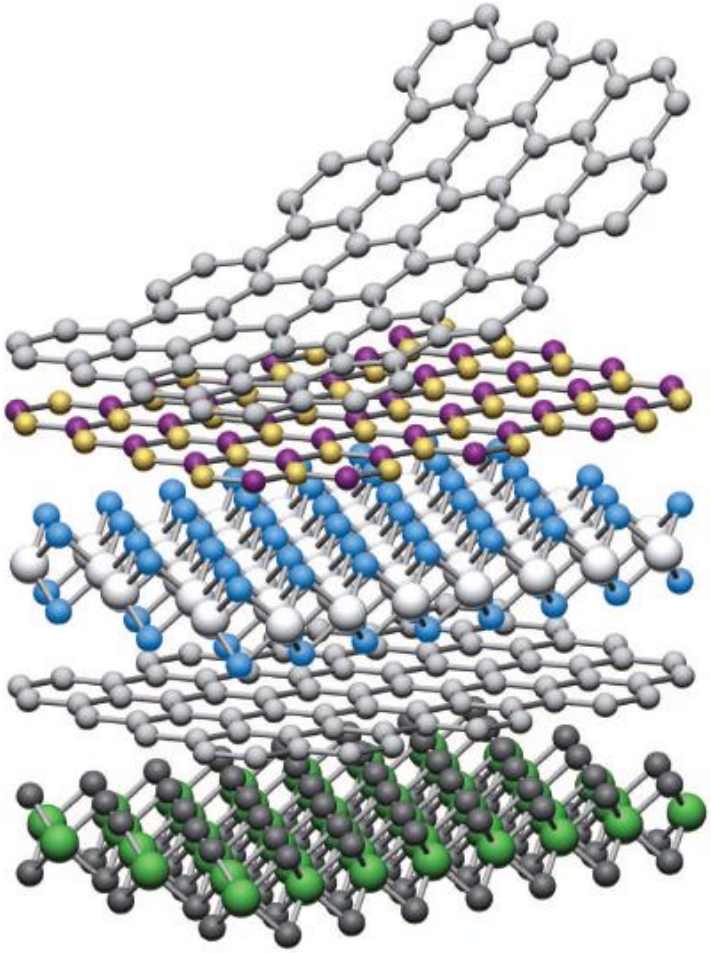
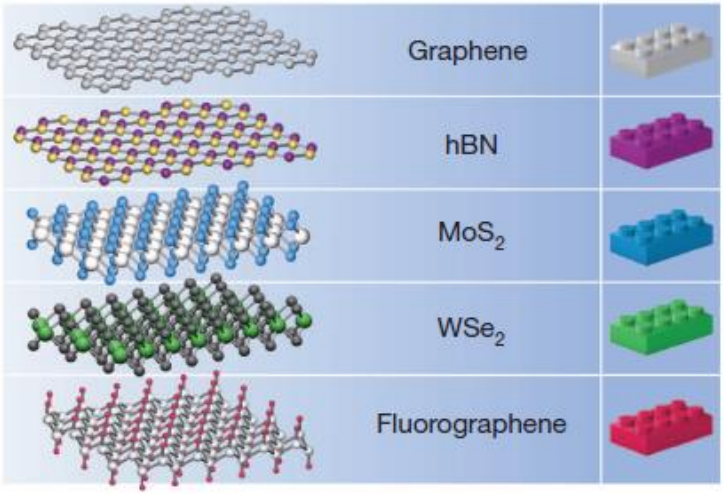
Angle-resolved photoemission spectroscopy on emergent quantum materials

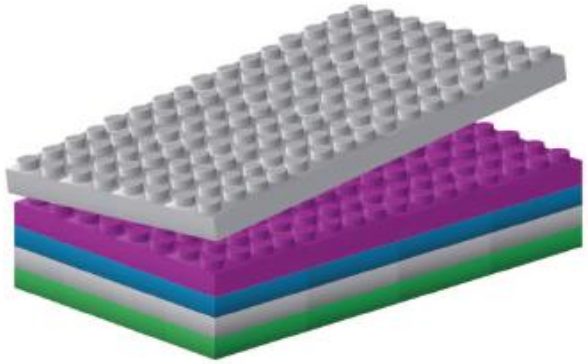
Part -2

A crucial problem to understand the electronic of exfoliated graphene

Van der Waals heterostructures







Geim, Nature (2013)

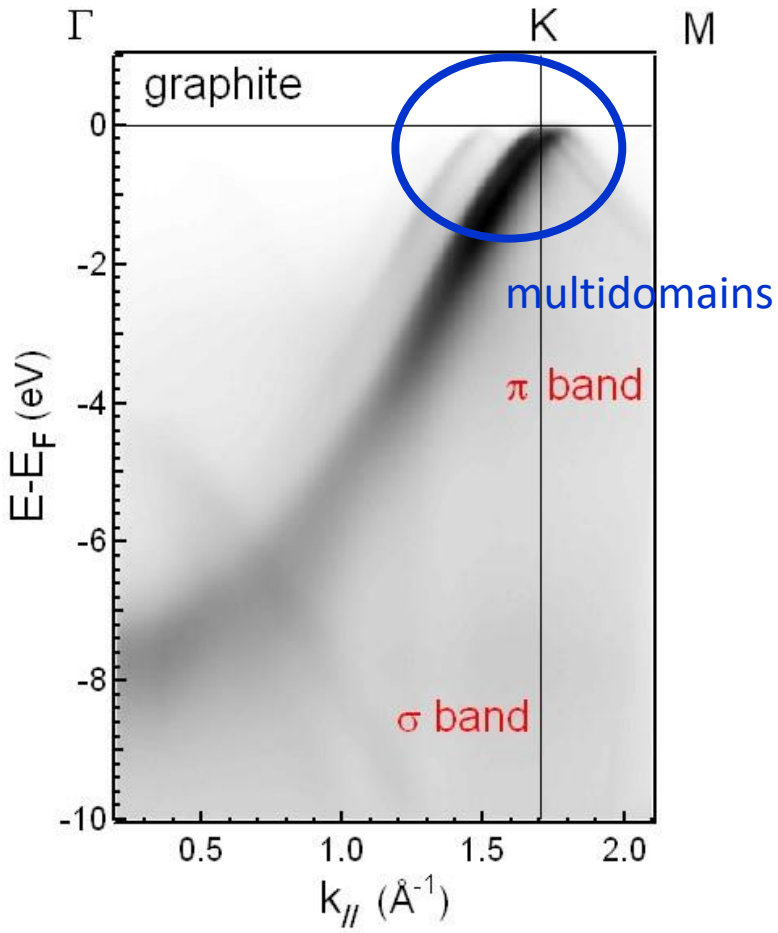
The difficulties for studying the electronic structure of exfoliated graphene

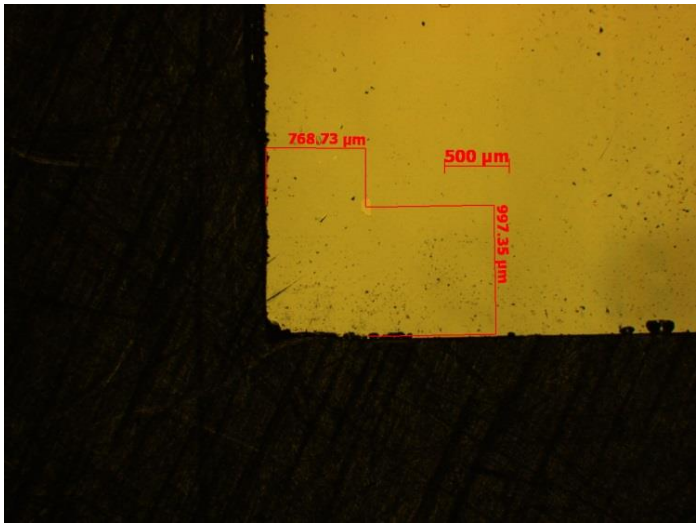
- Insulating substrate induces the strong charging effect.

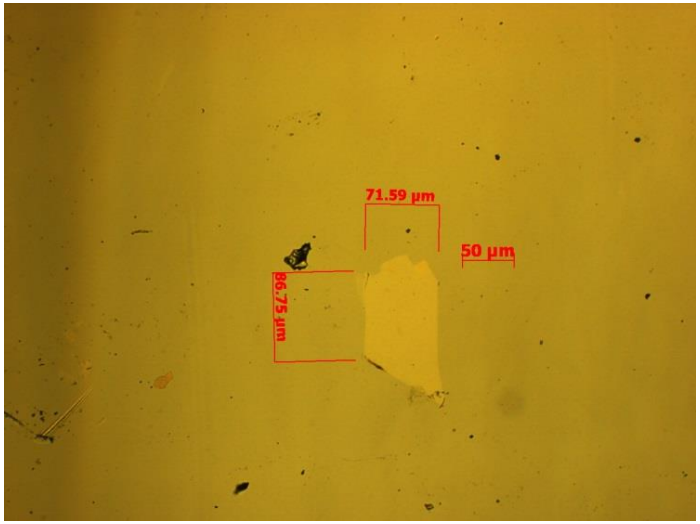
- Sample size : only several tens microns sample is obtained, but this sample size is quite small for current ARPES beam spot (> 100 μm) in VUV region. Nano-ARPES provides an advantage to study the electronic structure of exfoliated graphene, but the used photon energy is above 100 eV due to the short 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.

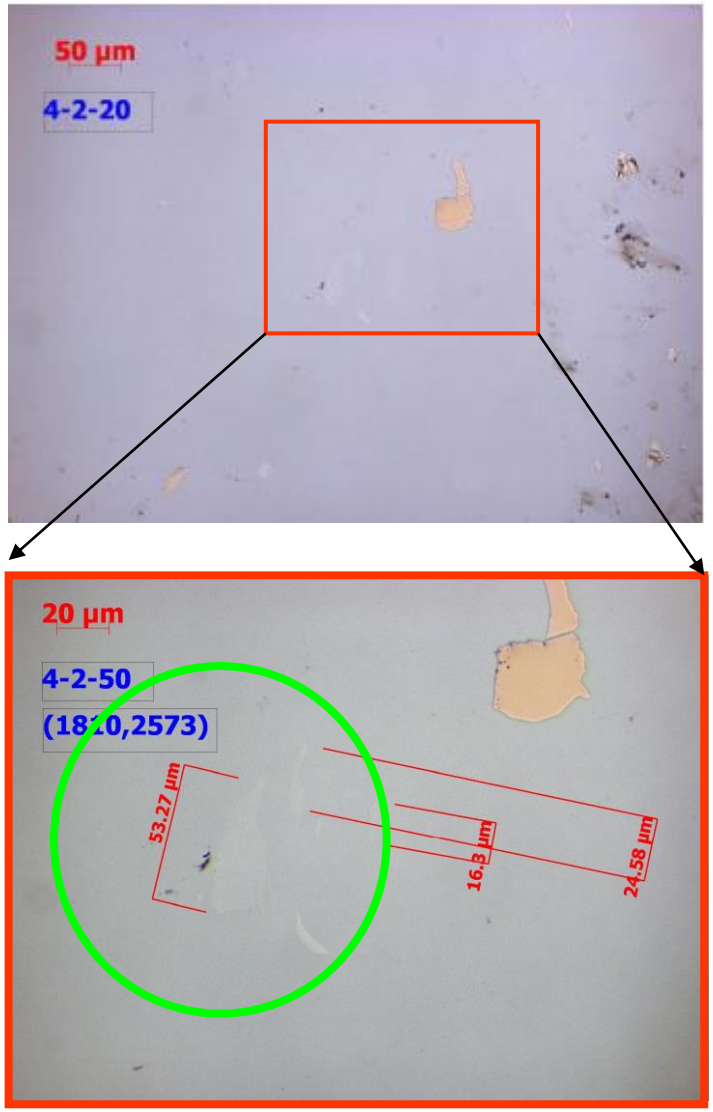
The band mapping result of Kish graphite

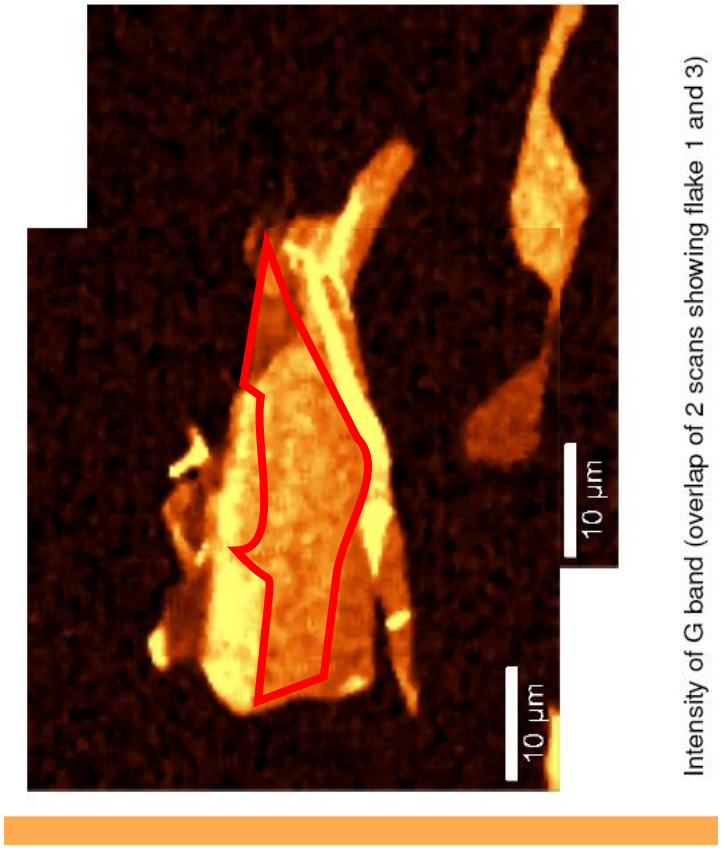






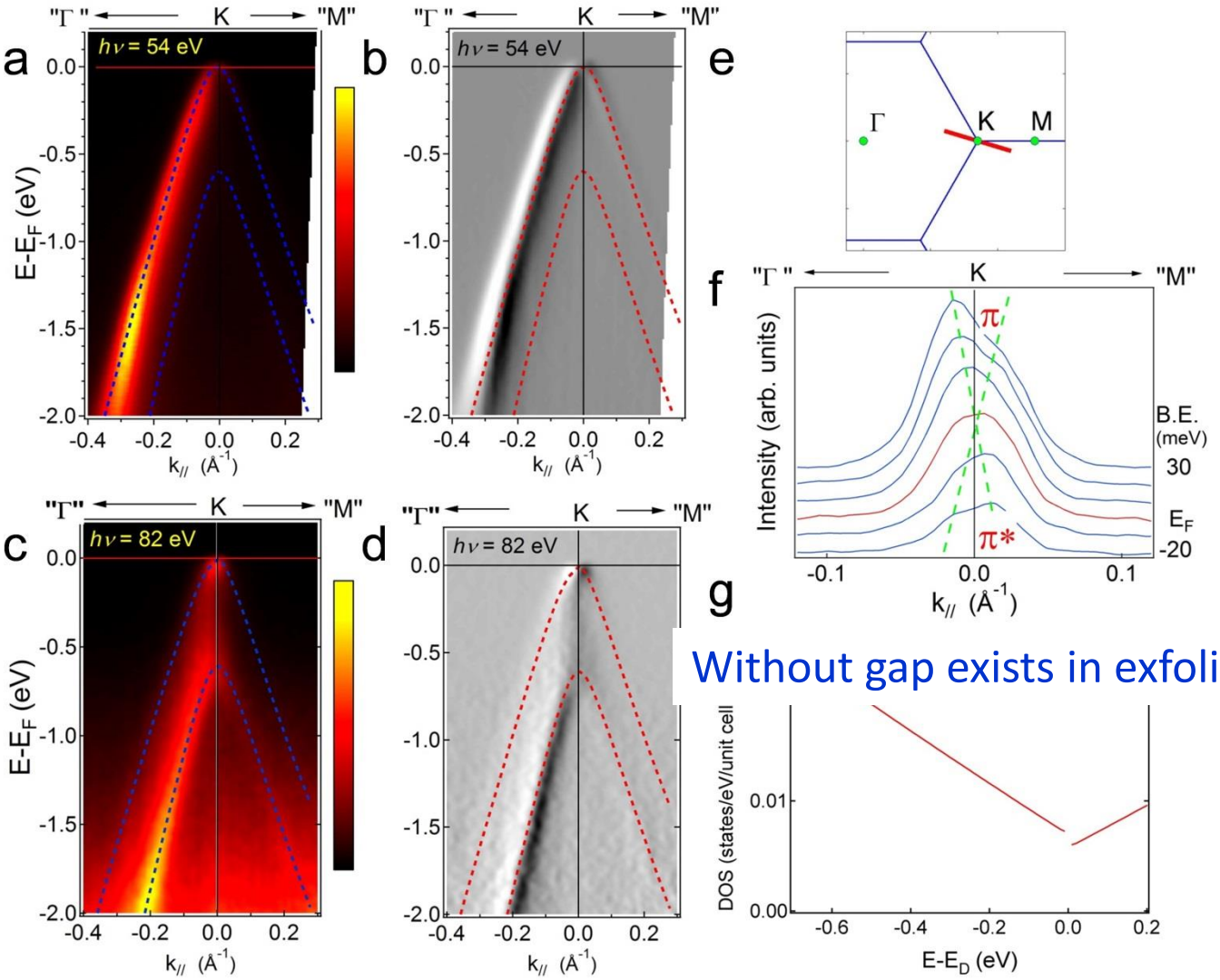
Bilayer graphene / Highly doped Si substrate





