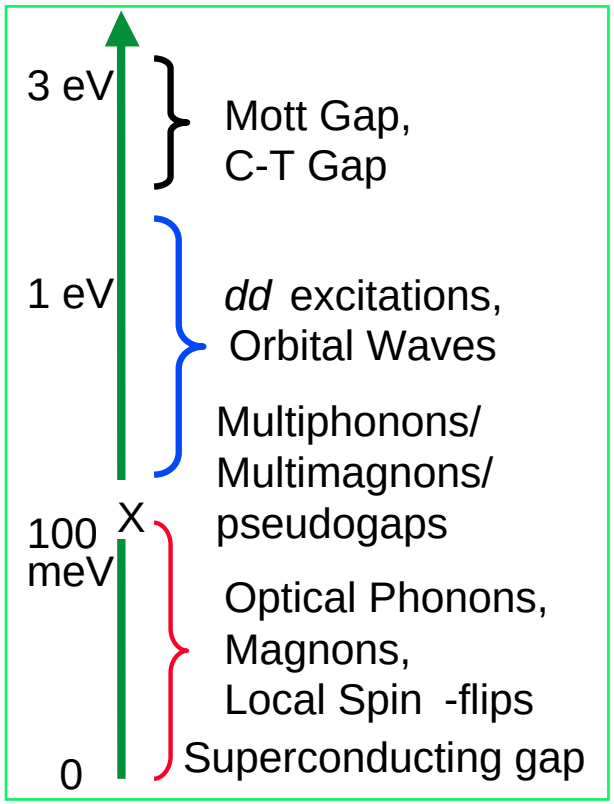
No. of states bounded between $\mathcal{E}(k)$ and $\mathcal{E}(k) + d\mathcal{E}$ per unit volume

$$D(\mathcal{E}) = \frac{1}{\mathcal{V}} \frac{dN}{d\mathcal{E}} = \frac{\sqrt{2m^3\mathcal{E}}}{\pi^2\hbar^3}$$

Single particle description of energy levels (Density of States) (most convenient in PE)



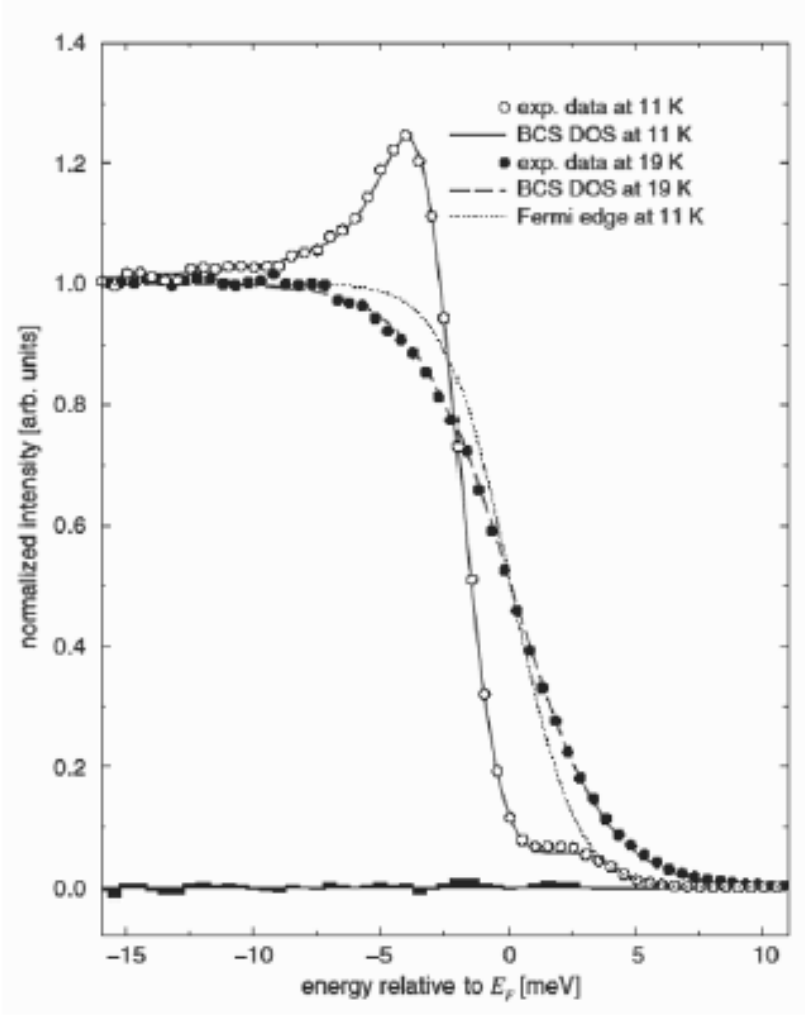
Energy scale and important excitations

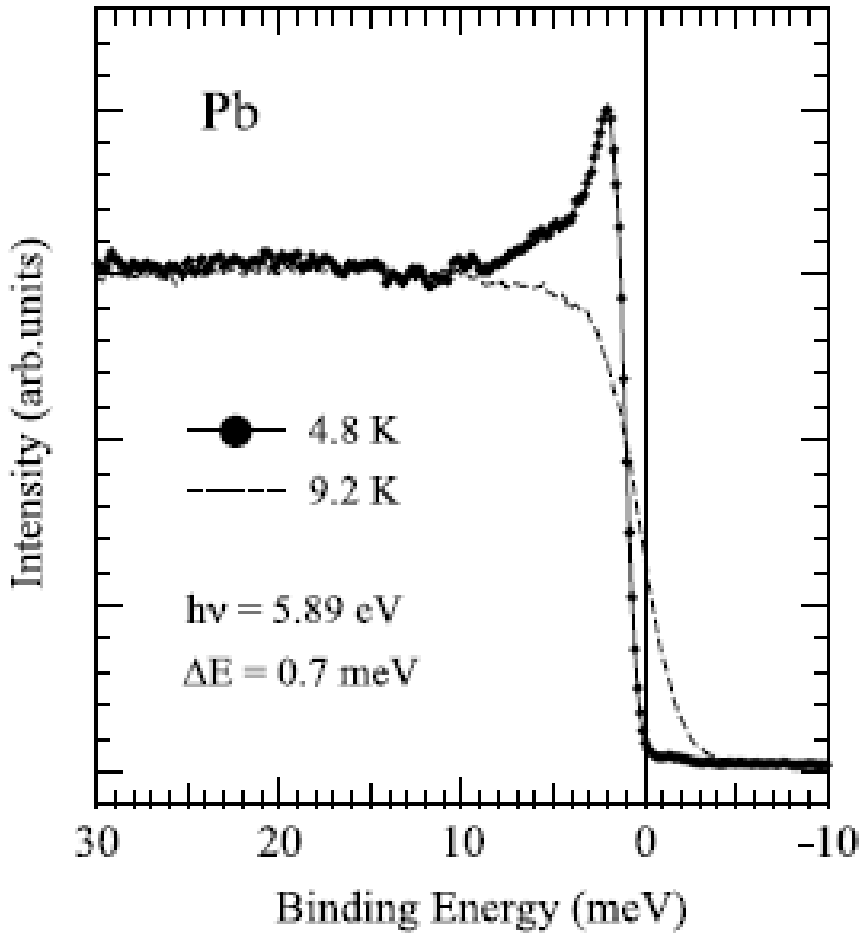


- Superconducting gap ~ 1 – 100meV
- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Pseudogap ~ 30-300 meV
- Multiphonons and multimagnons ~ 50-500 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~ 100 meV - 1.5 eV

Requirement: High Energy Resolution with High Intensity

Superconducting gap





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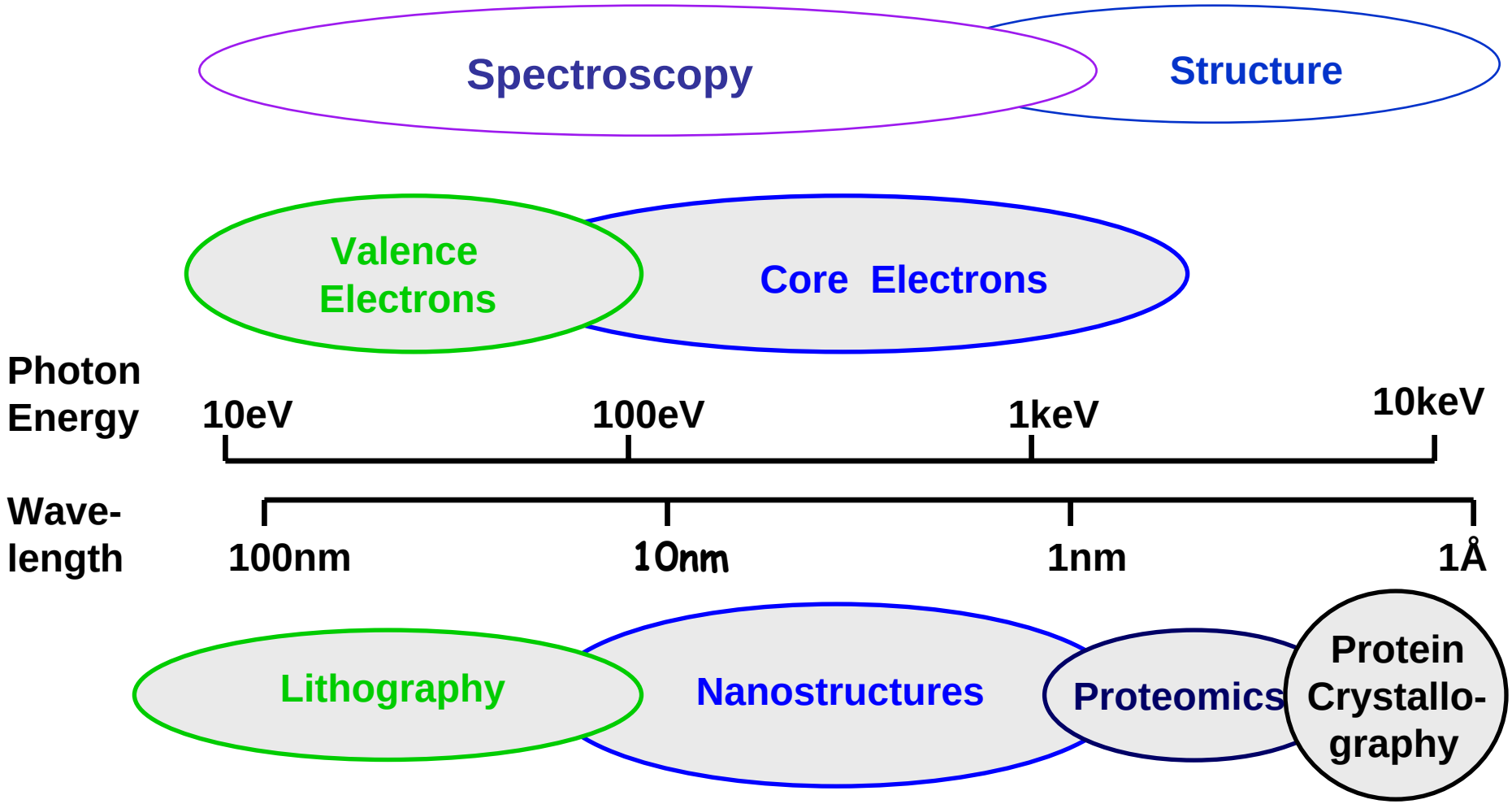
Hufner, very high resolution photoelectron spectroscopy

Science with Light Sources



Adopted from: Franz Himpsel, CMMP '07

Light sources and terminology

- **Ultraviolet Photoemission Spectroscopy (UPS)**
  - UV He lamp (21.2 eV, 40.8 eV)
  - Laser (high harmonic generation): 6 eV (BBO), 8 eV (KDDP), 11 eV (gas cell)
  - 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

3rd Synchrotron Radiation light source

Synchrotron Radiation

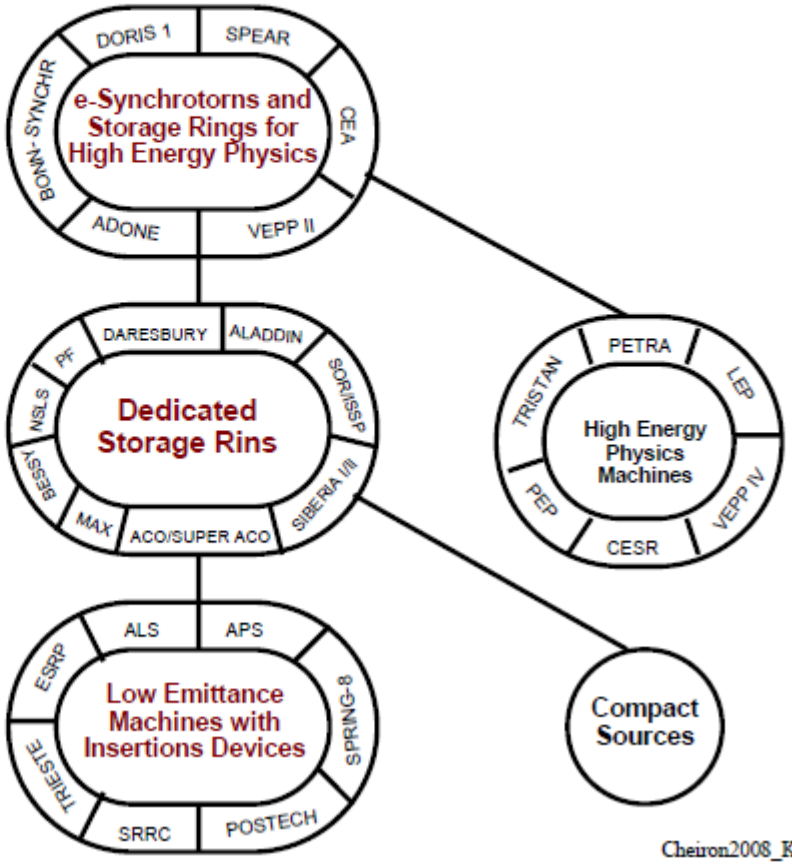
Year 1947: First Synchrotron Radiation observed in weak focusing synchrotron betatrons

1st G :1960-1970

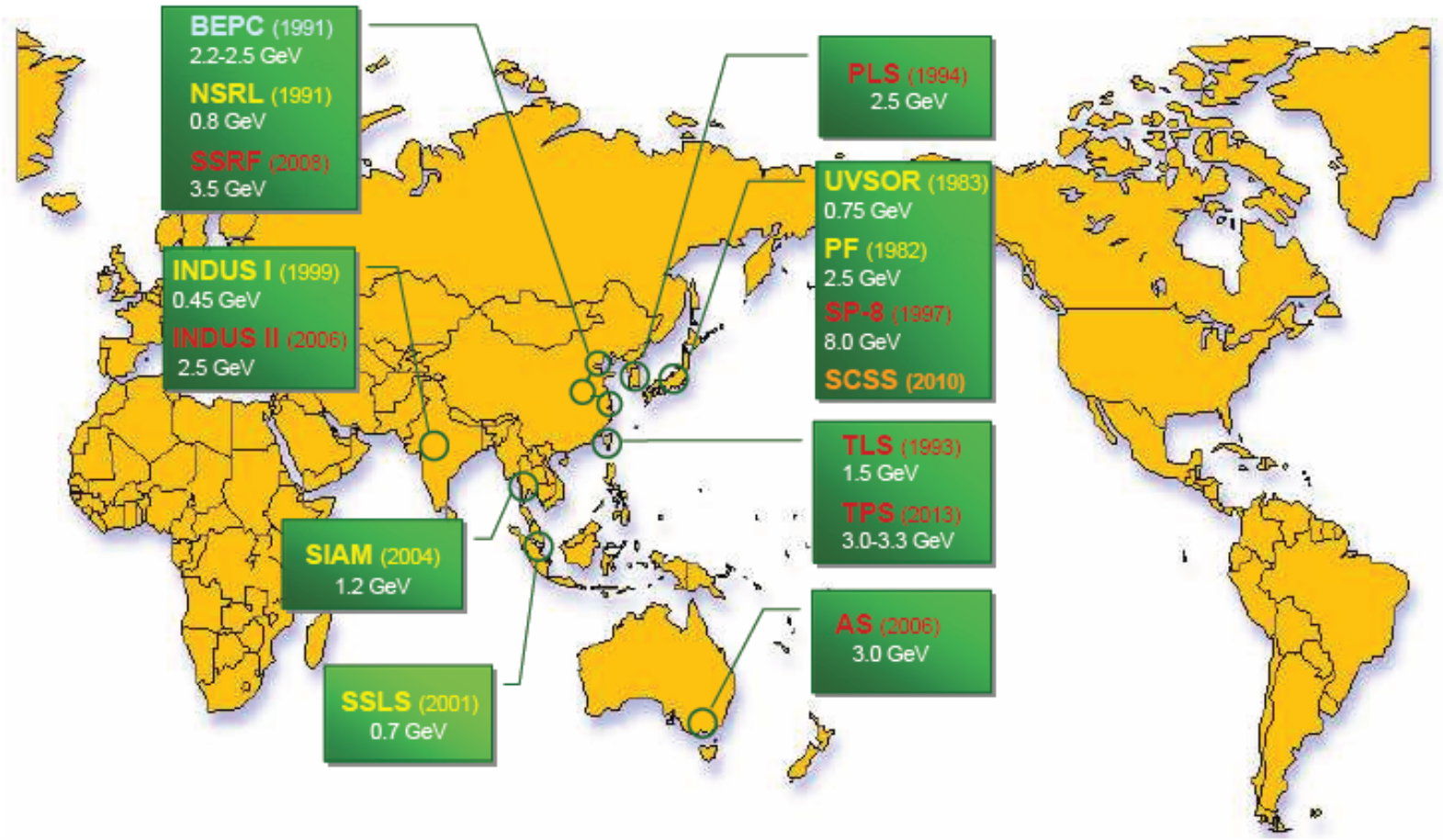
2nd G :1970-1980

3rd G :1980-

- Straight sections for insertion devices
- Low emittance

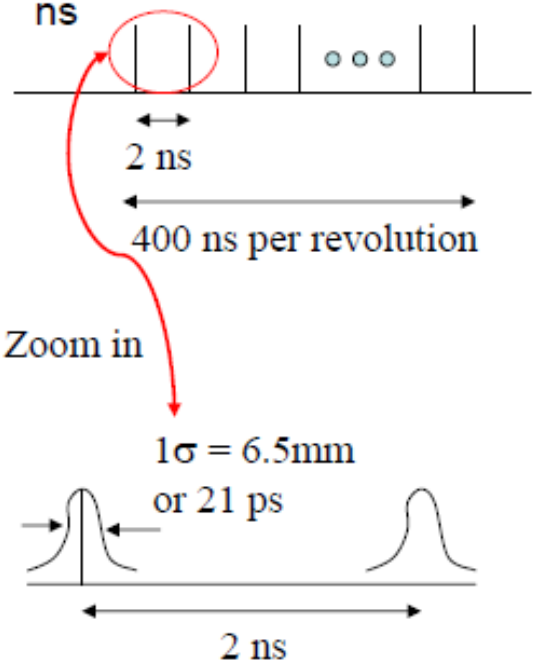


SR Facilities in Asia Oceania Region

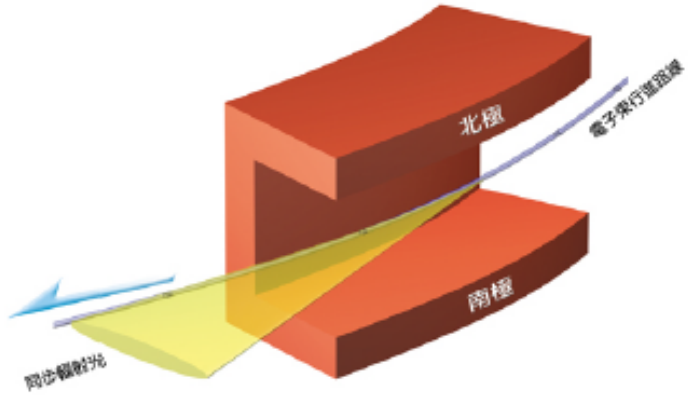


Basic Parameters of Taiwan Light Source

- Interval between bunches: 2ns
- Bunch length (1σ@1.6MV): 6.5 mm
- Bunch duration (1σ): 21 ps
- SC Cavity length: 24 cm
- Flight time through SC cavity: 0.8 ns



- Bunch current (180/200 filling to I_{avg}=300 mA): 1.67 mA/bunch or $4.17*10^9$ electrons/bunch

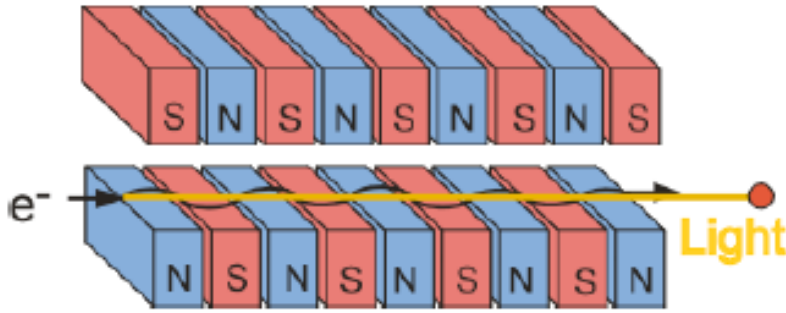


- Critical energy of SR

$$Ec(keV) = 0.665\ E^2\ (GeV)\ B(T)$$

Light source properties vs electron beam performance(1)

Main devices to supply SR to users are "undulators", which are installed in magnet-free straight sections in 3rd-generation SR sources.



5. Current limiting factors(4)

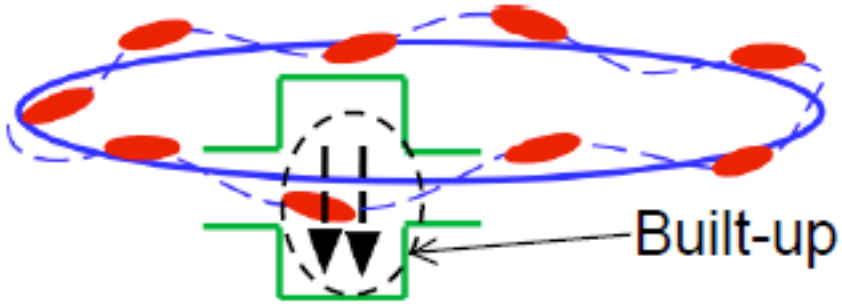
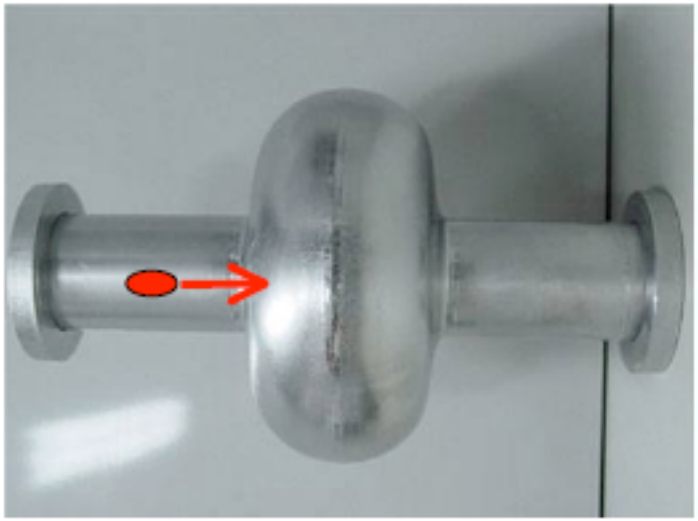
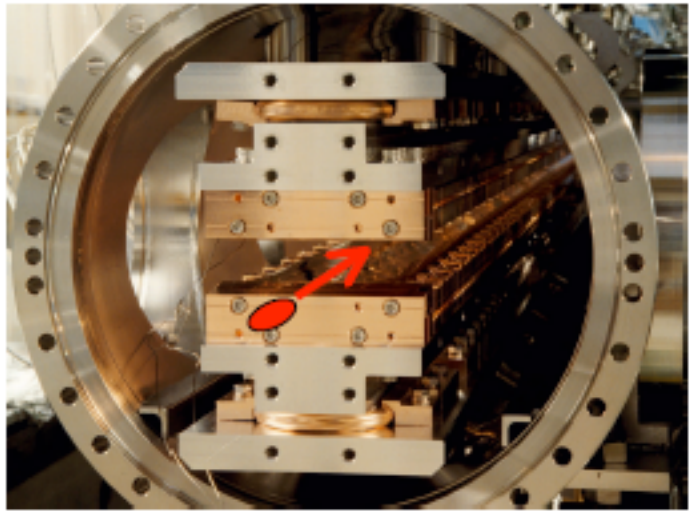


Image of the coupled bunch instability



High Q structure (RF cavity)



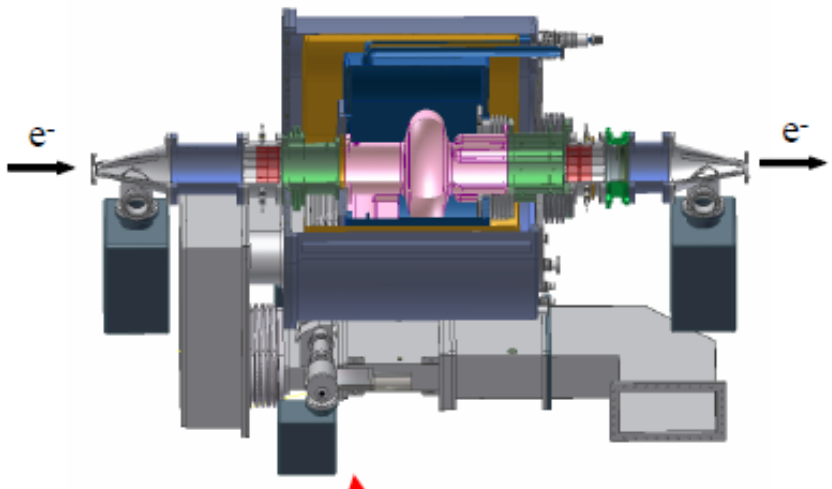
Narrow gap undulator

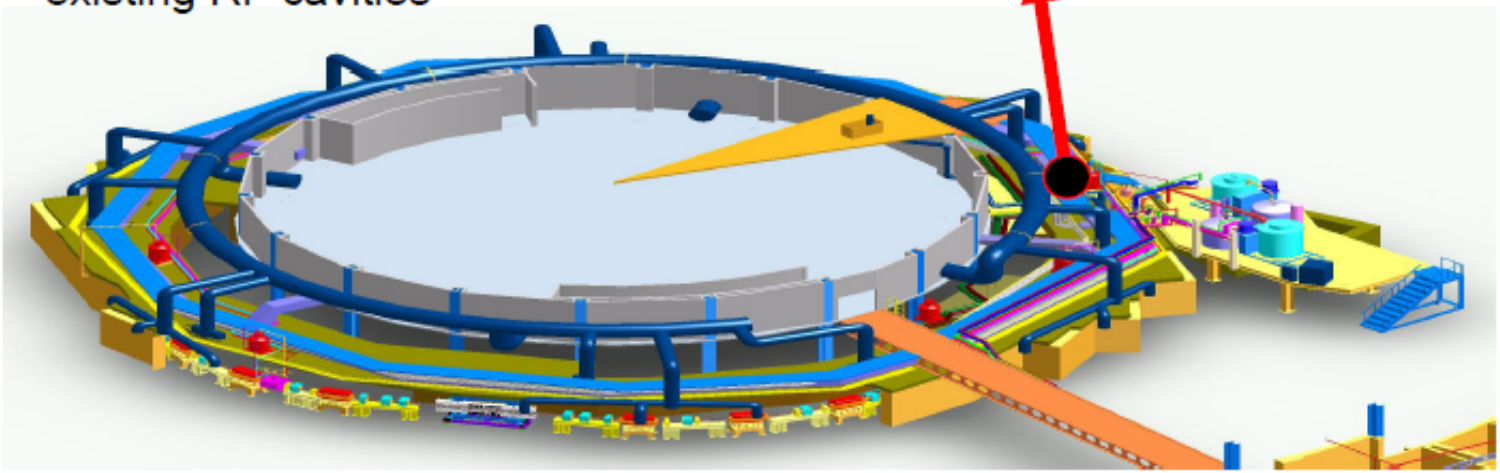
Superconducting RF Cavity

Goals :

- To increase the maximum electron beam current of the storage ring from 240 mA to 500 mA

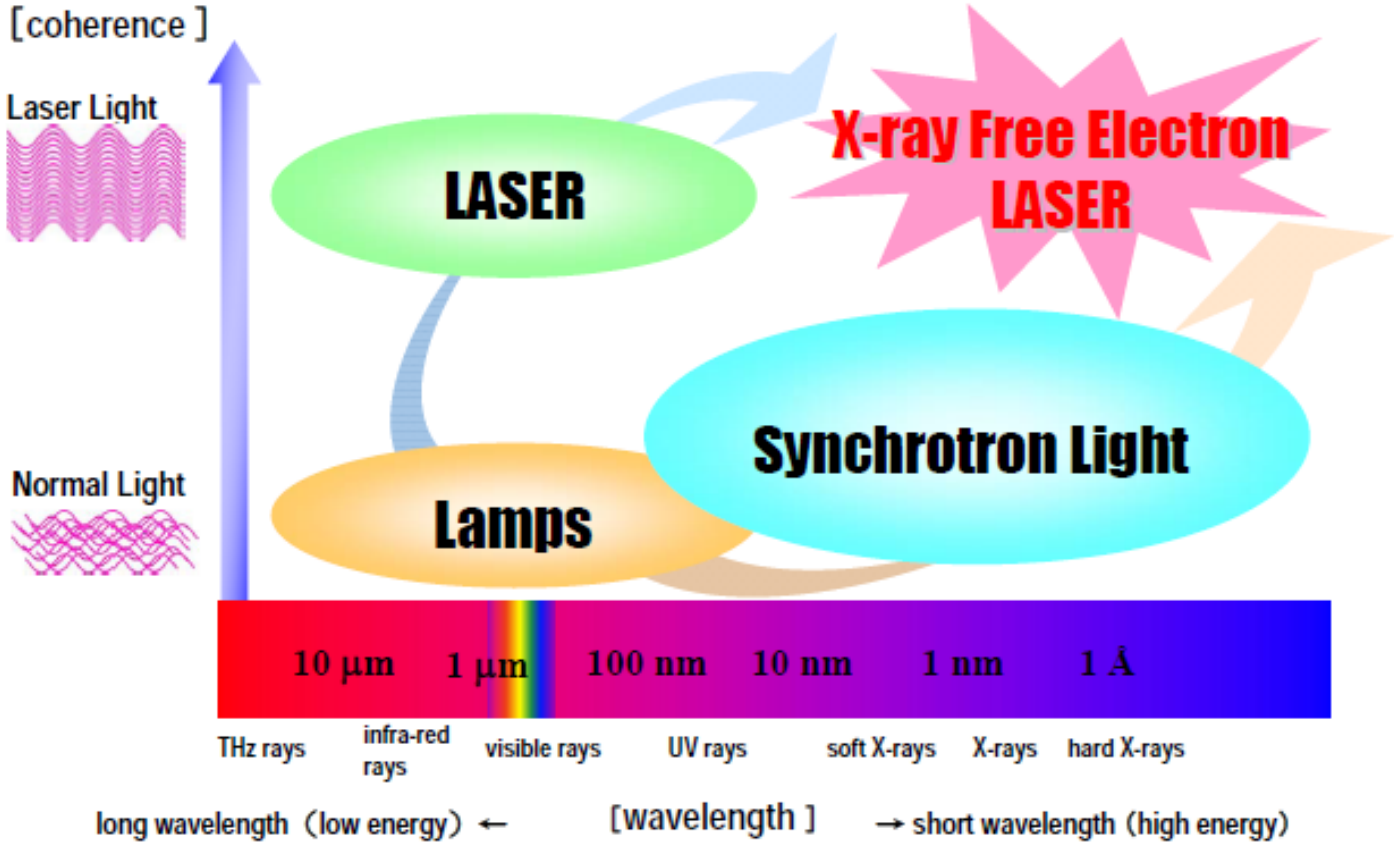
- To eliminate beam instabilities caused by the strong higher-order modes (HOMs) of the existing RF cavities



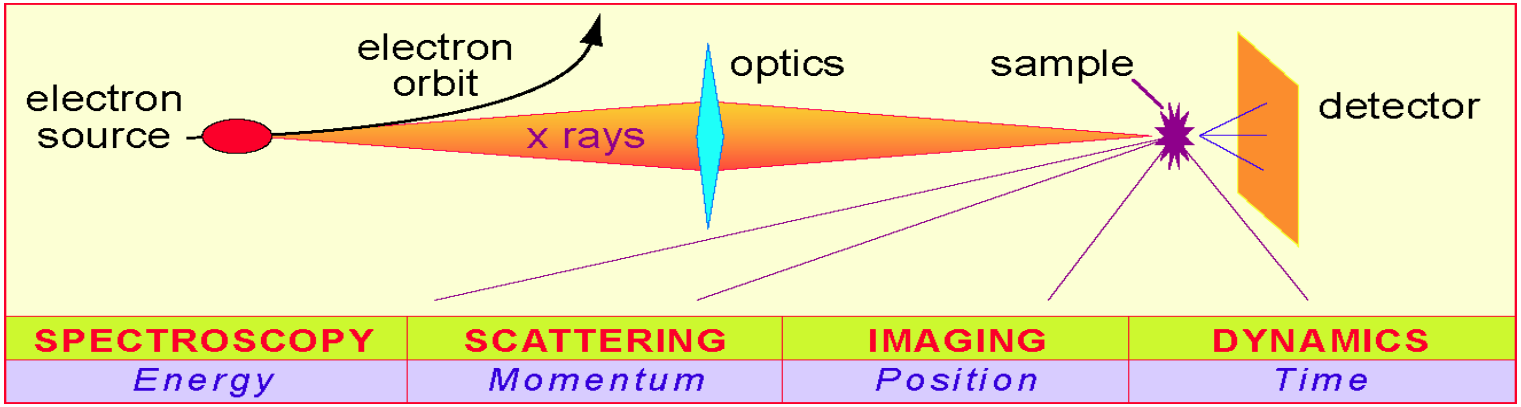


"X-ray Free Electron Laser, XFEL"

coherent light to explore nano-world



Techniques of Synchrotron Radiation (SR)



The fundamental parameters necessary for perception of physical world:

- **Energy (spectroscopy, state of matter)**
- **Momentum (scattering)**
- **Position (imaging, spatial distribution)**
- **Time (dynamics)** → numerous techniques of SR

Spectroscopy	Scattering	Imaging
01 Low-Energy Spectroscopy	05 Hard X-Ray Diffraction	09 Hard X-Ray Imaging
02 Soft X-Ray Spectroscopy	06 Macromolecular Crystallography	10 Soft X-Ray Imaging
03 Hard X-Ray Spectroscopy	07 Hard X-Ray Scattering	11 Infrared Imaging
04 Optics/Calibration/Metrology	08 Soft X-Ray Scattering	12 Lithography

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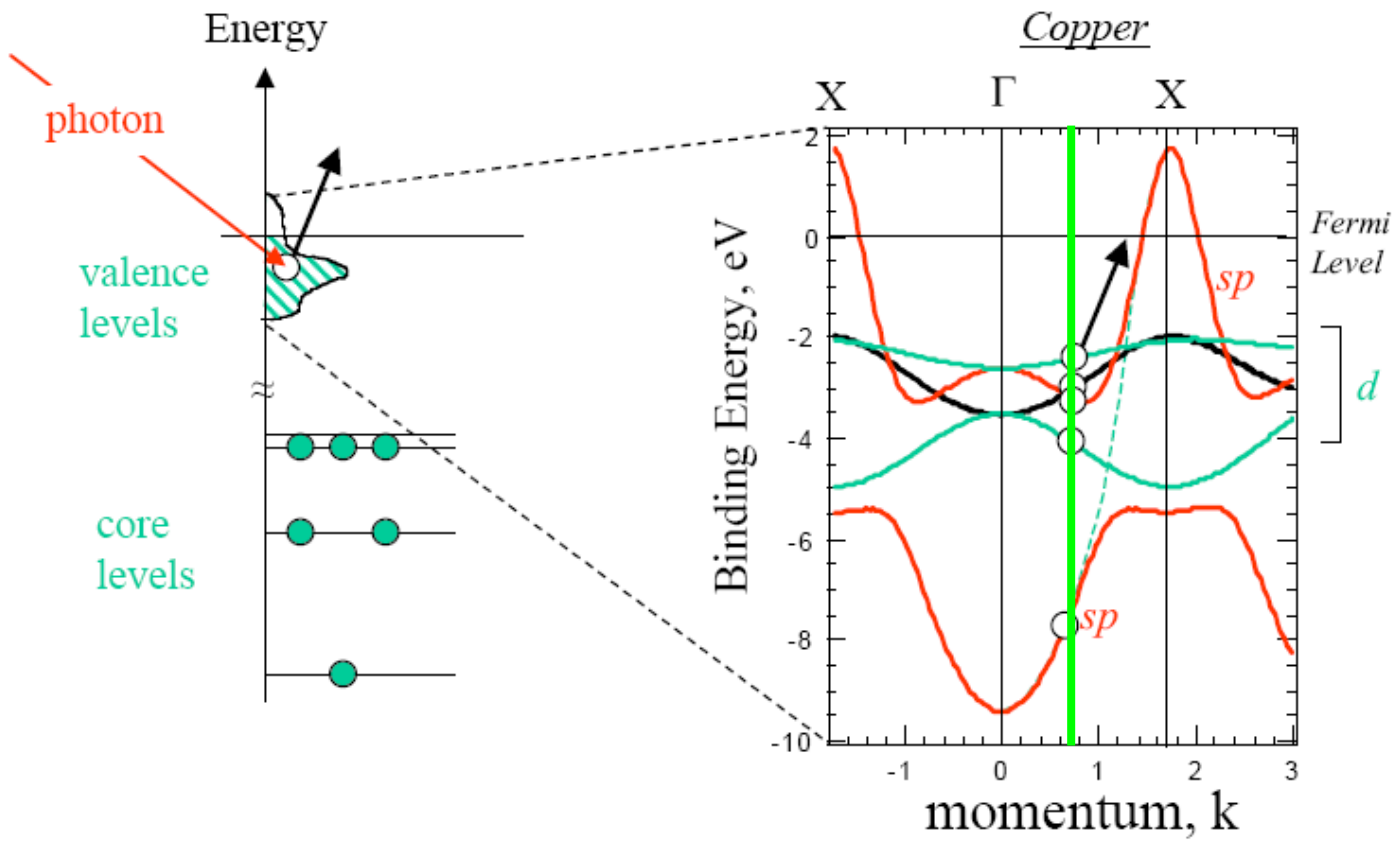
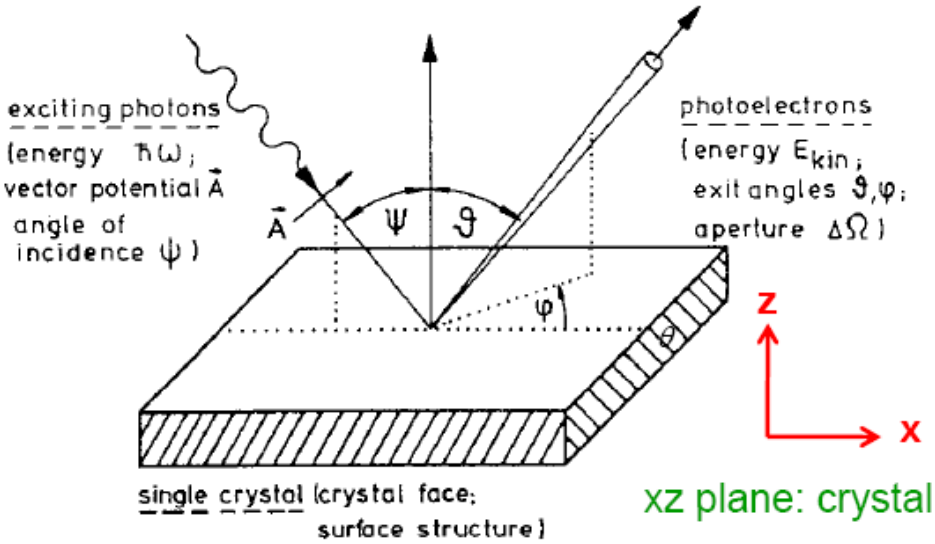
Angle-integrated photoemission (AIPES) and angle-resolved photoemission (ARPES)



Angular Resolved Photoemission Spectroscopy(ARPES)



xz plane: crystal symmetry plane

Electron emission angle: θ

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

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

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

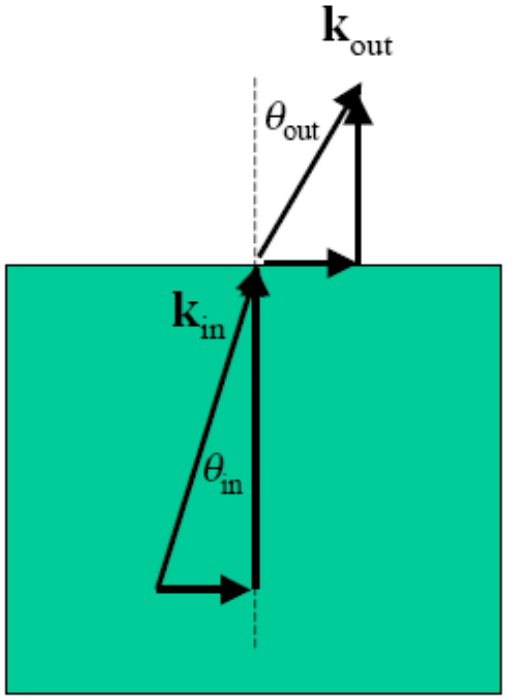
$k_{||}$(inside) = $k_{||}$(outside)

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

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

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

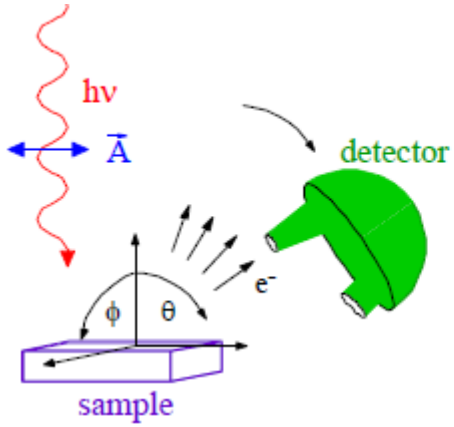
$$k_{out,\parallel} = k_{in,\parallel} \equiv k_{\parallel}$$

"Snell's Law"

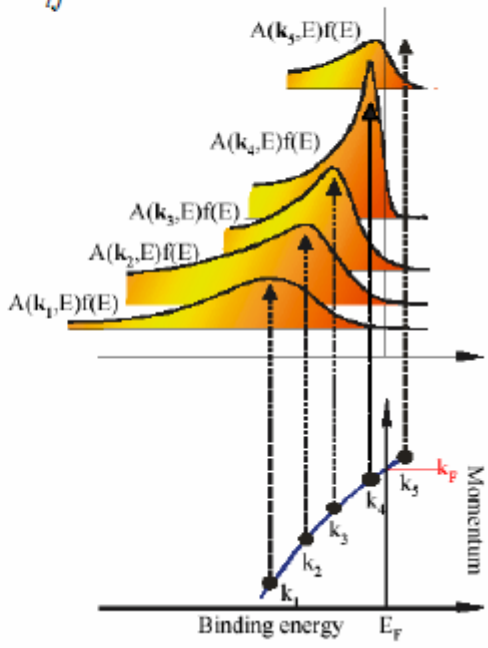
$$k_{\parallel} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission

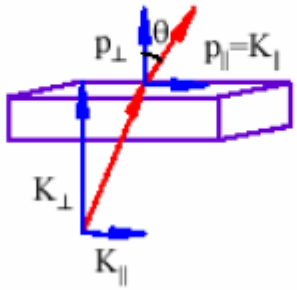
$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$



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



Electron momentum
Parallel to the surface is
conserved

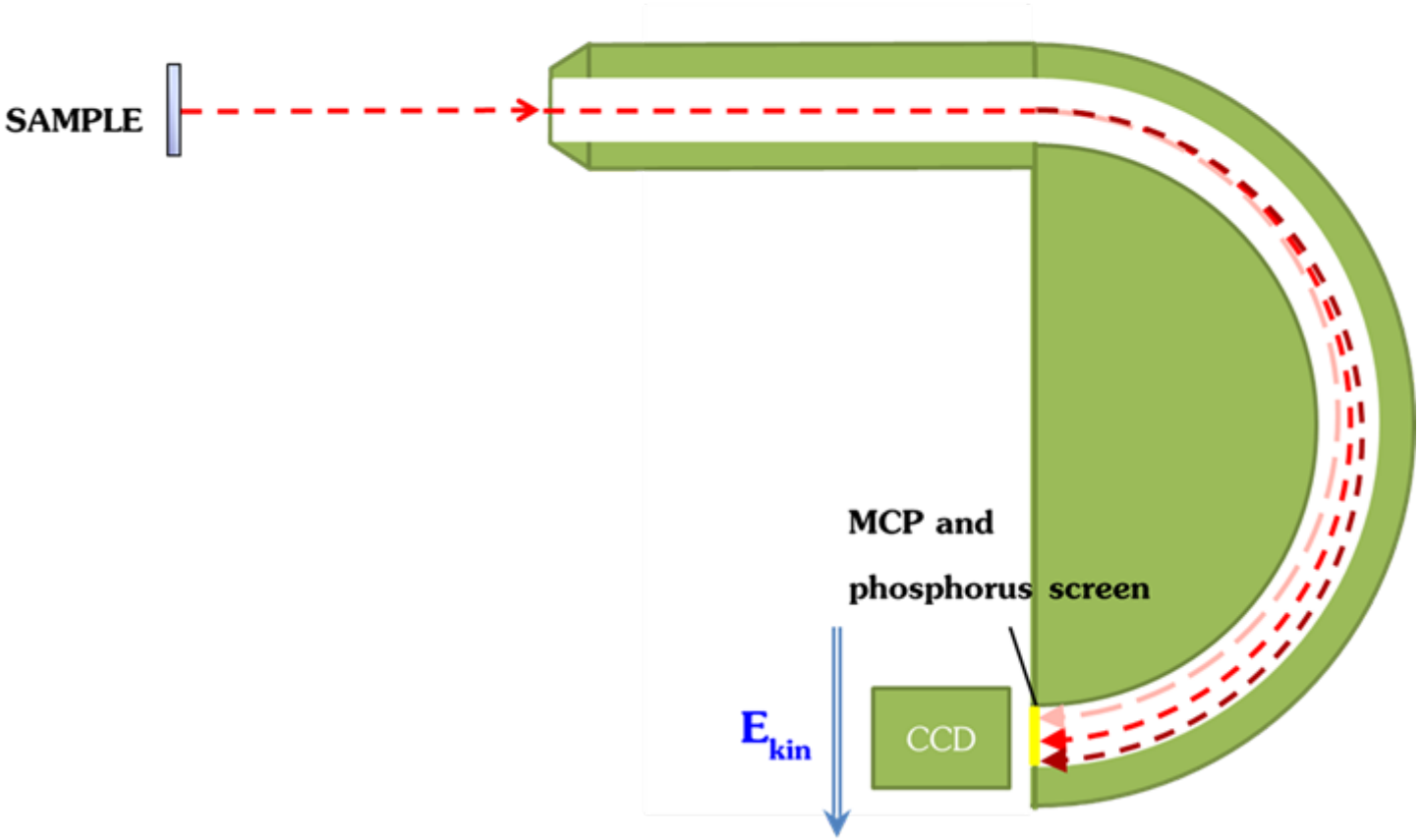


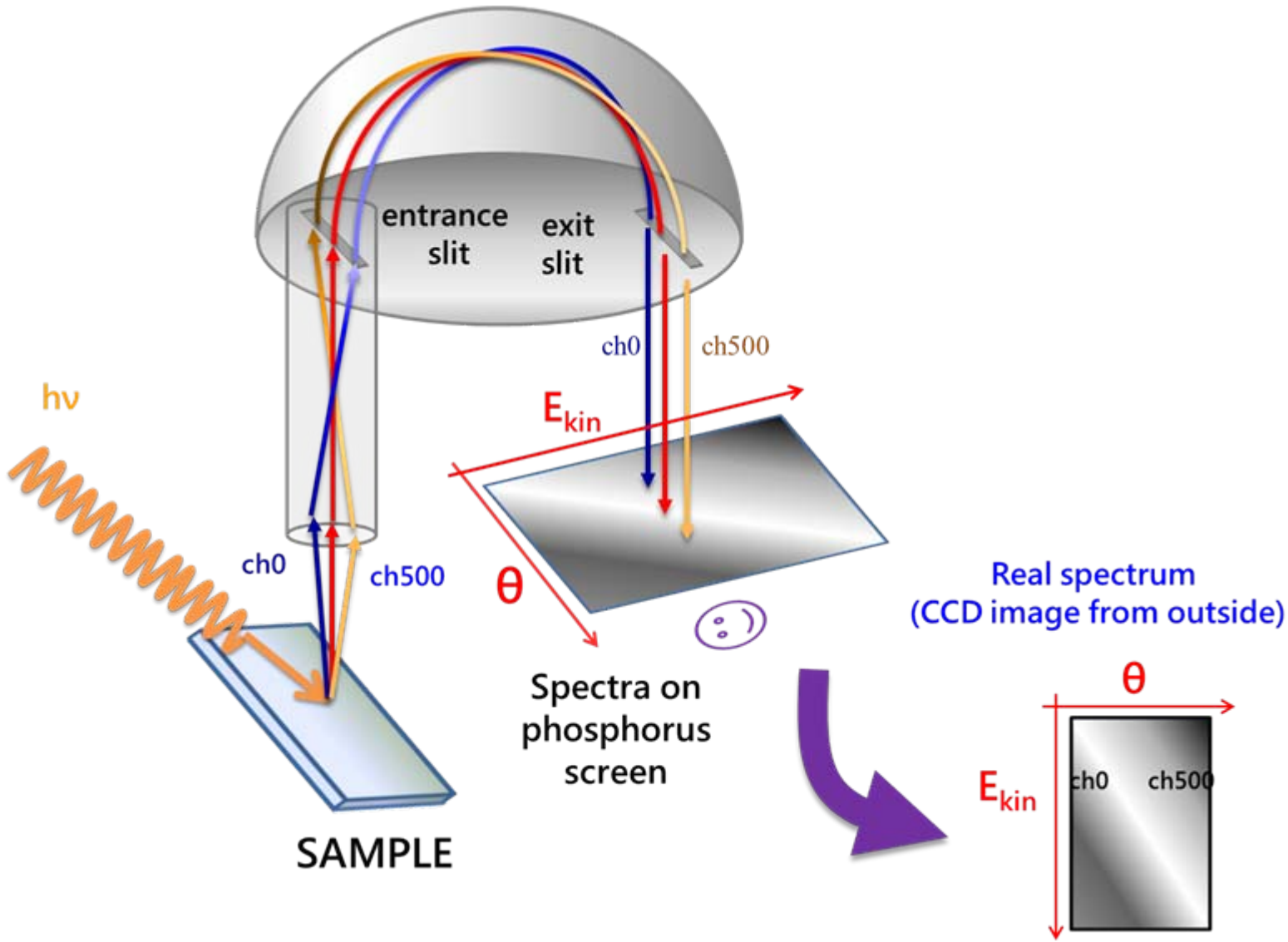
$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

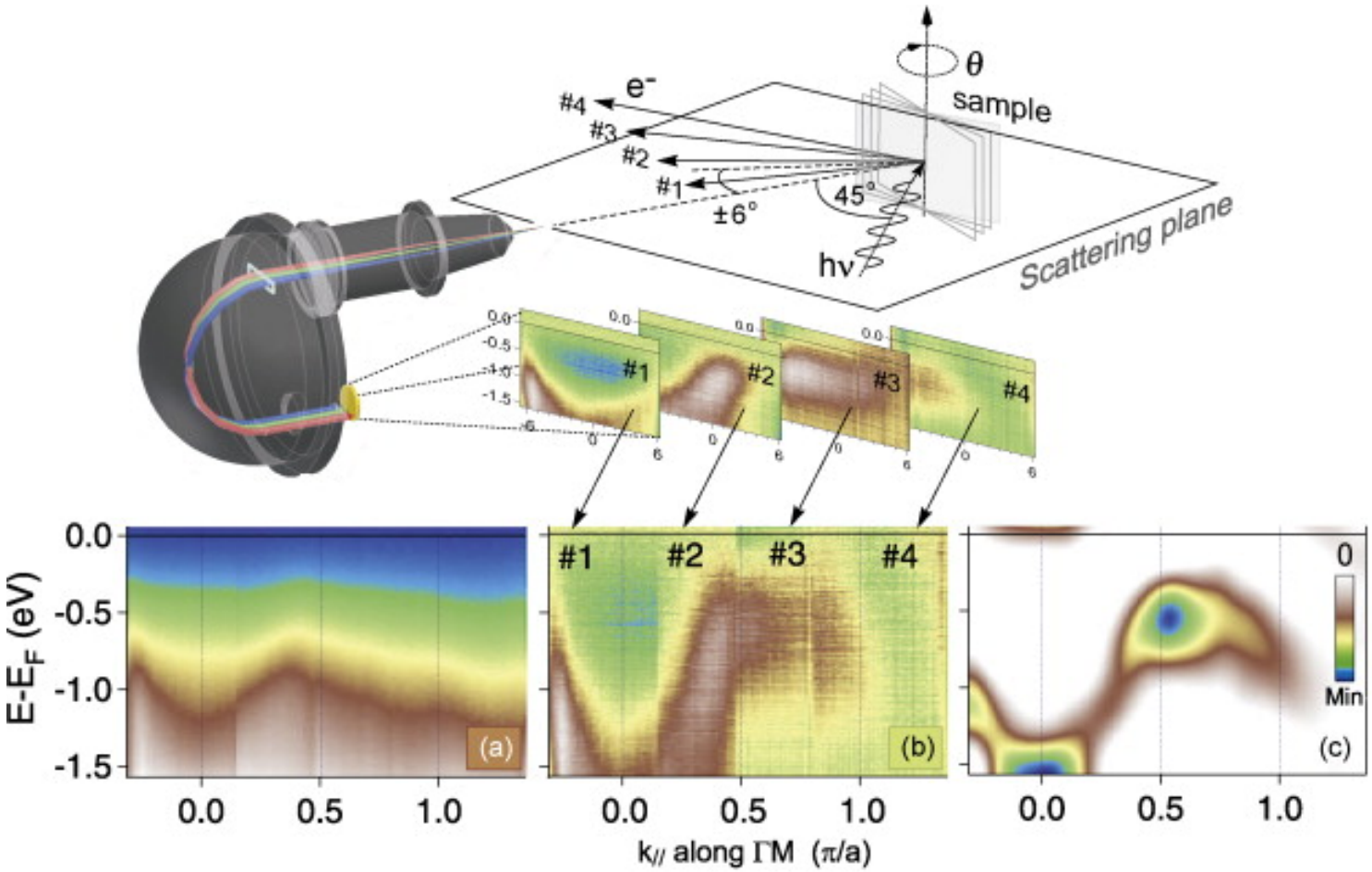
$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

- Low photon energy provides better momentum resolution.
- We expect to study the electronic structure of solids at low photon energies (10 eV~ 100 eV).

SCIENTA R4000 Side View




entrance slit
exit slit
ch0
ch500
hν
E_{kin}
ch0
ch500
θ
SAMPLE
Spectra on phosphorus screen
Real spectrum
(CCD image from outside)
θ
E_{kin}
ch0
ch500



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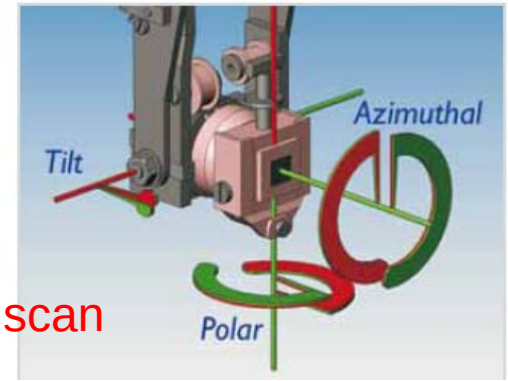
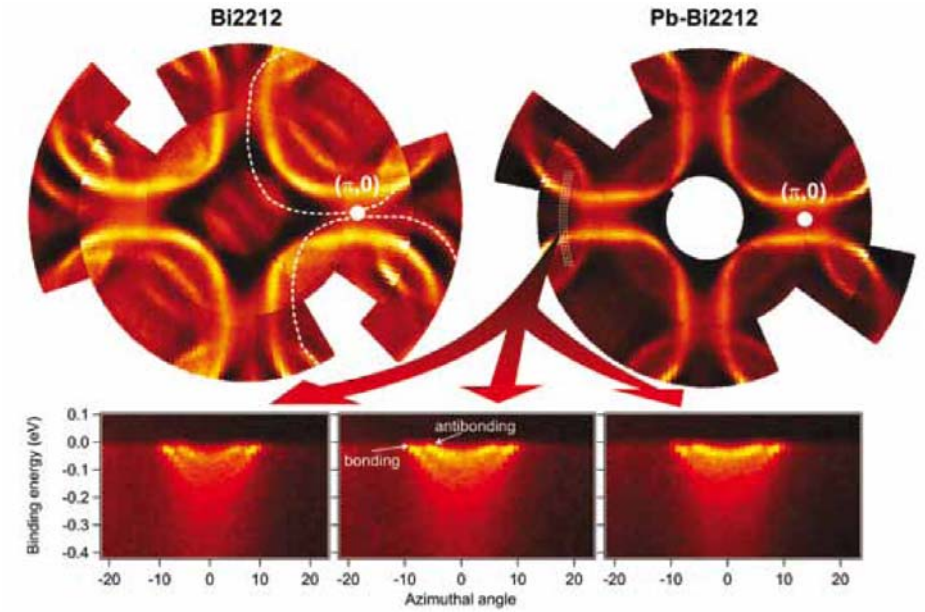
Krempasky et al., JESRP (2010)

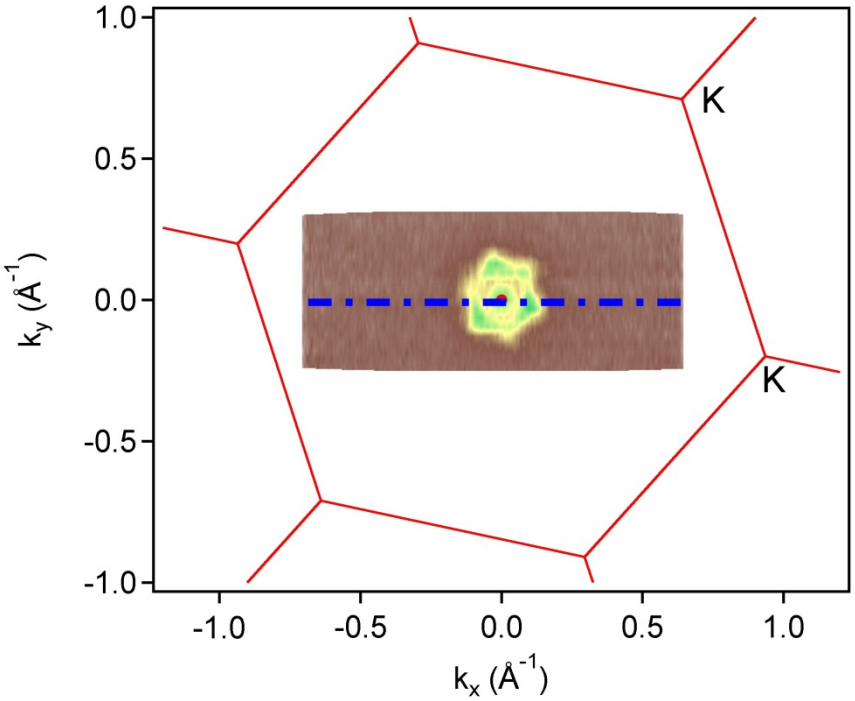
Angle is the soul of ARPES: Band mapping



Azmuthal angle scan

Tilt angle scan





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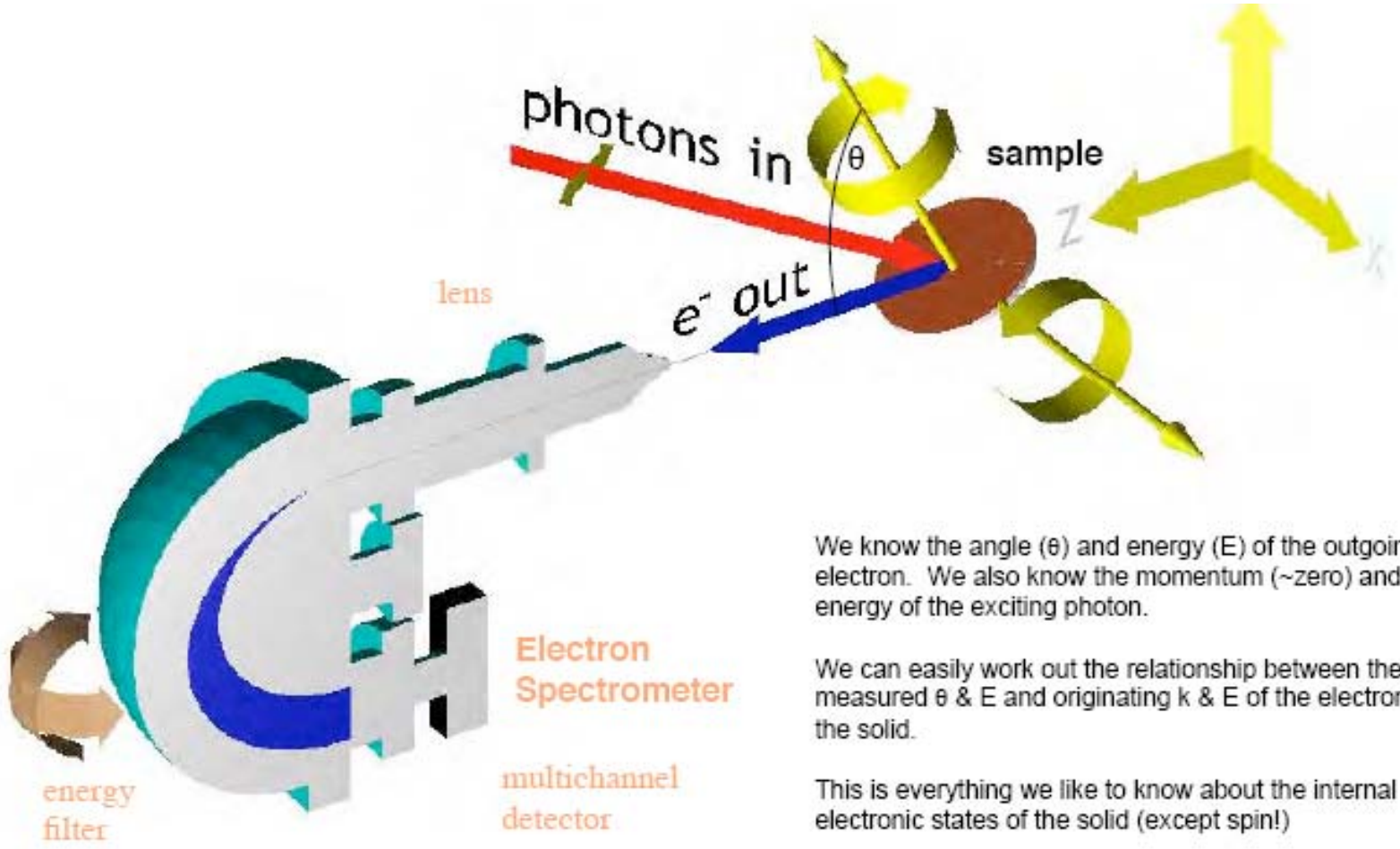
Experimental geometry

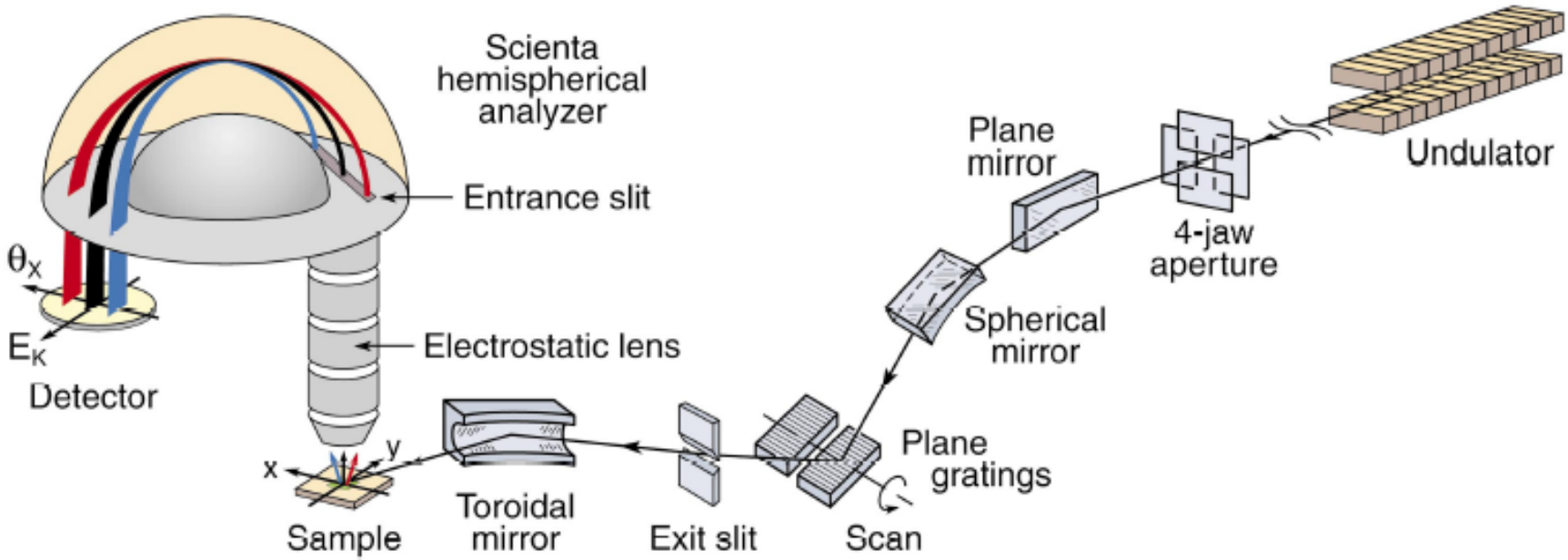


We know the angle (θ) and energy (E) of the outgoing electron. We also know the momentum (~zero) and the energy of the exciting photon.

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

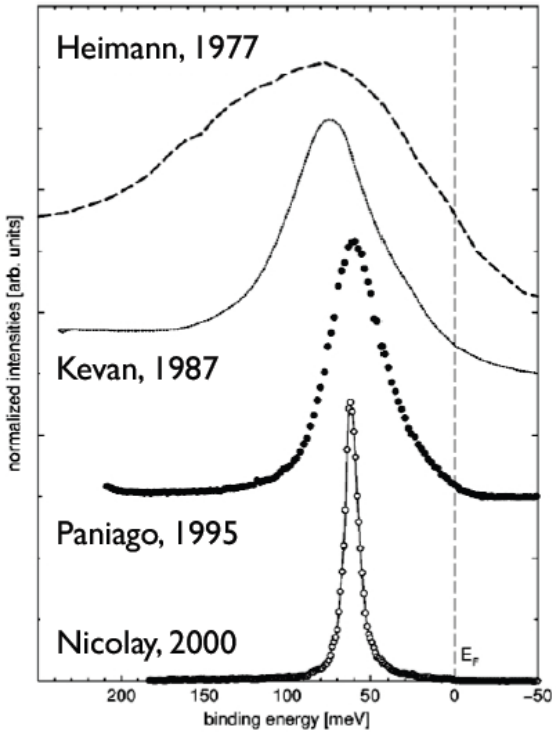
This is everything we like to know about the internal electronic states of the solid (except spin!)

Beamline design for modern high resolution photoemission spectroscopy

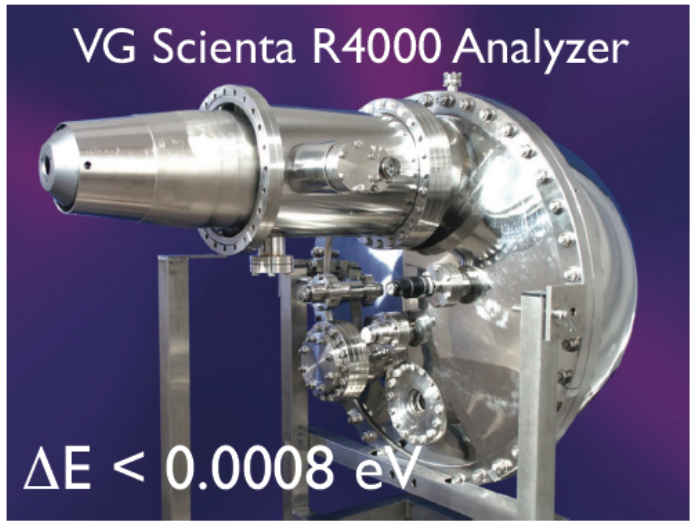


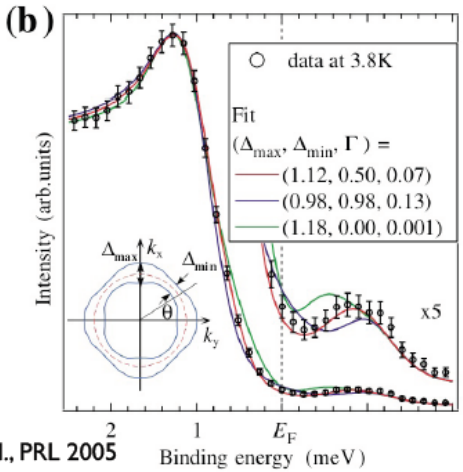
The state-of-the-art in electron spectroscopy

Evolution of instrumental resolution over time



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





T. Kiss et al., PRL 2005

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Kyle Shen, IGERT Lecture 2008

Early ARPES experimental result

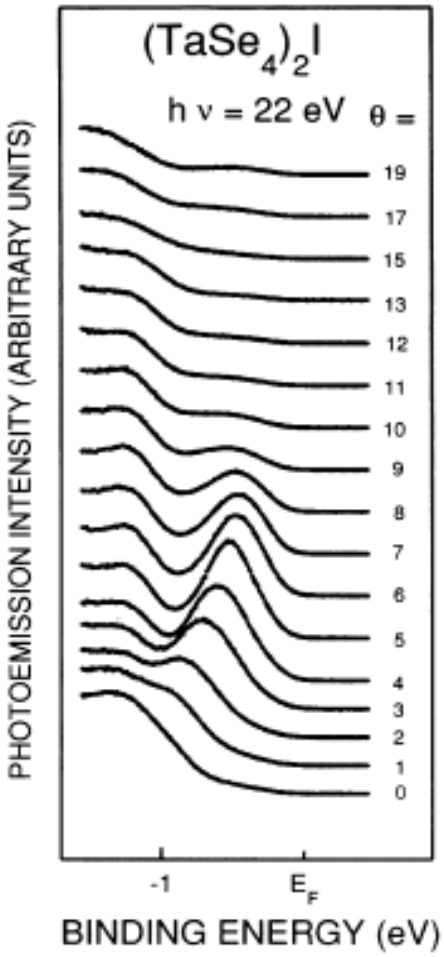


FIG. 1. A series of high-energy-resolution angle-resolved photoemission spectra, taken along the direction of the sample and for different values of the azimuthal angle.