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

The electronic structure of bilayer graphene



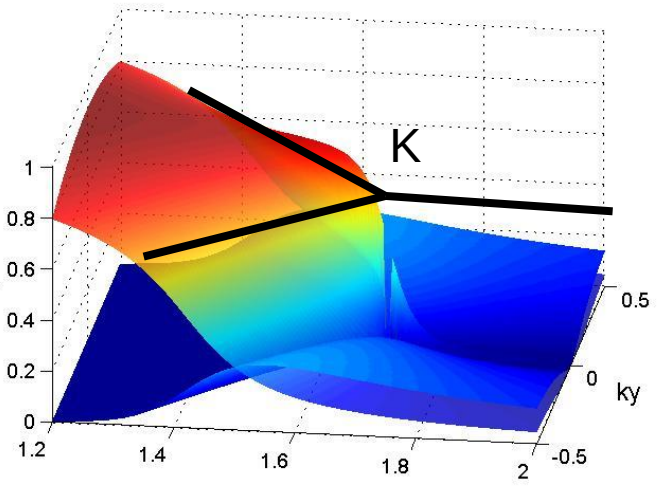
Without gap exists in exfoliated BLG

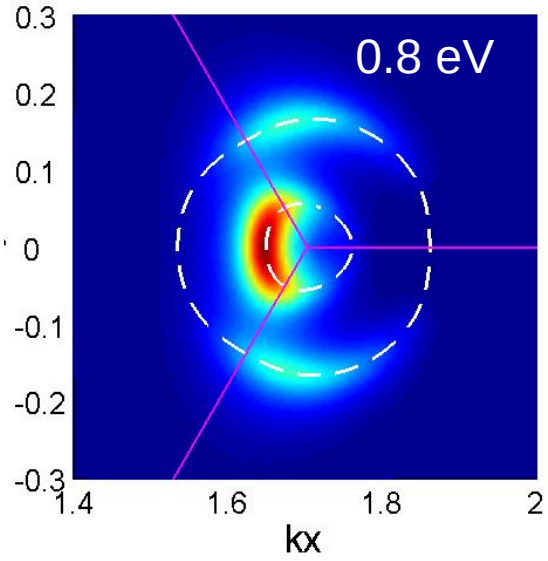
Cheng et al., Scientific Report (2015)

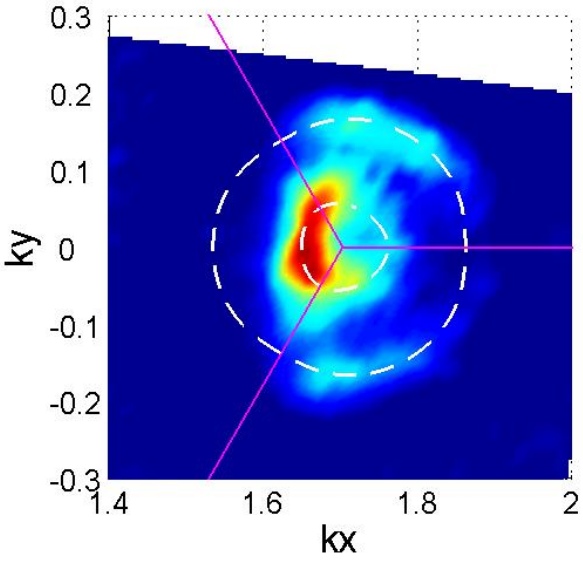
82 eV ME effect

Simulated result

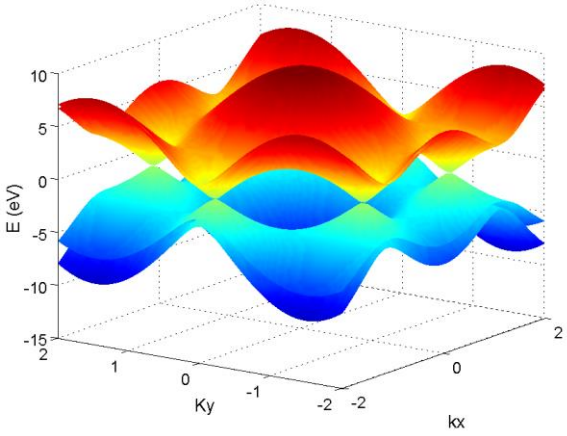
Experimental result

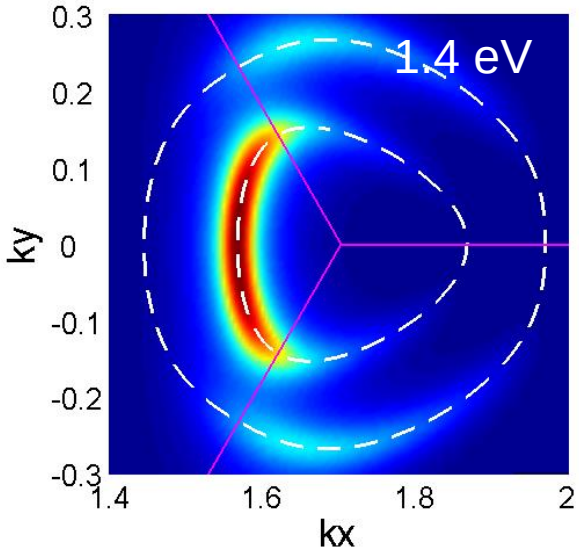


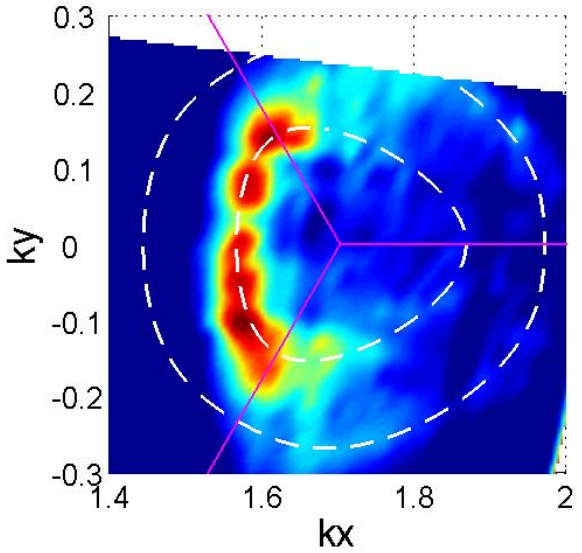




Electronic structure of BLG







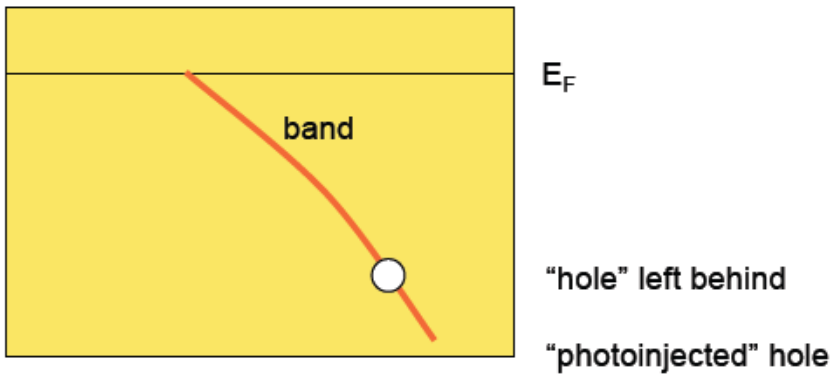
What does ARPES measure

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

Matrix element

Spectra function

ejected photoelectron



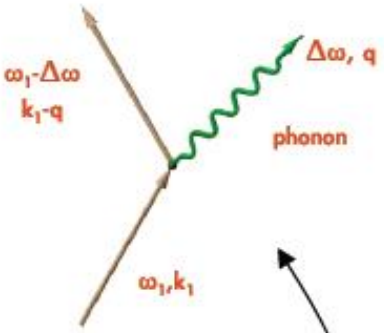
we believe the properties of the photoelectron reflect the properties of the injected hole

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

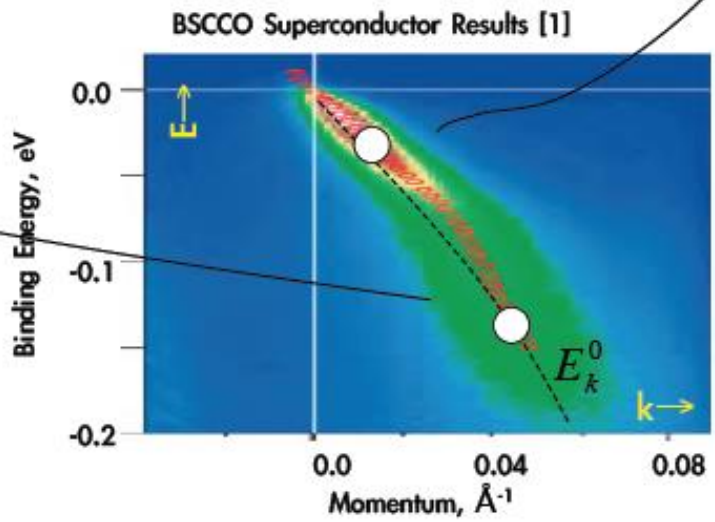


electron emits a phonon : change of energy **ω** and momentum *k*

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



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

Eli Rotenberg, ALS summer school

Self energy in photoemission spectra

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

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

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

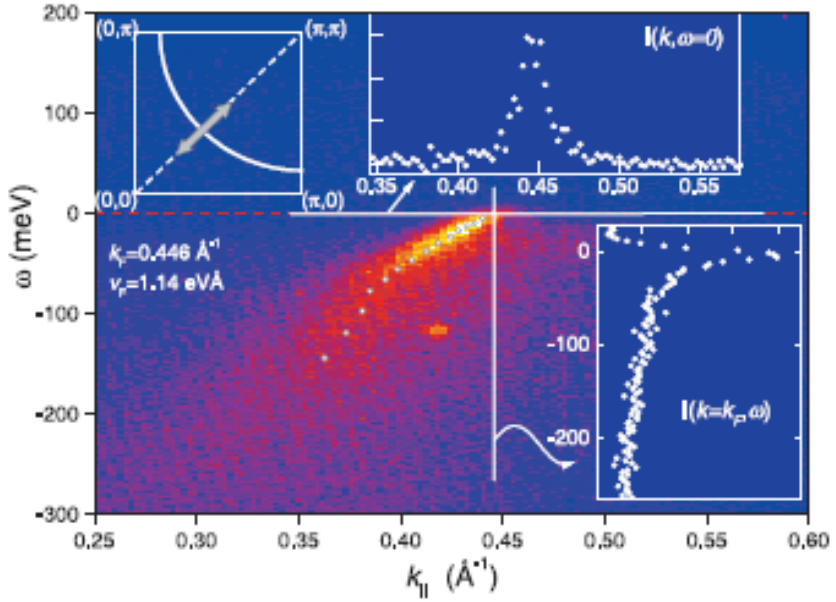
$$\hbar v_k \Delta k = \frac{\hbar v_k}{l} = |2\,\mathrm{Im}\Sigma(k,\omega)|$$

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

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

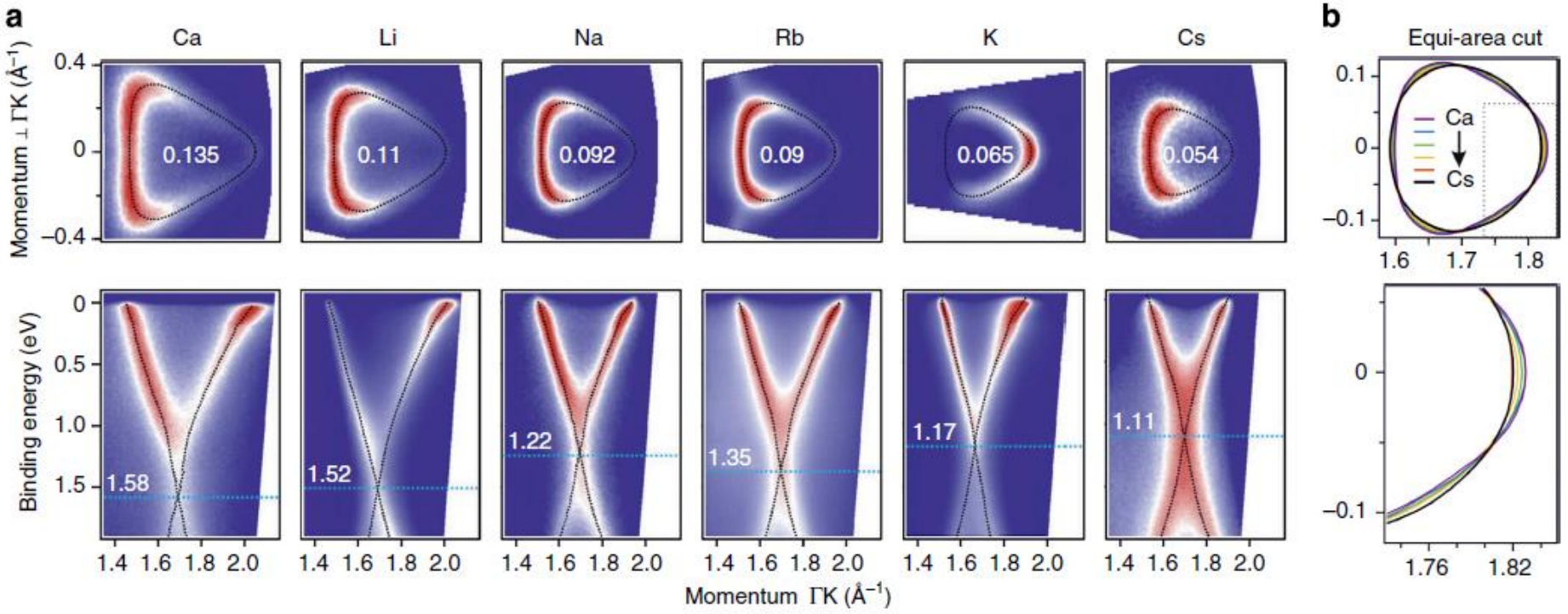
Scattering rate (Lifetime)