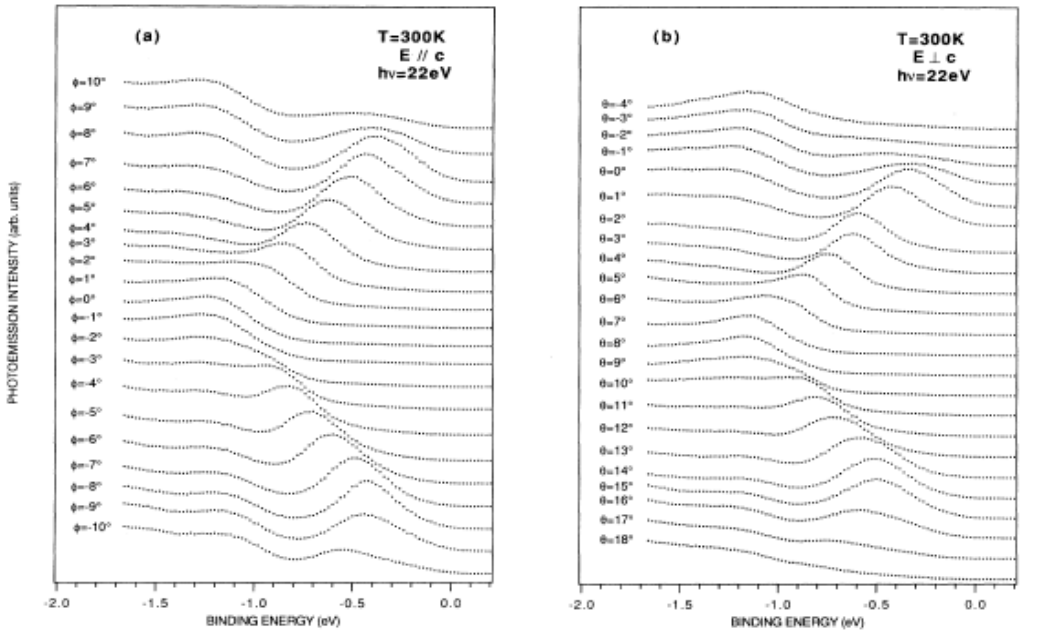
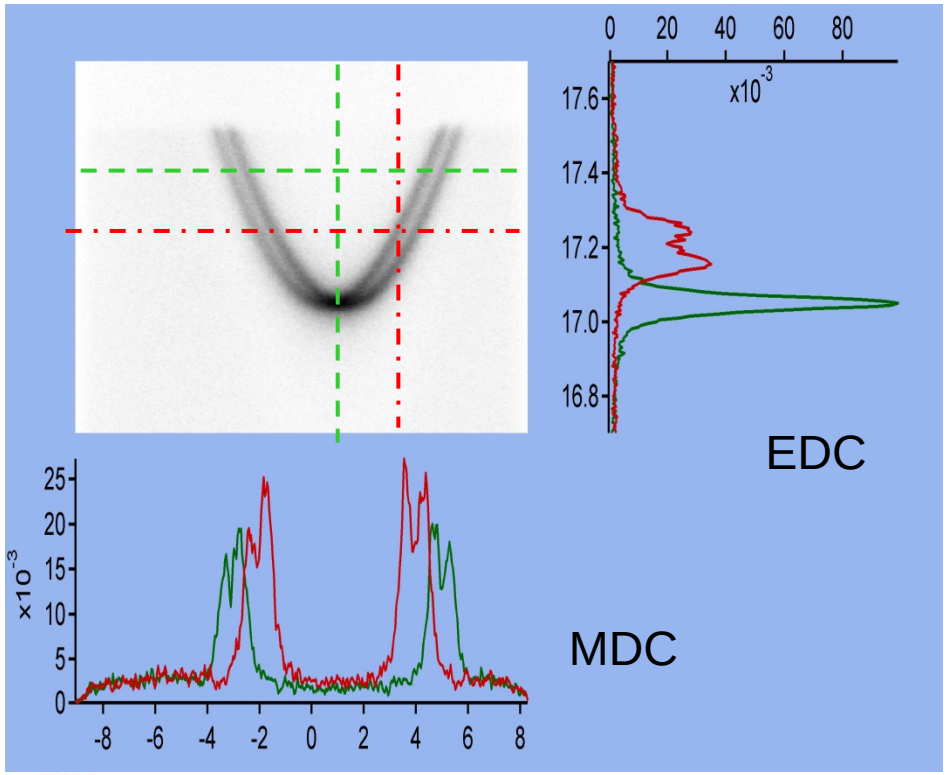


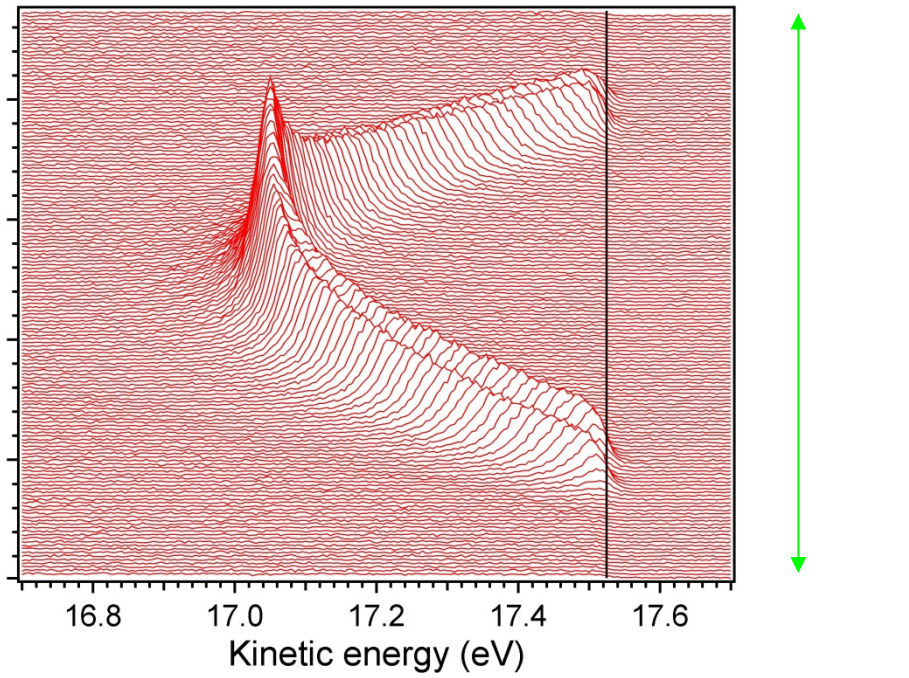
FIG. 1. Angle-resolved photoemission spectra taken using 22-eV photon energy, at room temperature, for photon electric field (a) parallel and (b) perpendicular to the conducting axis. The emission angle is along the conducting axis, with the surface normal defined as 0°.

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

Typical Experimental Result

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





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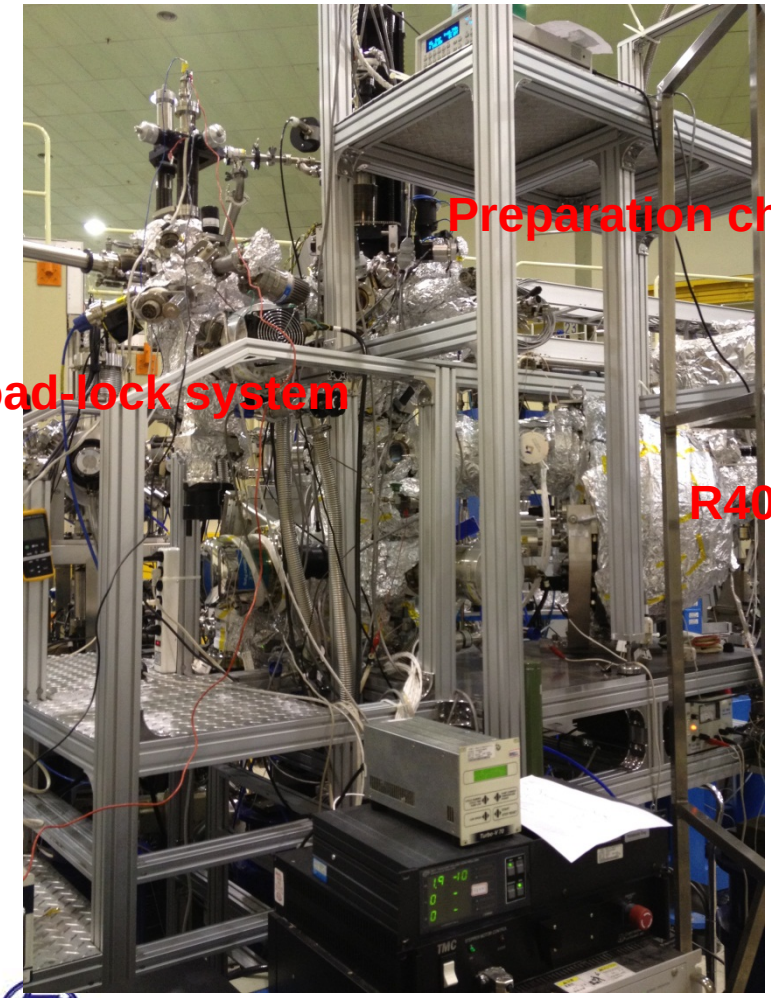
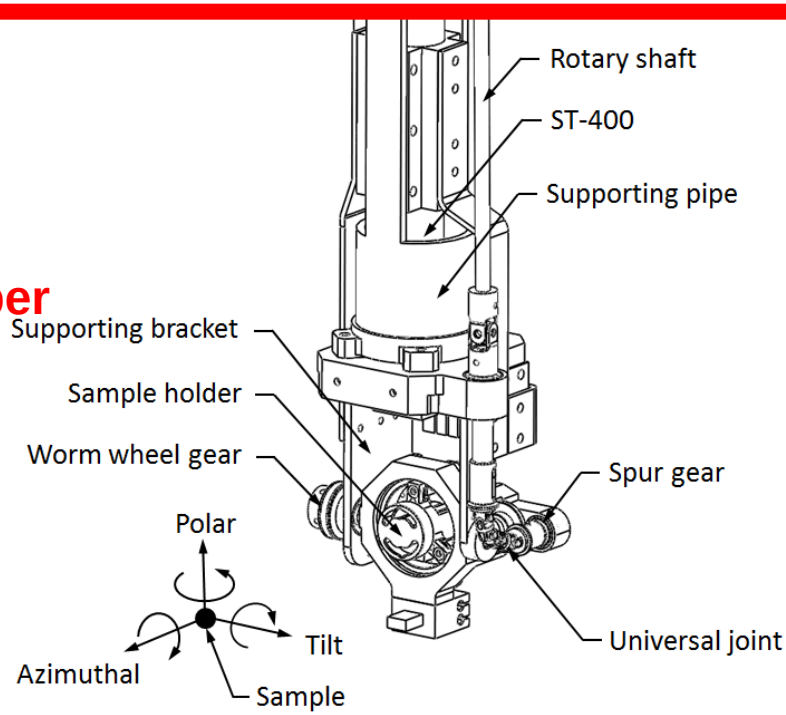
Current status of ARPES end station





Base pressure : 4.5×10^{-11} torr
Sample Preparation: *in-situ* cleave, MBE growth
Lowest temperature range : 10 K
Manipulator : 6-axis motorized manipulator

Scienta R4000 analyzer, LEED, RHEED,
Sputtering, Load-lock system

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Probe the electronic structure of materials

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

- Scientific topics for current users :
  - Molecular thin film/metal systems
  - Metal/semiconductor systems
  - Cuprates and complex oxides
  - Graphene based materials
  - Topological insulators
  - Iron-based superconductors

Electron Escape Depth : Surface Sensitivity

Why are electrons so useful as probes of surfaces?

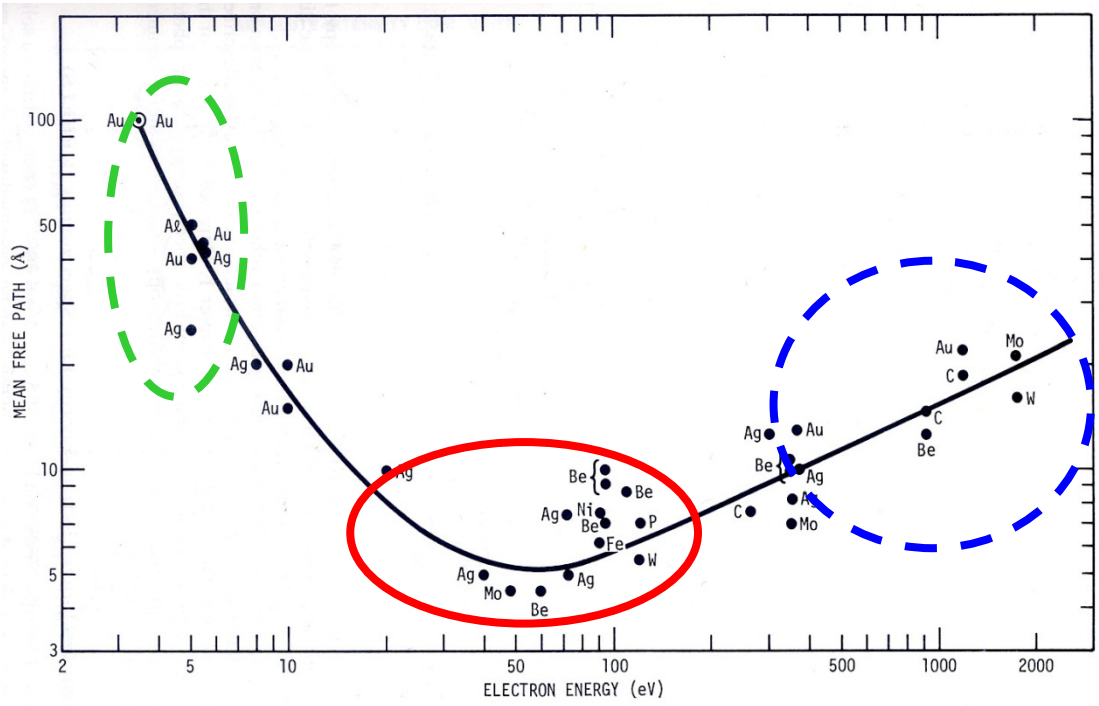
Or

Not so useful for studying bulk properties !!

Minimum due to electron-electron scattering, mainly plasmons

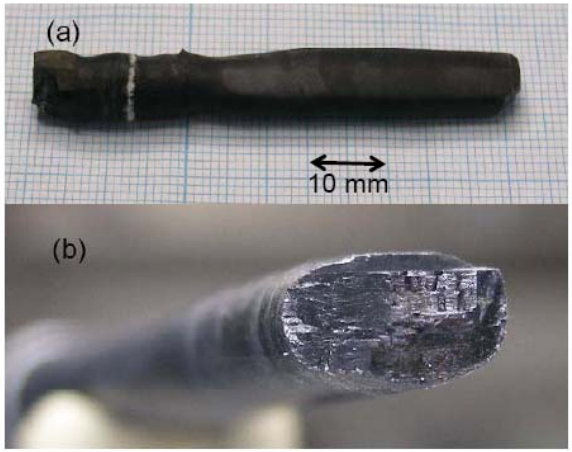
PES is a surface sensitive technique! (requires UHV)

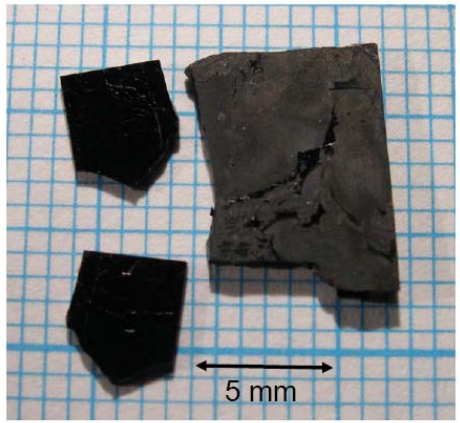
High energy photoemission: several keV to increase bulk sensitivity



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





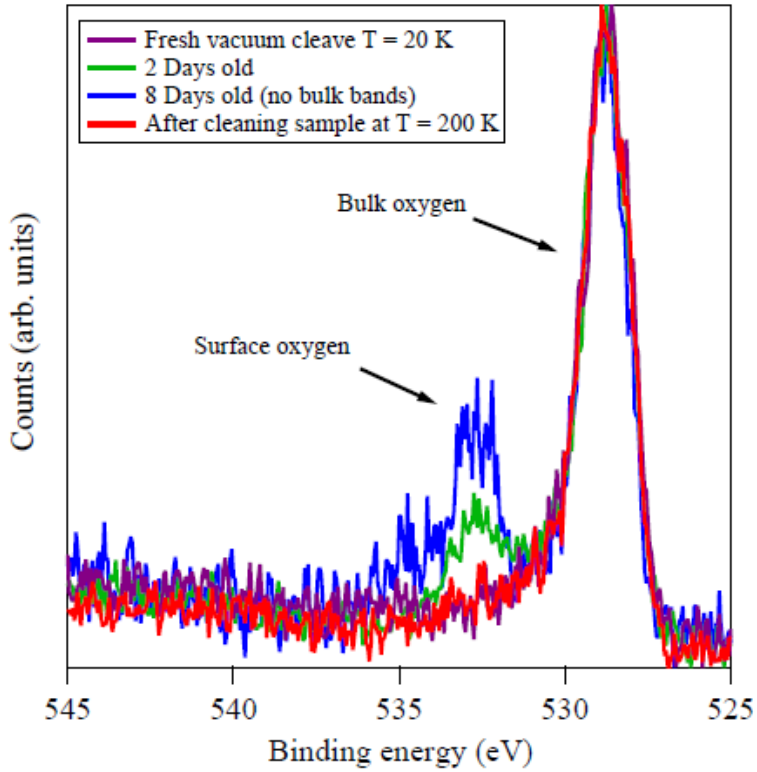


Figure 5.2: (color) The oxygen 1s peaks from Bi2212 at different times after the cleave. A constant background was subtracted from each spectrum to allow direct comparison. The peak derived from bulk oxygen is stable over time, while the surface oxygen peak grows as more oxygen sticks to the cold surface.

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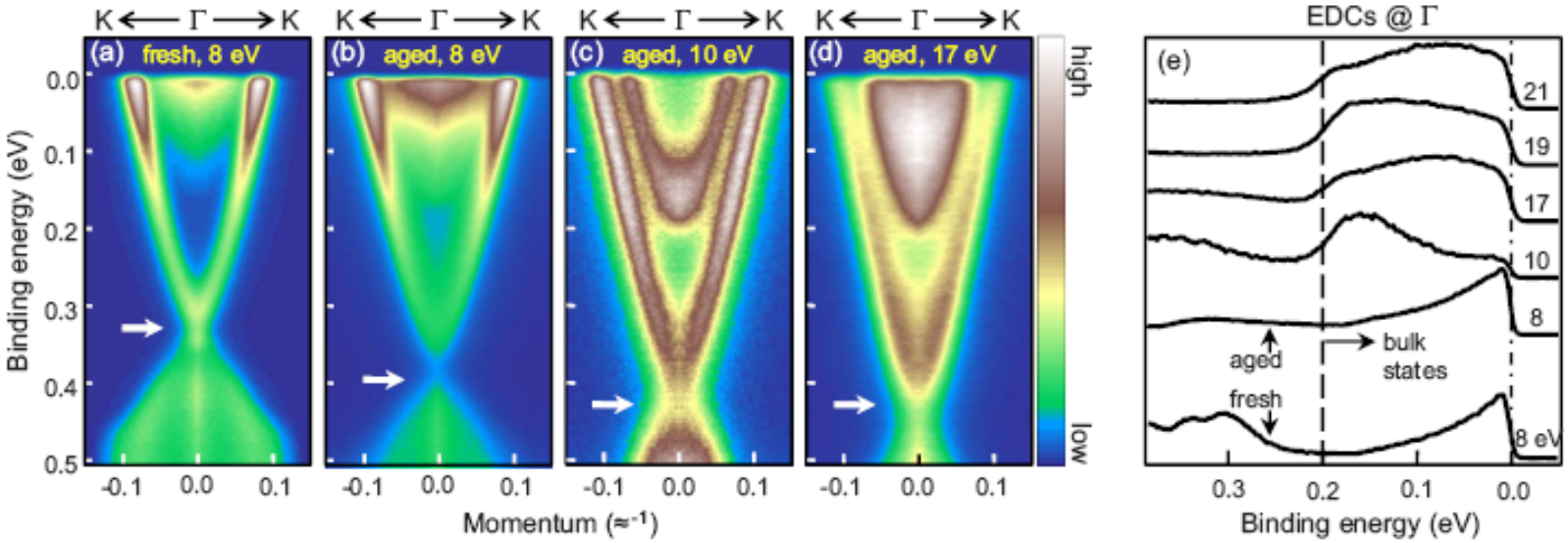
HC Hsu, Ph.D. Thesis NTNU(2010)
Koralek, U. Colorado Ph.D. Thesis (2007)

Impurity doping on topological insulators

Base pressure : $1x10^{-10}$ Torr

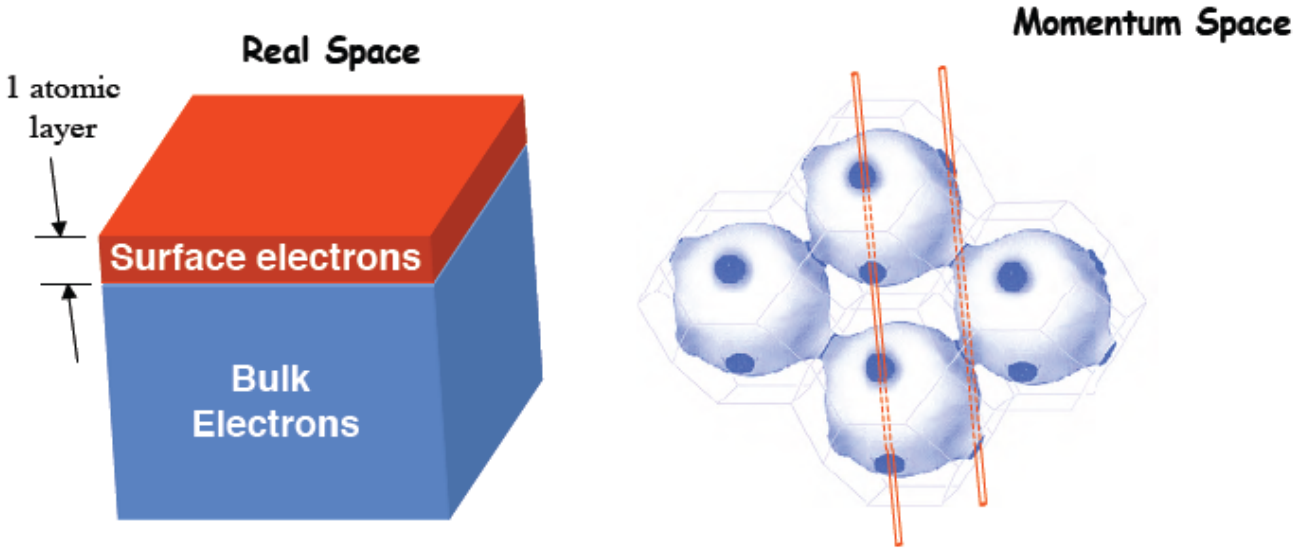
Bi_2Se_3 single crystal



Park *et al.*, PRB (2010)

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

Surface state



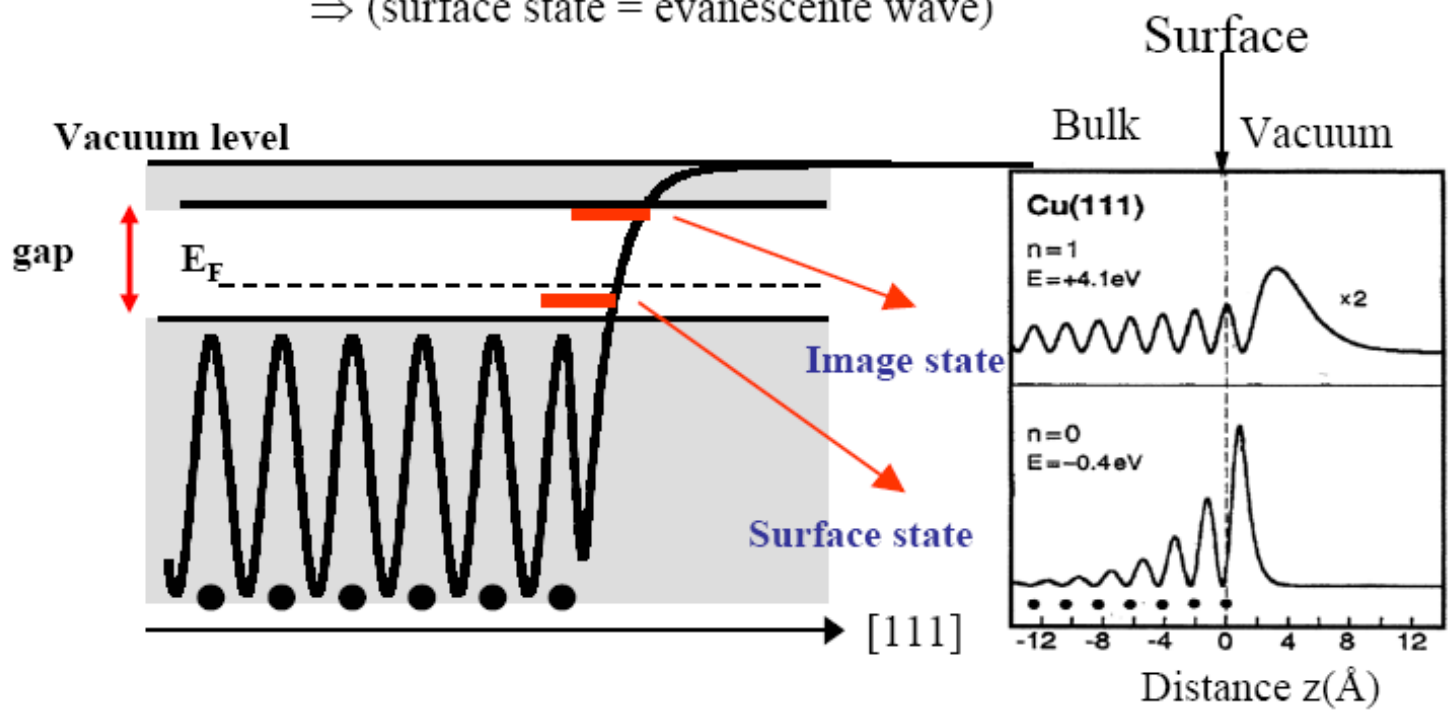
Surface states are highly localized in real space, therefore completely delocalized in k-space along kz.

– NO DISPERSION OF SURFACE STATES in kz direction

- Surface = Breakdown of the translational symmetry

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

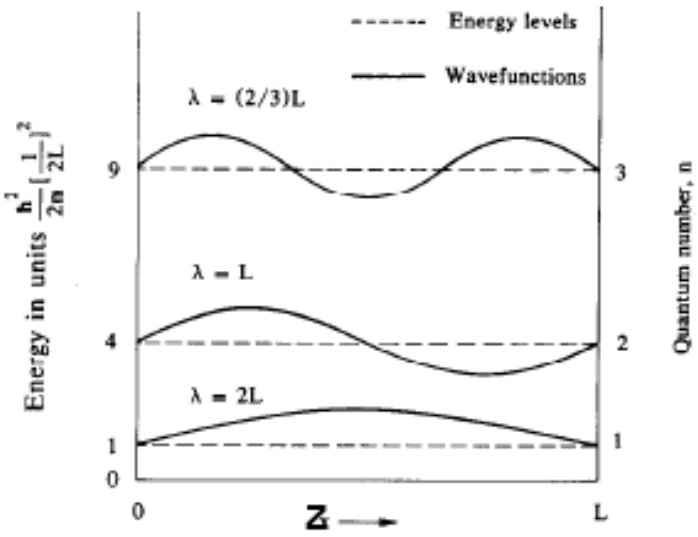
⇒ (surface state = evanescente wave)



→localisation of the electronic density at the surface

Surf. State is very sensitive to any structural modification

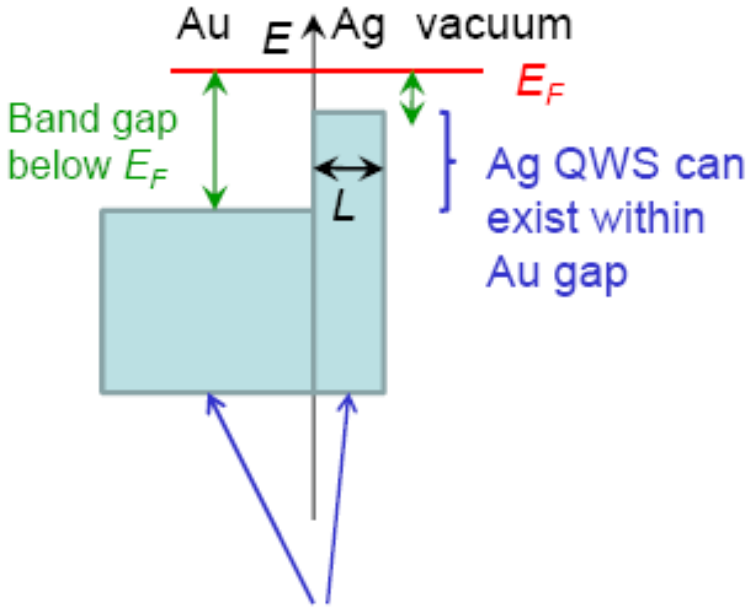
Quantum well states



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

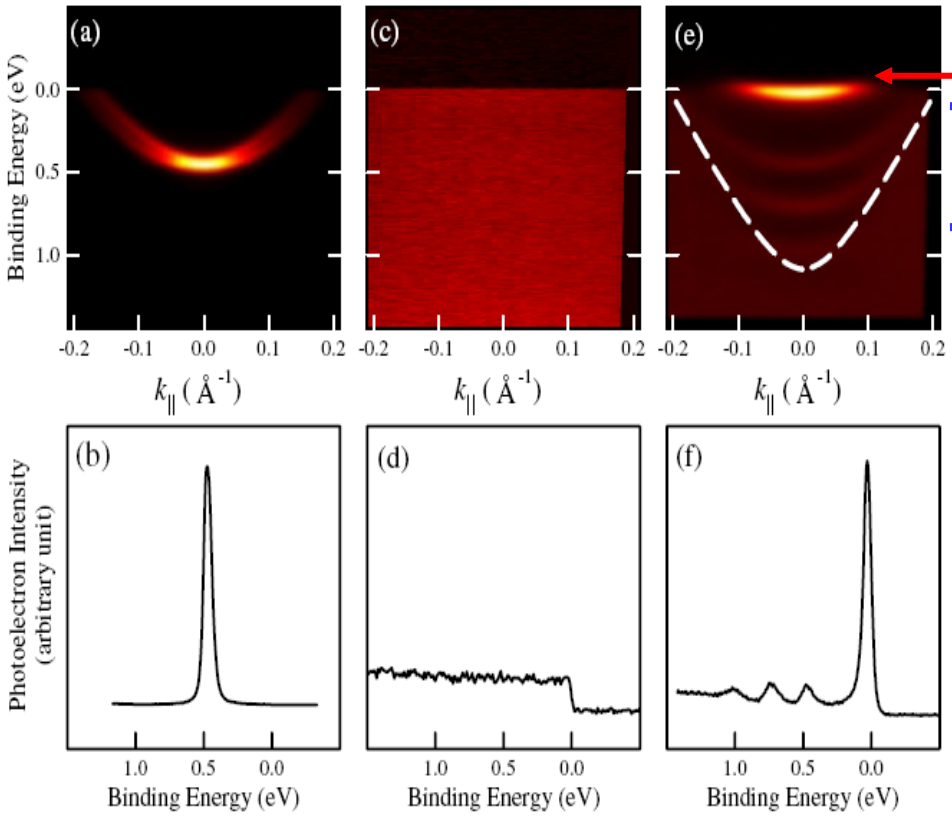
Nearly free electron like in xy-plane

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



Bulk projected bands along ΓL of Au and Ag, respectively

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



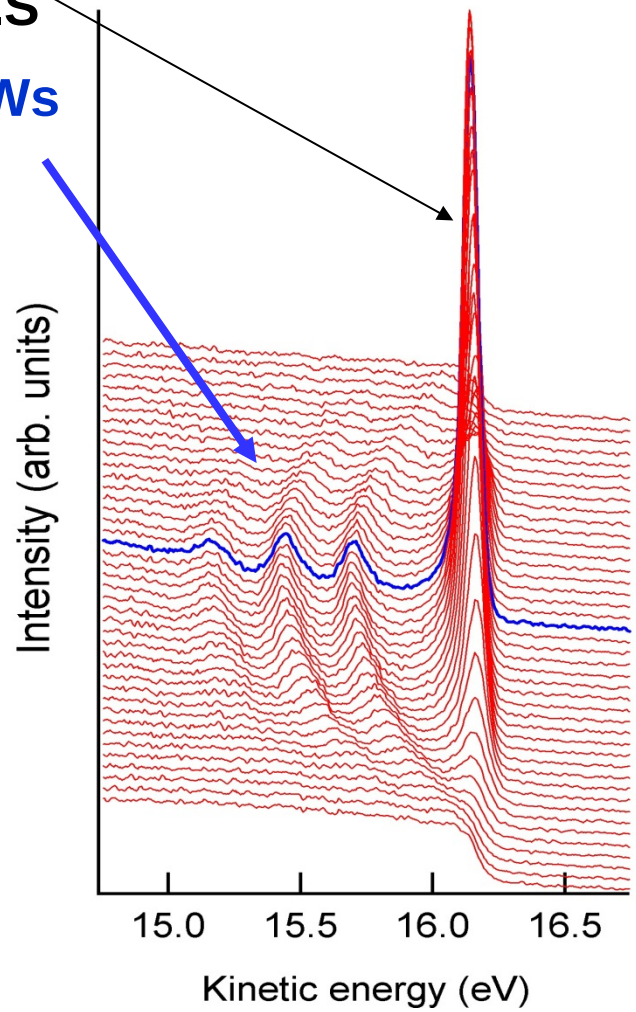
Clean Au(111)

LT deposite Ag/Au(111)

Anneal to near RT

Ag S.S

Ag QWs



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

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

Dynamically monitor the thin film growth mechanism

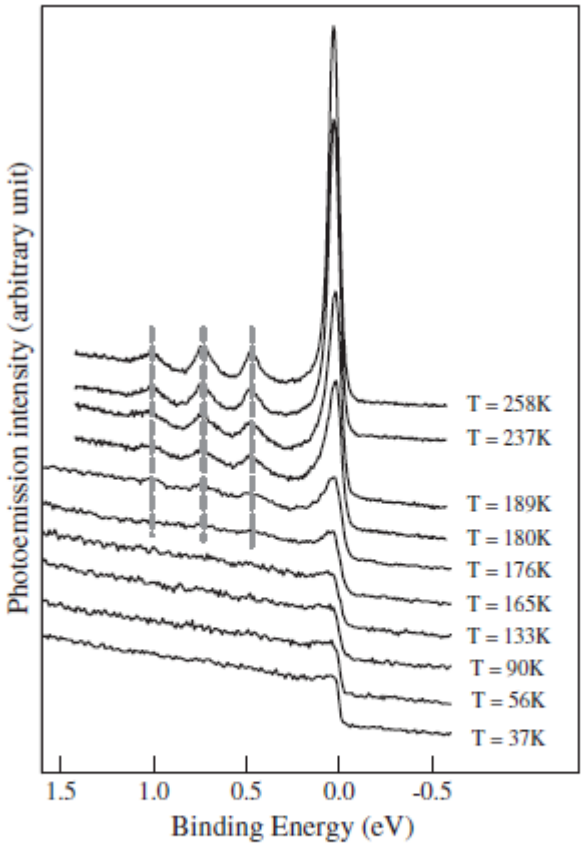
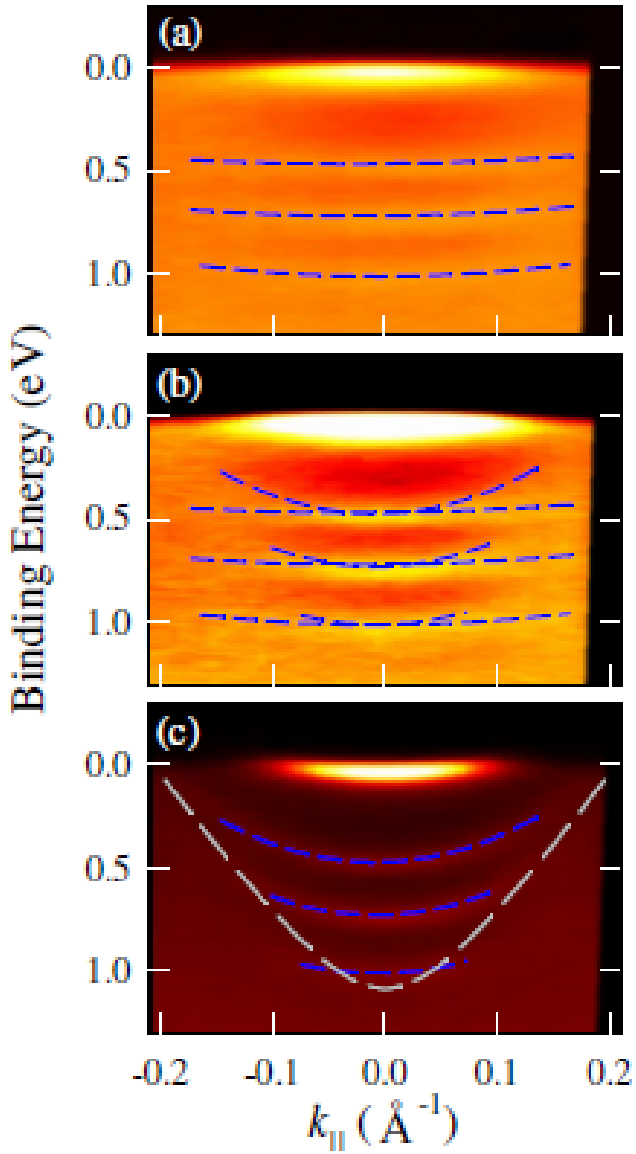
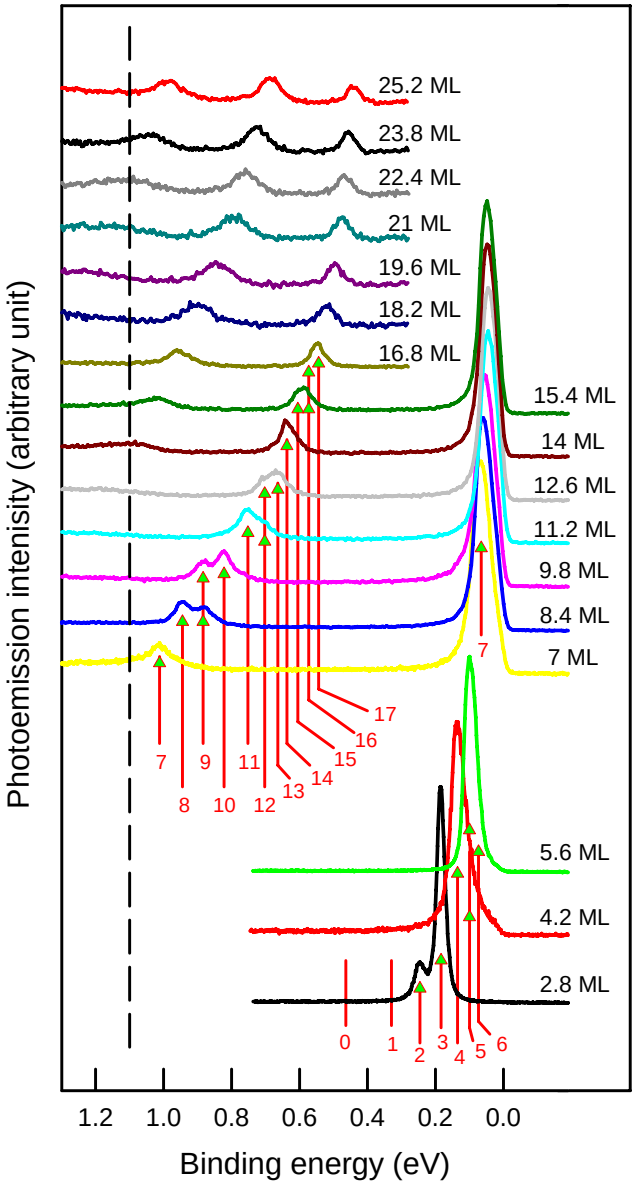
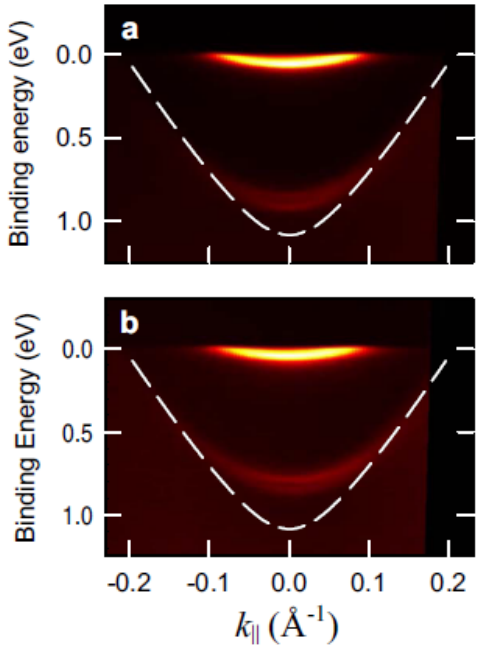
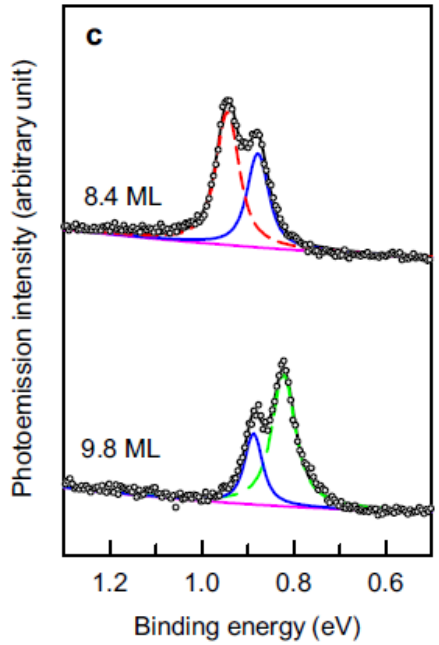


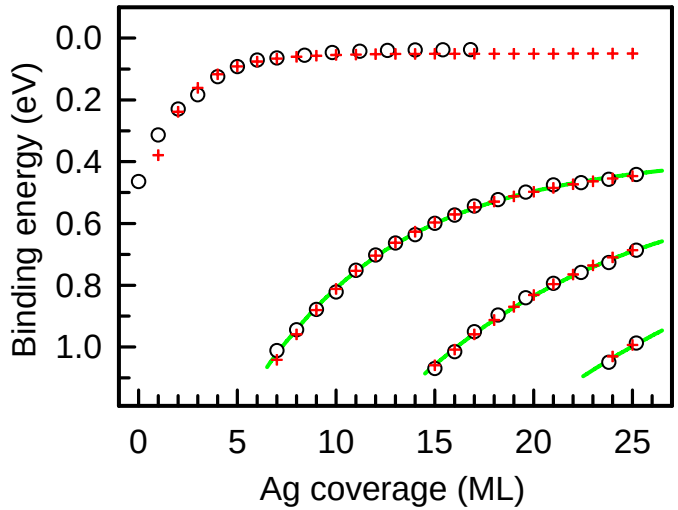
FIG. 2. Energy distribution curves of normal emission from Ag (22 ML) on Au(111) annealed at the indicated temperatures; intensities have been scaled variously for stacking presentation.











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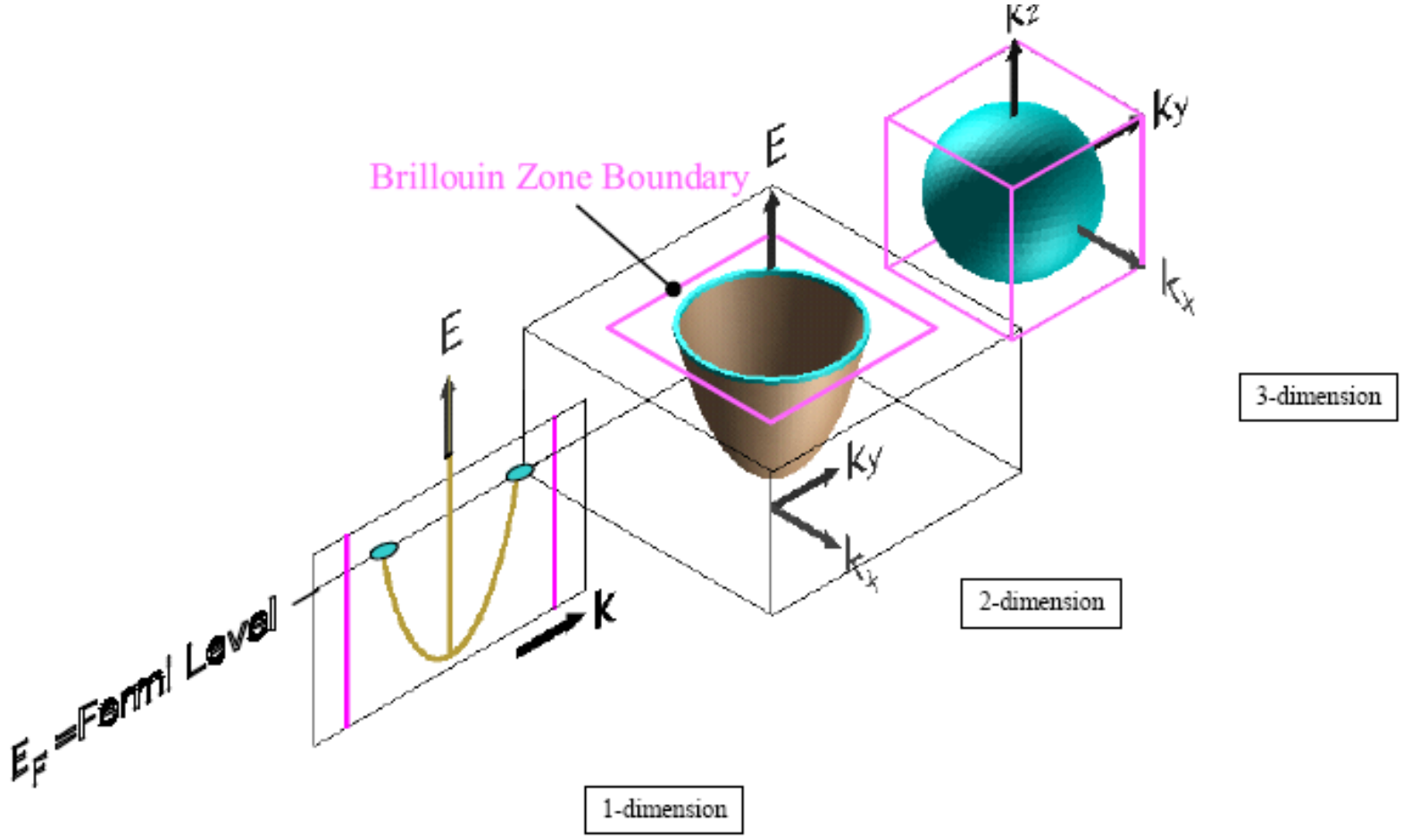
C.-M. Cheng et al., APL (2008)
C.-M. Cheng et al.,J. Phys. D: Appl. Phys. (2008)
D.-A. Luh et al., PRB (2008)

Fermi Surface

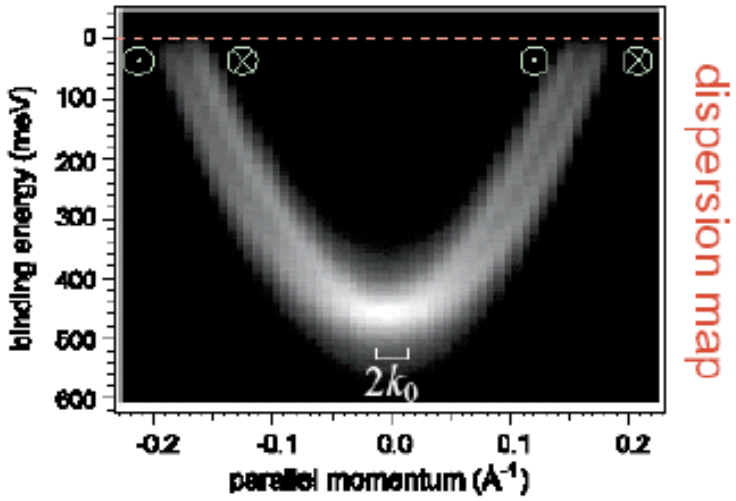


Surface state

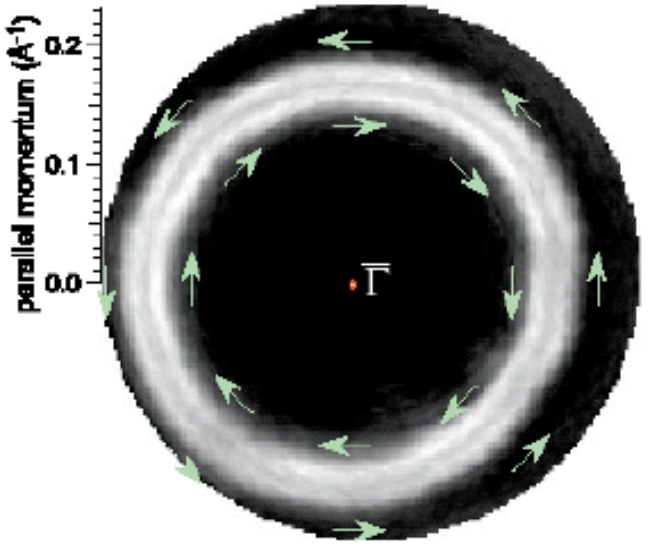
The Shockley surface state on Au(111)

spin-integrated photoemission at $h\nu$ = 21.1 eV, T = 160 K

instrumental resolution
ΔE = 25 meV, $\Delta\vartheta$ = 0.5° (FWHM)



dispersion map



Fermi surface map

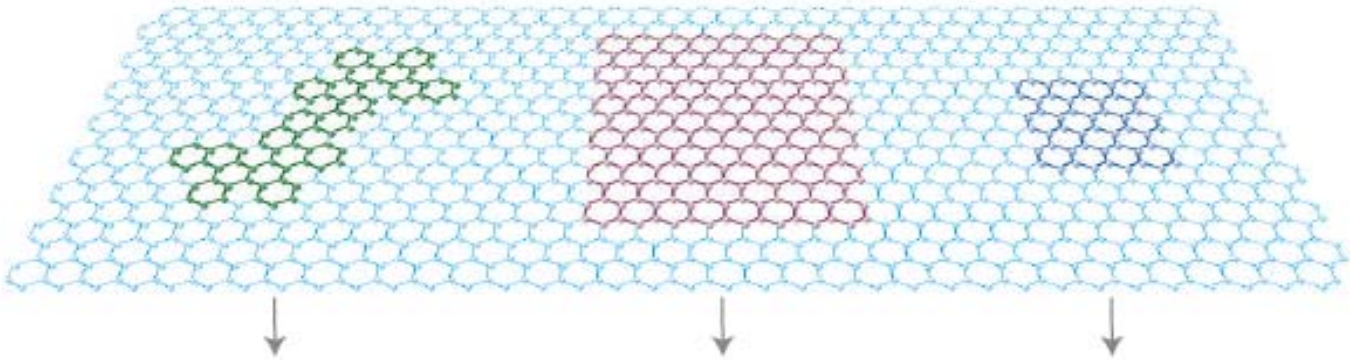
$2k_0 = 0.026$ Å^{-1} $\quad E_B = 470$ meV $\quad k_F = 0.173$ Å$^{-1} \pm k_0$ $\quad m^* = 0.24\ m_e$

The electronic structure of graphene

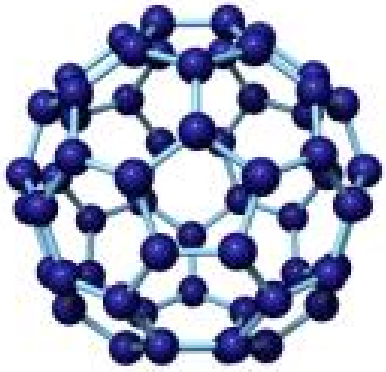
Graphene is the mother of them all !

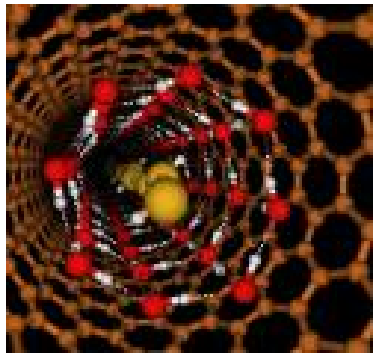
Very good conductors

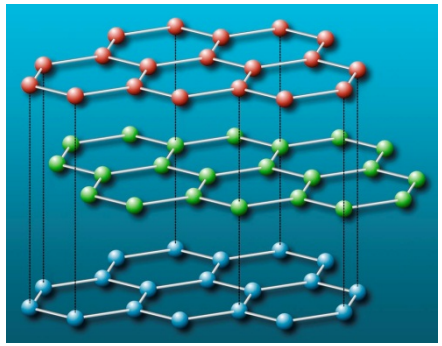
Extremely thin and resistant



wrapped **Rolled** **stacked**







Zero dimensional: fullerenes

One dimensional: carbon nanotubes

Three dimensional: graphite

Why graphene

- The strictly two-dimensional material

  - *Exceptionally high crystal and electronic quality*

- Unusual electronic spectrum

  - *New paradigm of 'relativisity' condensed-matter physics*

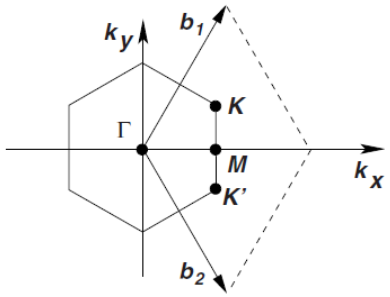
- Graphene-based electronics : new cadidate material to take over from Si

  - *High mobility, high carrier density, high v_F*

  - Tunable gap by electrical field : Field-effect transistor (FET), Single-electron-transistor (SET)

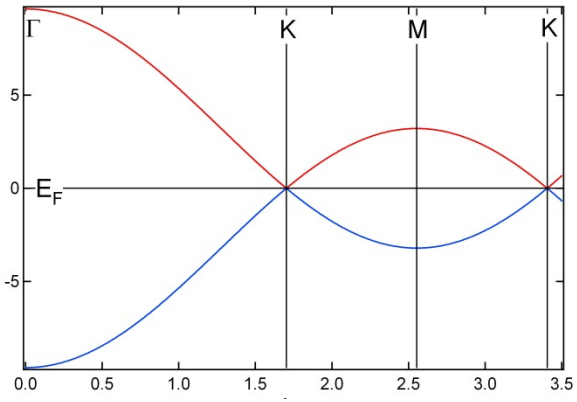
  - Superconducting field effect transistor and Spin valve, Composite material for electric battery, hydrogen storage material

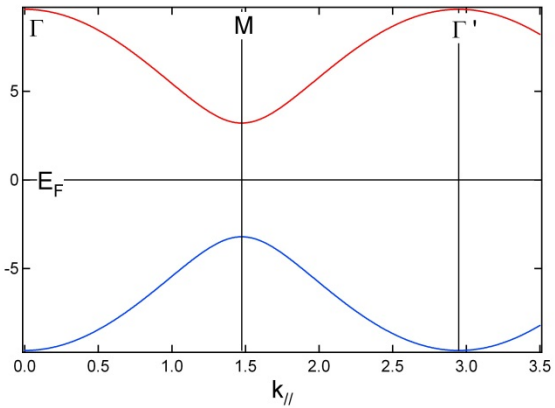
Pure 2D material : graphene

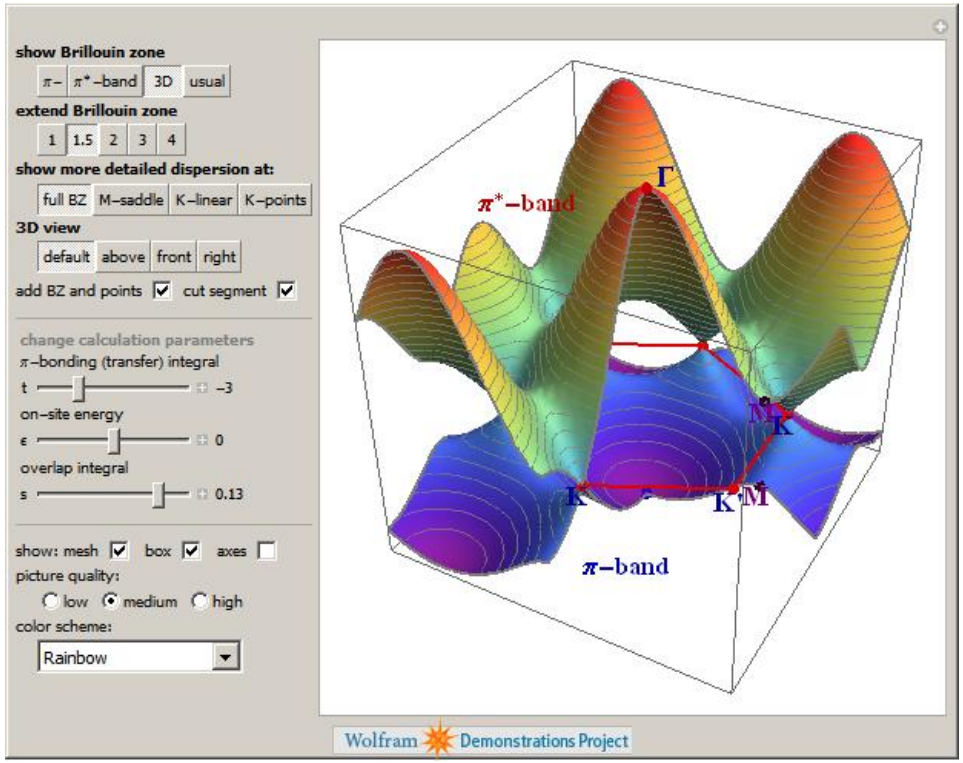


$$\boldsymbol{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \boldsymbol{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3})$$

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





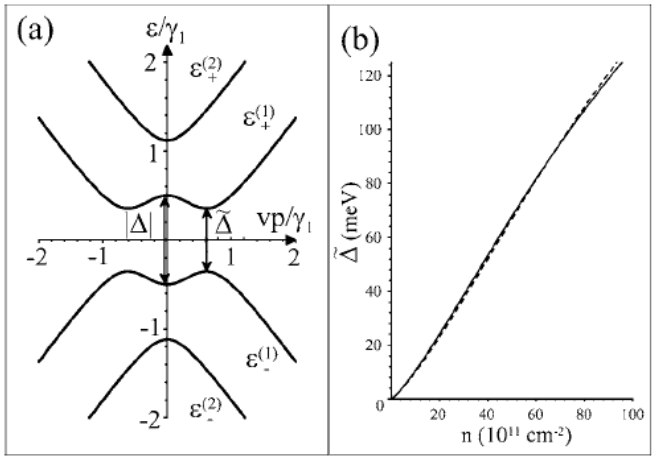


Bilayer graphene : tunable energy gap

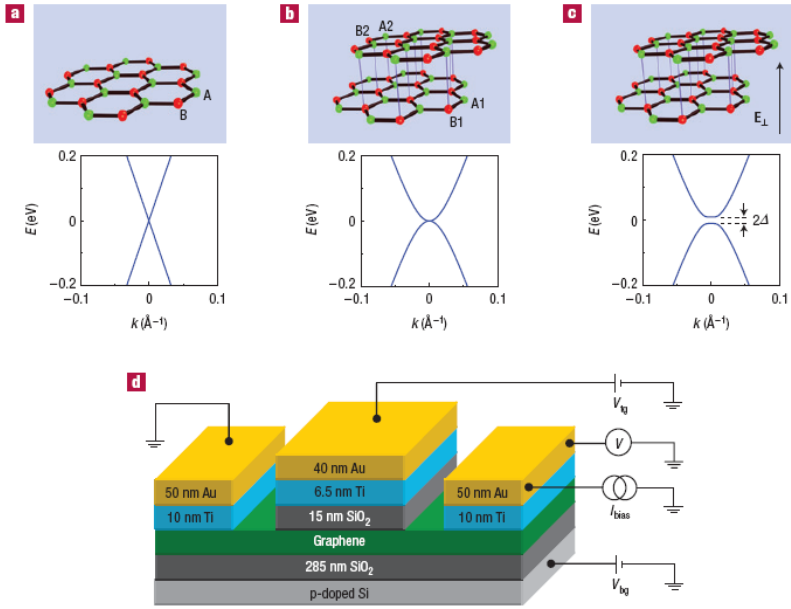
Bilayer graphene

Max. 250 meV by IR detection

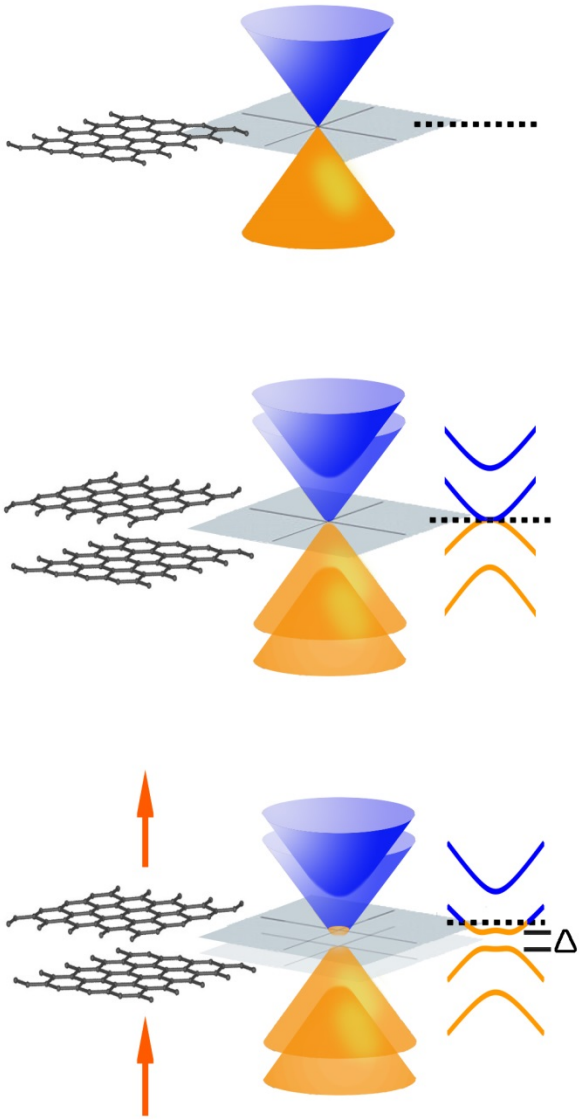
Zhang et al., Nature (2009)

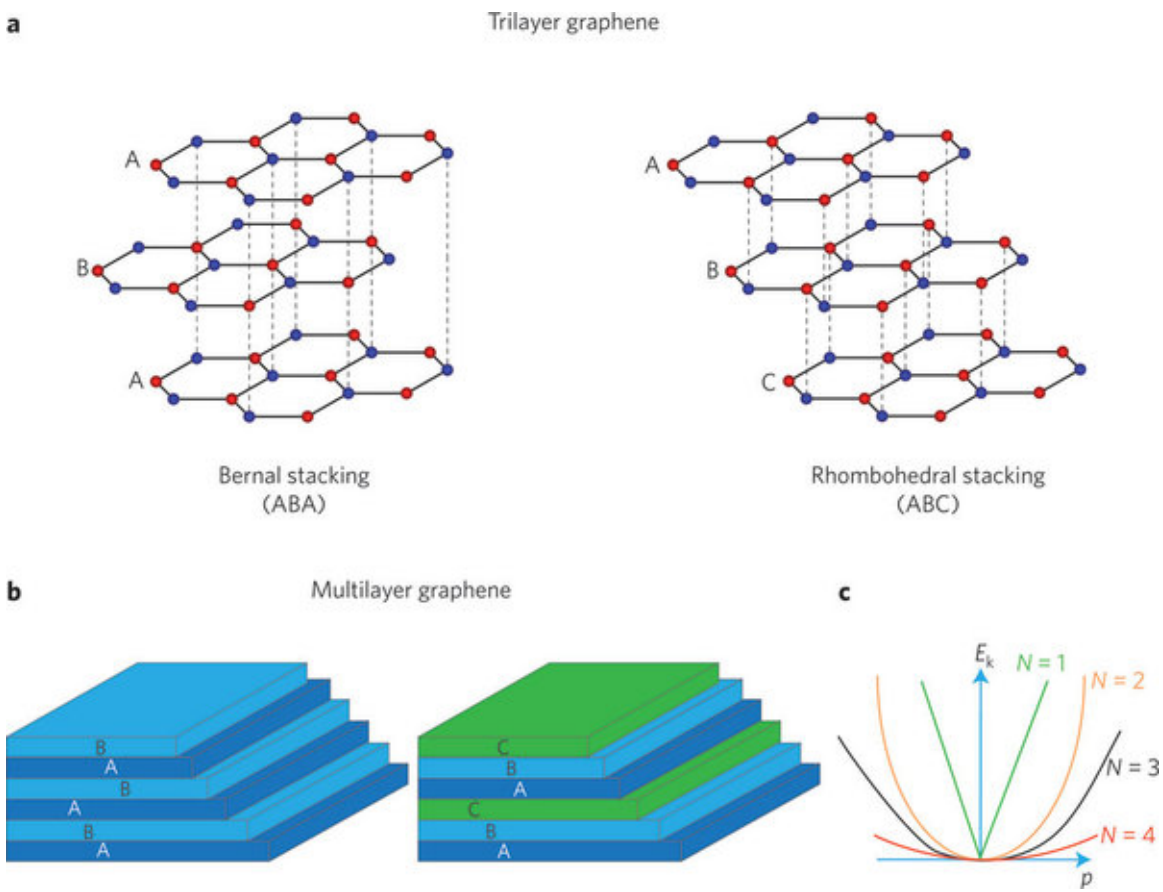


McCann, PRB (2006)



J.B. Ostinga et al., Nature Mat. (2007)



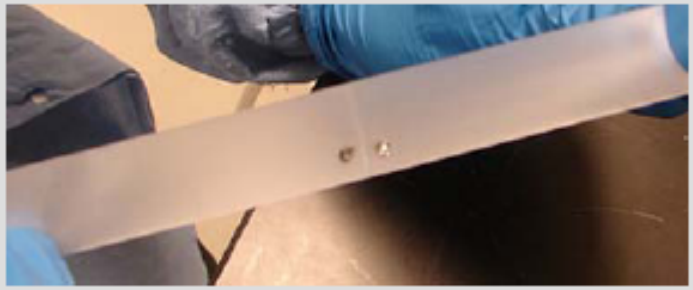


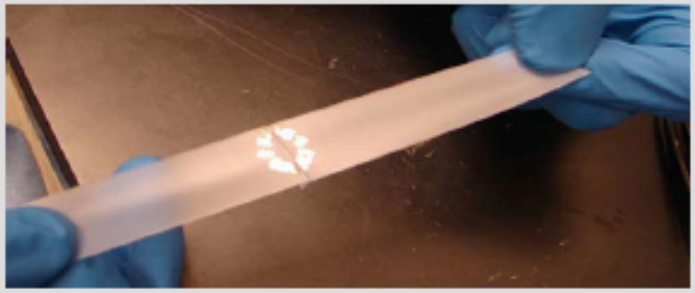
Yacoby, Nature Physics (2011)
infared.lbnl.gov.tw

How to prepare graphene

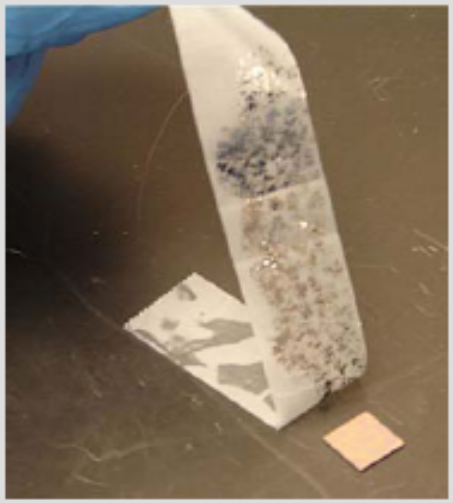
mechanical cleavage

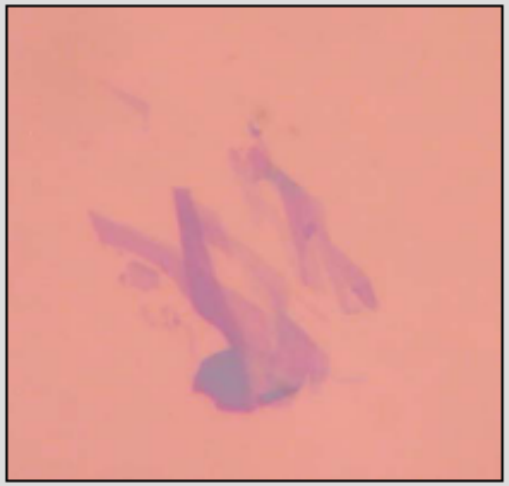
peeling off layers of graphite with a sticky tape





transfer onto substrate





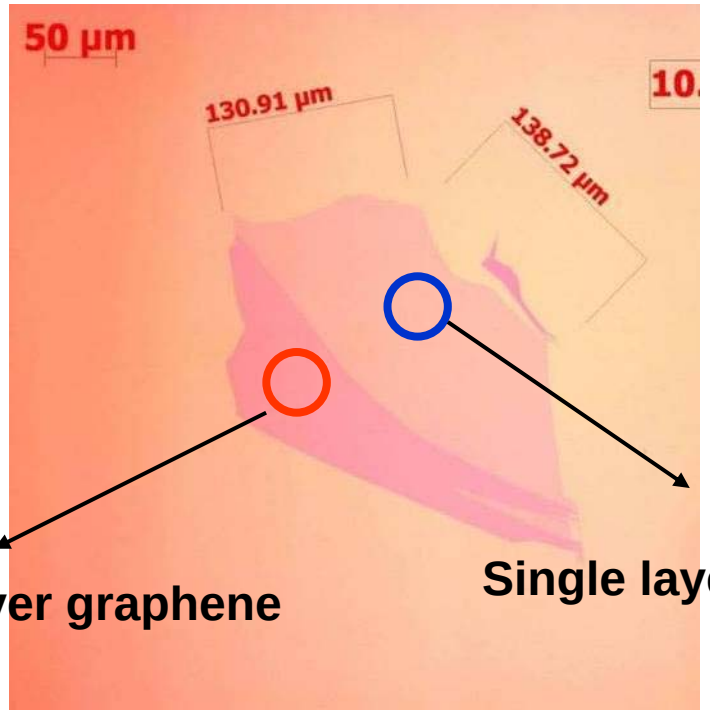
optical microscope image of resulting flakes

Novoselov et al., Nature (2005)

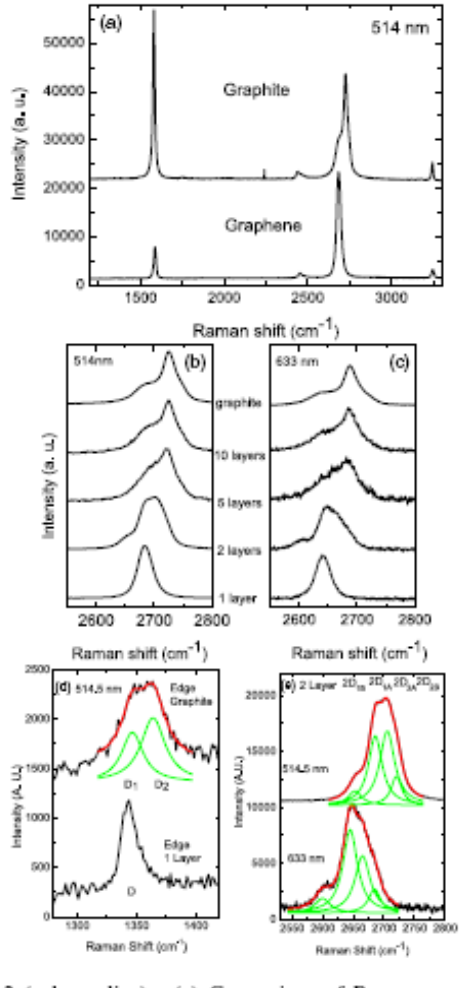
How to distinguish the thickness of graphene

SiO_2(200 nm)/Si

Optical microscopy



Raman spectroscopy

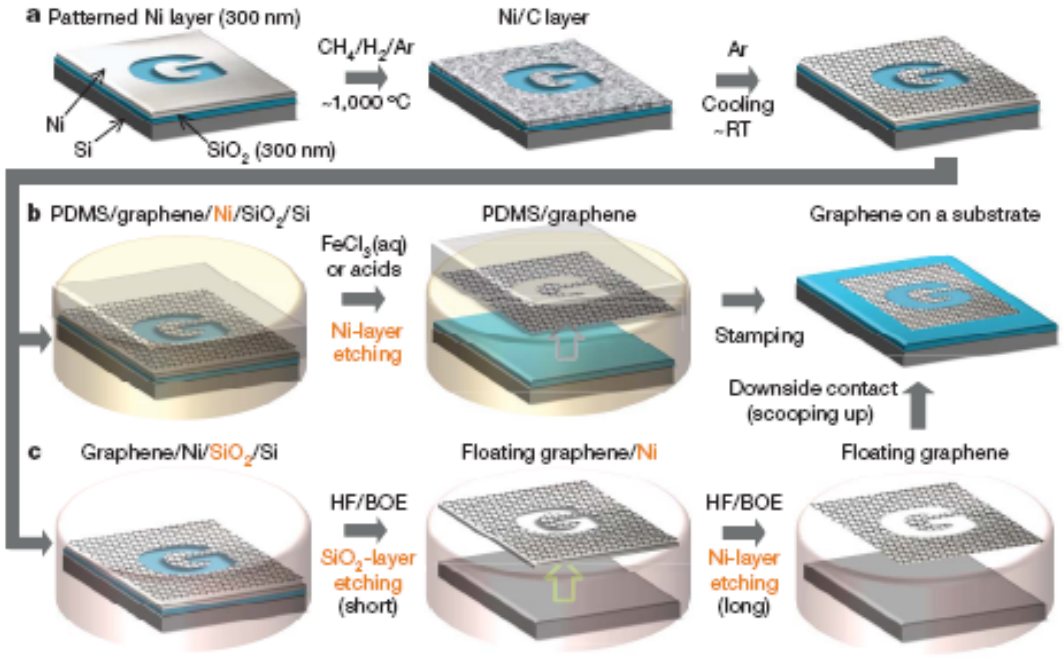


國家同步輻射研究中心
National Synchrotron Radiation Research Center

Barbaros, NUS, Singapore

A. Ferrari et al. PRL 97,187401 (2006)

CVD for large scale graphene film



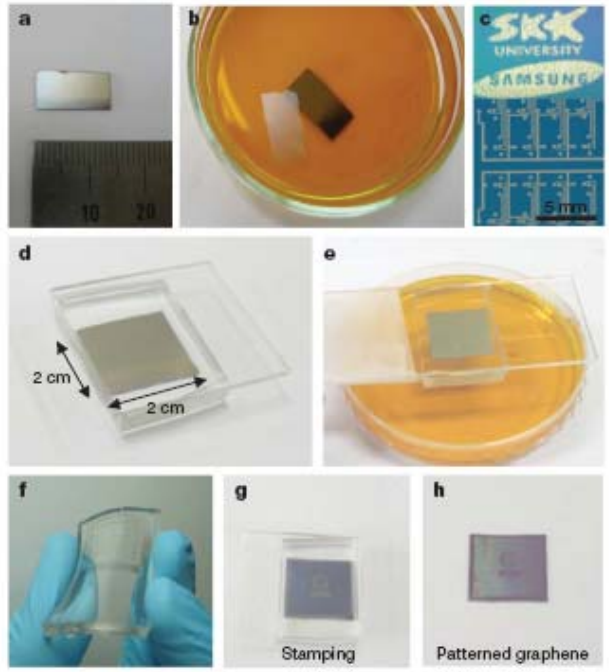
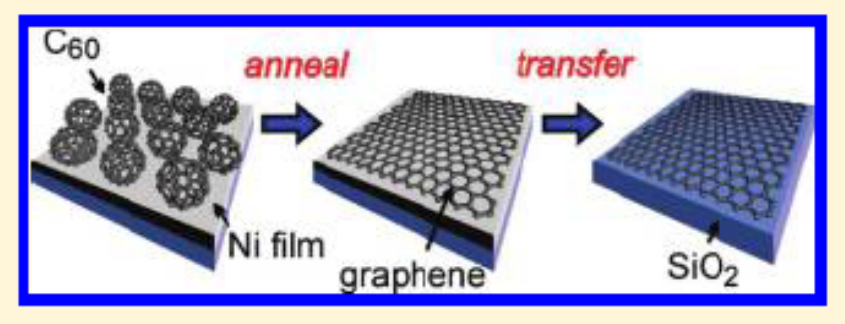
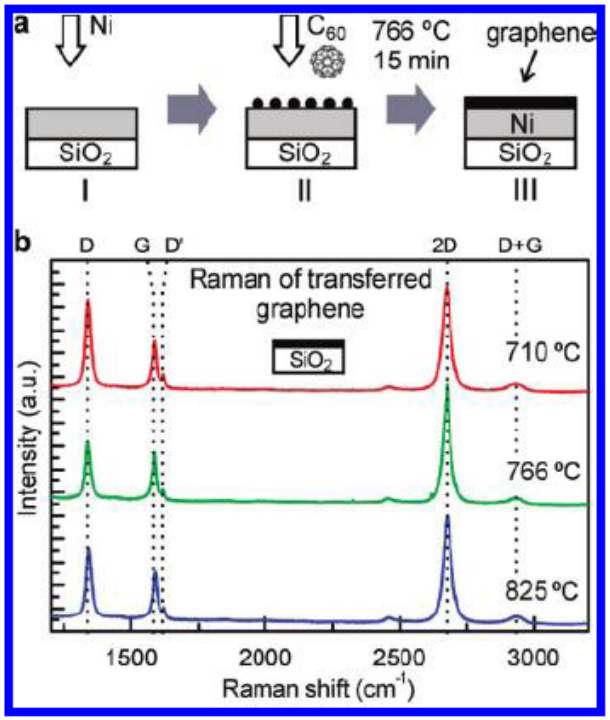