Optimally doped Bi-2212 cuprate



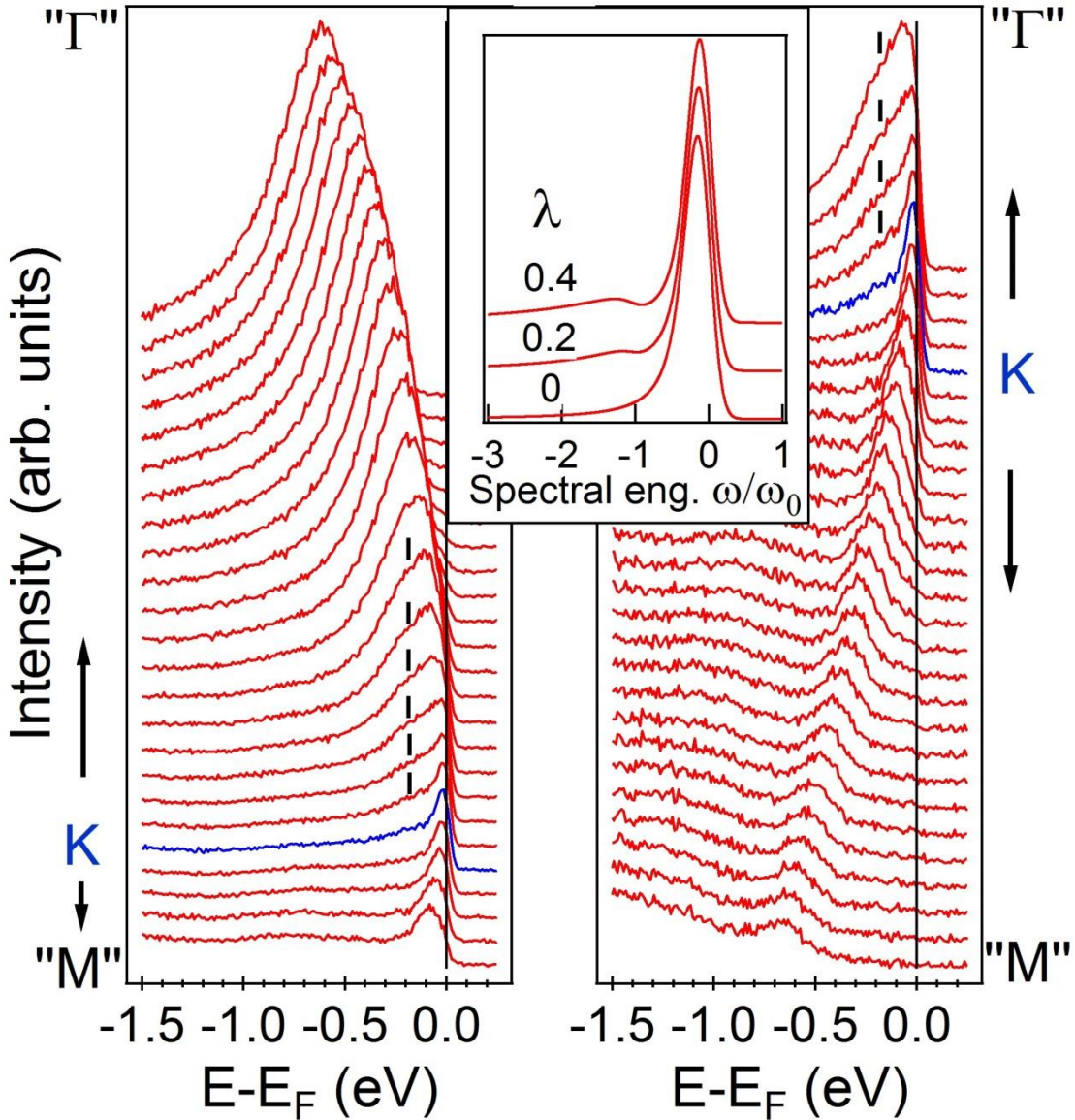
T. Valla et al., Science 285, 2110 (2000)

Electron-phonon interaction in doped graphene

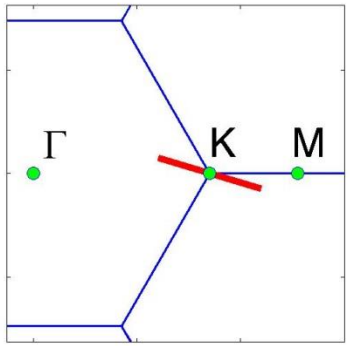


Fedorov, Nat. Comm. (2014)

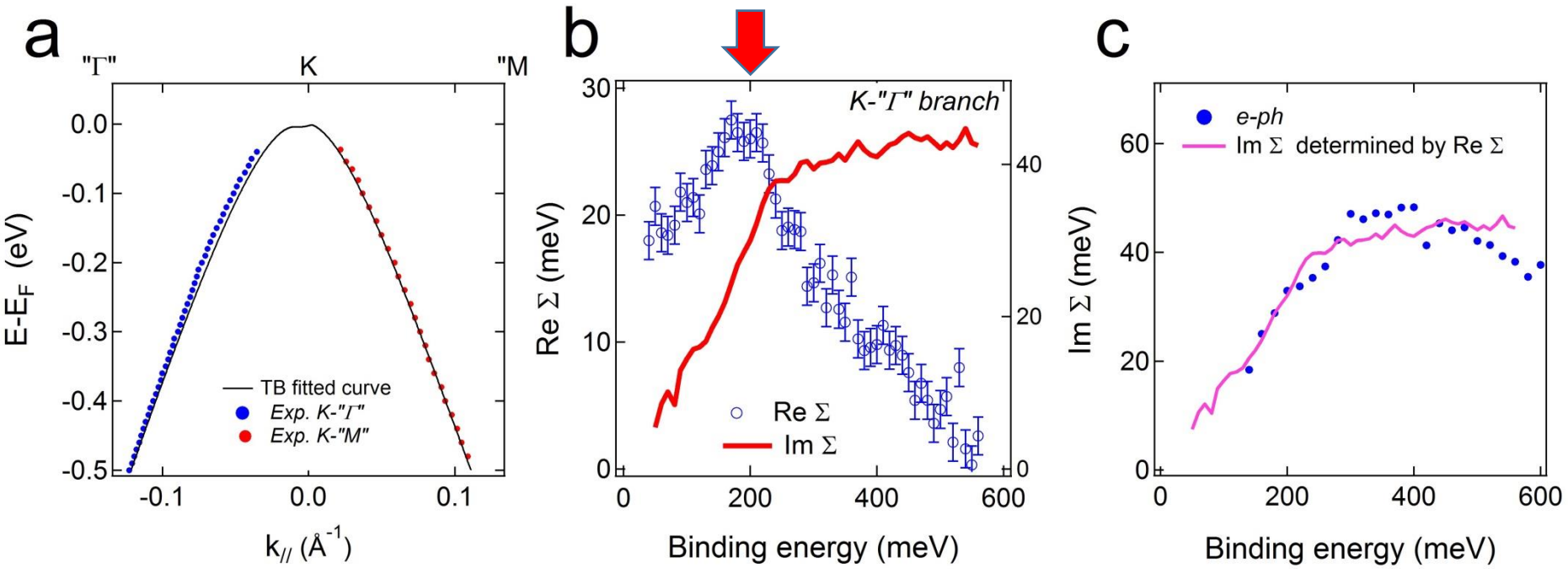
Anisotropic *e-ph* interaction property on K-Γ and K-M branches



A bump appears at 200 meV due to the optical phonon

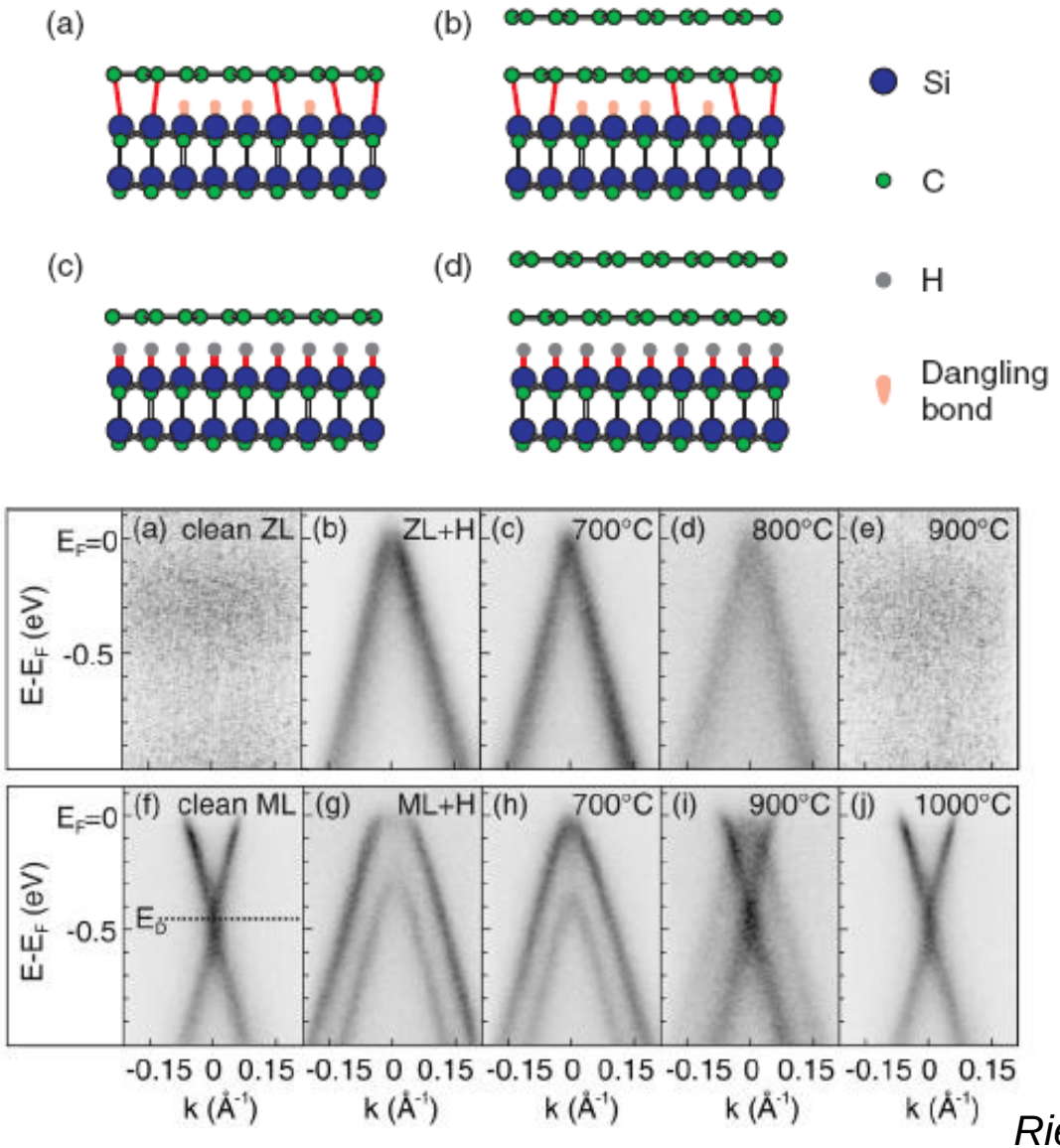


The KK transformation between Re Σ and Im Σ



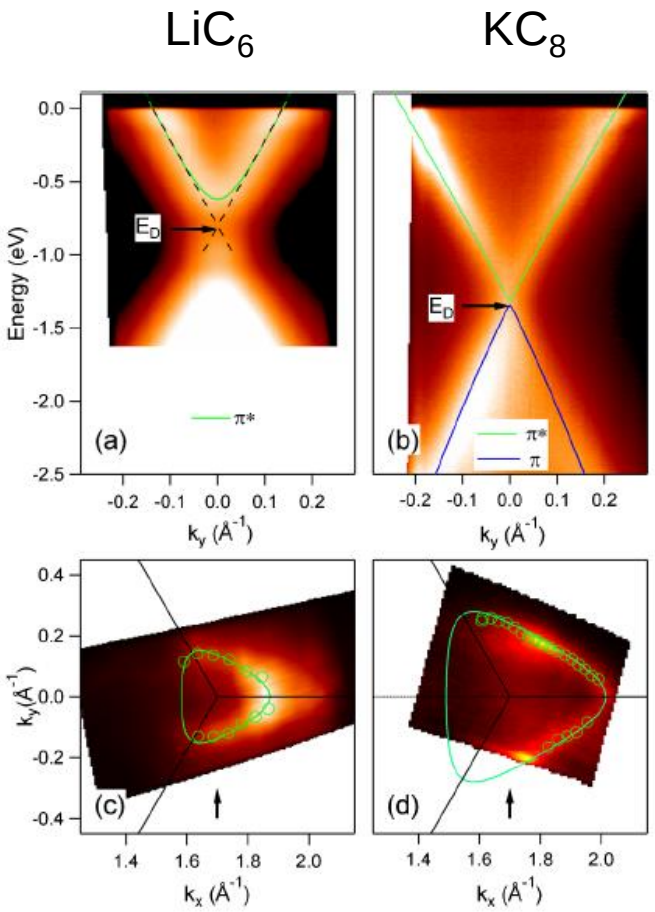
Im Σ extracted from the width of line shape analysis is consistent with Im Σ determined by Re Σ

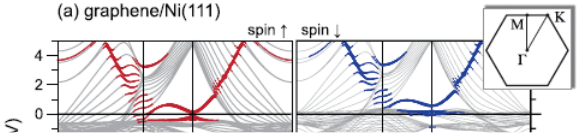
Hydrogen intercalated graphene/SiC

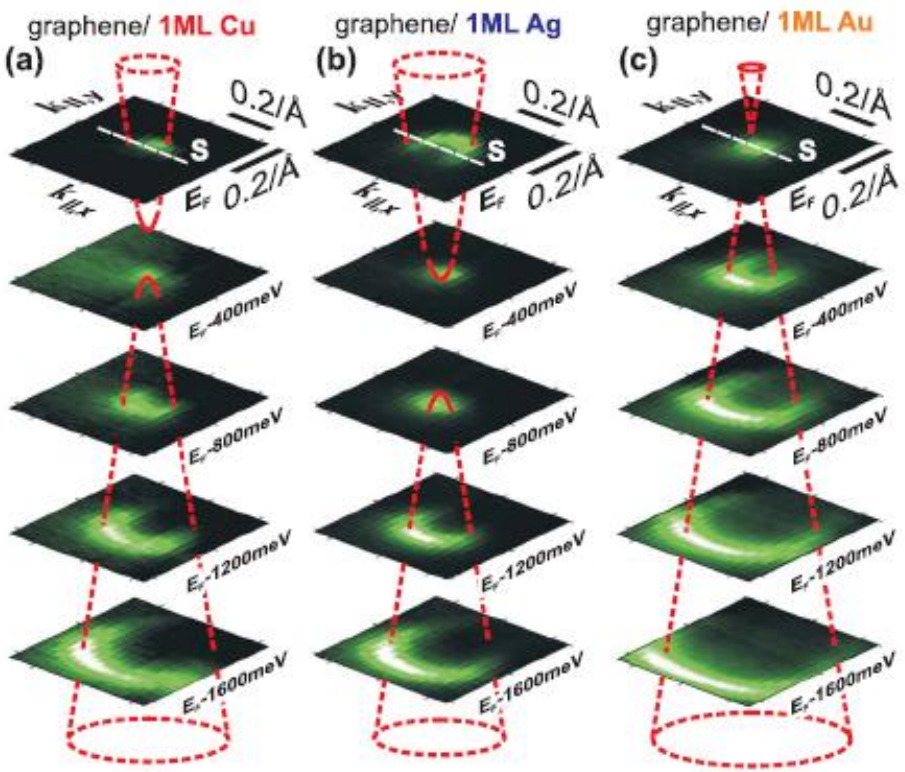


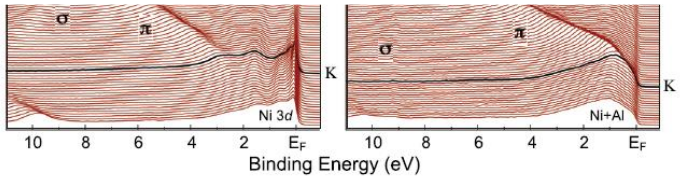
Riedl et al., PRL (2009)

Graphene intercalated compounds (GICs)









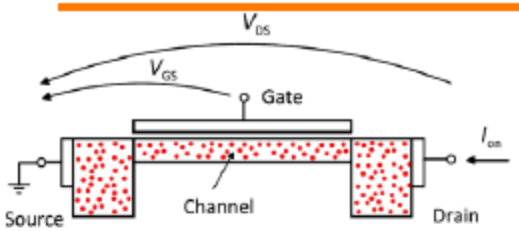
Pan et al., PRL (2011)

Voloshina et al., NJP (2011)

Varykhalov et al., PRB (2010)

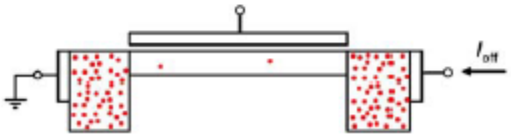
Beyond Graphene :
Graphene nanoribbons (GNRs), transition metal dichalcogenides (TMDs), black phosphorus (BP), stanene and van der Waals heterstructure

FET Basics – Digital CMOS

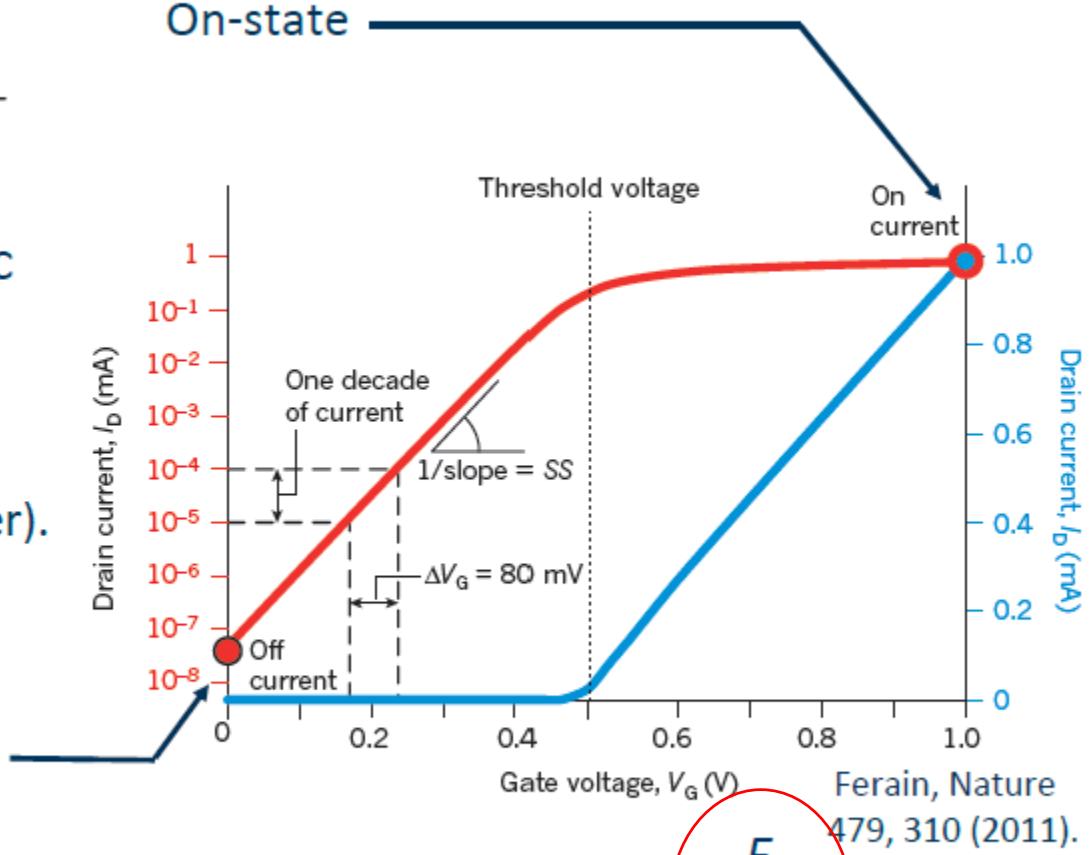


Requirements for logic

- 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*.



Off-state



Ferain, Nature 479, 310 (2011).

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

A sizeable gap is mandatory!

Frank Schwierz, Nanoscale (2015)

2D materials :potential candidates for future applications

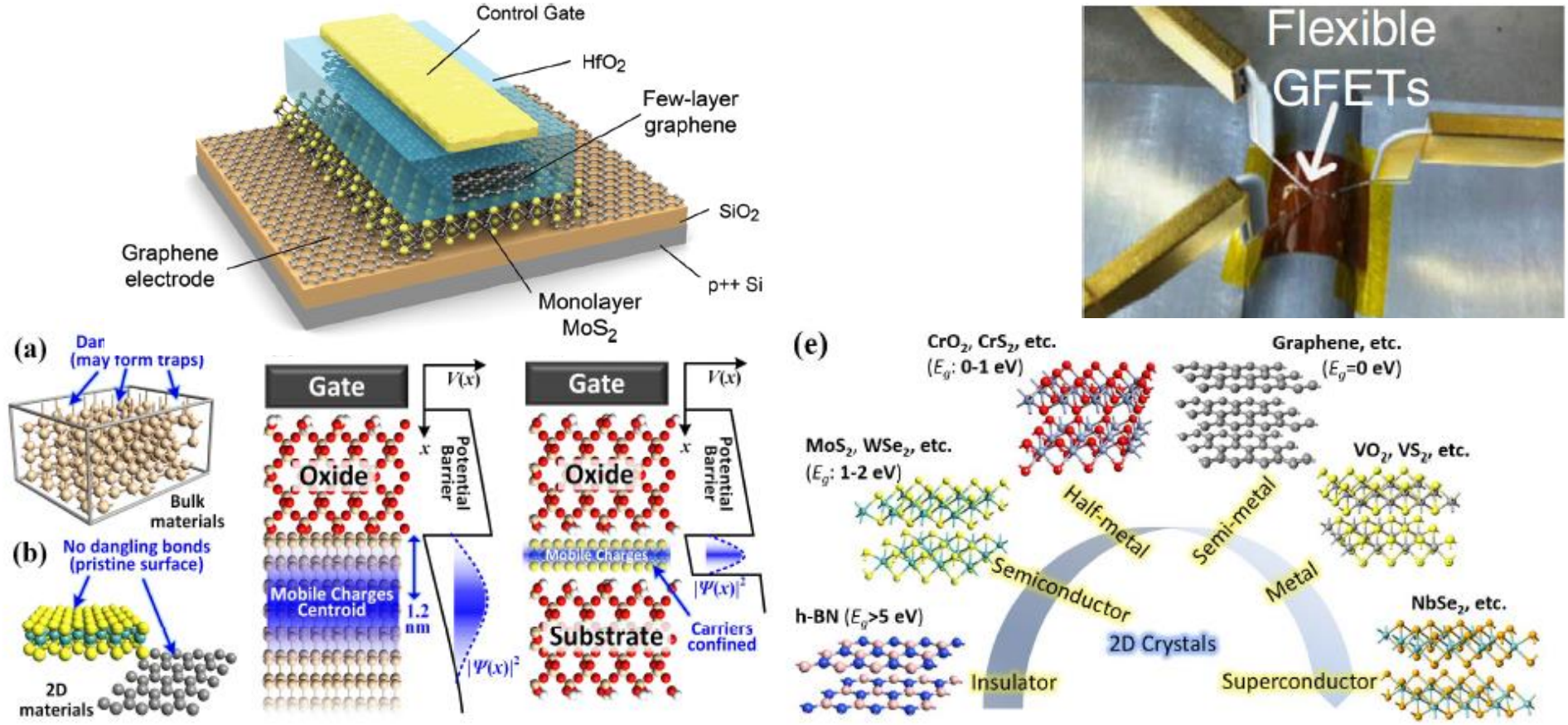


Figure 1. Schematic illustrating advantages of 2D materials: surfaces of **(a)** 3D and **(b)** 2D materials. The pristine interfaces (without out-of-plane dangling bonds) of 2D materials help reduce the interface traps. Mobile charge distribution in **(c)** 3D and **(d)** 2D crystals used as channel 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

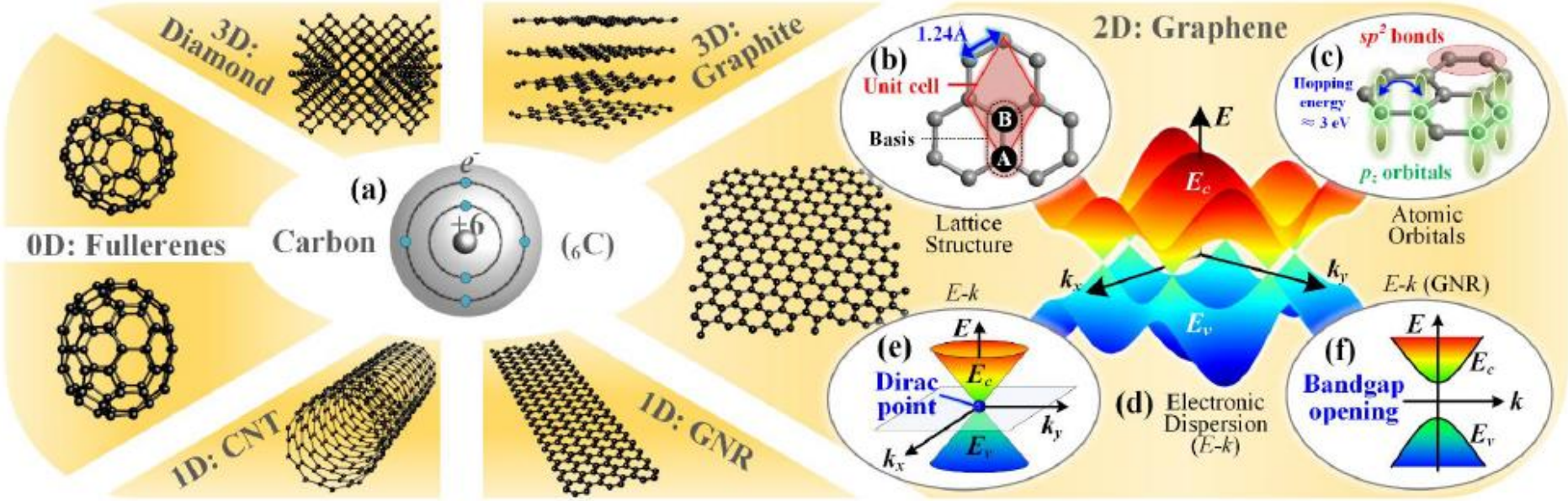
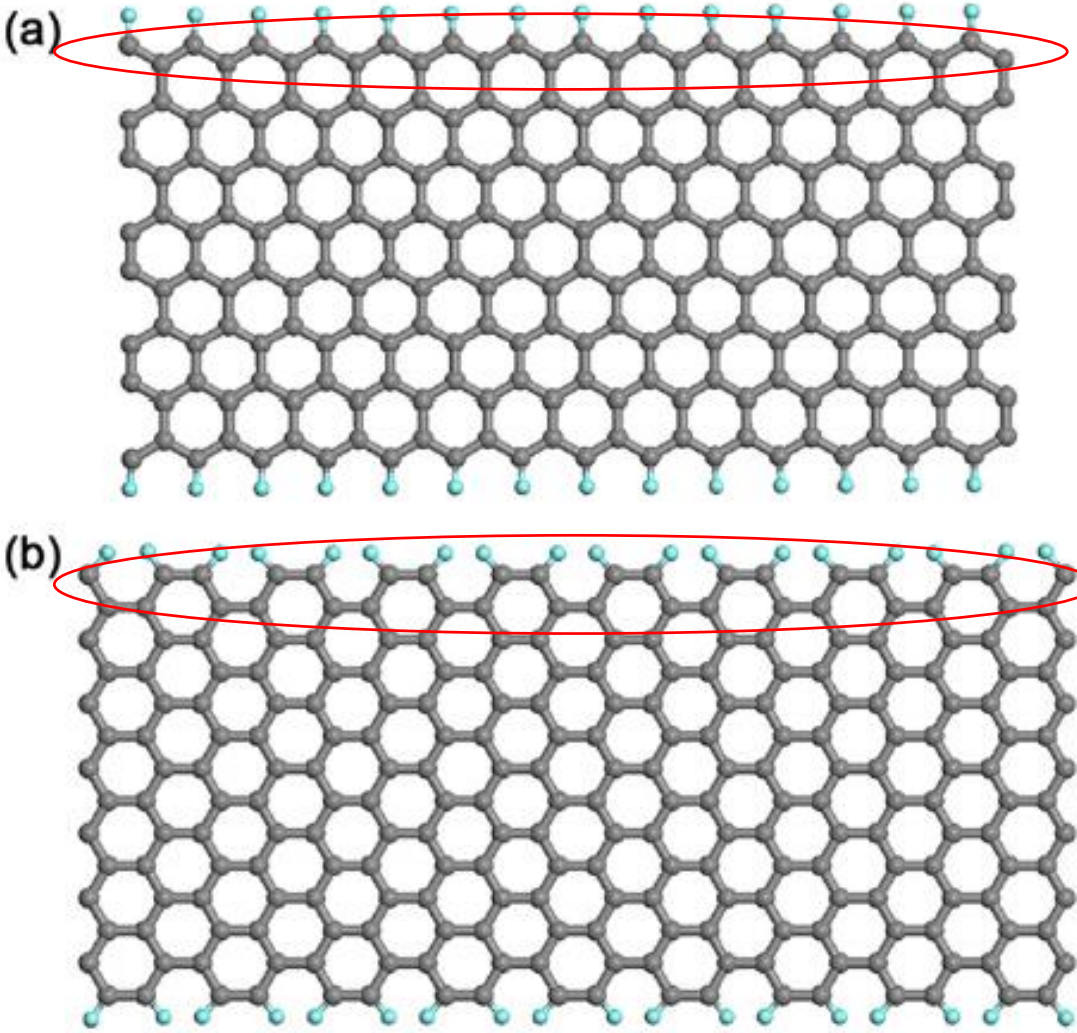


Figure 2. **(a)** Schematic of carbon atom and carbon allotropes, from 0D to 3D; **(b)** unit cell, basis and bond length of graphene; **(c)** atomic orbitals of graphene; **(d, e)** energy dispersion of graphene, where the energy dispersion is linear for low energies near the six corners (Dirac points)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

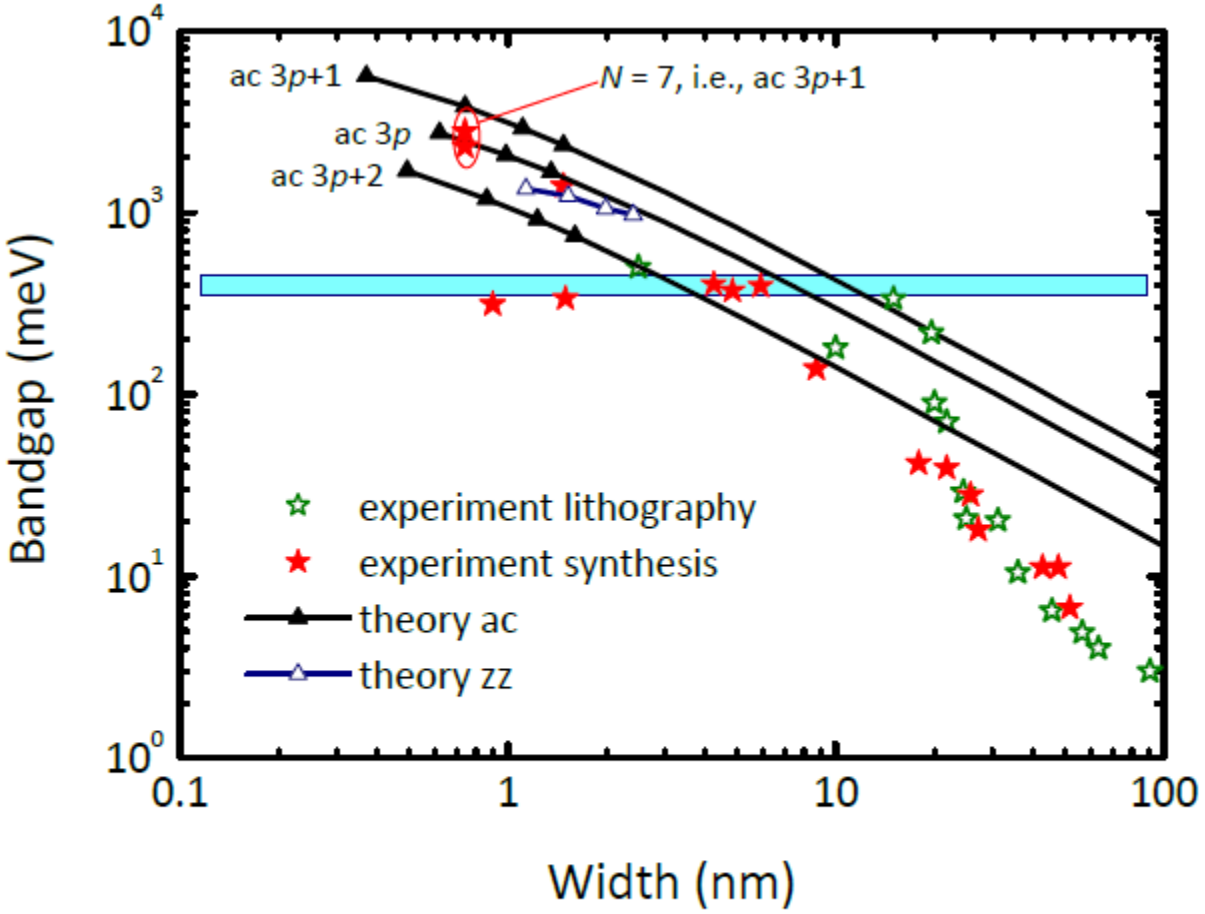
Kang et al., Proc. SPIE (2014)