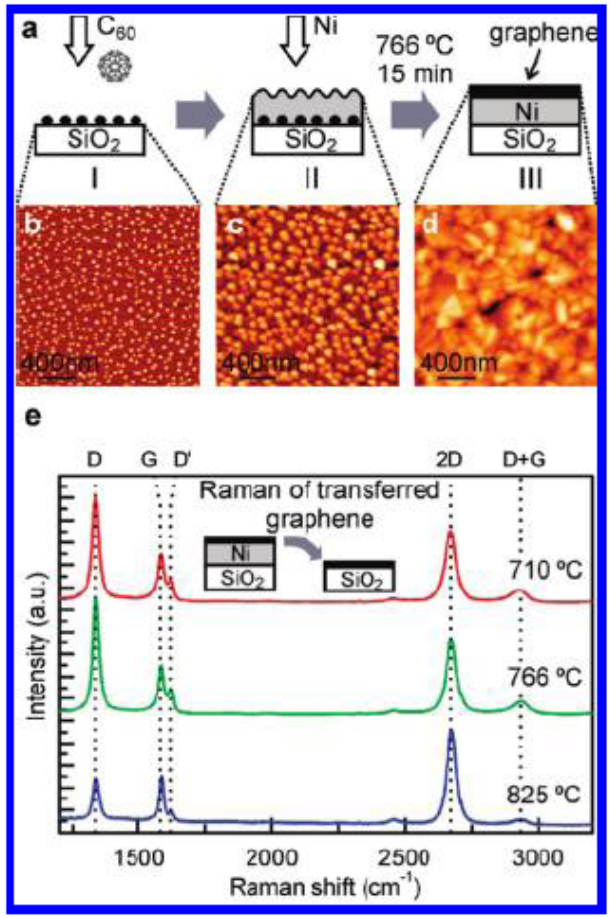
Figure 3 | Transfer processes for large-scale graphene films. a, A

Kim et al., Nature (2009)

Graphene formation by decomposition of C_{60}

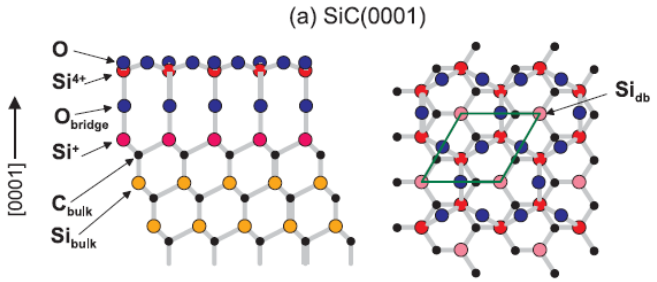


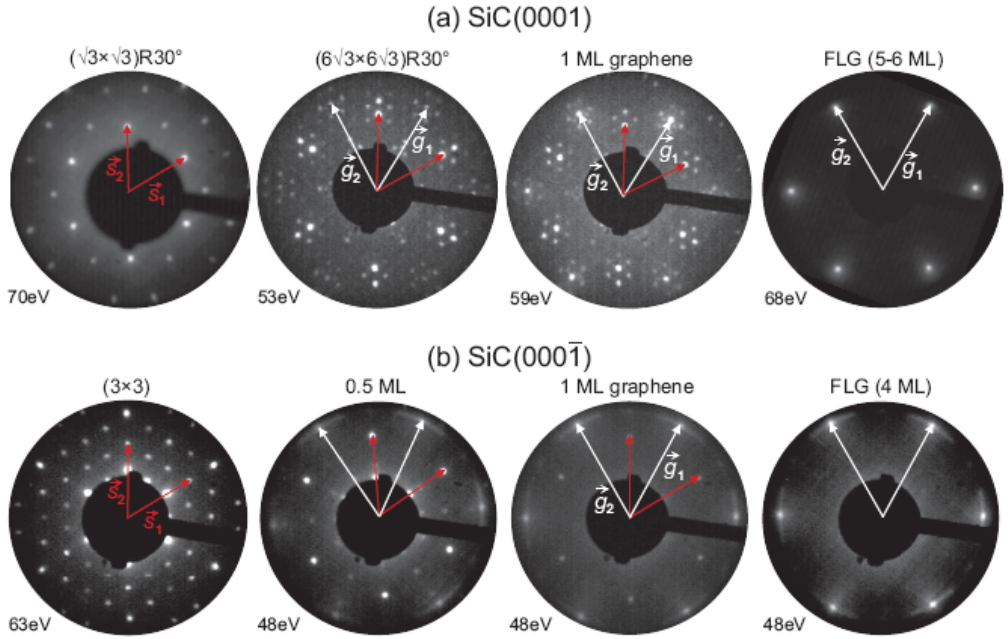


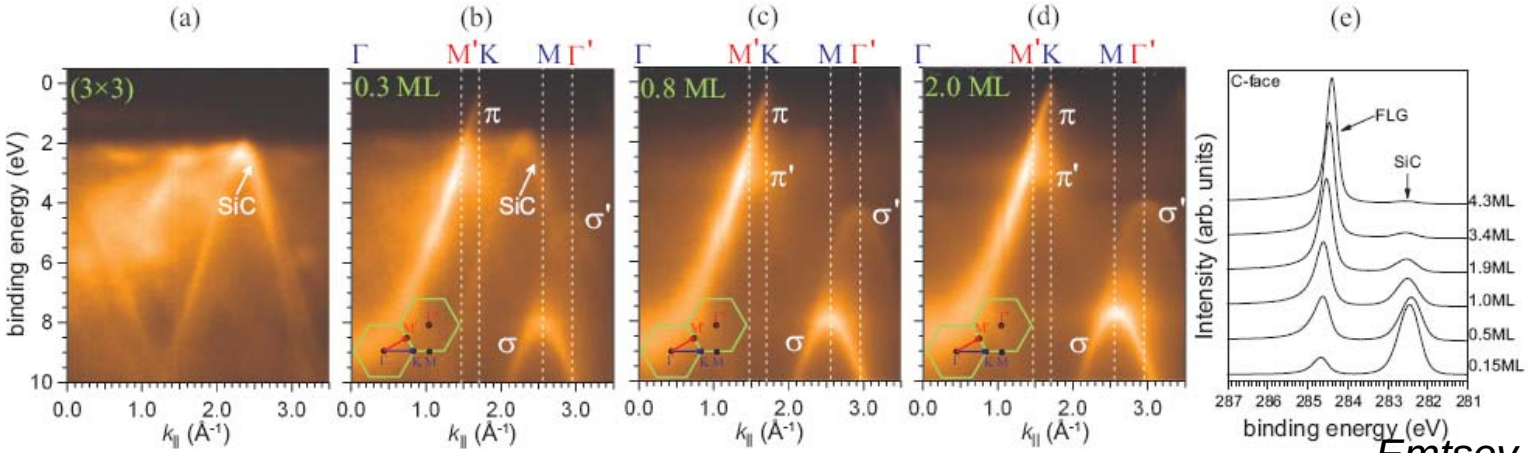


Perdigao *et al.*, J. Physical Chemistry C (2011)

Epitaxial growth graphene on SiC

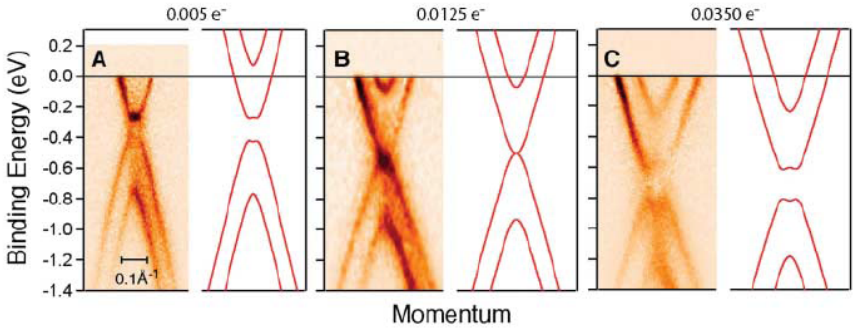




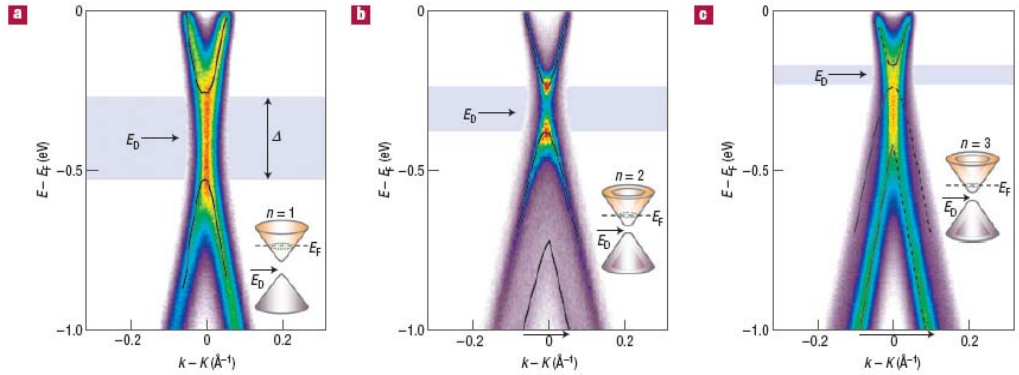


Emtsev et al., PRB (2008)

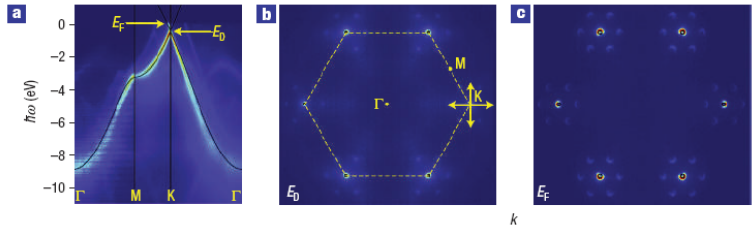
Epitaxial growth graphene on SiC

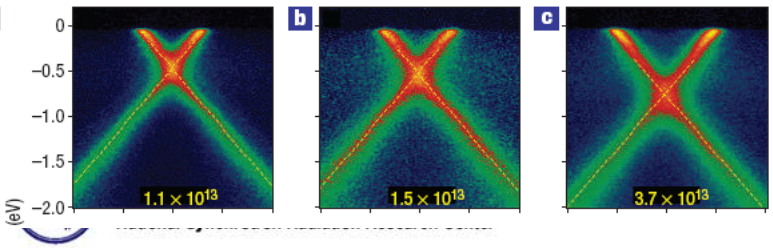


Ohta et al., Science (2007)

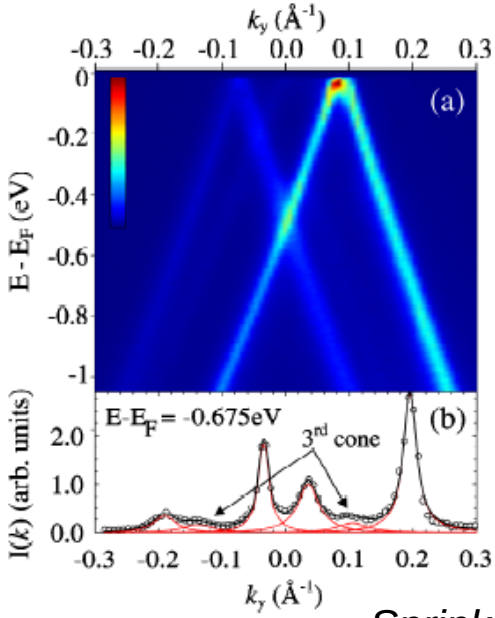


Zhou et al., Nat. Mat. 6,770 (2008)





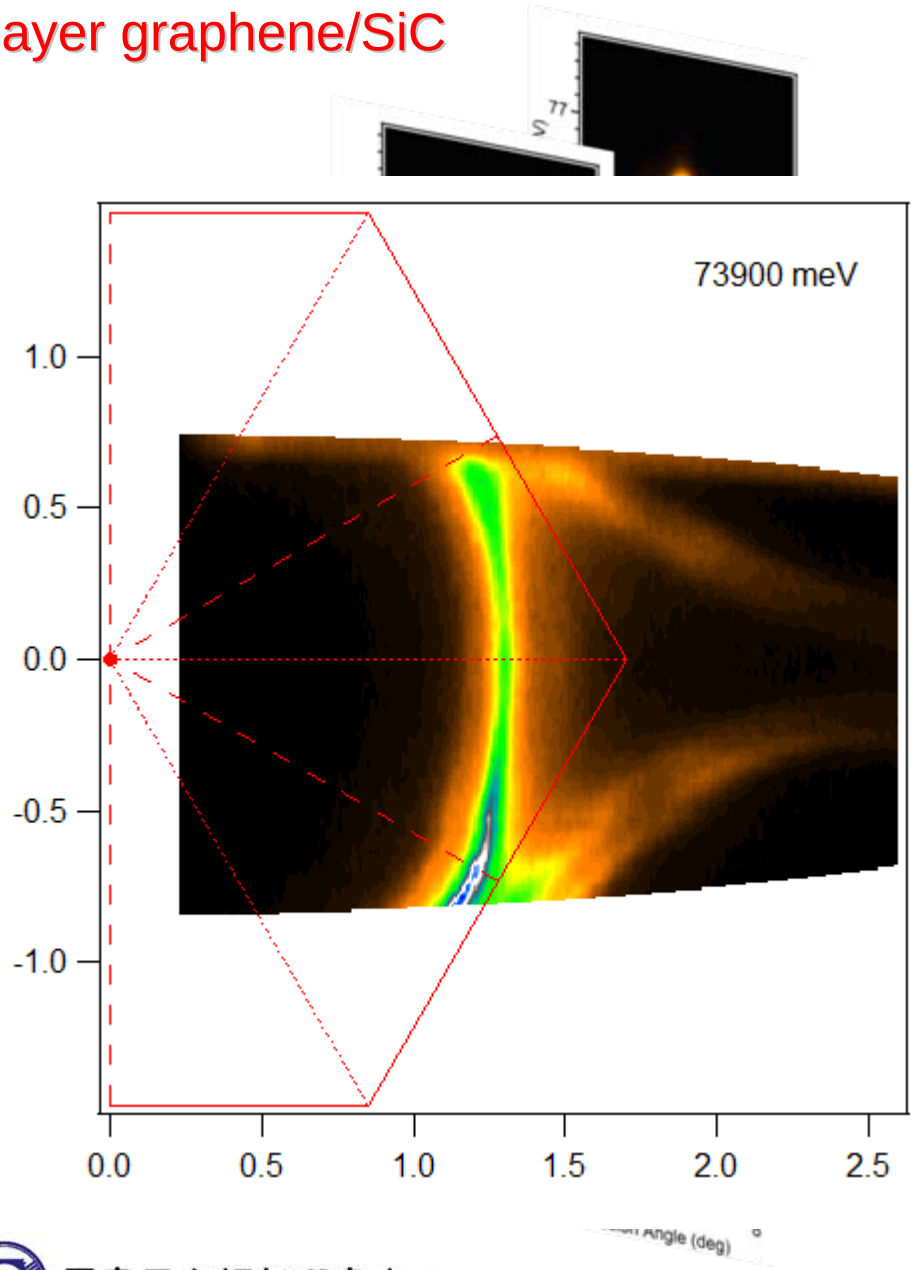
Bostwick et al., Nat. Phys. 3,36 (2007)

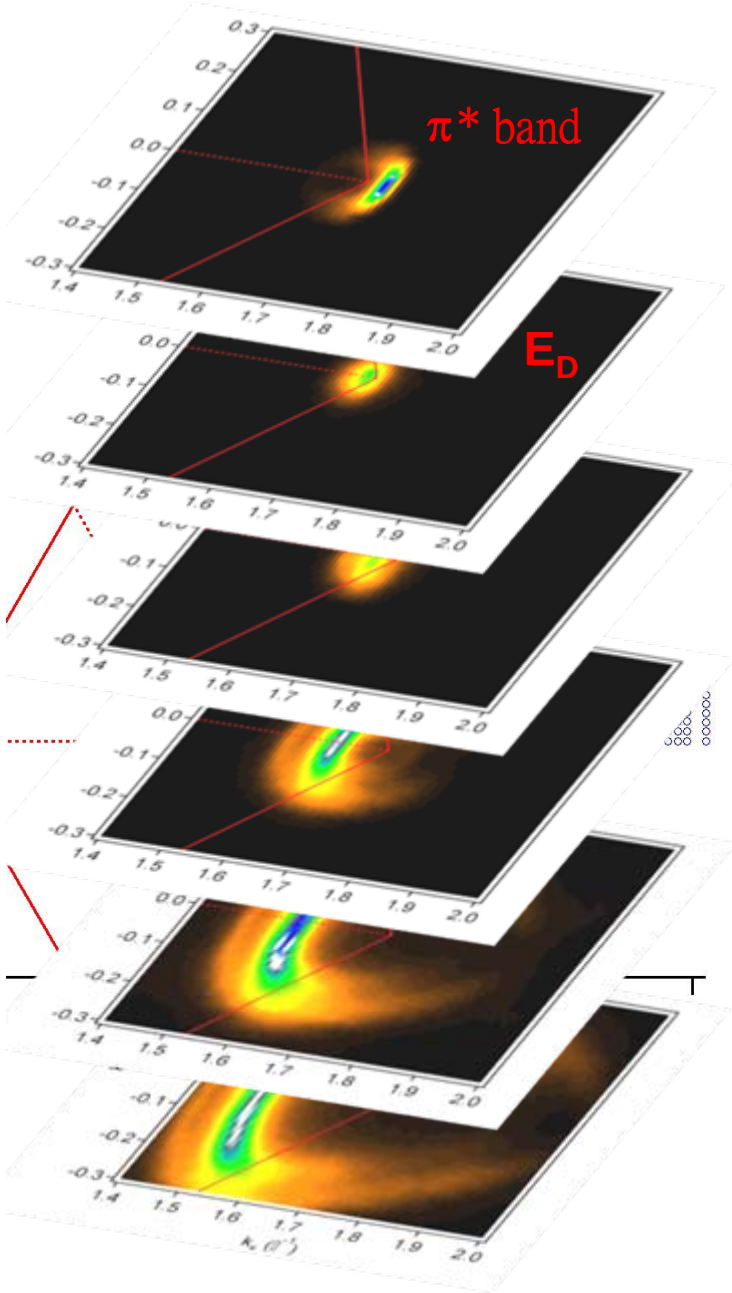


6H-SiC(000 -1)

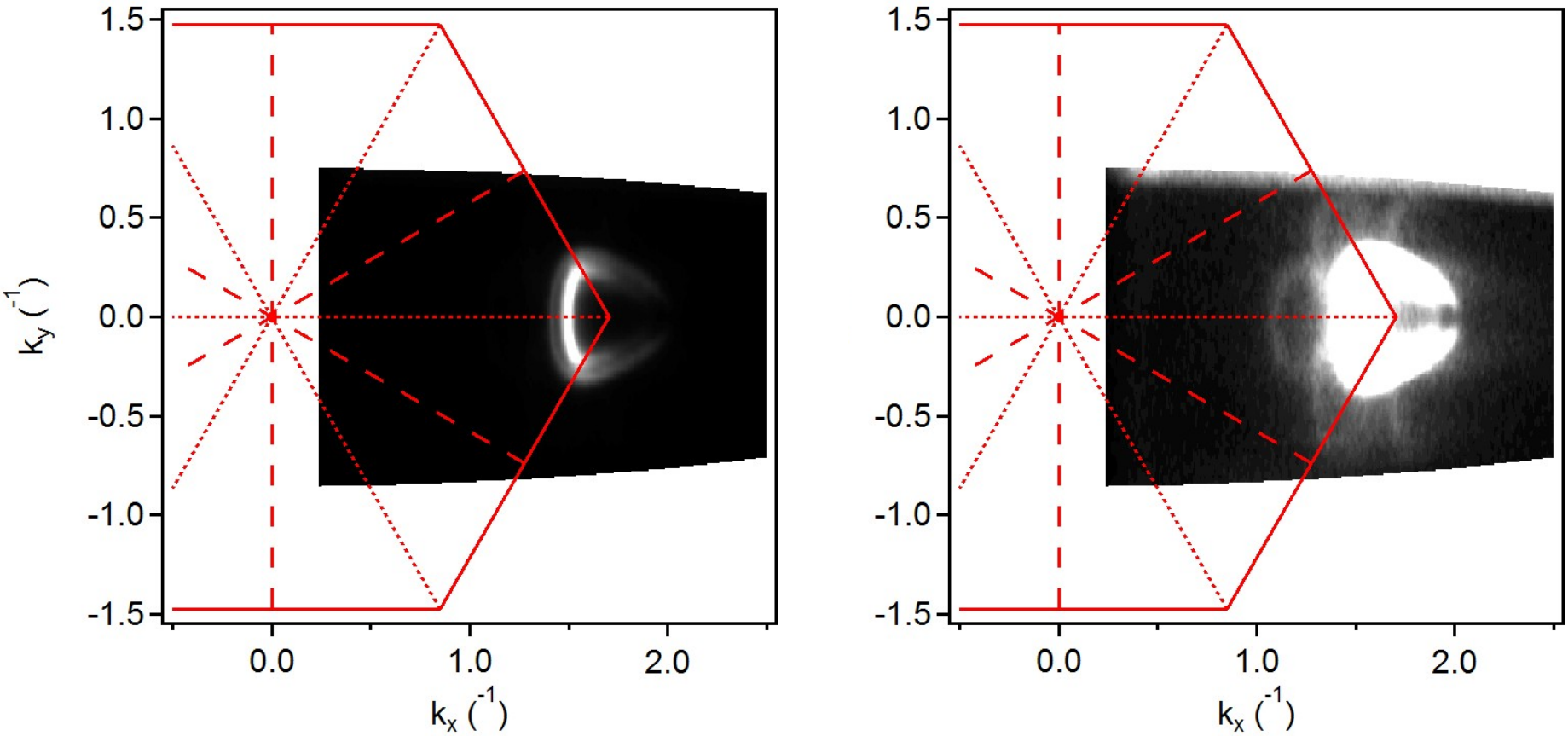
Sprinkle et al., PRL (2009)

Bilayer graphene/SiC



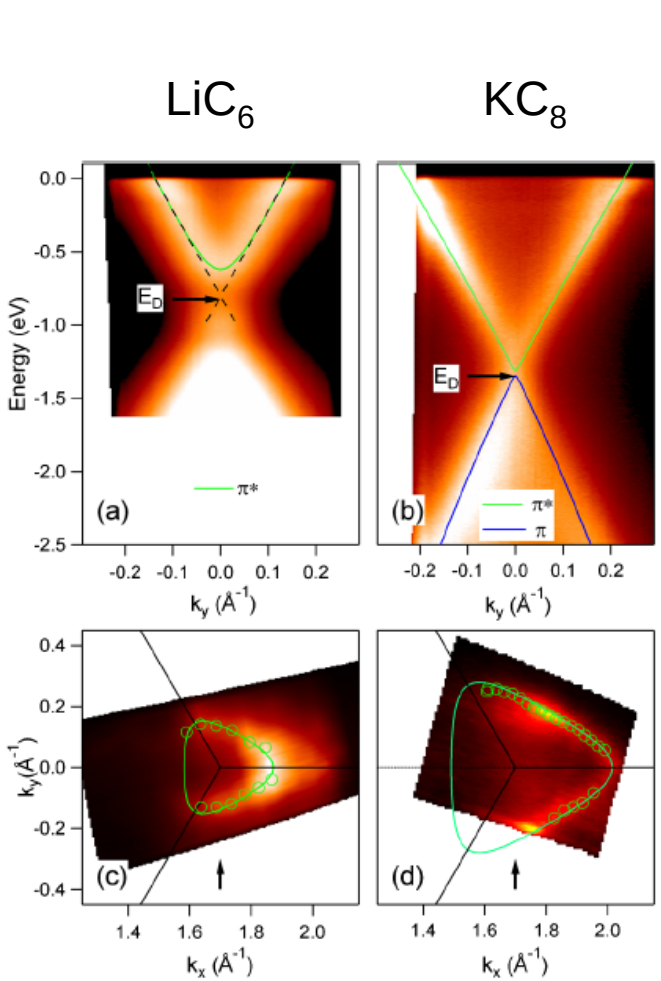


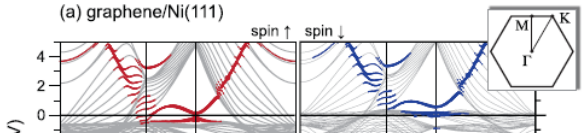
High quality graphene/SiC

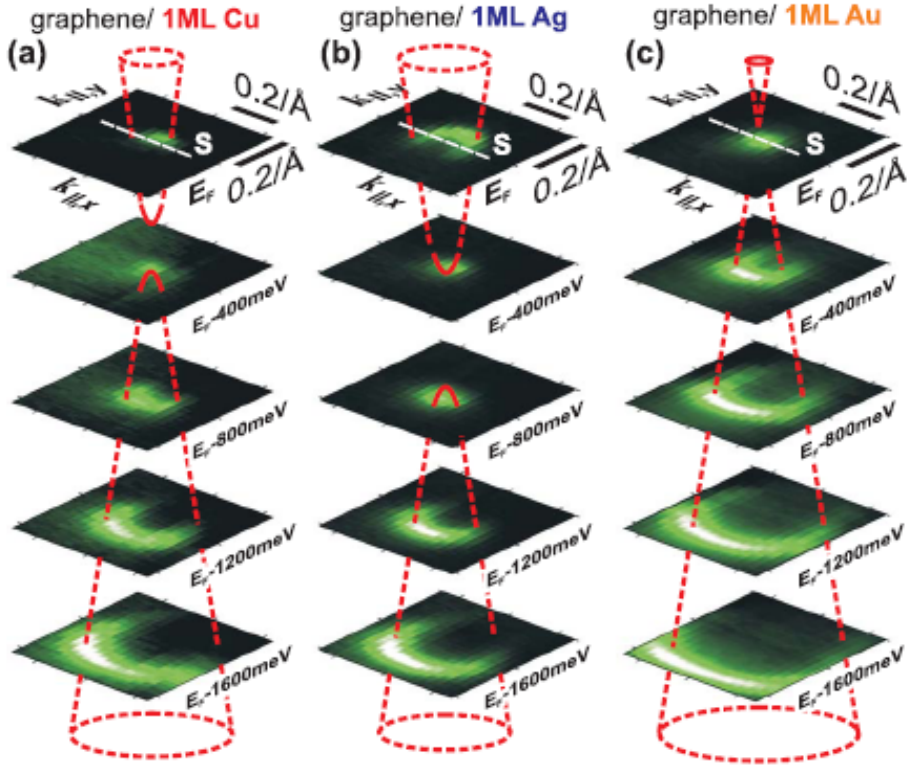


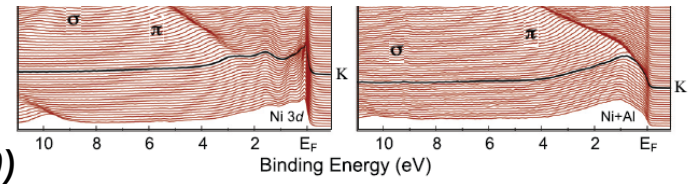
Spectra line shape analysis and intercalated compounds

Graphene intercalated compounds (GICs)



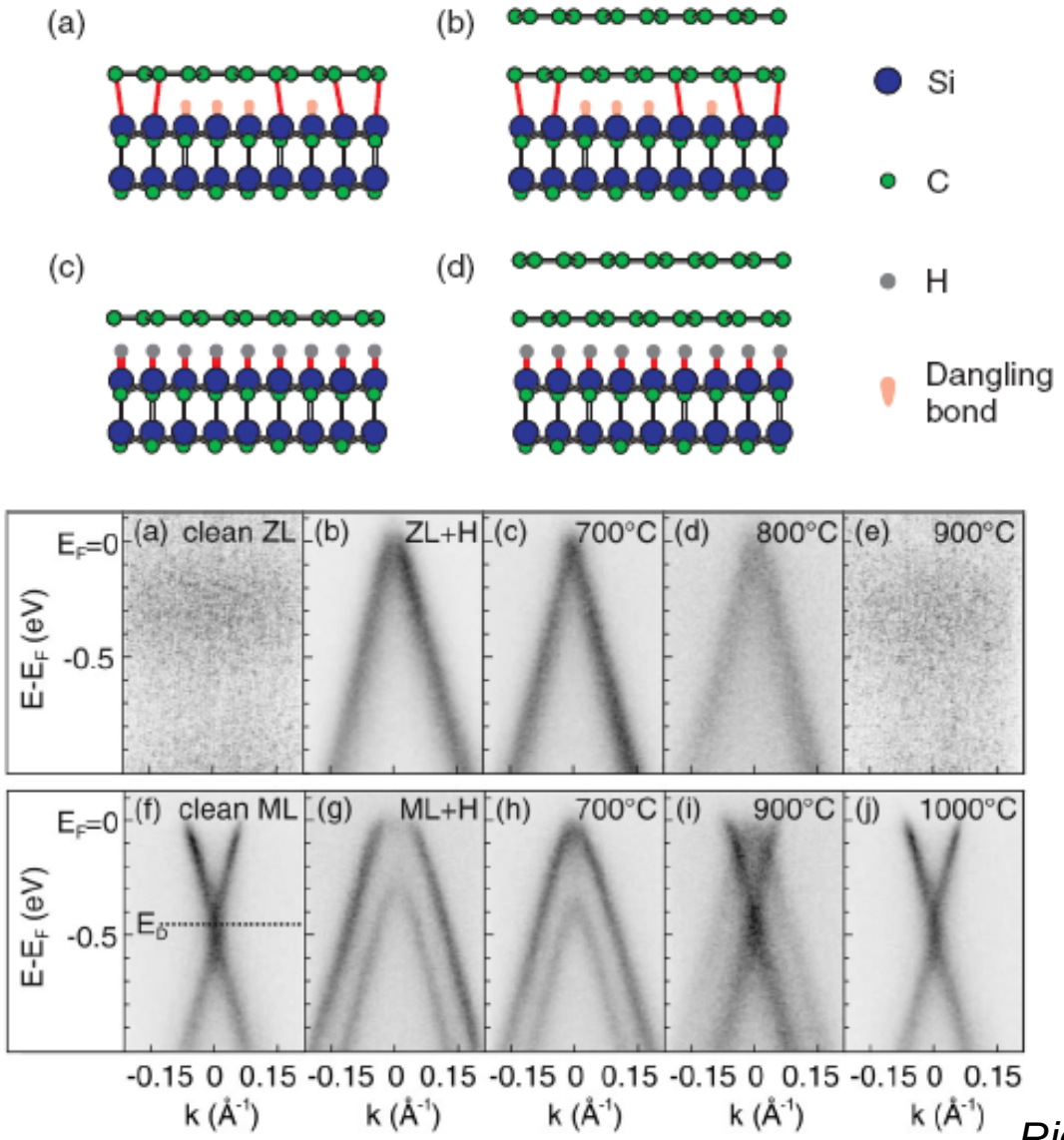






Pan et al., PRL (2011)
Voloshina et al., NJP (2011)
Varykhalov et al., PRB (2010)

Hydrogen intercalated graphene/SiC



Riedl et al., PRL (2009)

A intrinsic gap exists or not ?

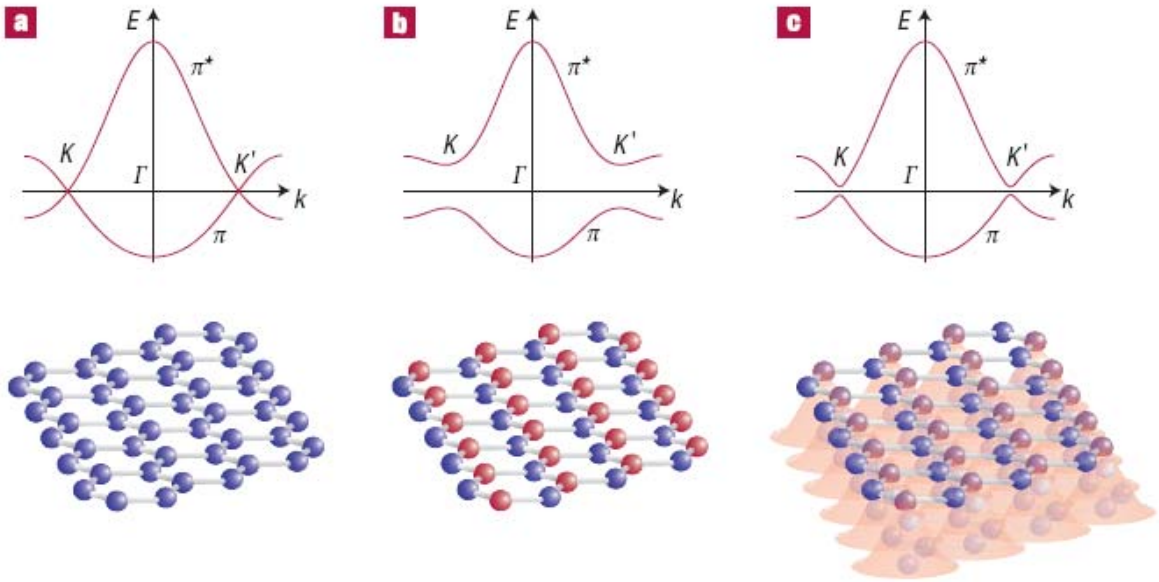


Figure 1 Schematic representation of crystal and electronic band structures (only π-bands are shown). **a**, Free-standing graphene. **b**, Boron-nitride. **c**, Epitaxial graphene. Symmetry between the sublattices in graphene guarantees gapless spectra around *K* points. This symmetry is broken in boron-nitride (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)

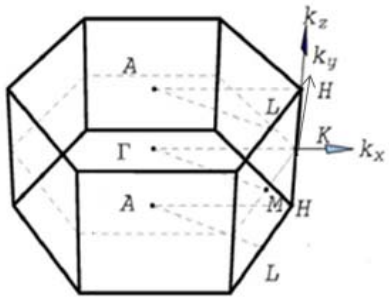
The difficulties for studying the electronic structure of exfoliated graphene

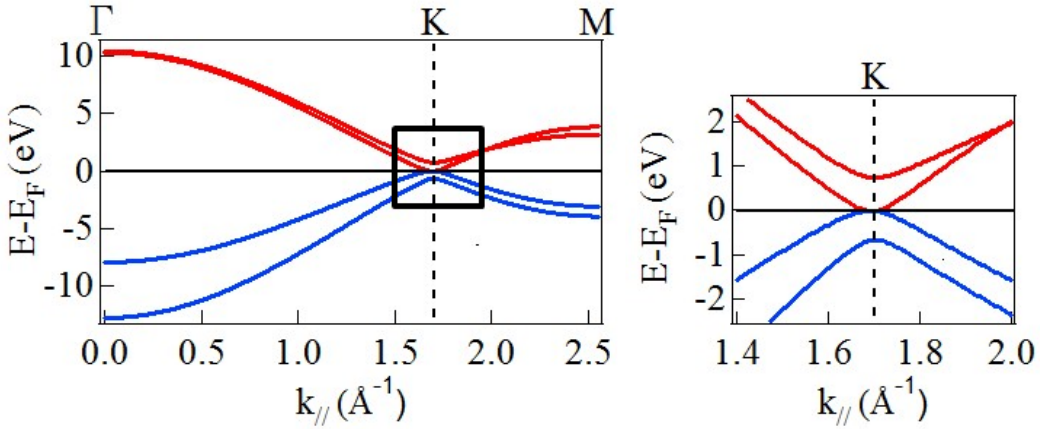
- Insulating substrates induce the strong charging effect
- Sample size : only several tens microns sample is obtained, the size is small for current ARPES beam spot in VUV region
- *ex-situ* sample preparation is not good for ARPES experiments

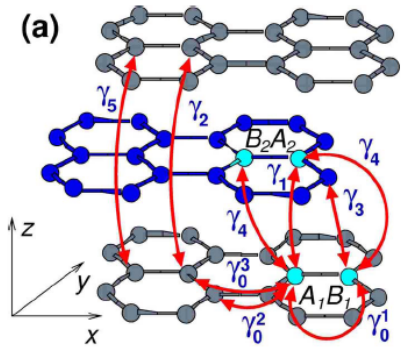
Sample preparation

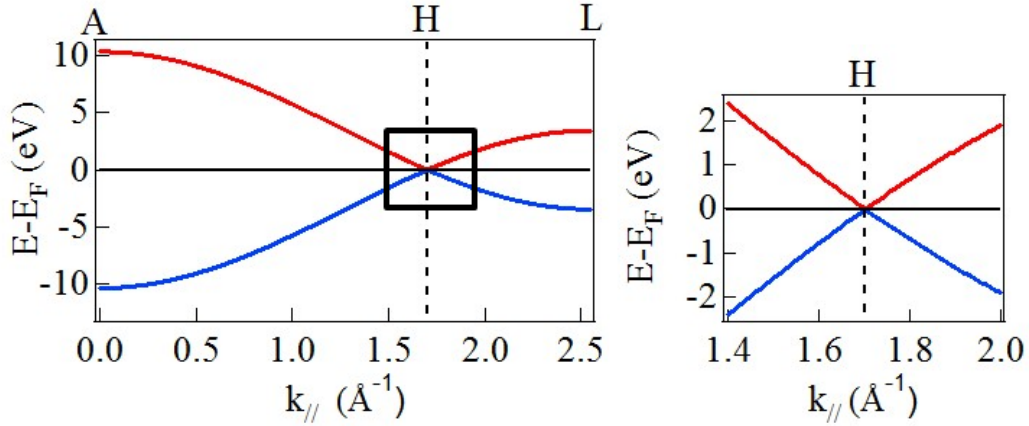
- Use highly-doped Si-substrate to replace Si capped with 200nm SiO_2 substrate.
- Anneal sample above 400 ℃ to flash gas condensations in UHV environment.
- Choose suitable photon energy to enhance the cross section of carbon.