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



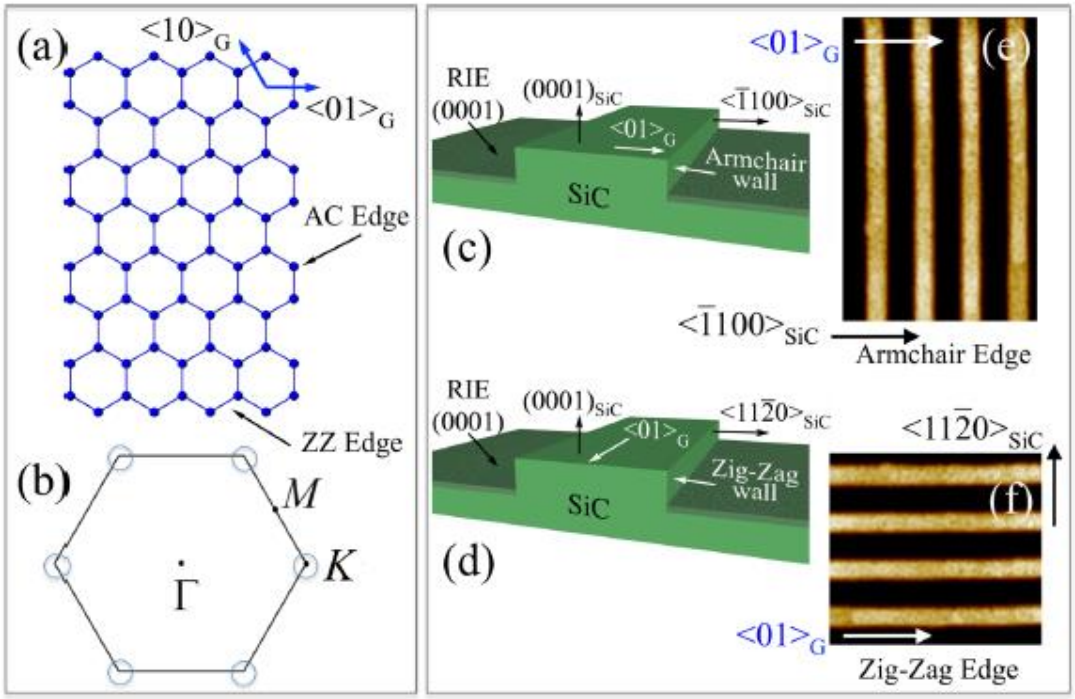
GNR bandgap vs width.

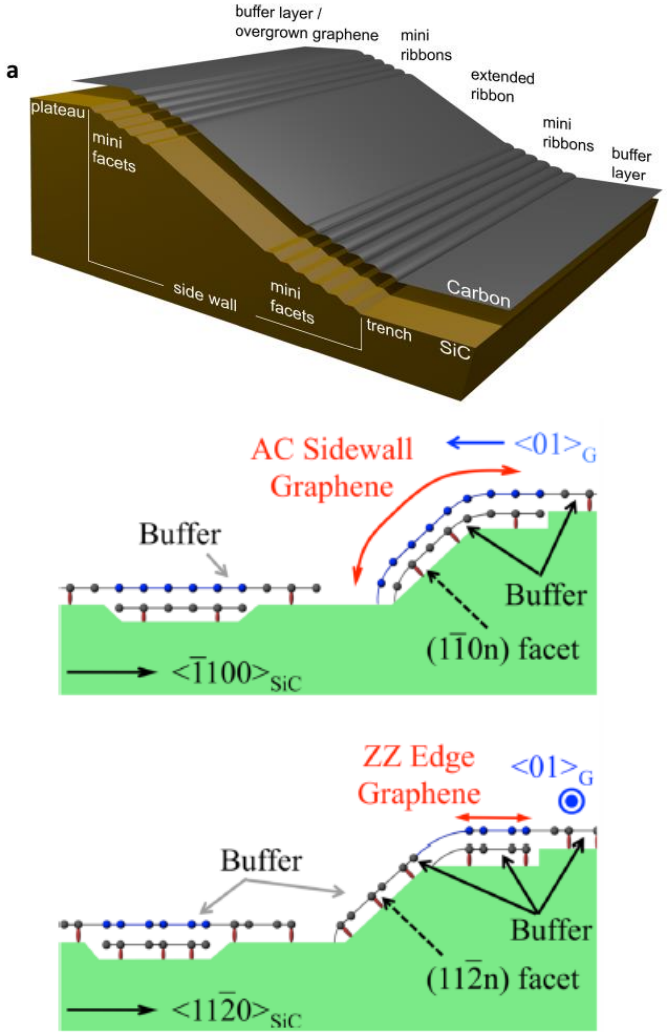
FS, Pezoldt, Granzner, Nanoscale 2015.

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

Frank Schwierz, Nanoscale (2015)

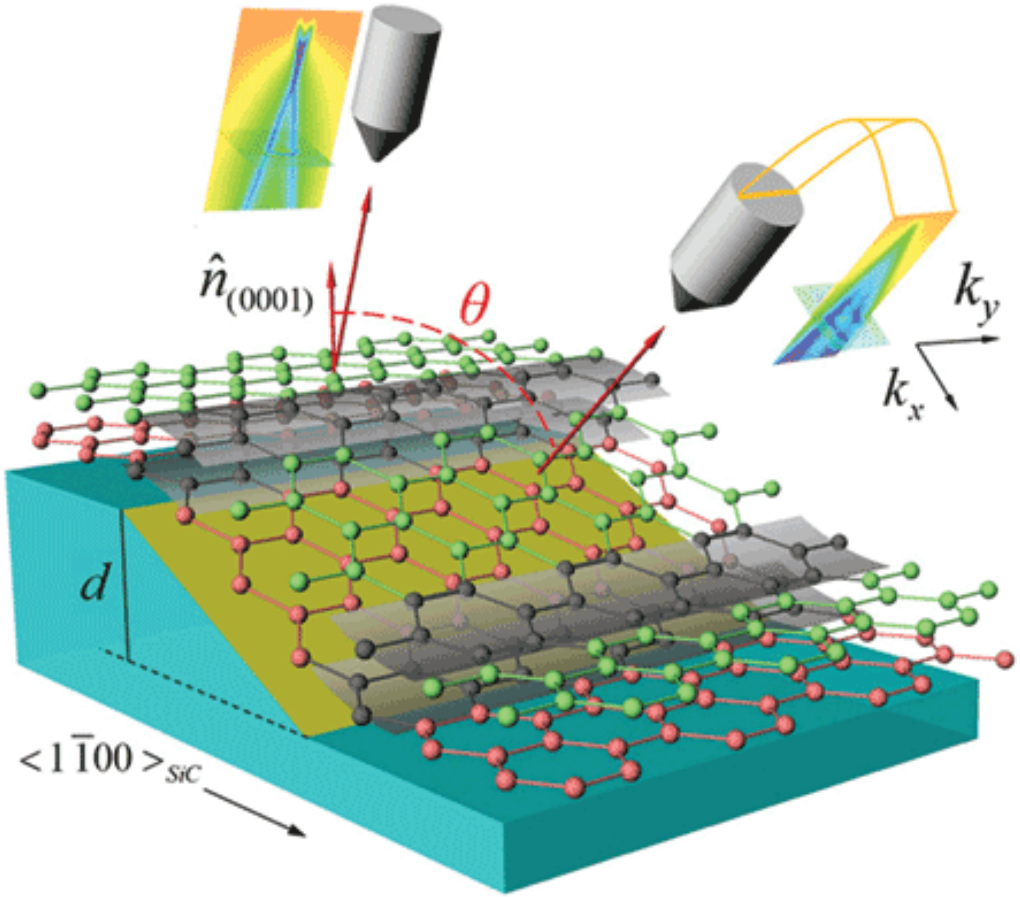
Sample preparation for GNRs

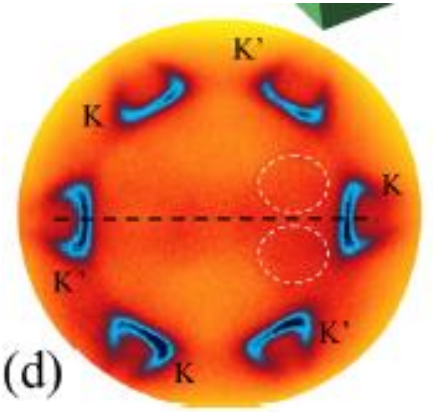


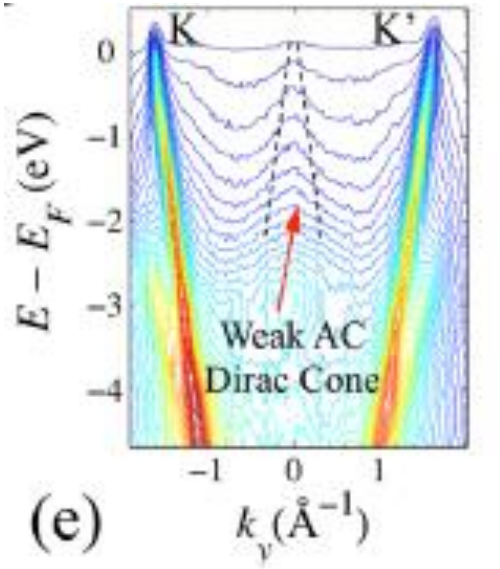


Nevius et al., Nano Lett. (2014)
Palacio et al., Nano Lett. (2014)

Using ARPES to probe GNRs/SiC

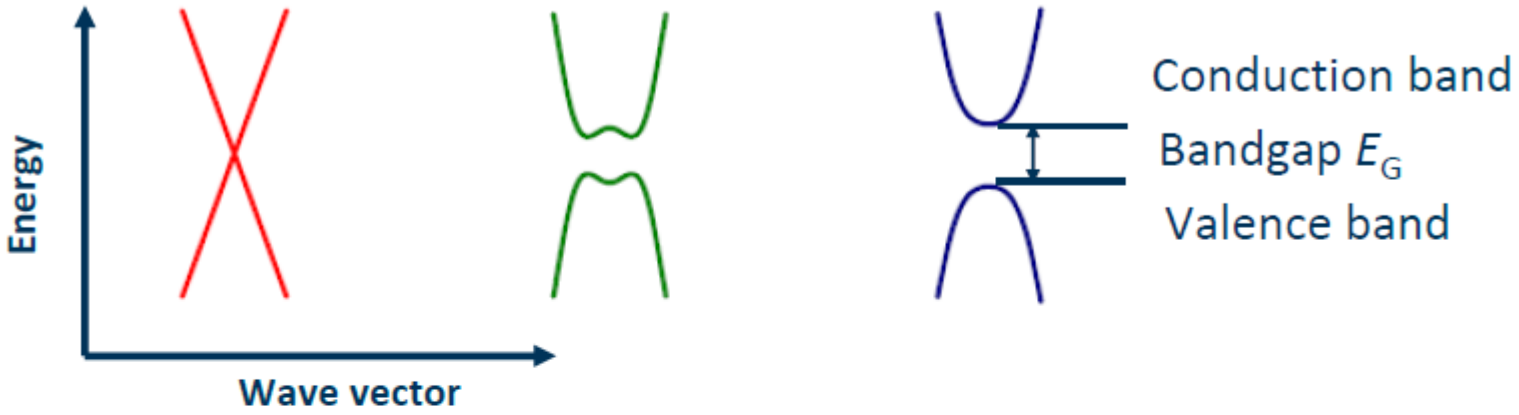






Nevius et al., Nano Lett. (2014)

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

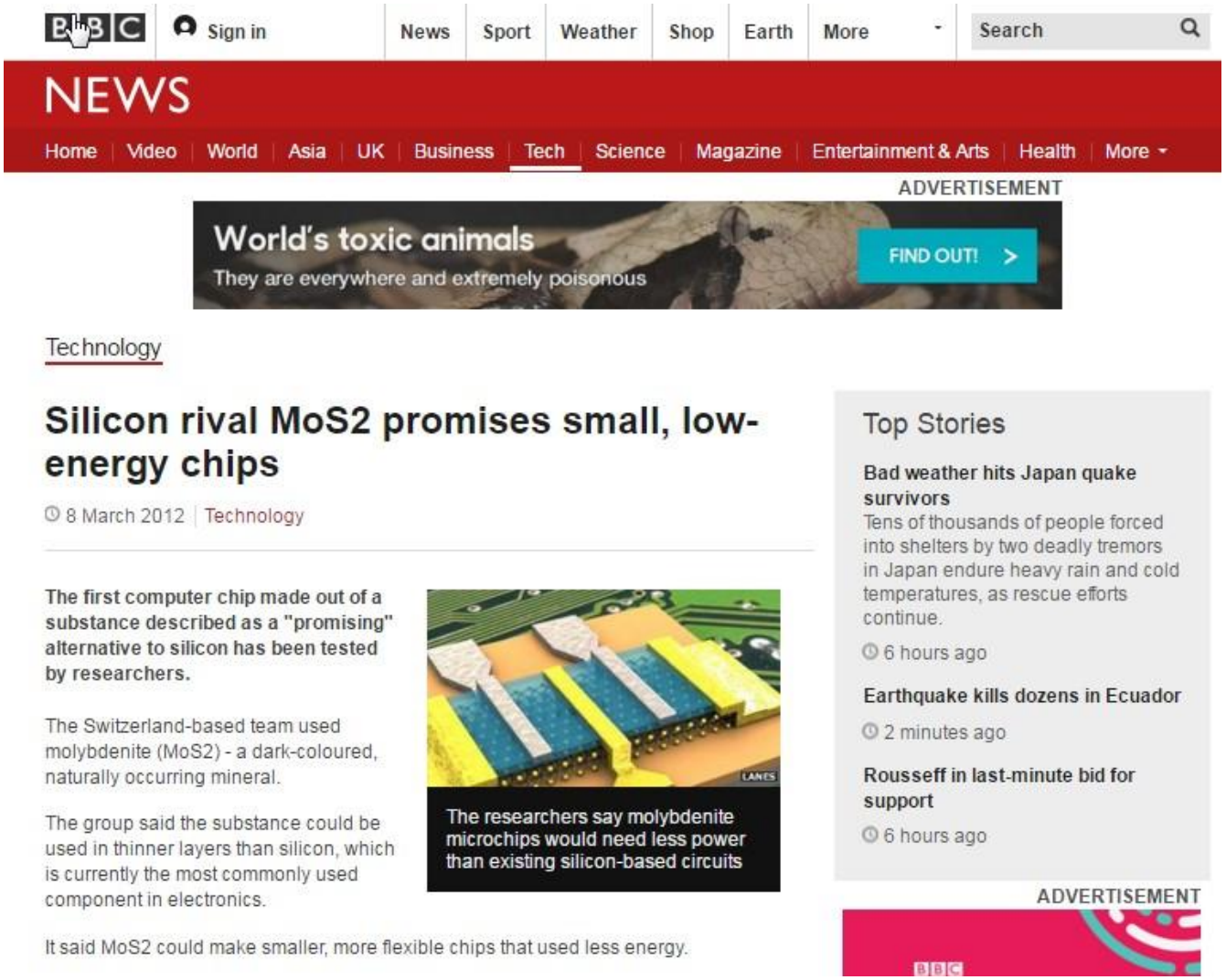
MX-enes
- Sc_2CF_2
- $TiCO_2$

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

etc., etc.

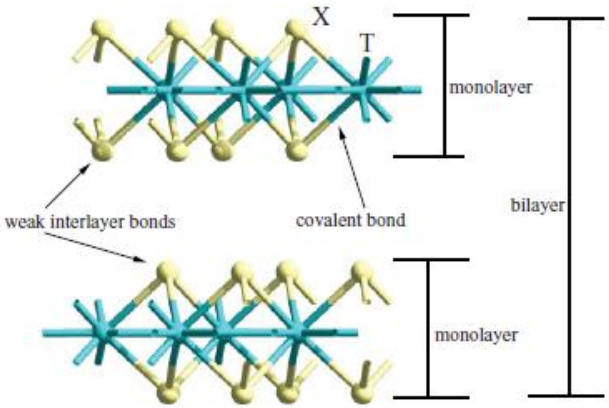
Many of these materials have a gap E_G = 0.5... 2.5 eV, perfect for transistors.

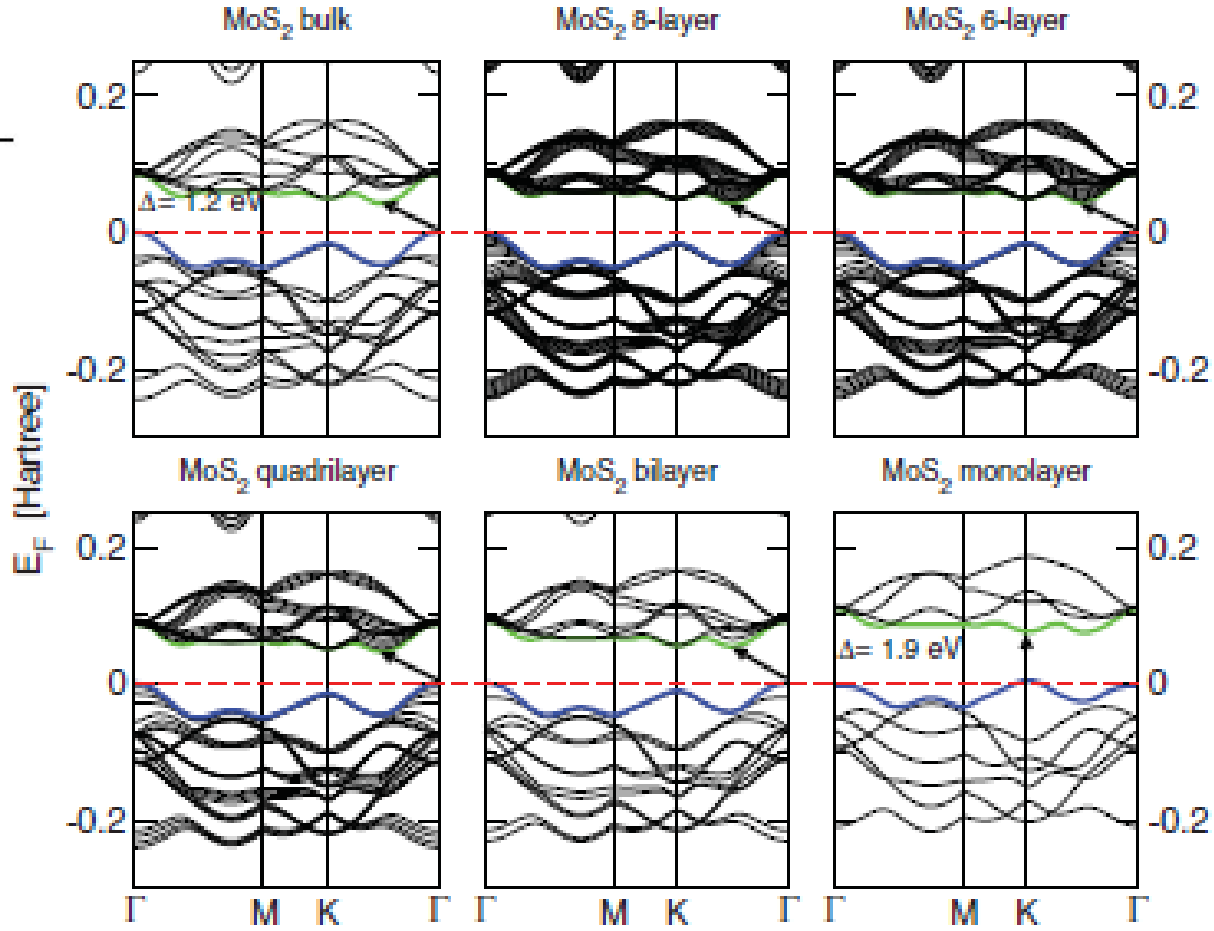
Frank Schwierz, Nanoscale (2015)



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.

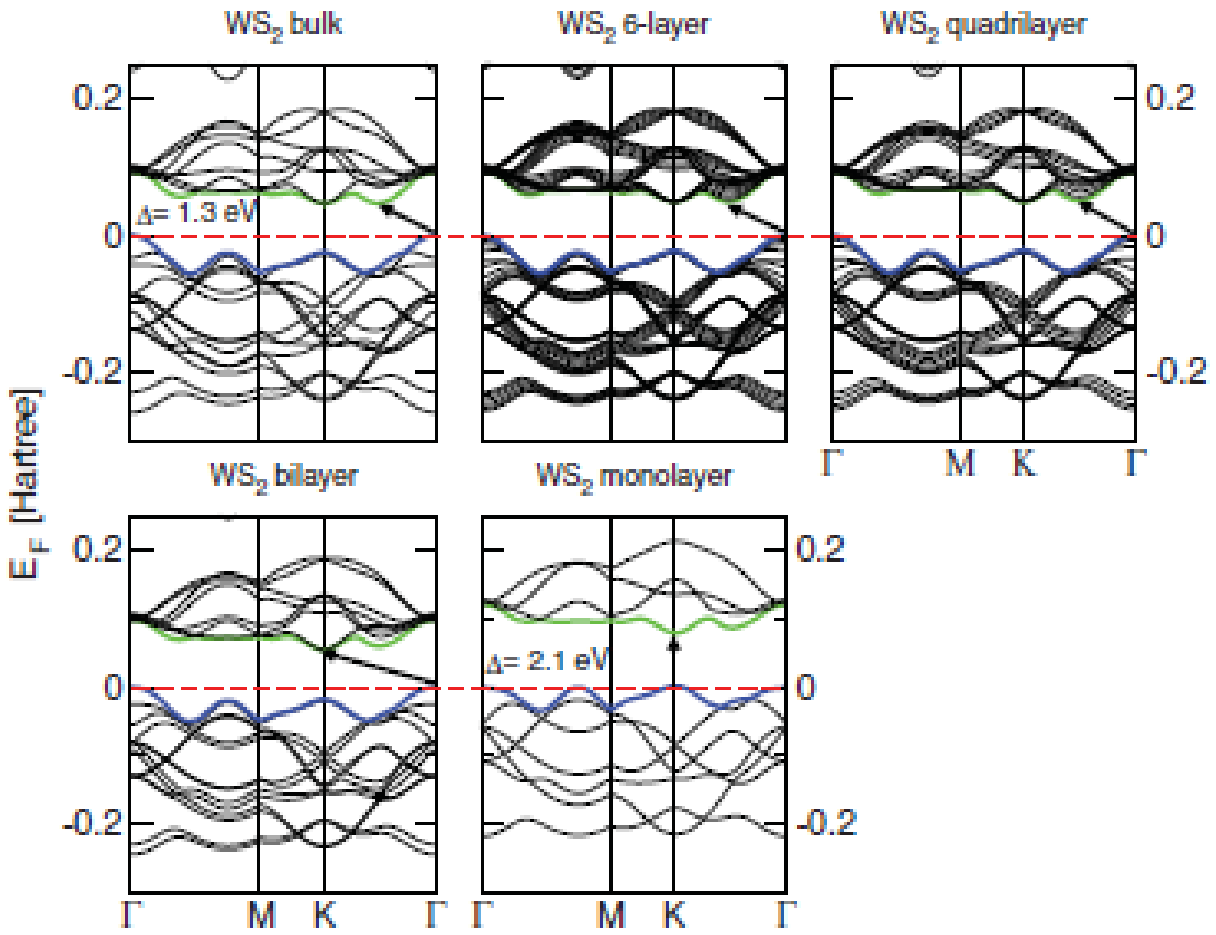
The band structure of MoS_2





Kuc et. al., PRB (2011)

The band structure of WS_2

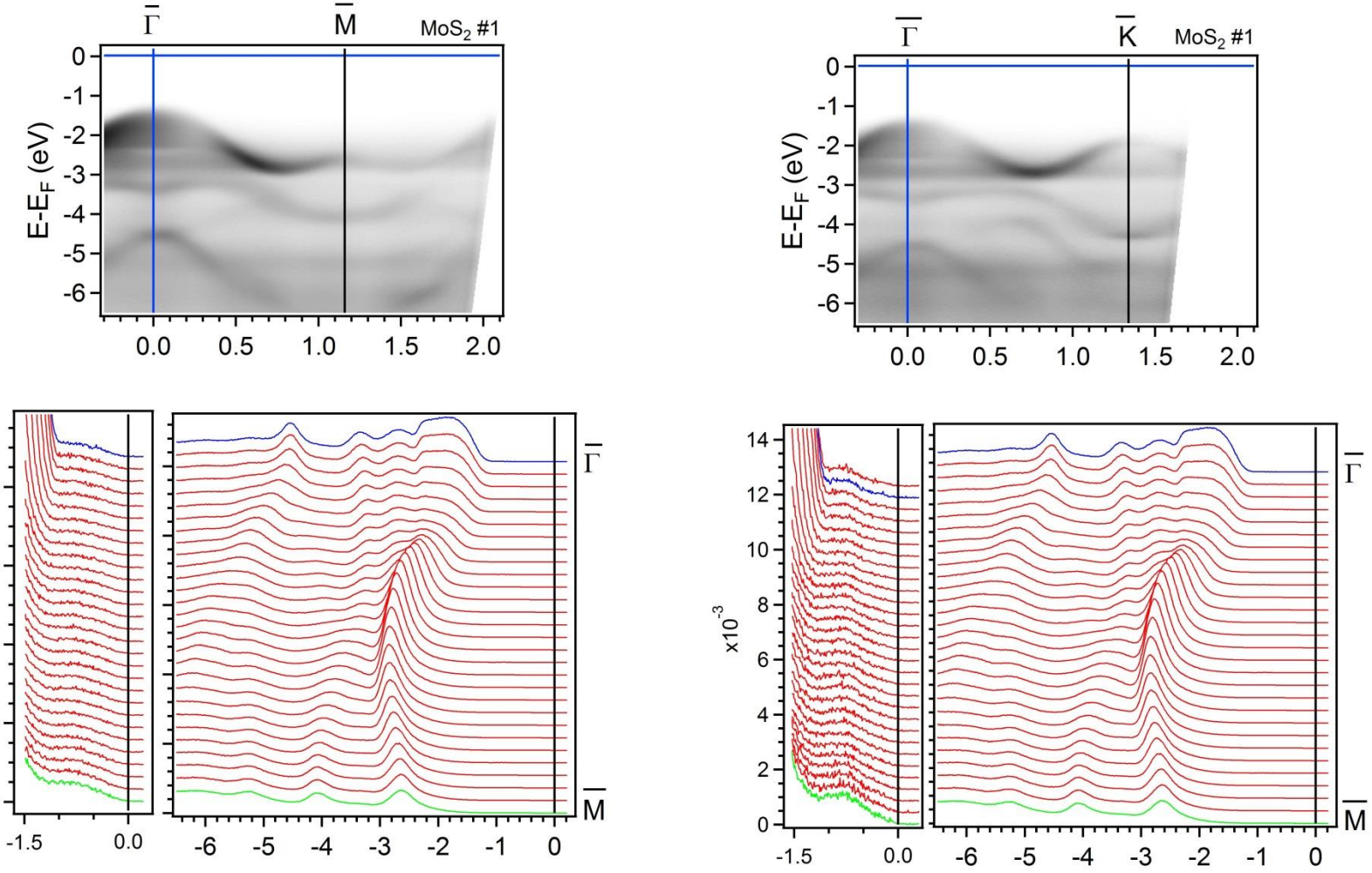


Kuc et. al., PRB (2011)

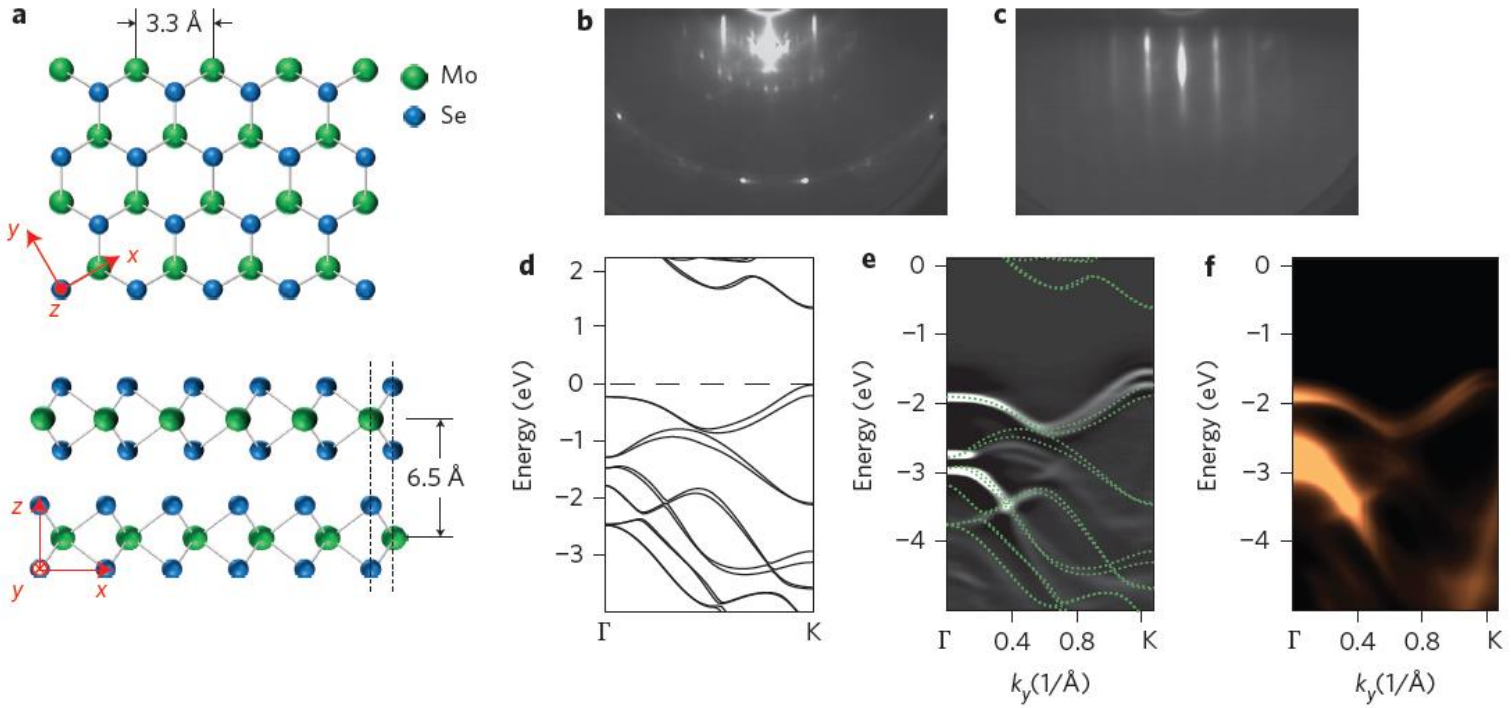
MoS2 #1

Photon energy : 42 eV, measurement temperature : 100 K, Sample cleaved in air
A state located at -0.8 eV of binding energy was observed below the Fermi level.