The electronic structure of graphite

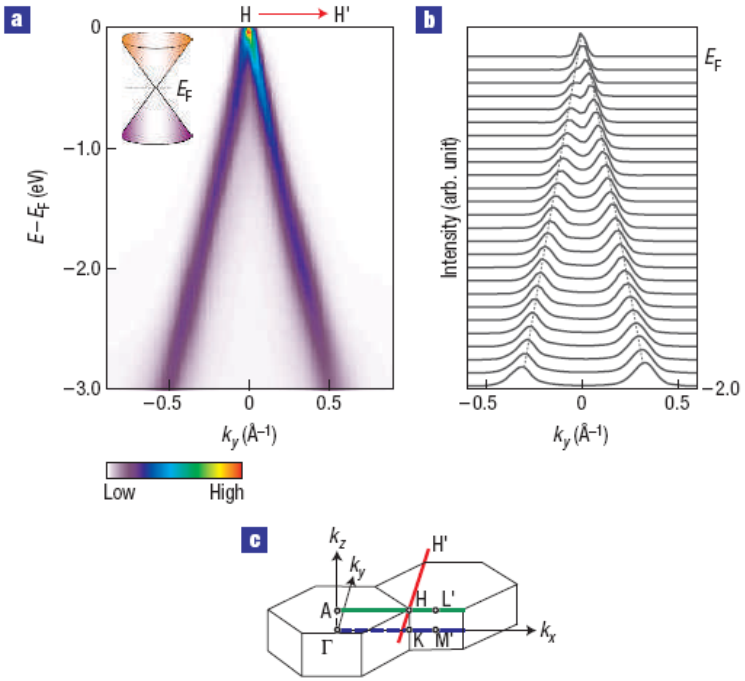


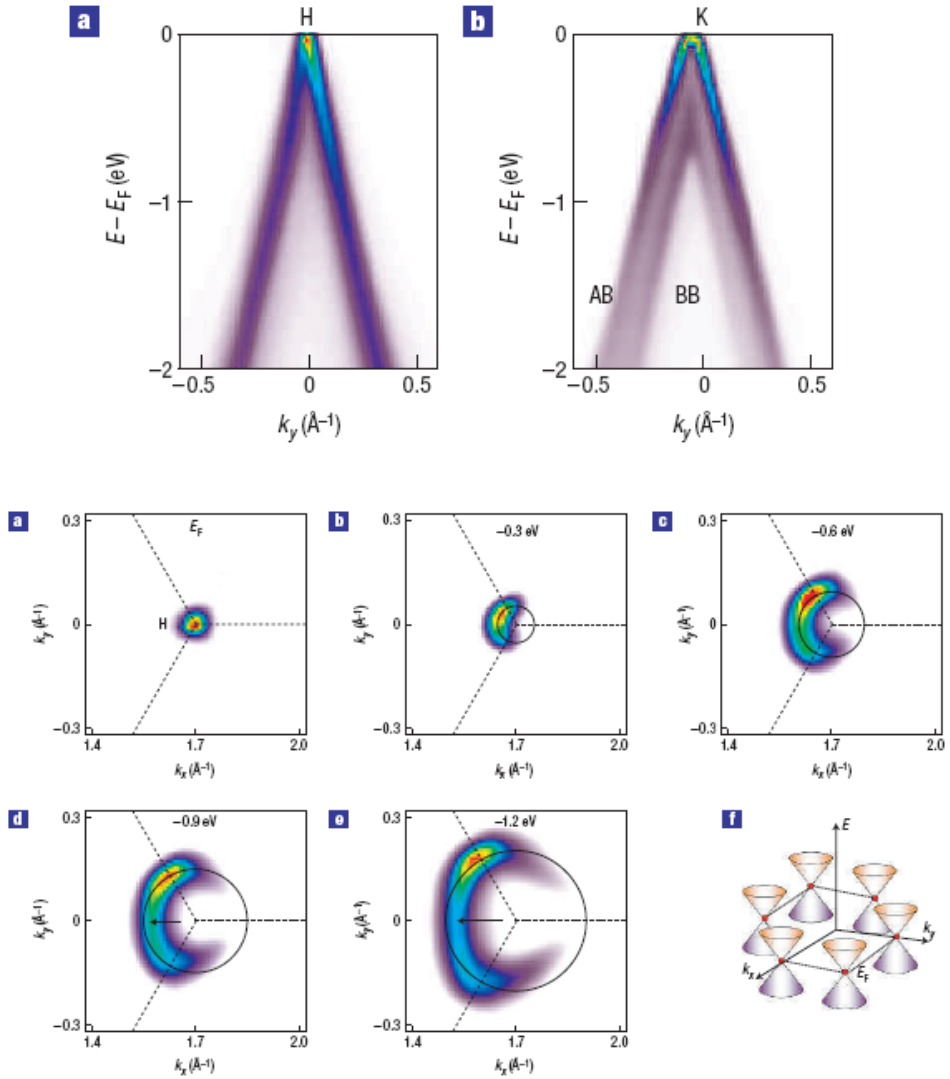






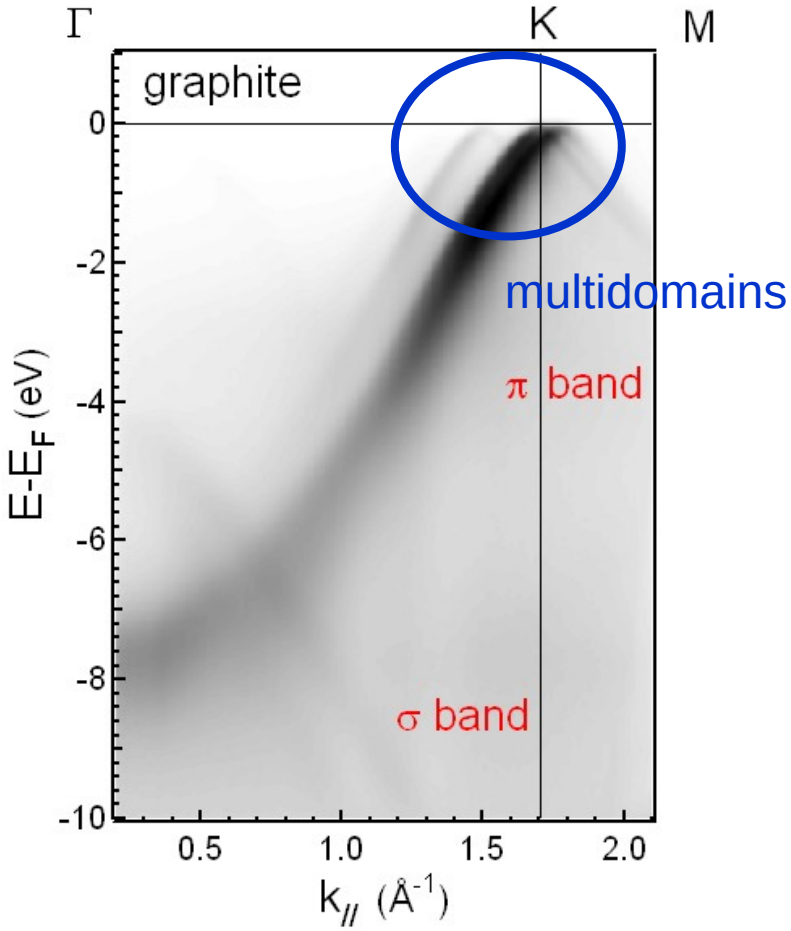
Early ARPES work on graphite

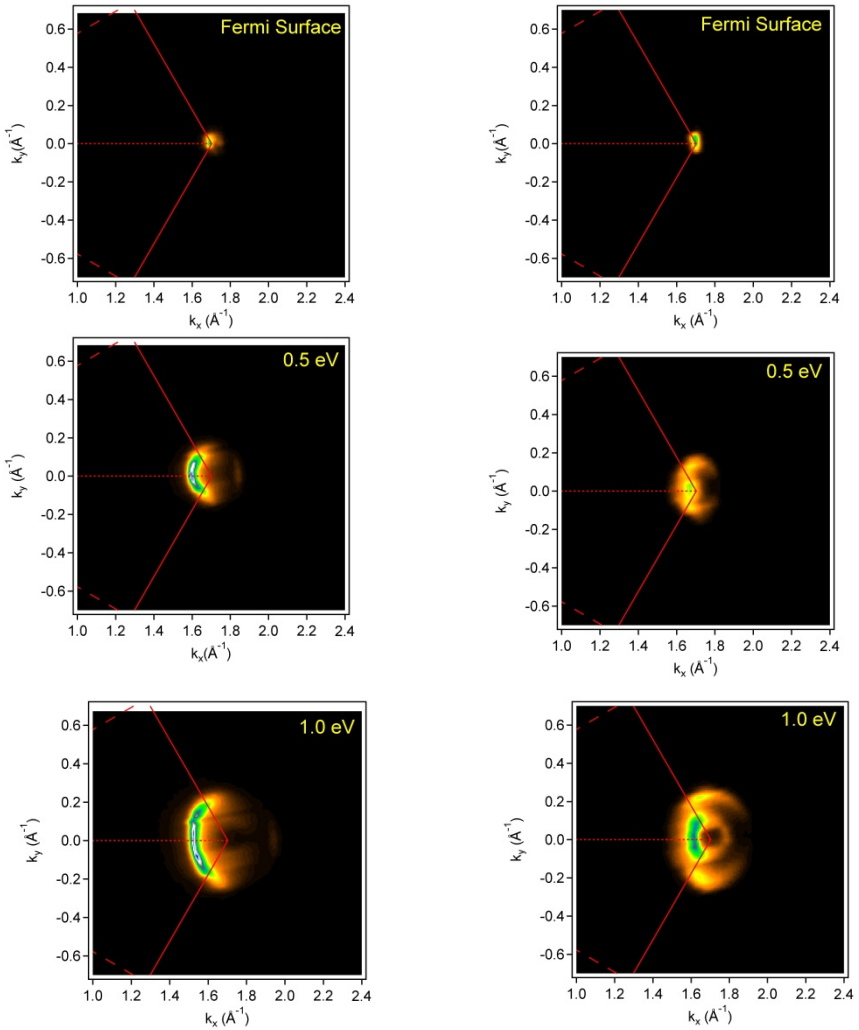




Zhou et al., Nature Physics 2, 595(2006)

The band mapping result of Kish graphite





52 eV ~ H point

87 eV ~ K point

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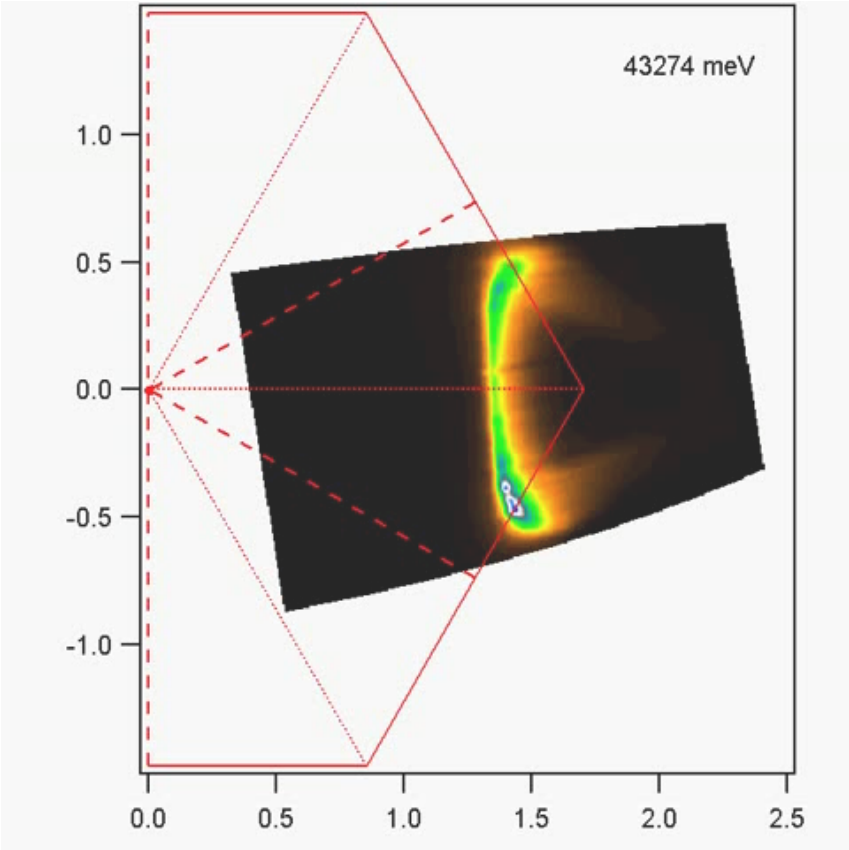
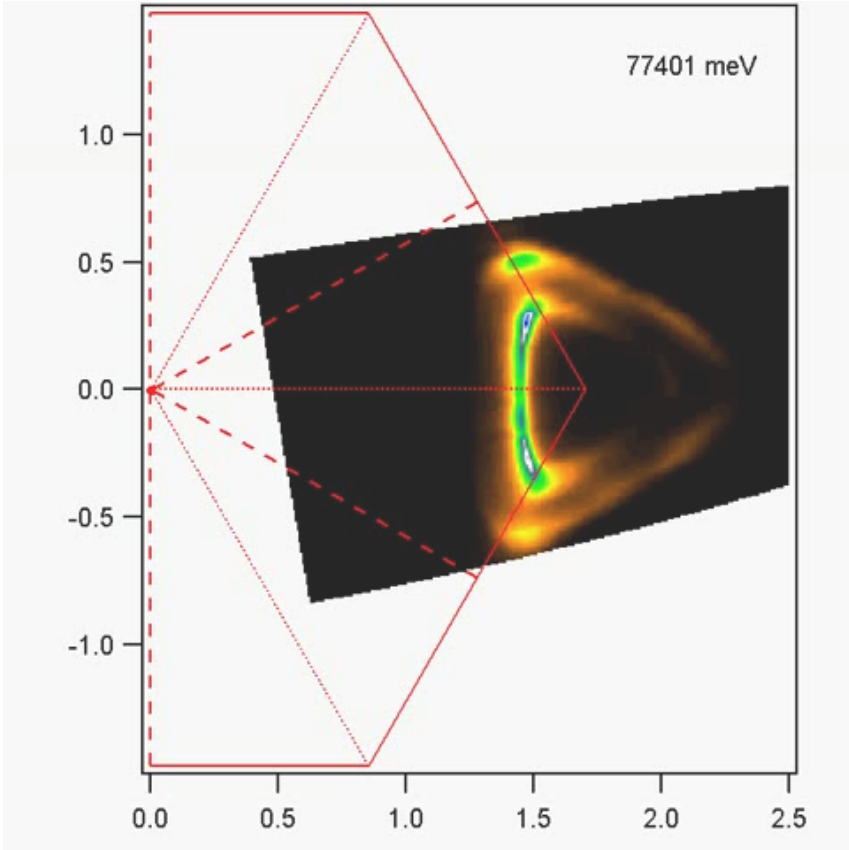
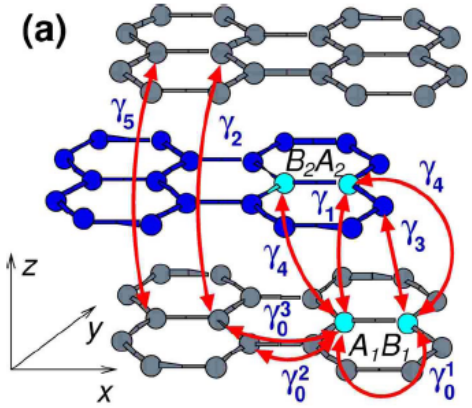
Constant energy mapping of graphite





3NNN SWMc Hamiltonian of bilayer graphene



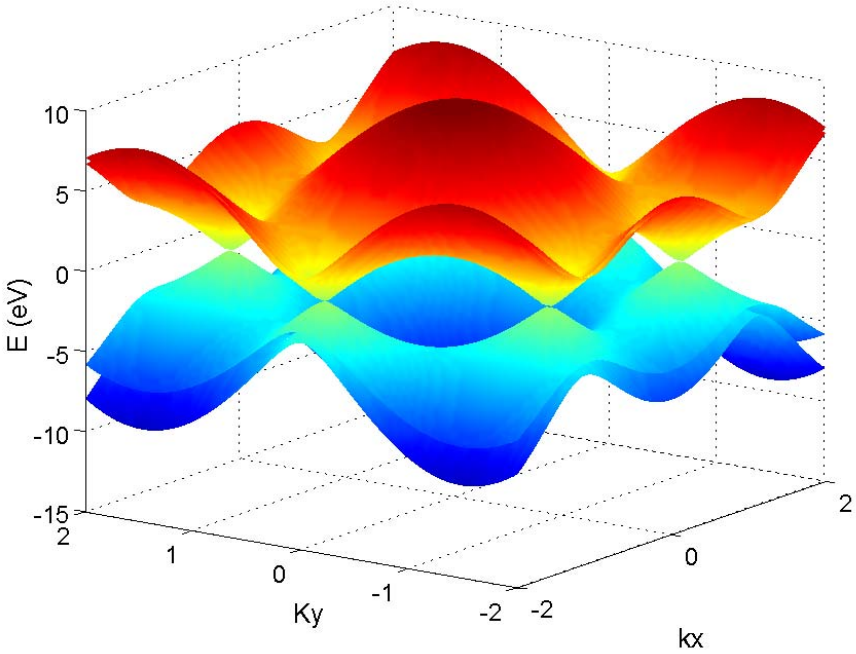
$$H(\mathbf{k})c(\mathbf{k}) = S(\mathbf{k})E(\mathbf{k})c(\mathbf{k}).$$

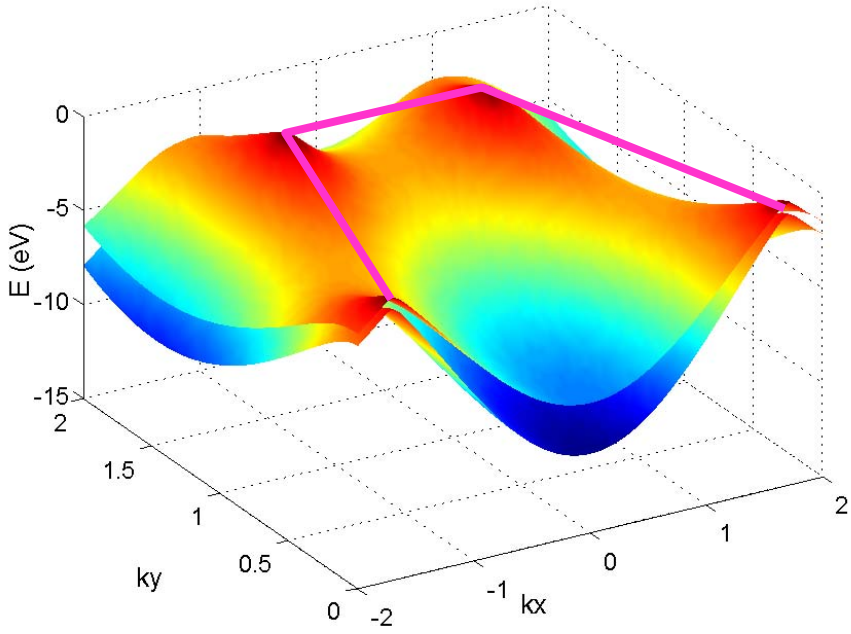
$$H(\mathbf{k}) = \begin{pmatrix} E_0 + \Delta + \gamma_0^2 f_2(\mathbf{k}) & \gamma_0^1 f_1(\mathbf{k}) + \gamma_0^3 f_3(\mathbf{k}) & \gamma_1 & \gamma_4 f_1(\mathbf{k})^* \\ \gamma_0^1 f_1(\mathbf{k})^* + \gamma_0^3 f_3(\mathbf{k})^* & E_0 + \gamma_0^2 f_2(\mathbf{k})^* & \gamma_4 f_1(\mathbf{k})^* & \gamma_3 f_1(\mathbf{k}) \\ \gamma_1 & \gamma_4 f_1(\mathbf{k}) & E_0 + \Delta + \gamma_0^2 f_2(\mathbf{k}) & \gamma_0^1 f_1(\mathbf{k})^* + \gamma_0^3 f_3(\mathbf{k})^* \\ \gamma_4 f_1(\mathbf{k}) & \gamma_3 f_1(\mathbf{k})^* & \gamma_0^1 f_1(\mathbf{k}) + \gamma_0^3 f_3(\mathbf{k}) & E_0 + \gamma_0^2 f_2(\mathbf{k}) \end{pmatrix}$$

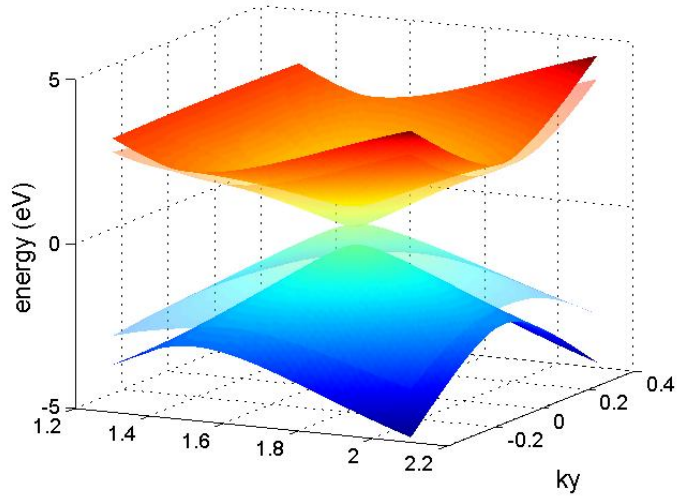
$$S(\mathbf{k}) = \begin{pmatrix} 1 + s_0^2 f_2(\mathbf{k}) & s_0^1 f_1(\mathbf{k}) + s_0^3 f_3(\mathbf{k}) & 0 & 0 \\ s_0^1 f_1(\mathbf{k})^* + s_0^3 f_3(\mathbf{k})^* & 1 + s_0^2 f_2(\mathbf{k})^* & 0 & 0 \\ 0 & 0 & 1 + s_0^2 f_2(\mathbf{k}) & s_0^1 f_1(\mathbf{k})^* + s_0^3 f_3(\mathbf{k})^* \\ 0 & 0 & s_0^1 f_1(\mathbf{k}) + s_0^3 f_3(\mathbf{k}) & 1 + s_0^2 f_2(\mathbf{k}) \end{pmatrix}.$$

A. Gruneis et al., PRB (2008)

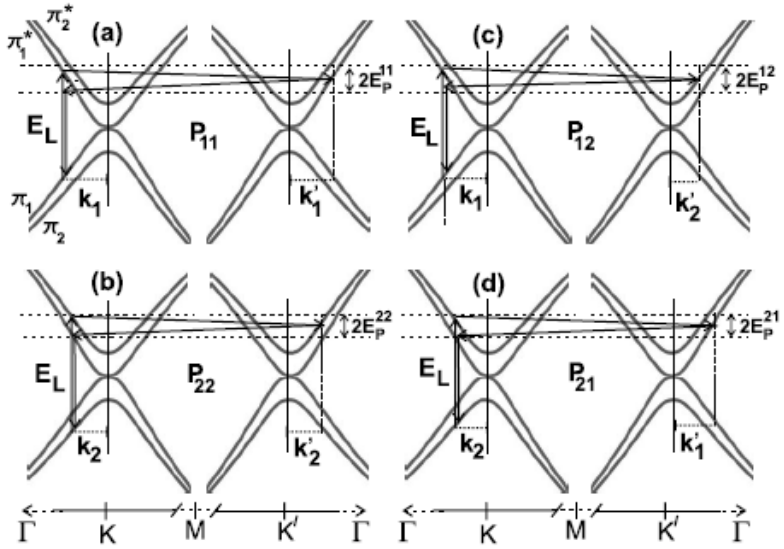
Simulation result of the π band for bilayer graphene

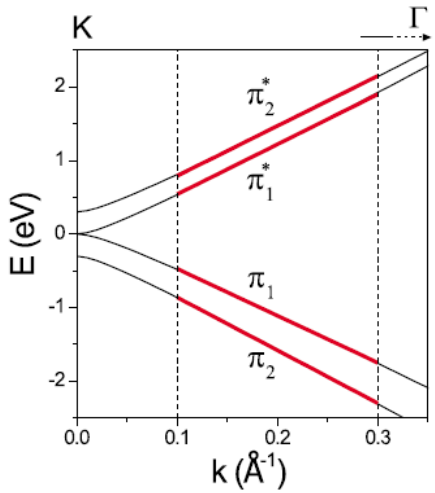






TBM parameters determined by rasonance Raman scattering





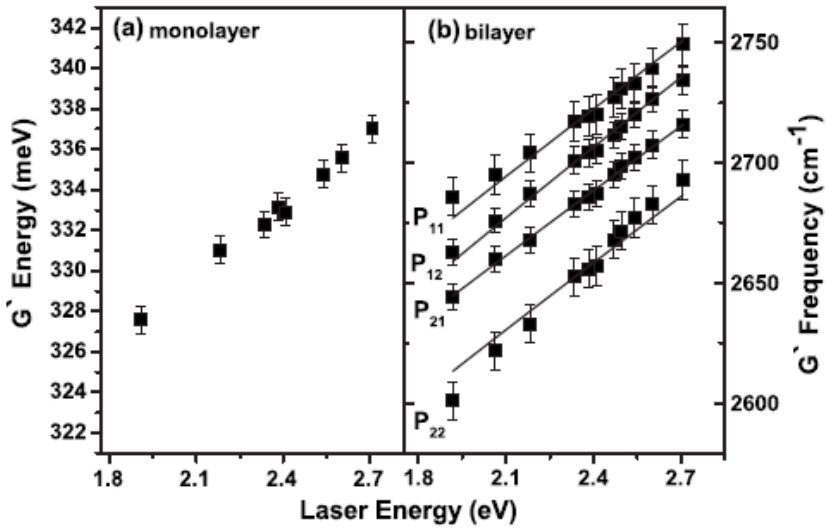
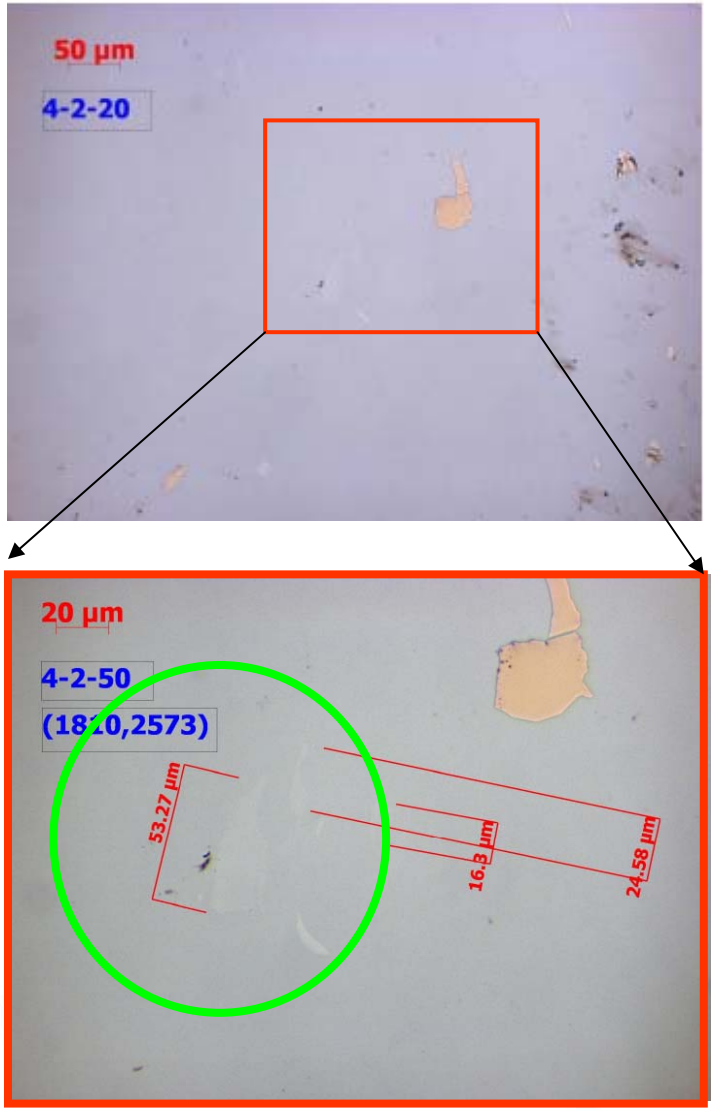


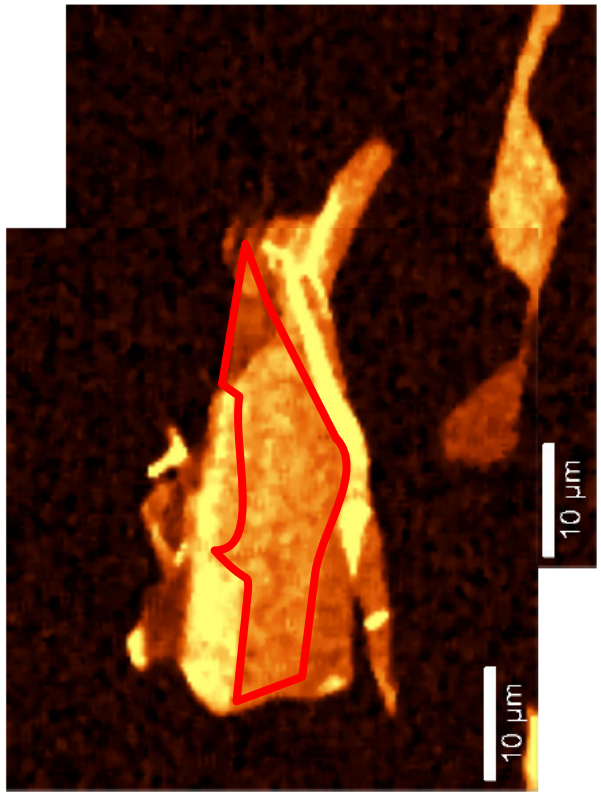
TABLE II. Experimental SWM parameters (in eV) for the band structure of bilayer graphene. The parameters for graphite are taken from Refs. 18 and 19.

	γ_0	γ_1	γ_2	γ_3	γ_4	γ_5	$\gamma_6=\Delta$
Bilayer graphene	2.9	0.30	n/a	0.10	0.12	n/a	n/a
Graphite	3.16	0.39	−0.02	0.315	0.044	0.038	0.008

Malard et al.,PRB (2007)

Bilayer graphene / Highly doped Si substrate

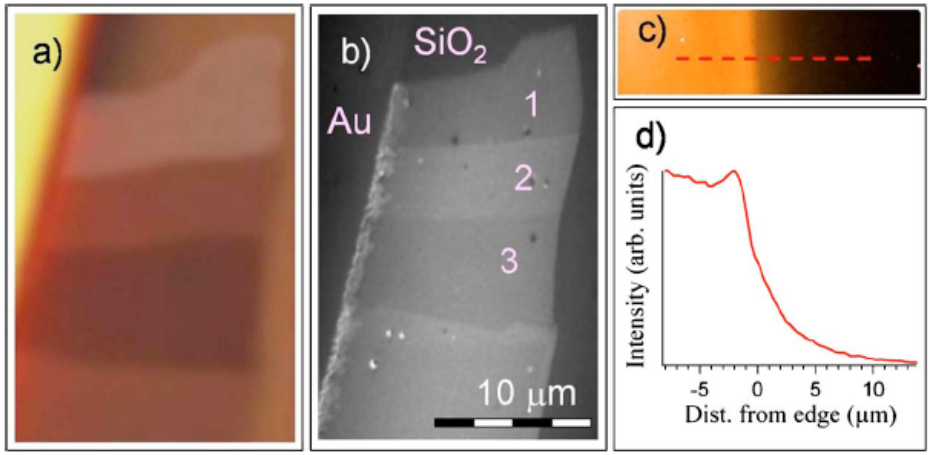


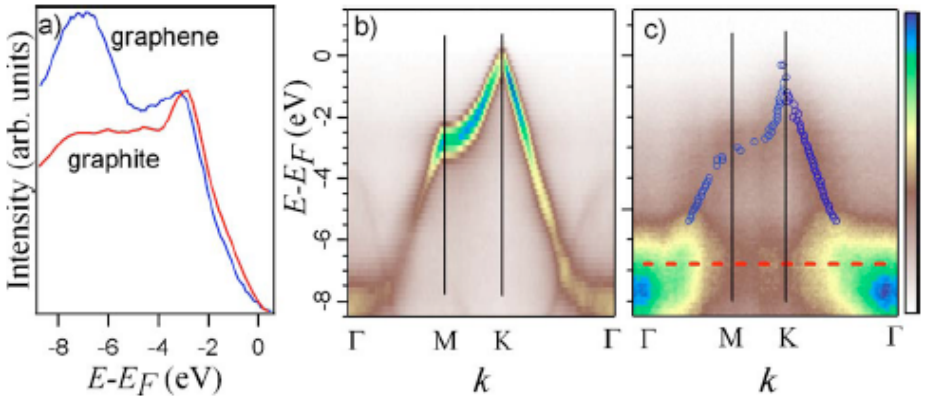


Intensity of G band (overlap of 2 scans showing flake 1 and 3)

Raman result from Germany,, the bilayer graphene should be the area marked in red.

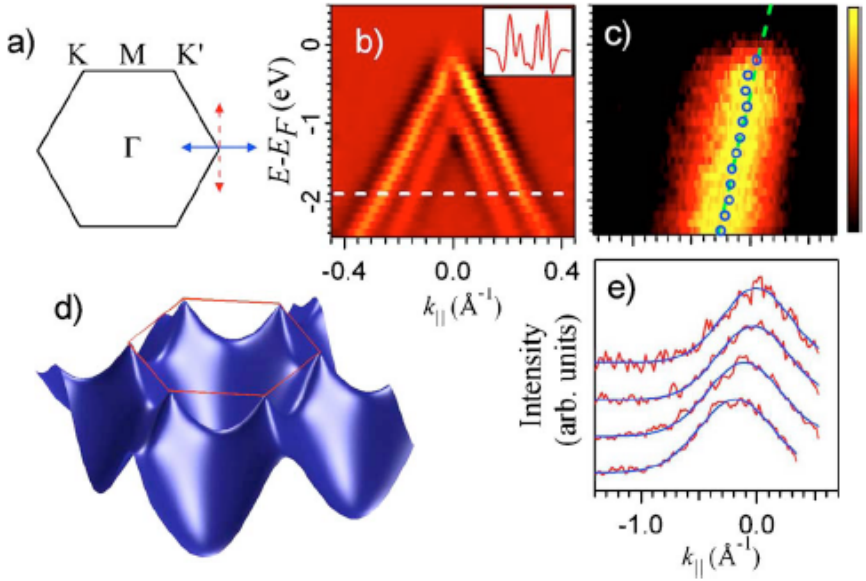
The electronic structure of single layer graphene on SiO_2 (200nm)





1. Use lithography to pattern graphene flake with gold contact

2. Microfocus beam size < 5 μ m



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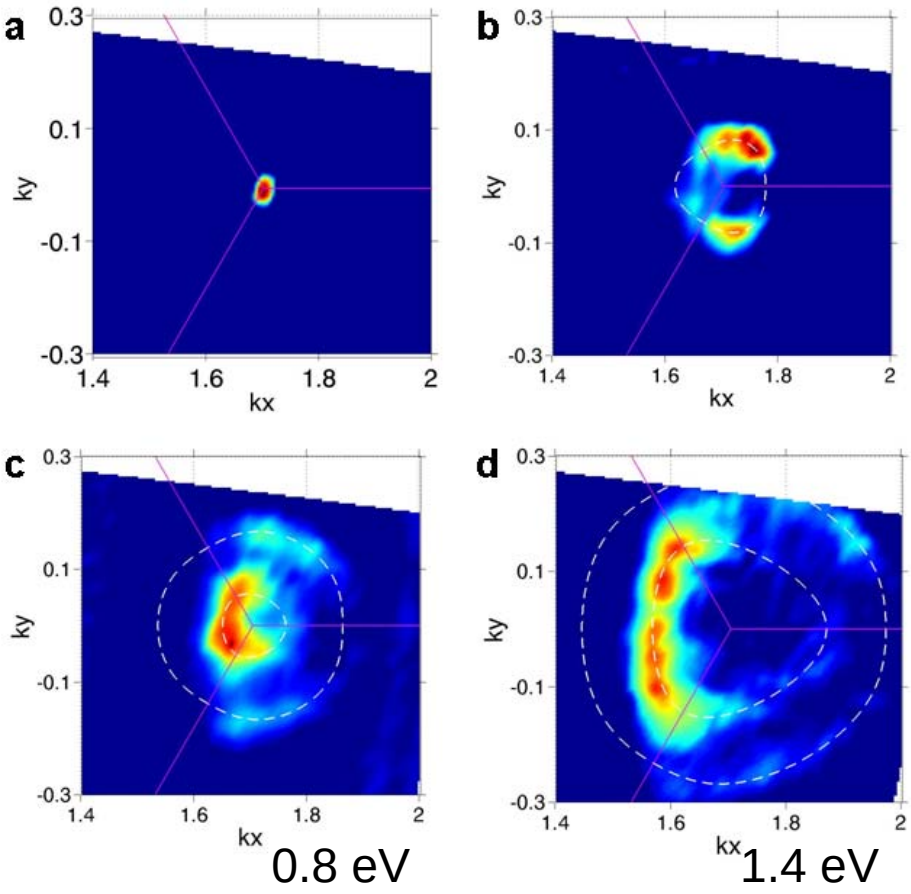
Knox et al., PRB 78, R201408 (2008)

Fit TBM parameters to high binding energy

Data were taken at 82 eV

FS

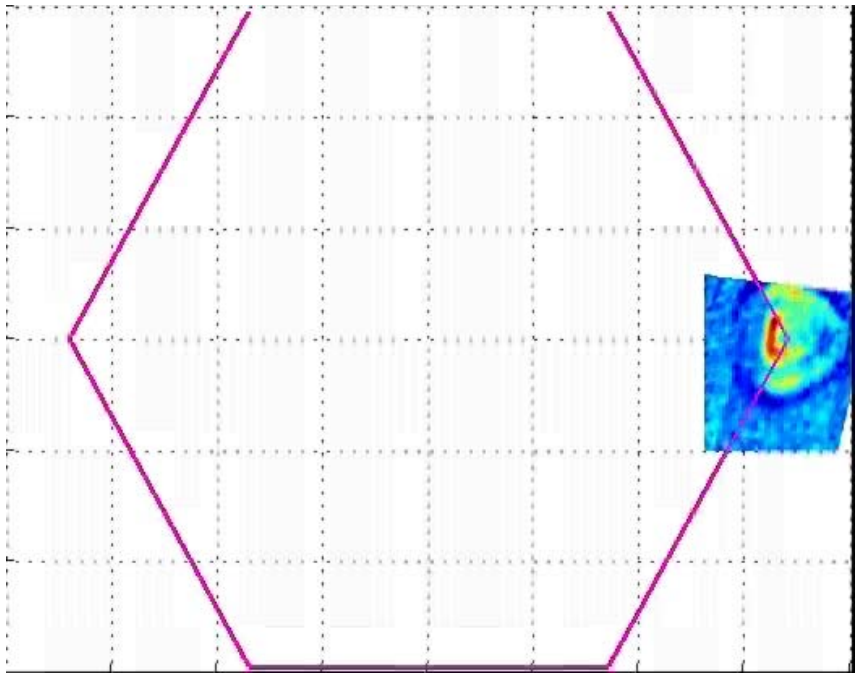
0.3 eV



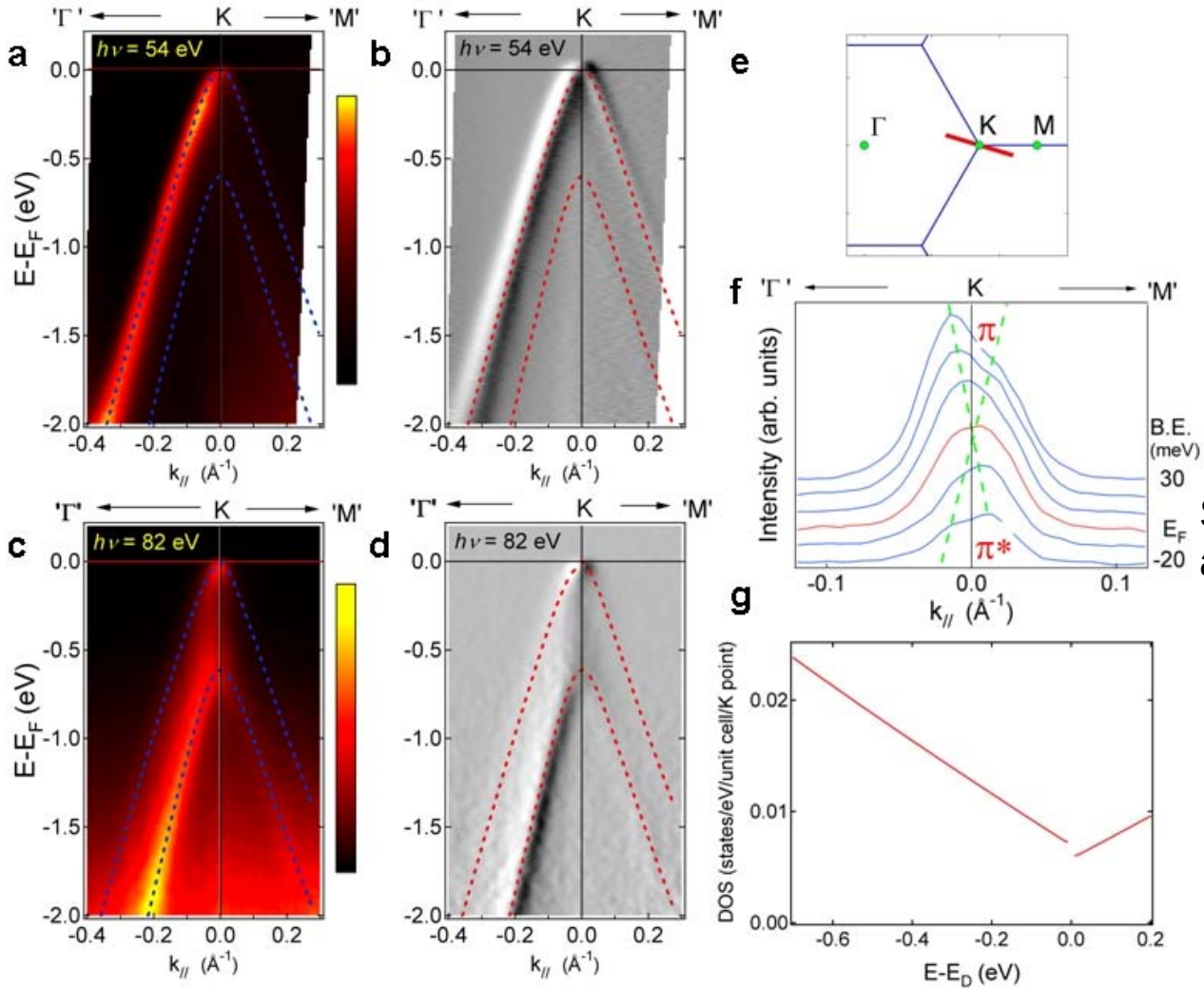
0.8 eV

1.4 eV

Exfoliated BLG/Si



The electronic structure of bilayer graphene



Sample temperature at 70 K

Without gap exists on charge neutral bilayer graphene

What does ARPES measure

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

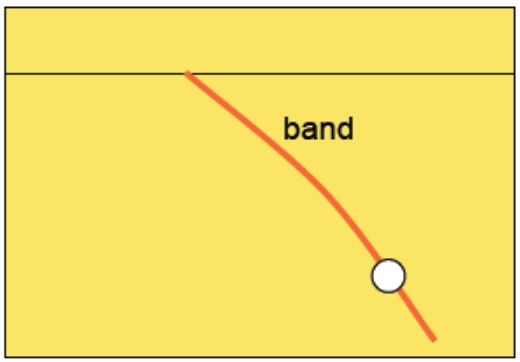
Matrix element

Spectra function

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

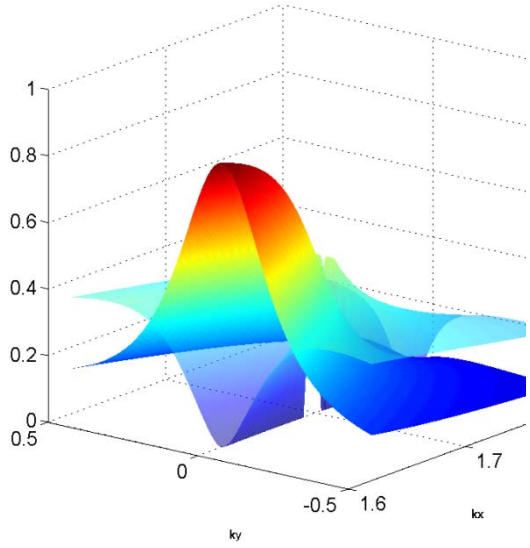
namely,

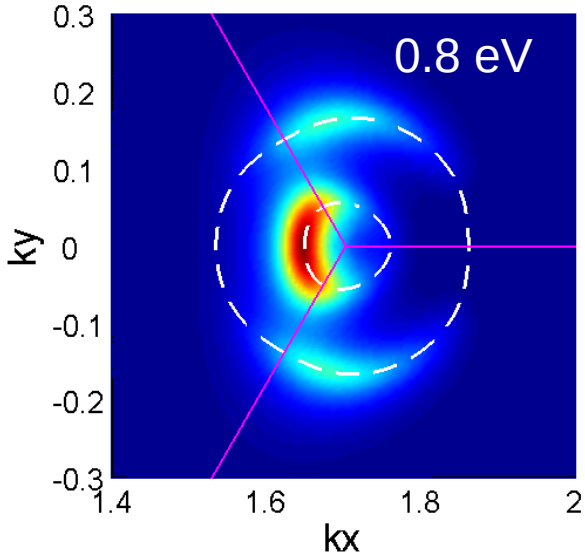
we can learn about the scattering and lifetime of the injected hole

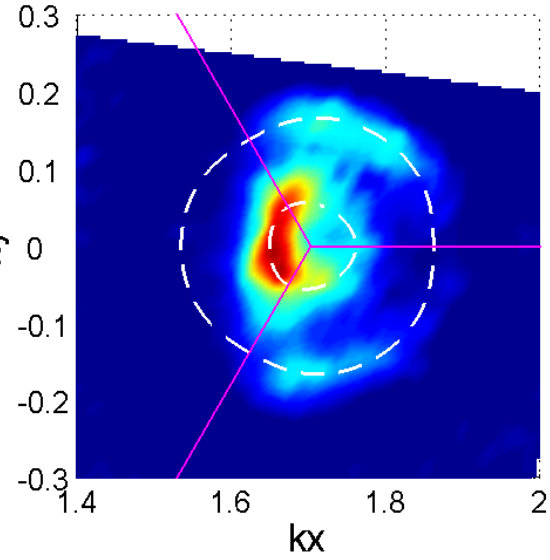


Eli Rotenberg, ALS summer school

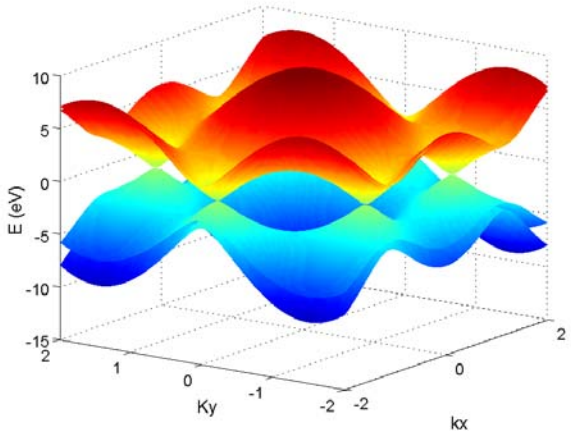
82 eV ME effect

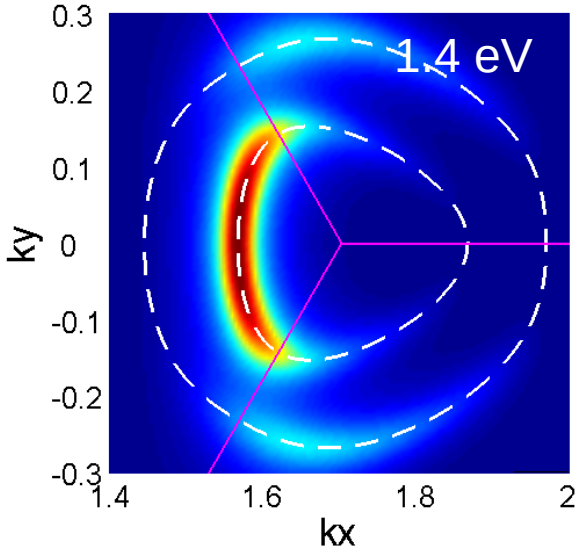


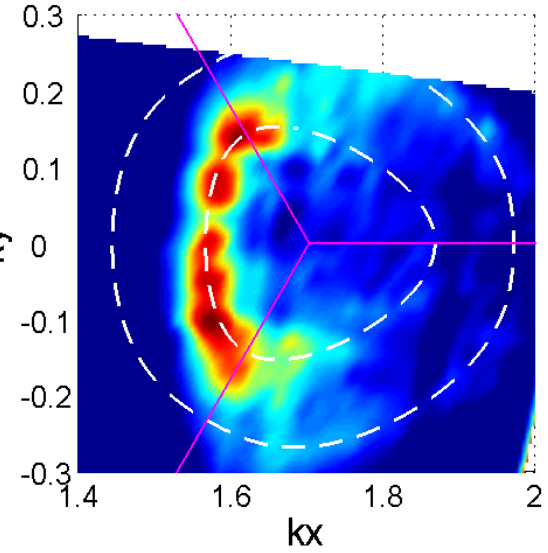




Electronic structure of BLG







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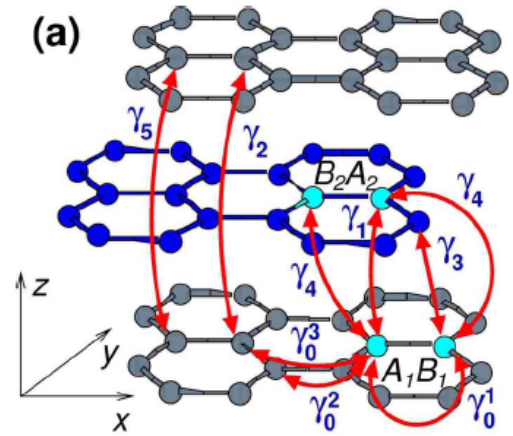
TB parameters for experimental and theoretical results

TABLE I. 3NN tight-binding parameters for few-layer graphene and graphite. All values except the ones for s_0^1, s_0^2, and s_0^3 are in eV. The parameters of fits to LDA and *GW* calculations are shown. The 3NN Hamiltonian is valid in the whole two (three) dimensional BZ of graphite (graphene layers).

Method	γ_0^1	γ_0^2	γ_0^3	s_0^1	s_0^2	s_0^3	γ_1	γ_2	γ_3	γ_4	γ_5	E_0	Δ
3NN TB-*GW* [a]	−3.4416	−0.7544	−0.4246	0.2671	0.0494	0.0345	0.3513	−0.0105	0.2973	0.1954	0.0187	−2.2624	0.0540[b]
3NN TB-LDA[a]	−3.0121	−0.6346	−0.3628	0.2499	0.0390	0.0322	0.3077	−0.0077	0.2583	0.1735	0.0147	−1.9037	0.0214
EXP[c]	−5.13	1.70	−0.418	−0.148	−0.0948	0.0743							
3NN TB-LDA[d]	−2.79	−0.68	−0.30	0.30	0.046	0.039						−2.03	

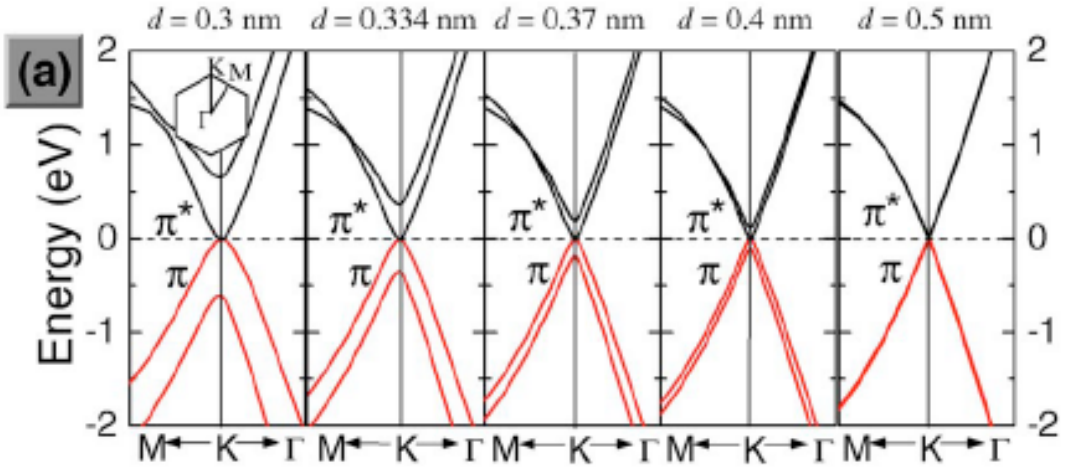
[a]This work.
[b]We adjusted the impurity doping level in order to reproduce the experimental value of Δ.
[c]Fit to ARPES by Bostwick *et al.* (Ref. 22).
[d]Fit to LDA by Reich *et al.* (Ref. 20).

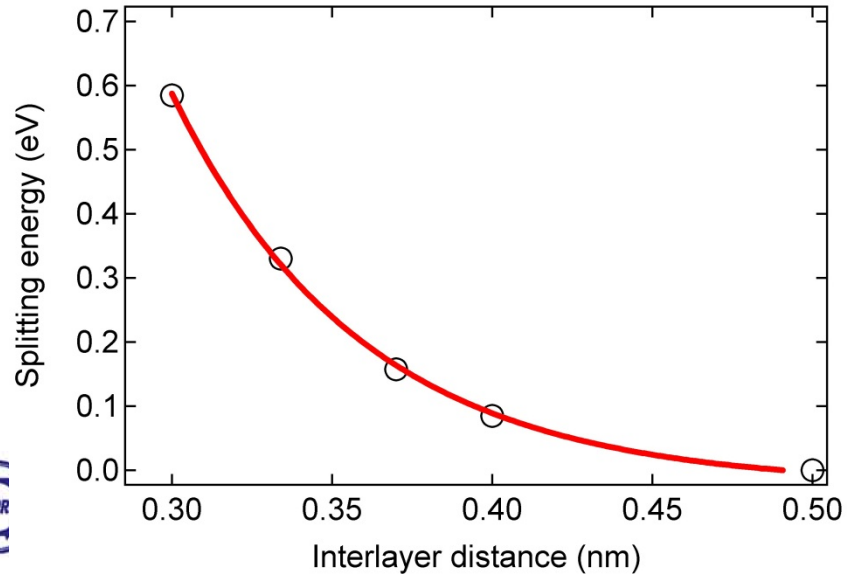


TB parameters	γ_0	γ_1	γ_3	γ_4
Pres. work	-3.21	0.61	0.39	0.15
Prev. bilayer/SiC	-3.24	0.48		
Prev. graphite	-3.16	0.39	0.315	0.044

Strong interlayer interaction induced smaller interlayer spacing on BLG ?

Interlayer spacing of neutral BLG





Graphite : 3.35 Å

BLG/SiO_2 with 0.61 splitting energy: 2.99 Å

Consistent with larger γ_1 in our case

Y. Guo et. al., APL (2008)

What does ARPES measure

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

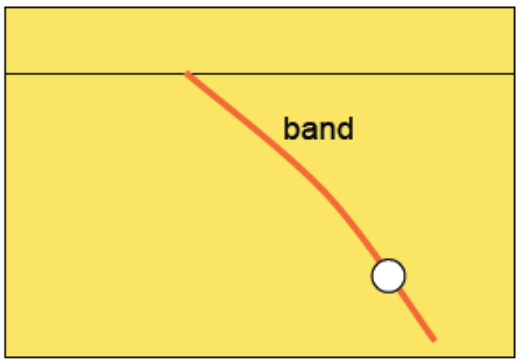
Matrix element

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



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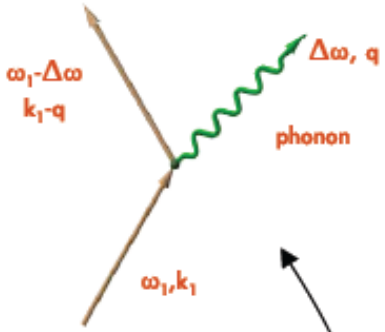
The carriers have a finite lifetime due to absorption and emission of phonons and other excitations

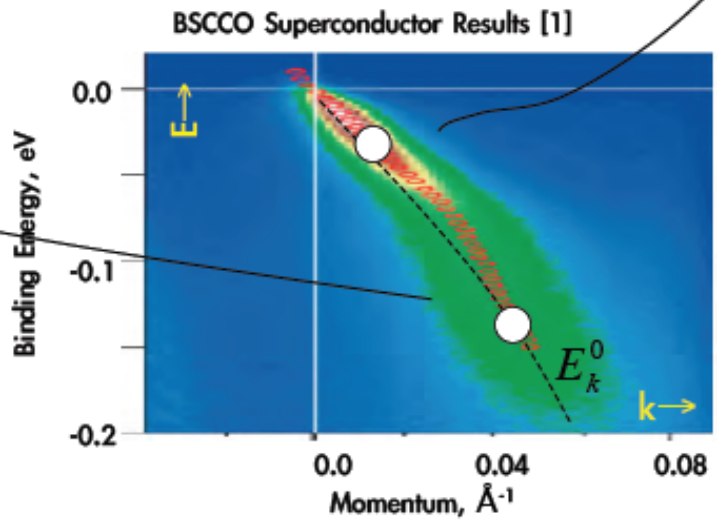


electron emits a phonon : change of energy ω and momentum k

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



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

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

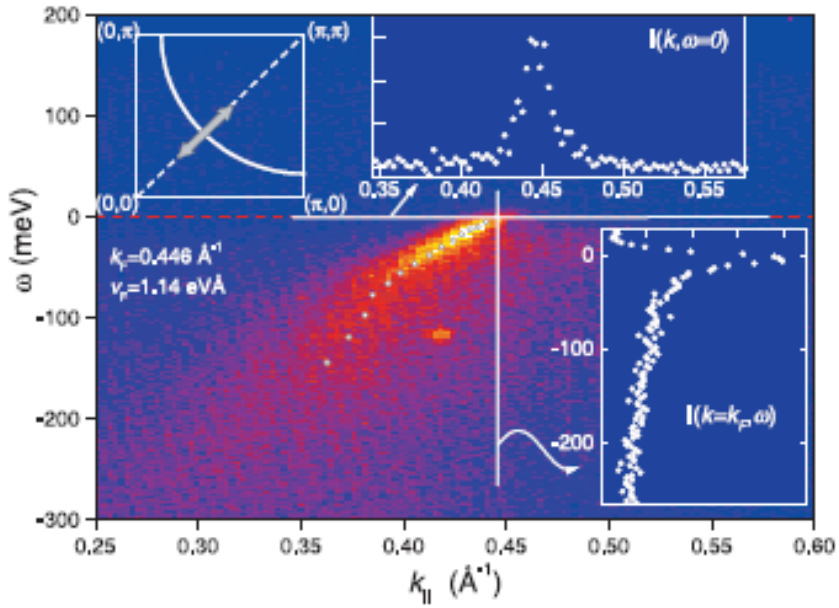
$$A(k,\omega) = \frac{\mathrm{Im}\,\Sigma(k,\omega)}{[\omega - \varepsilon_k - \mathrm{Re}\,\Sigma(k,\omega)]^2 + [\mathrm{Im}\,\Sigma(k,\omega)]^2}$$

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

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

Scattering rate (Lifetime)

Optimally doped Bi-2212 cuprate



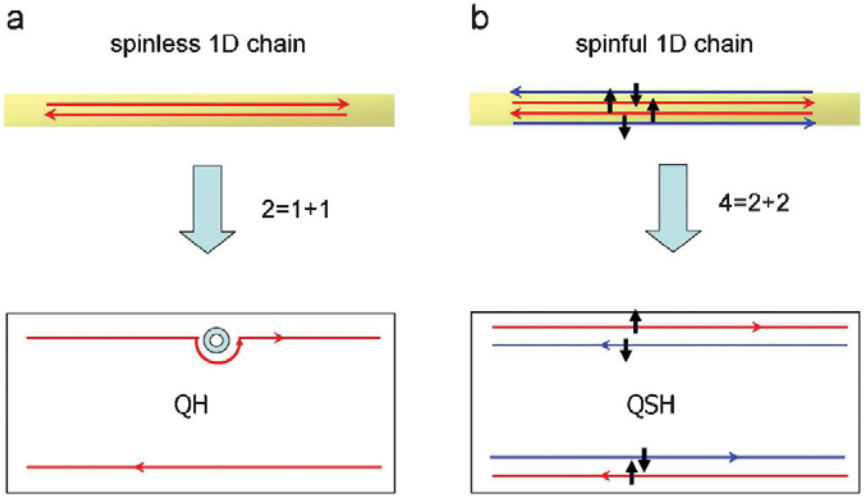
$$\hbar v_k \Delta k = \frac{\hbar v_k}{l} = \left|2\,\mathrm{Im}\,\Sigma(k,\omega)\right|$$

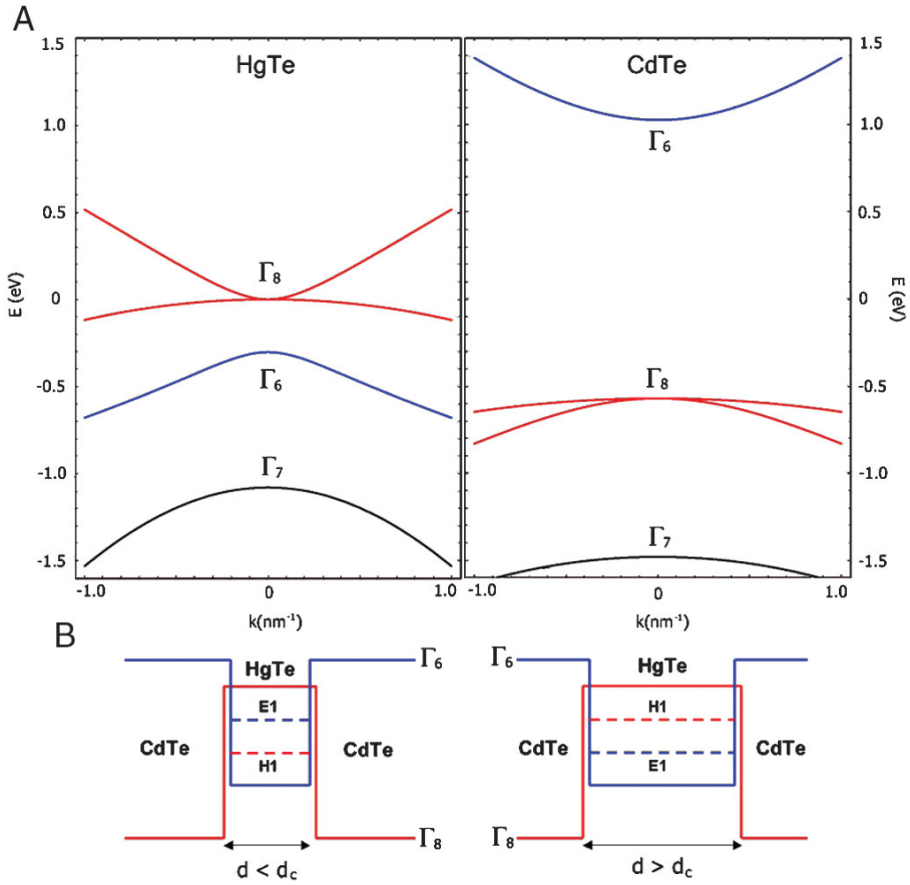
T. Valla et al., Science 285, 2110 (2000)

Summary for graphene

- The free standing bilayer graphene is gapless semiconductor.
- The splitting energy is larger than epitaxial graphene and bulk graphite due to the stronger screening effect.
- A reliable TBM parameters be obtained from presented experimental result.

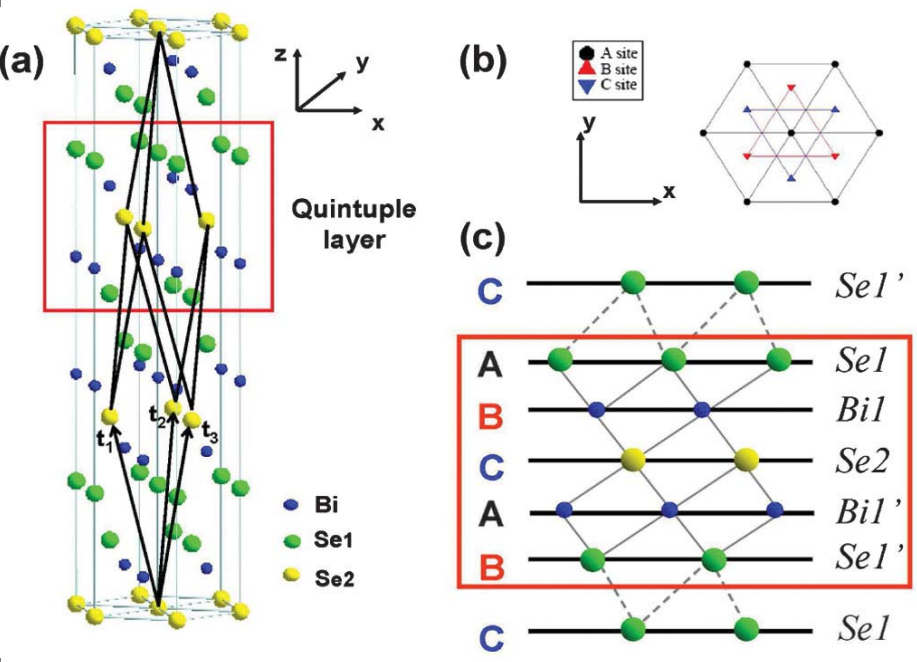
Topological insulators

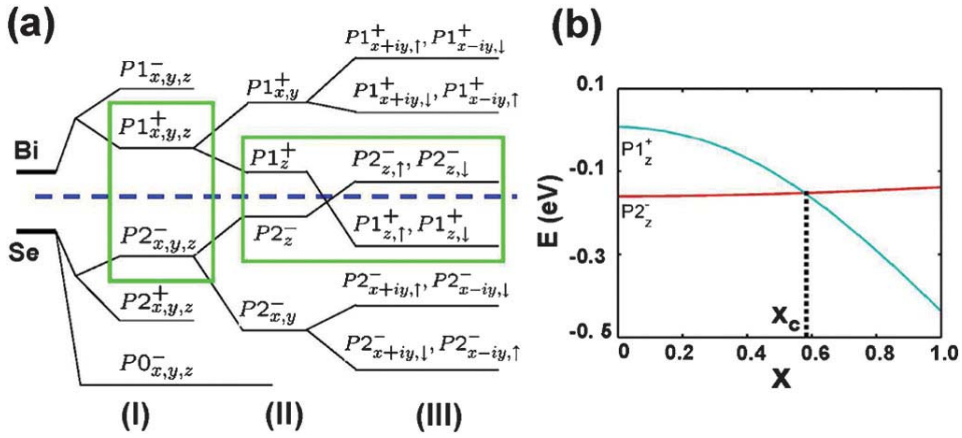




Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

3D topological insulators

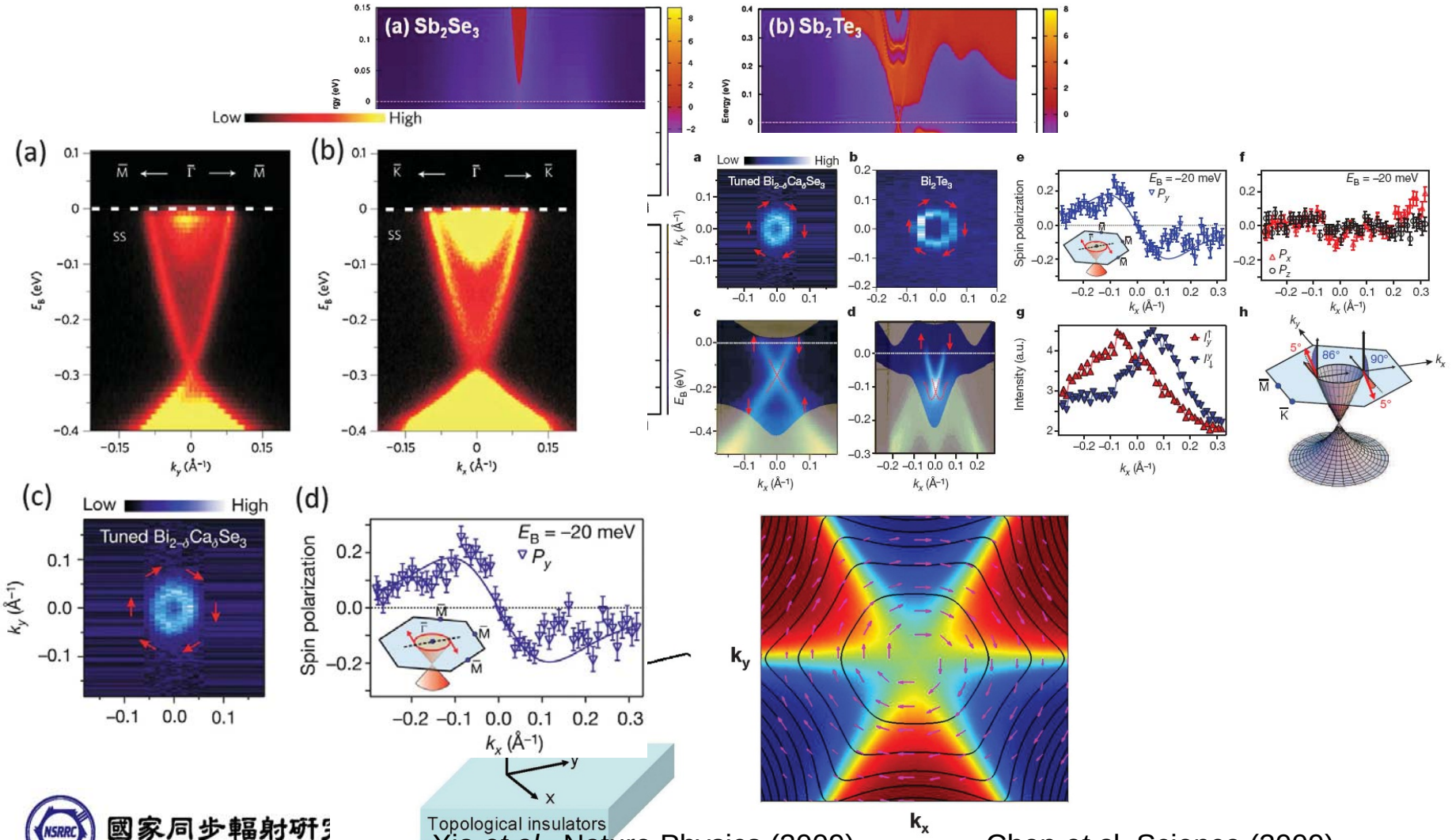




Strong spin-orbit coupling
Band inversion

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

Predictions for 3D topological insulators



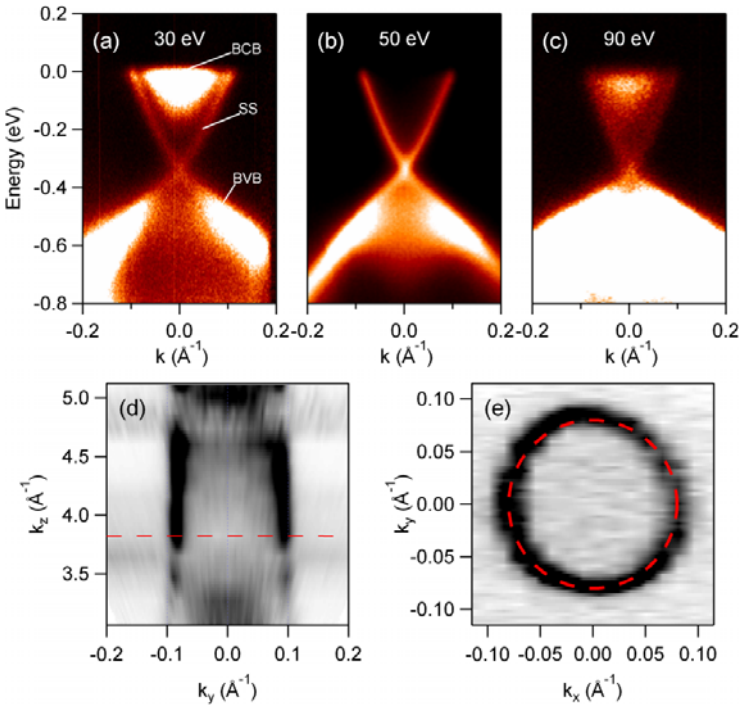
Xia *et al*., Nature Physics (2009)