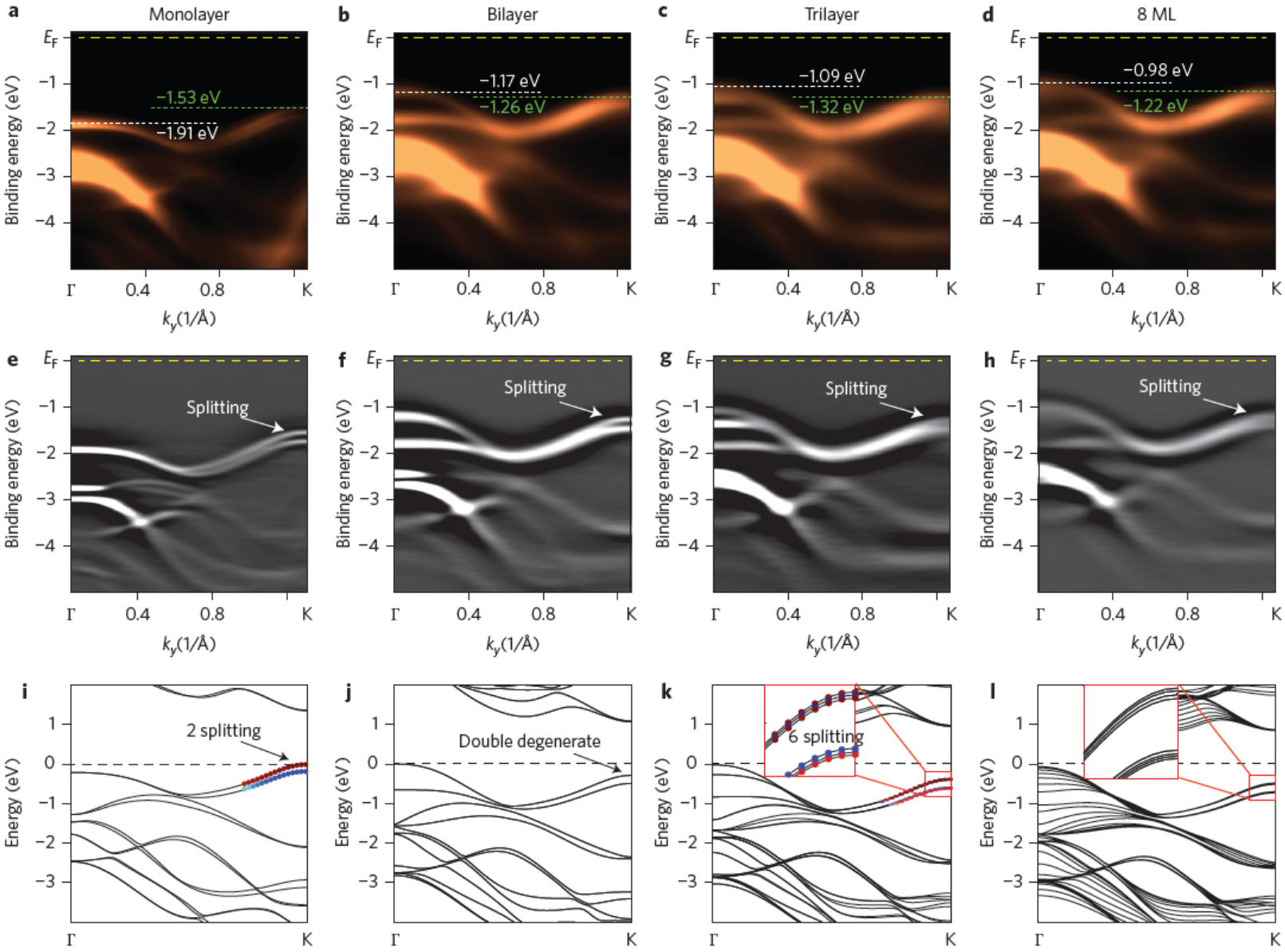
Upper: band mapping along the ΓK and ΓM directions
Bottom: EDCs and the enlargement for a energy scale between -1.5 eV and E_F



The electronic structure of $MoSe_2$

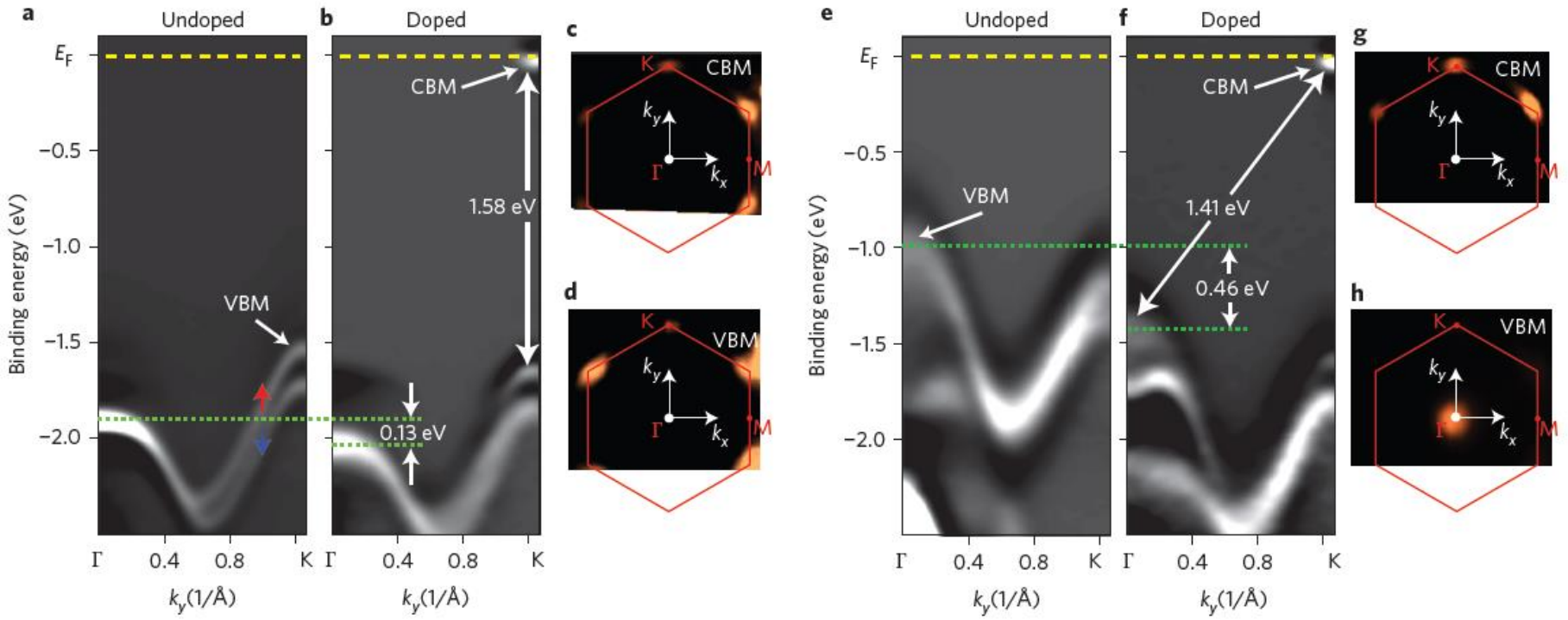


Zhang et al., Nat. Nano. (2013)



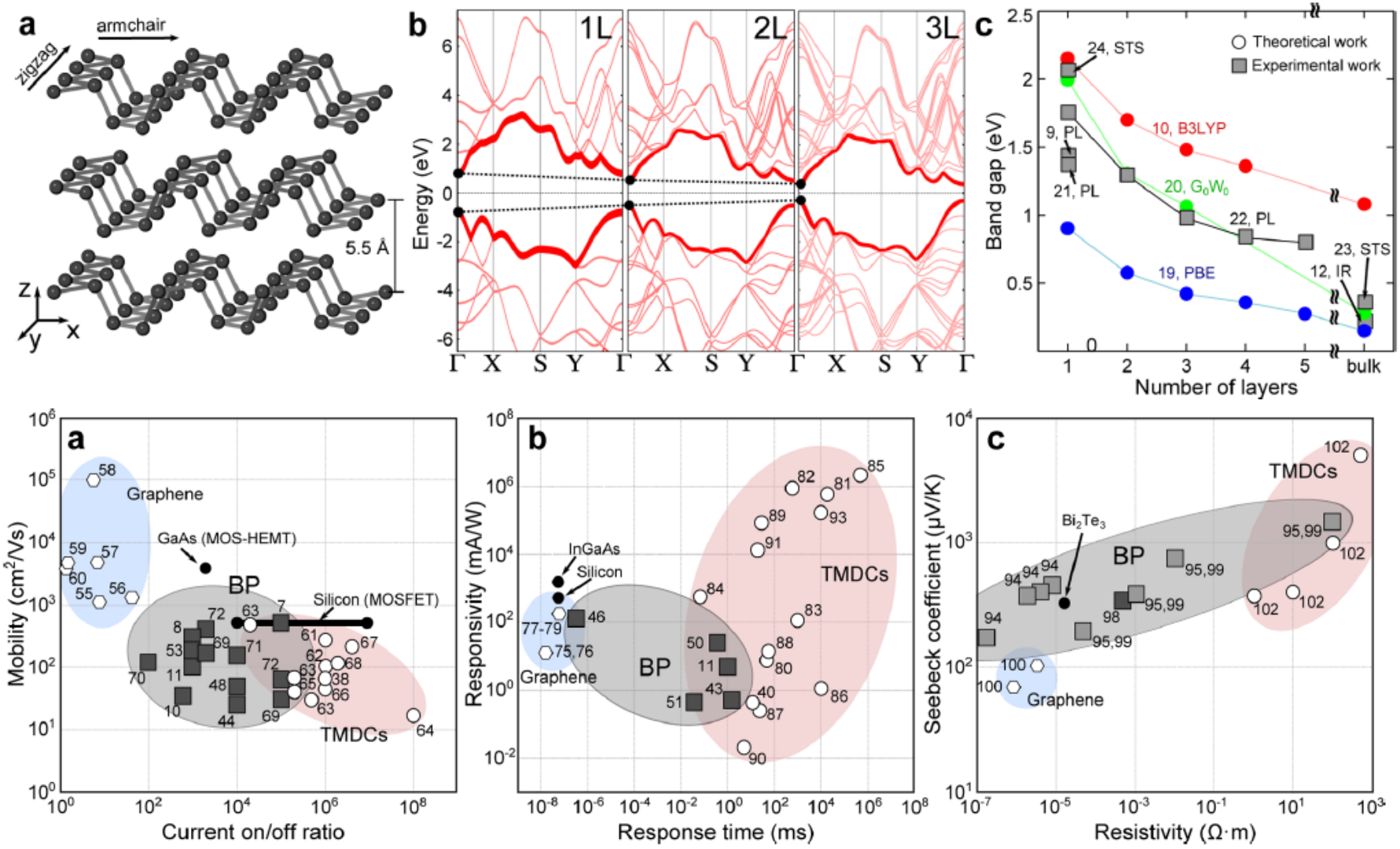
Zhang et al., Nat. Nano. (2013)

Alkali metal doped $MoSe_2$



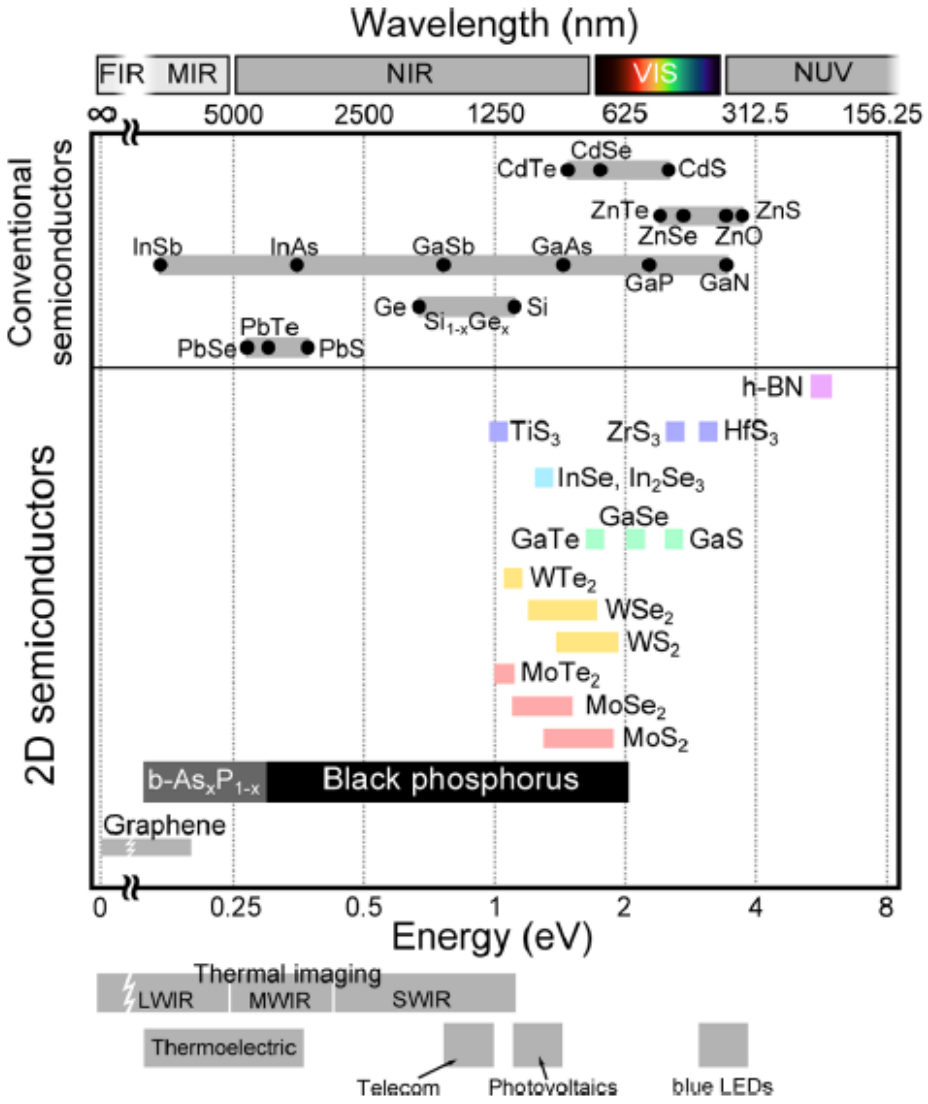
Zhang et al., Nat. Nano. (2013)

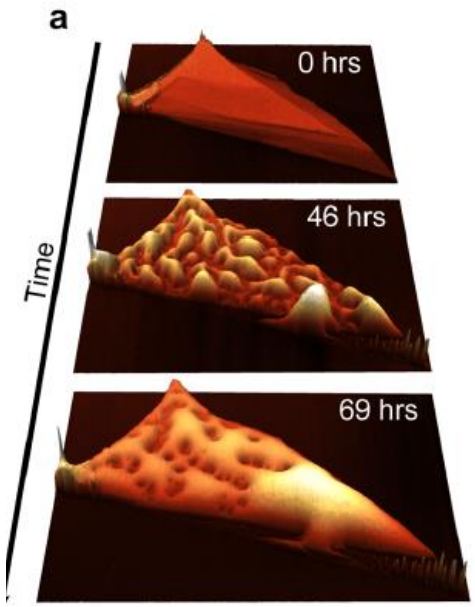
Black phosphorus (BP)