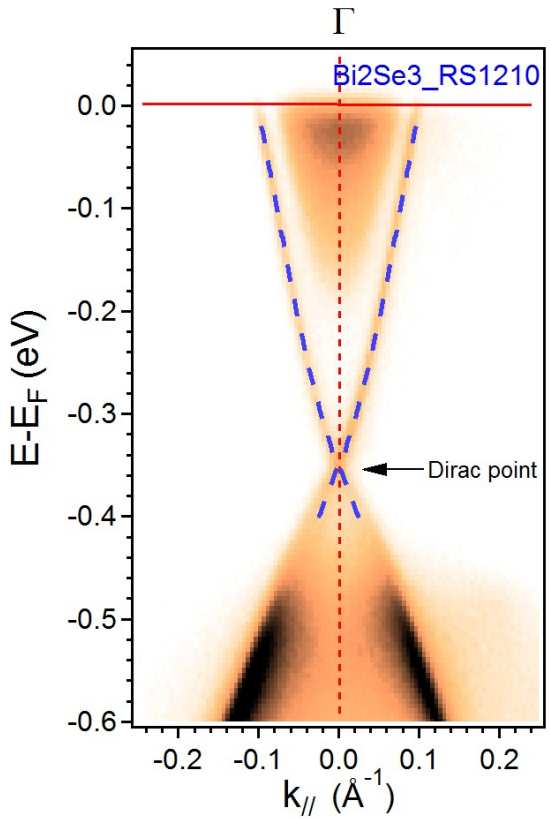
Hsieh *et al*., Nature (2009)

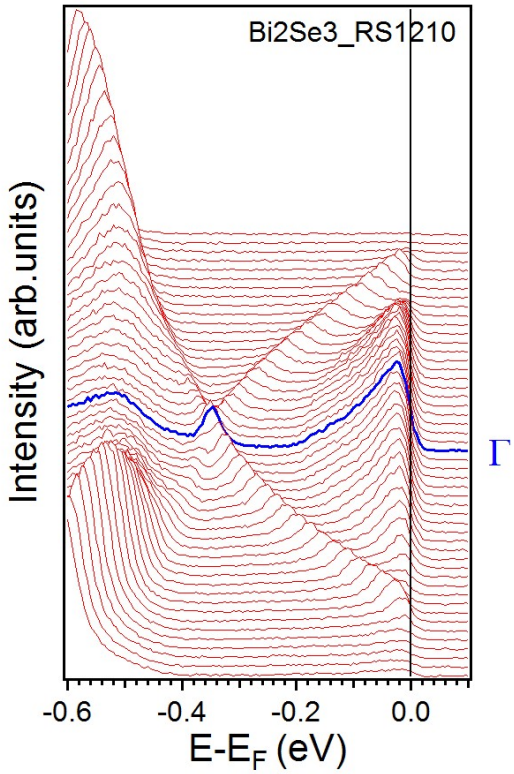
Chen *et a*l, Science (2009)

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

Typical experimental result at NSRRC

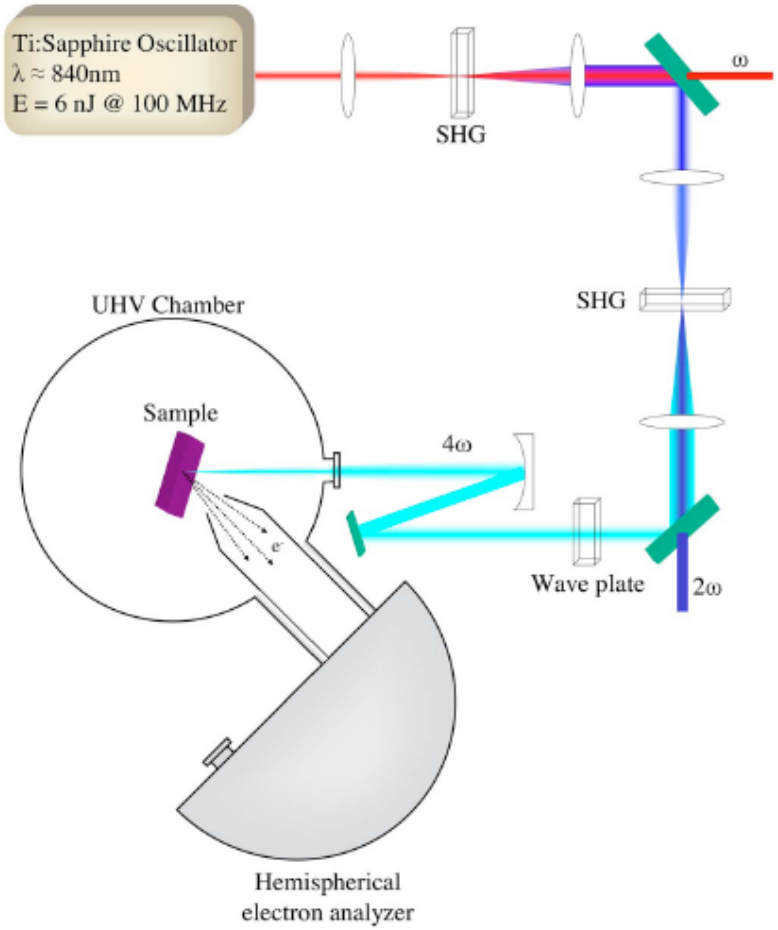




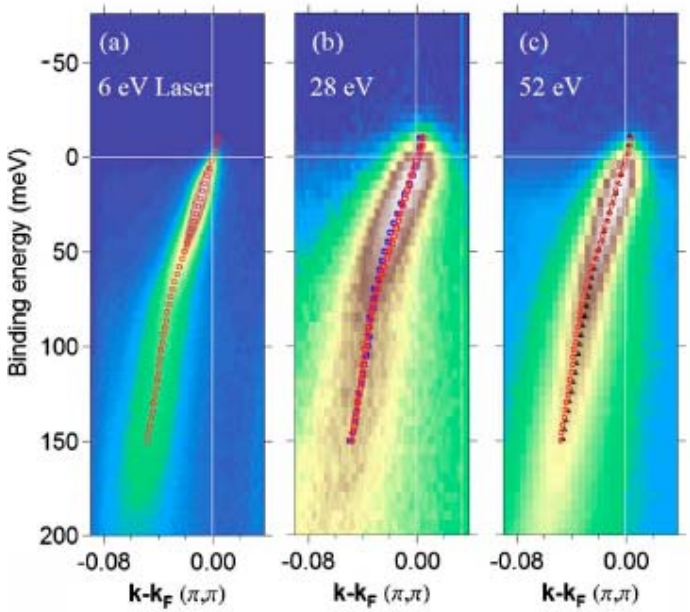


Pan *et al.*, PRL (2011)

Setup for Laser ARPES



Band mapping with various photon energies on Bi-2212



Koralek *et al.*, Rev. Sci. Instrum. (2007)

Time-resolved ARPES

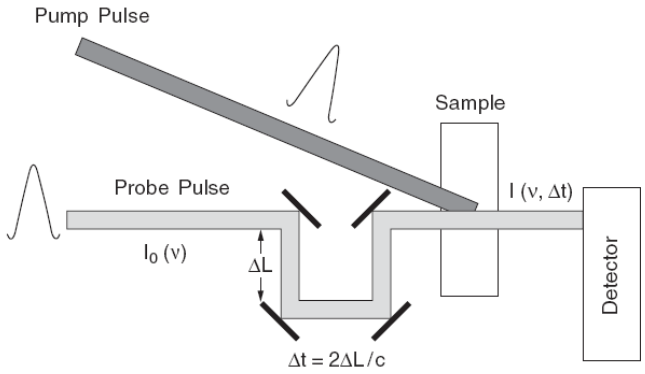


Fig. 8.1. Typical scheme of a "pump–probe" experiment

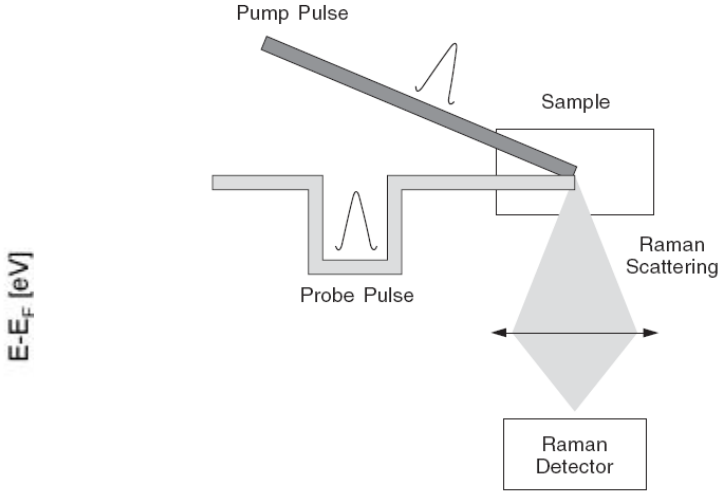
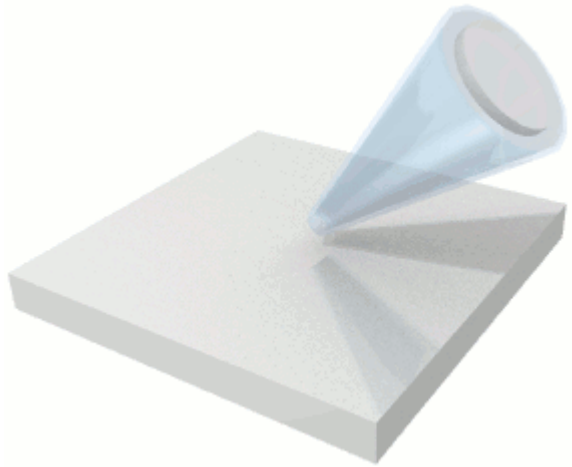
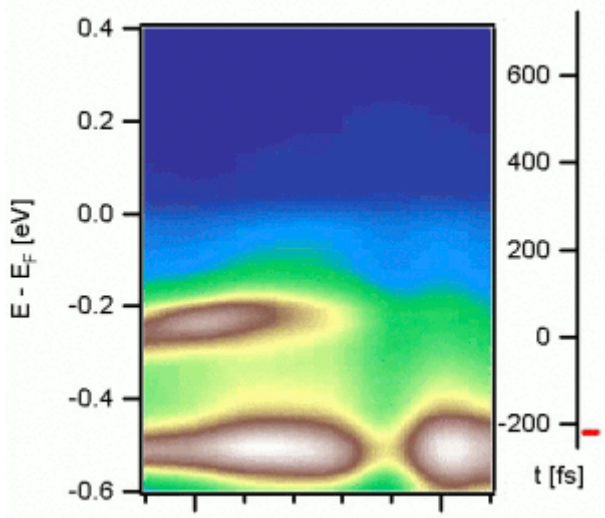


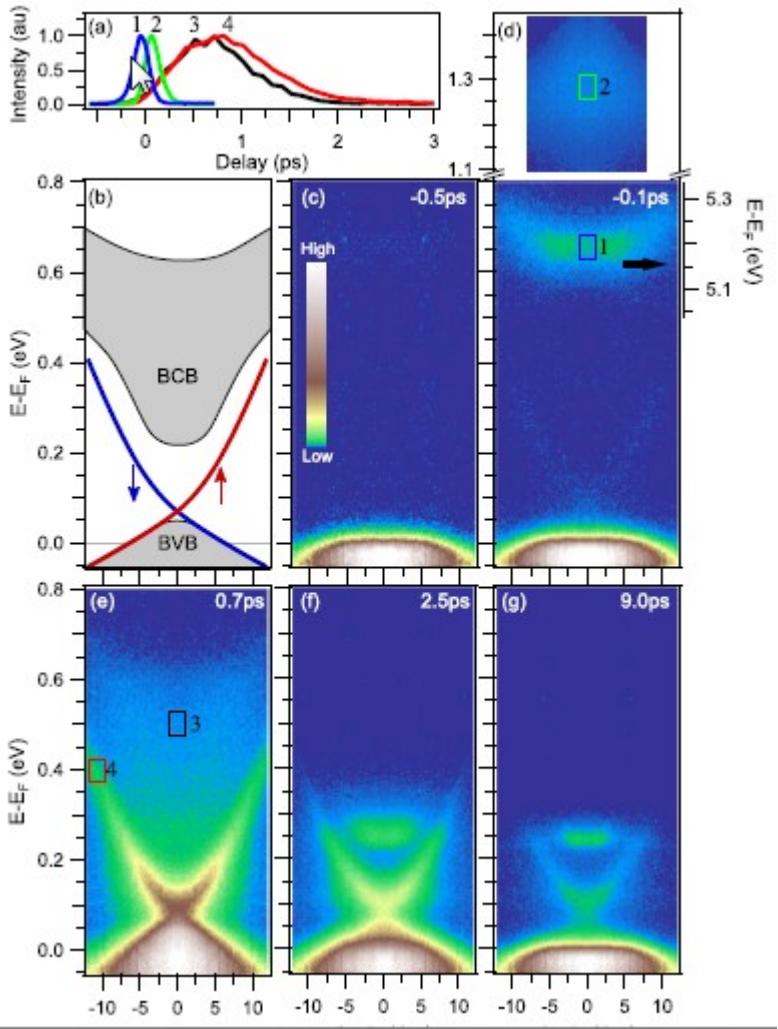
Fig. 8.12. Experimental setup for time-resolved Raman spectroscopy

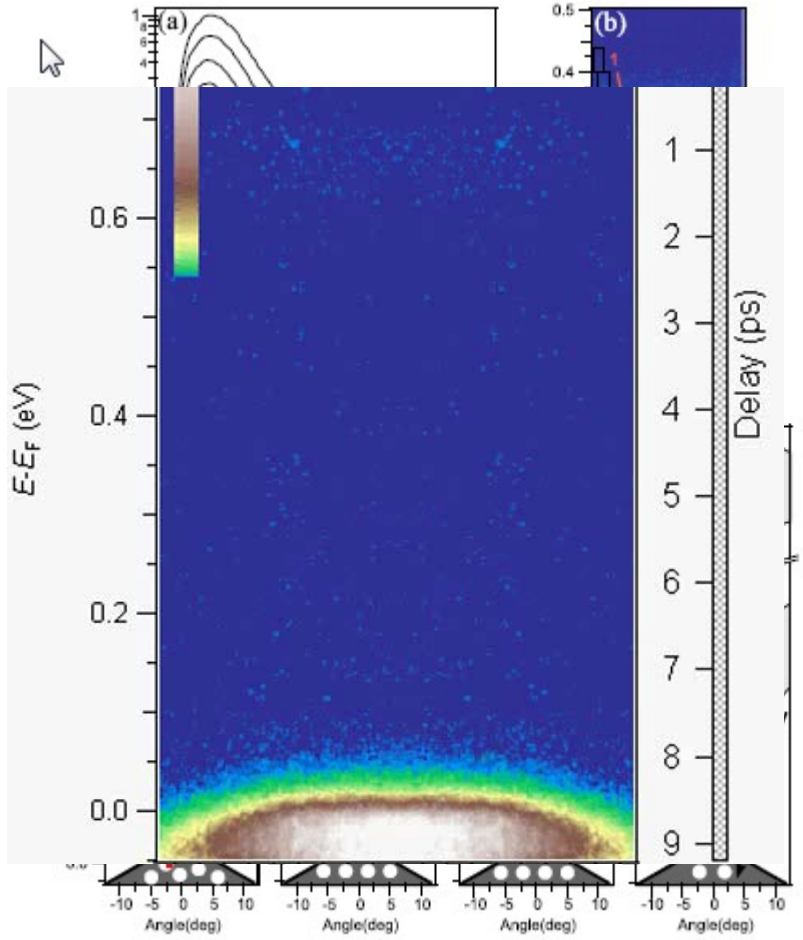




Pictures taken from Schmitt et al., Science 321, 1649-1652 (2008) and Prof. ZX Shen's group

Ultrafast Dynamics of Dirac Fermion in Topological Insulators





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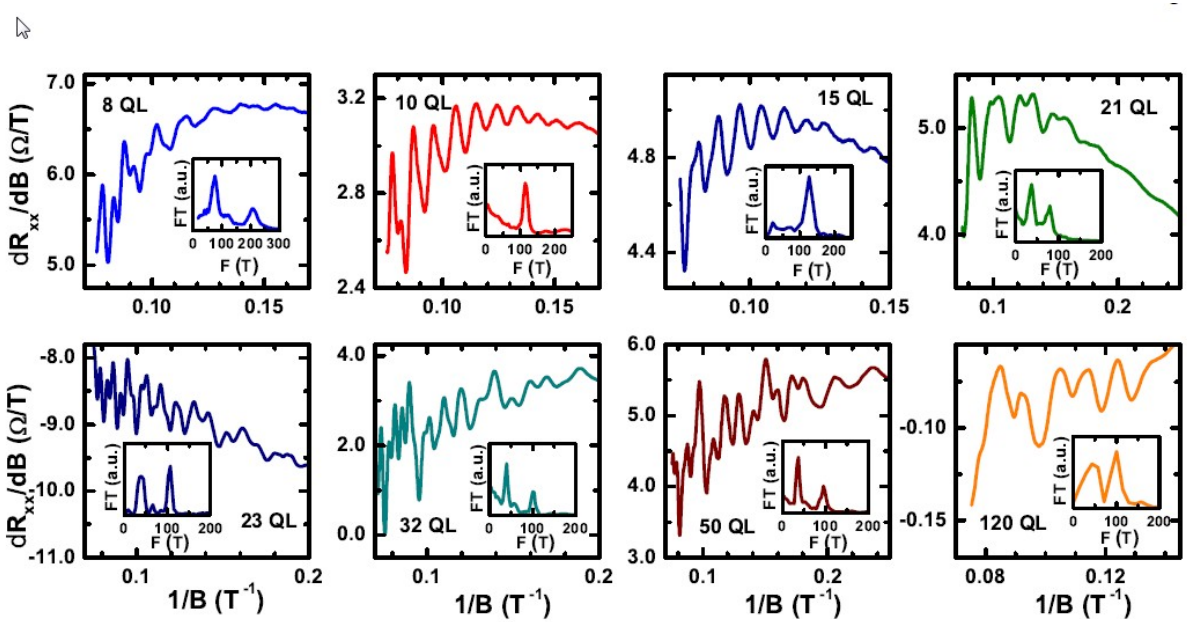
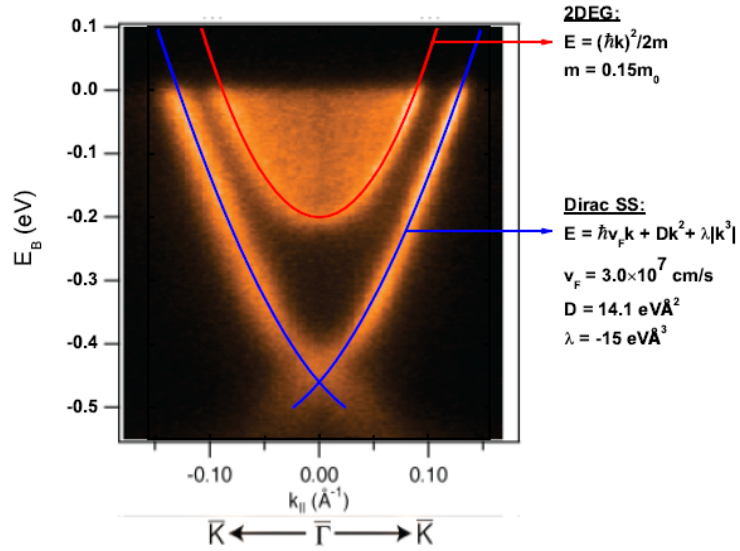
Sobota et al., PRL (2012)

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

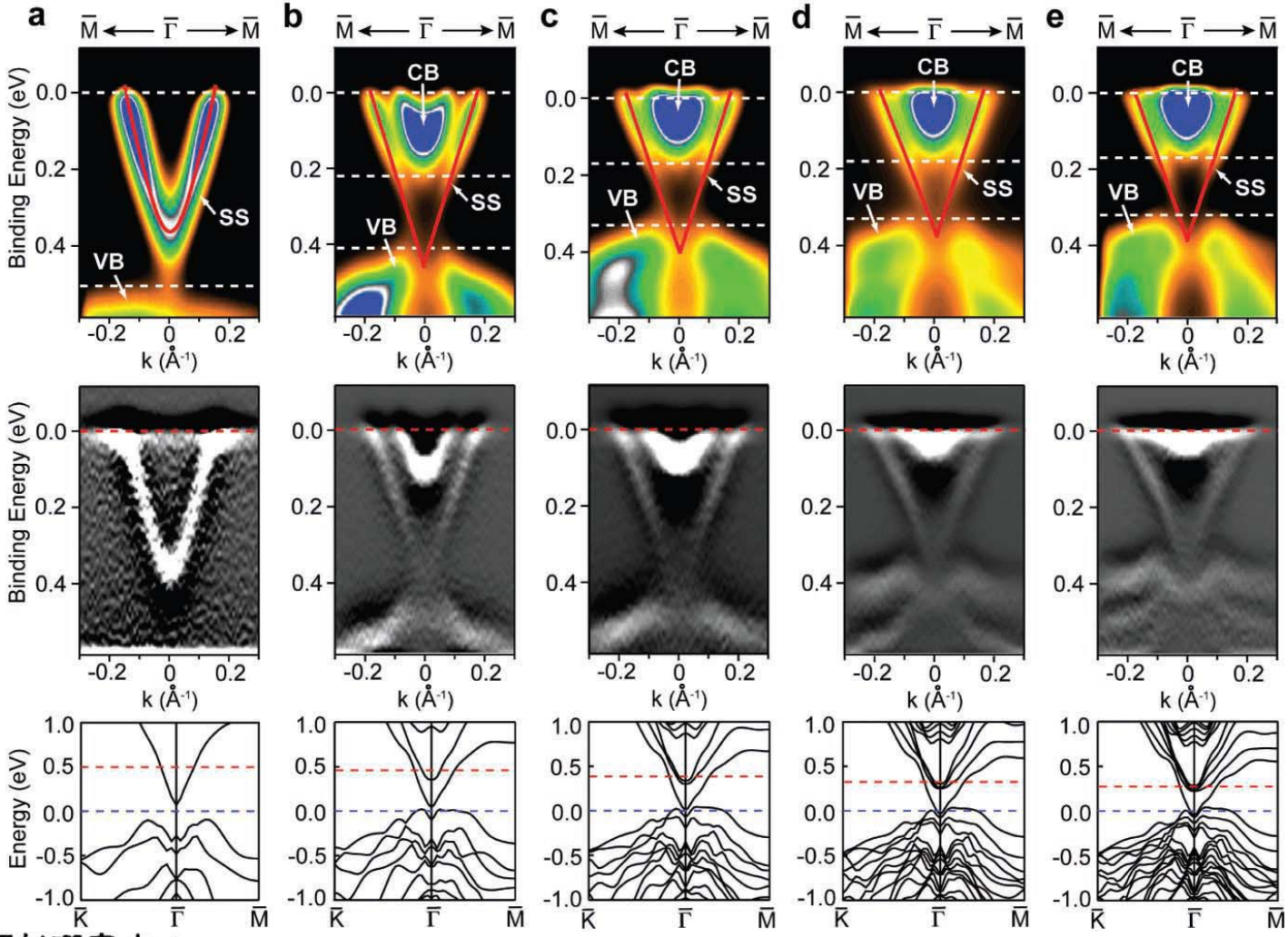


Estimate the surface charge carrier density : ARPES



MBE growth topological insulators (Bi_2Te_3)

Bi_2Te_3/Si



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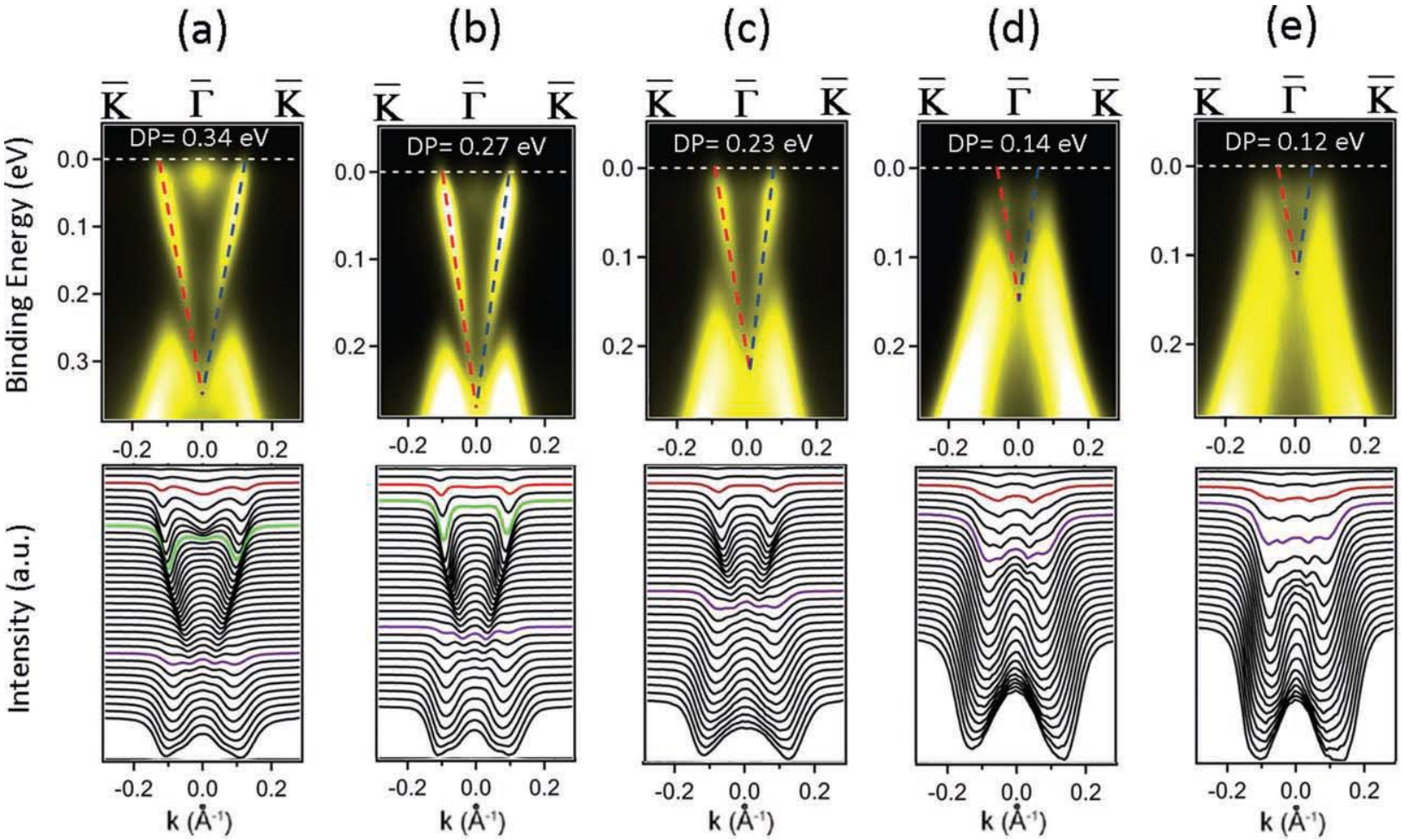
Li et al., Adv. Mat. (2010)



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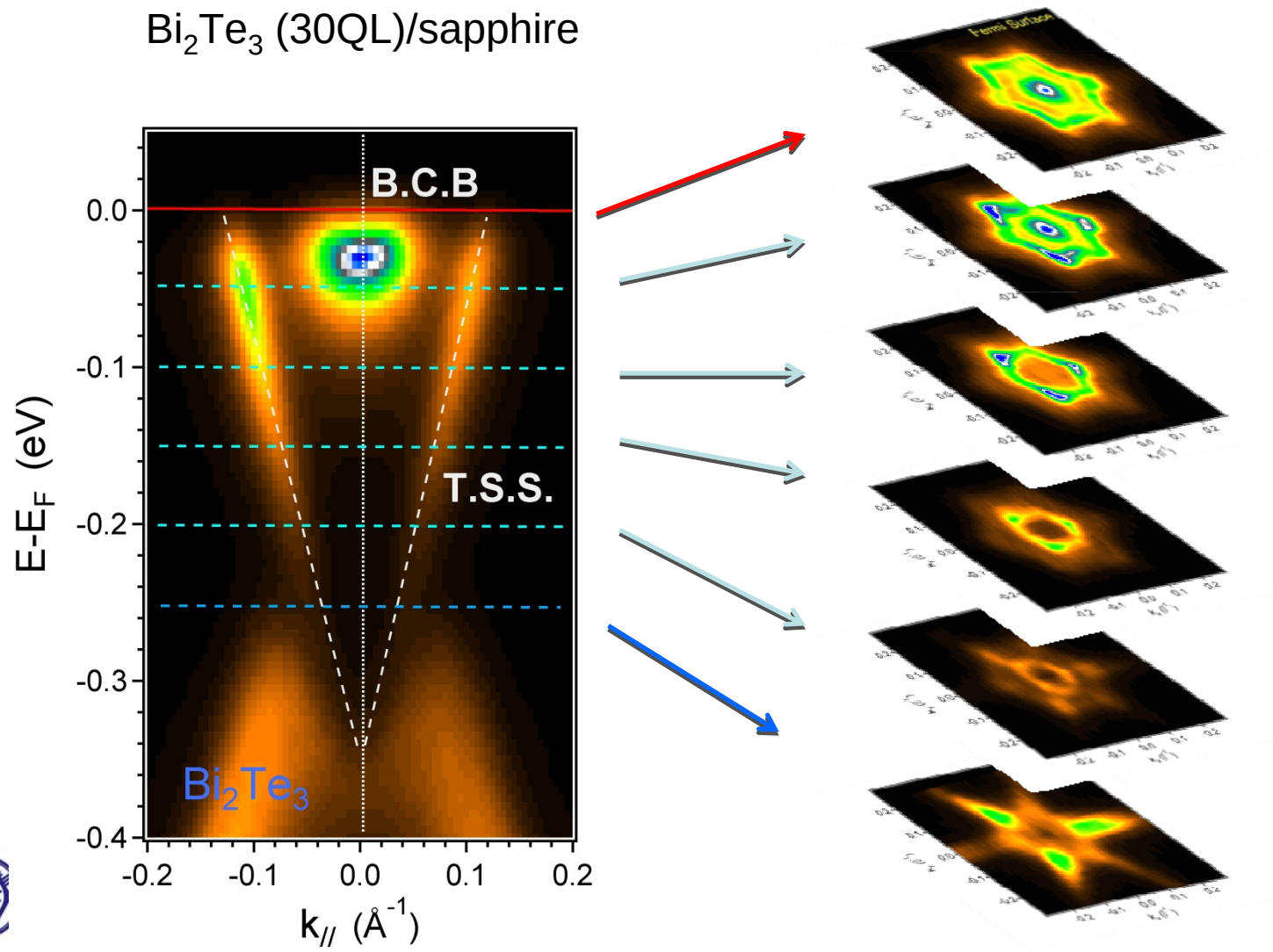
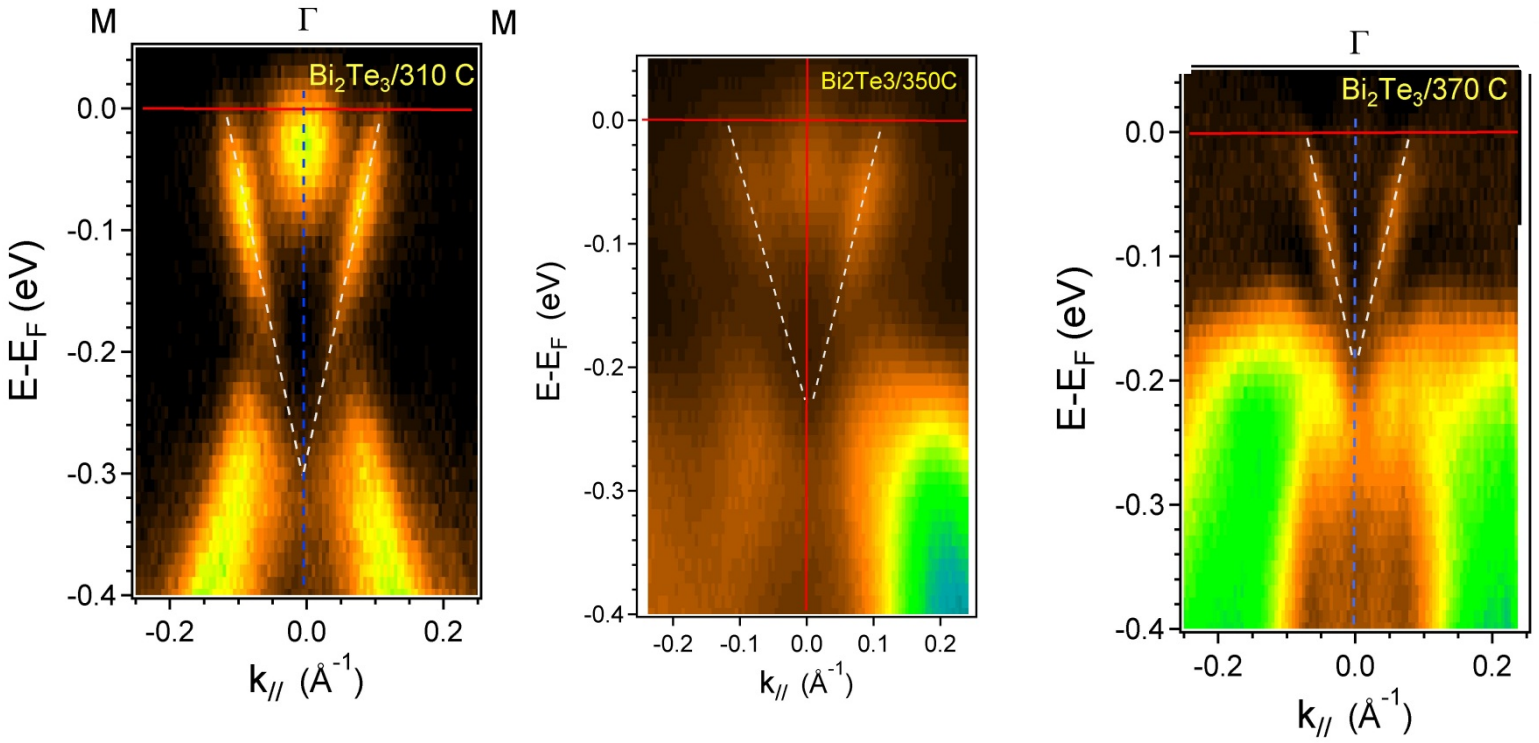
Wang *et al*., Adv. Mat. (2011)

Bi_2Te_3 /Sapphire





Controlling substrate temperature and Bi/Te flux ratio can vary the doping condition arbitrary

Topics for TIs

- New ternary Tis : Bi_2Te_2Se, $TlBiSe_2$, $GeBi_2Se_4$, SmB_6….
- Impurity doping : Cu, Mn, Cr….
- Heterostructure TIs for devices : spintronic devices, thermoelectric devices

Collaborators

Graphene

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TIs

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