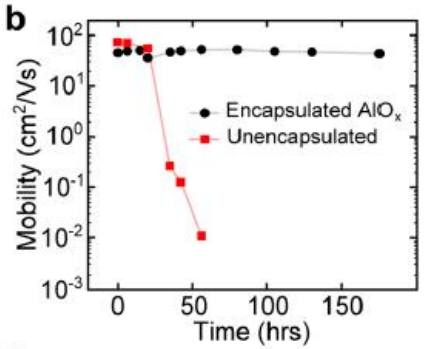


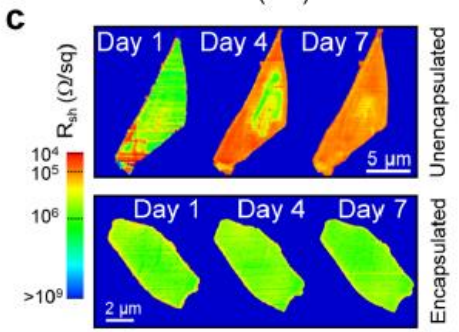
Catellanoas-Gomez, J. Phys. Chem. Lett. (2015)

The degradation of black phosphorus (BP)



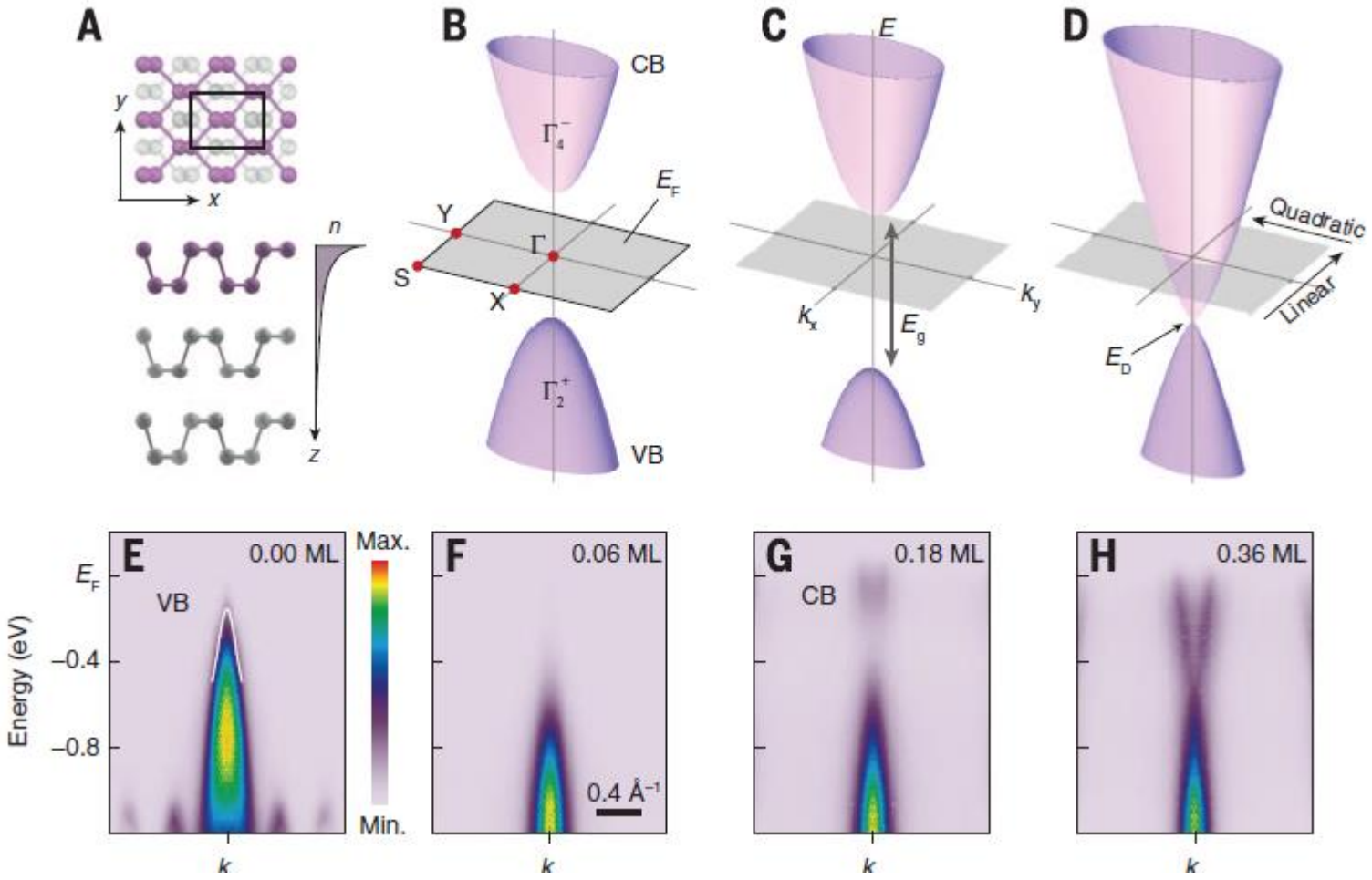




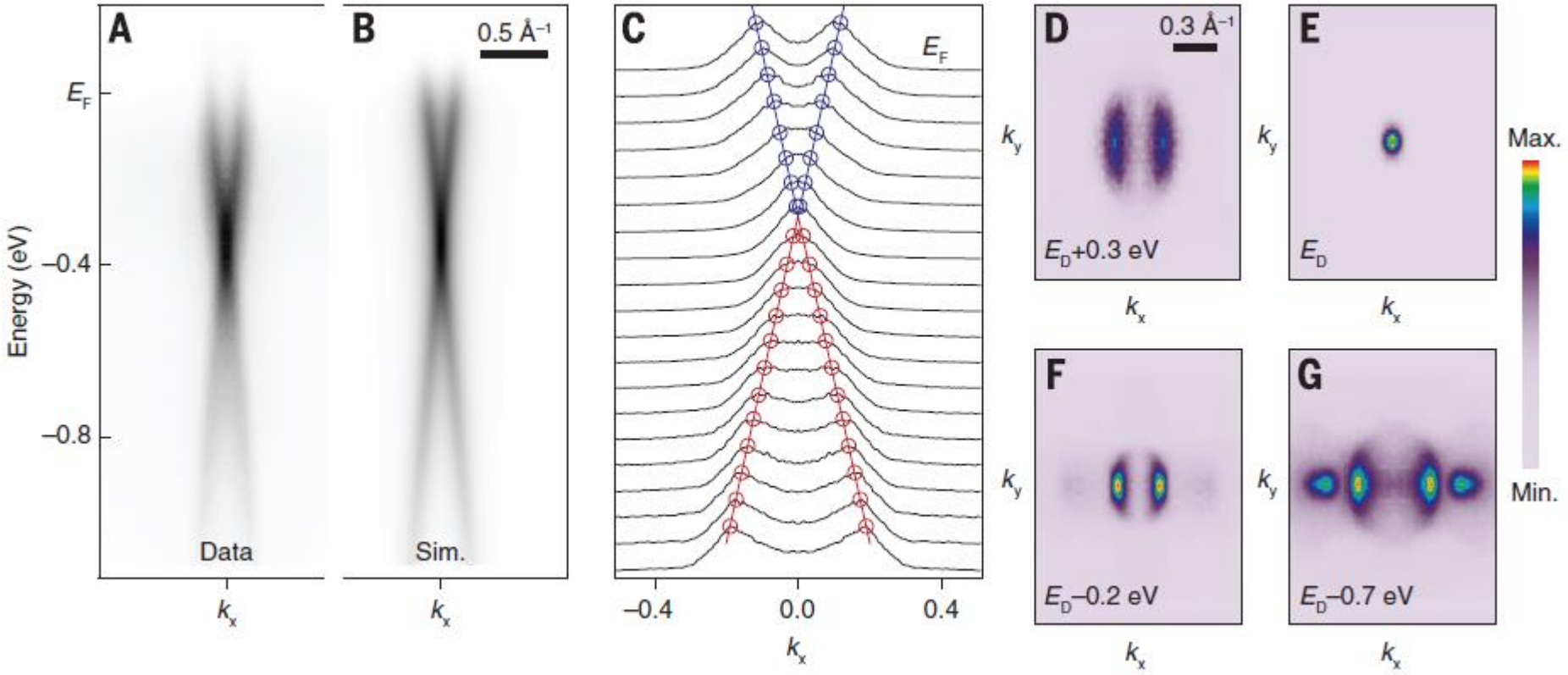


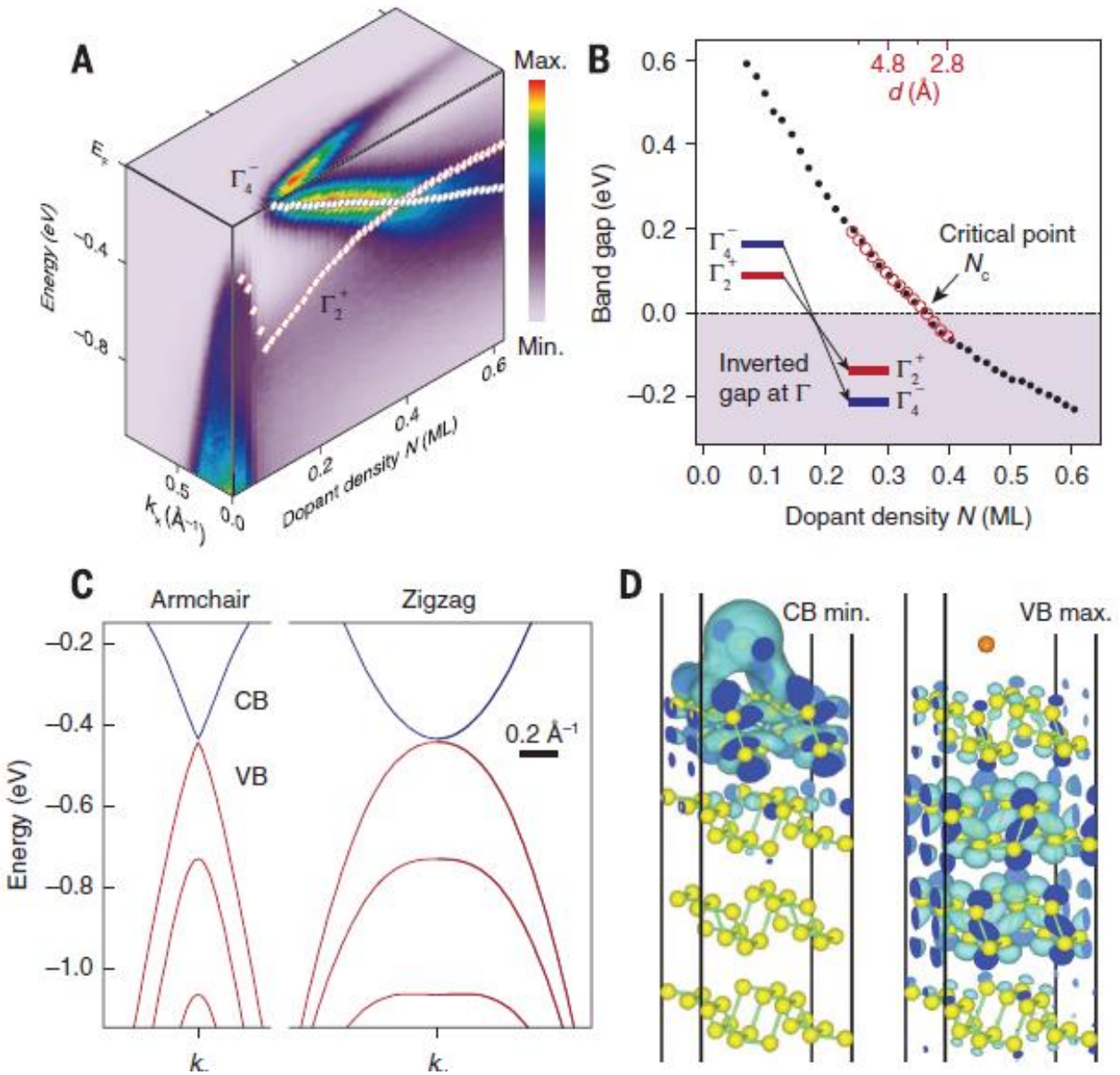
Catellanoas-Gomez, J. Phys. Chem. Lett. (2015)

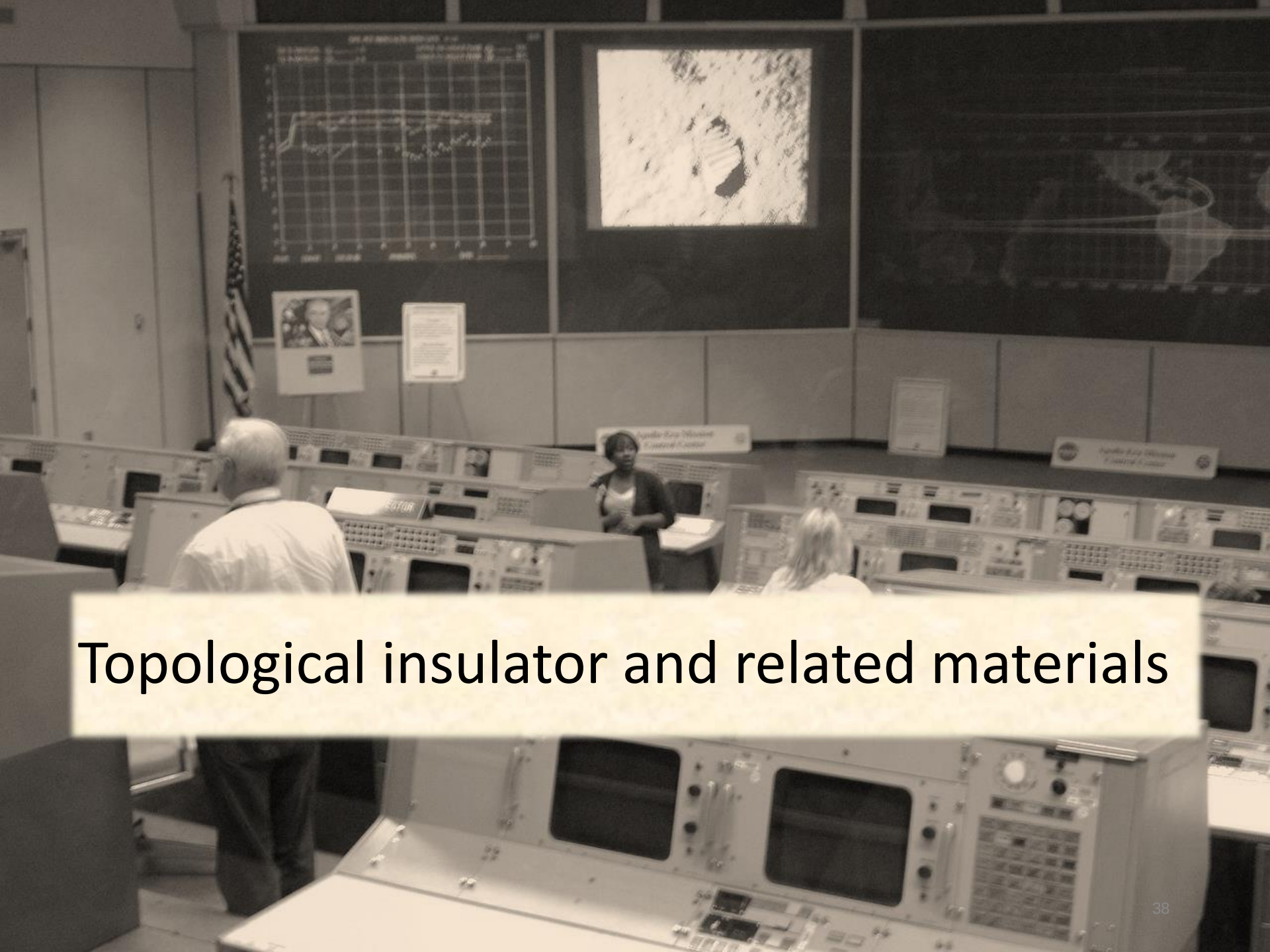
Anisotropic Dirac semimetal state in BP



Anisotropic Dirac semimetal state in BP

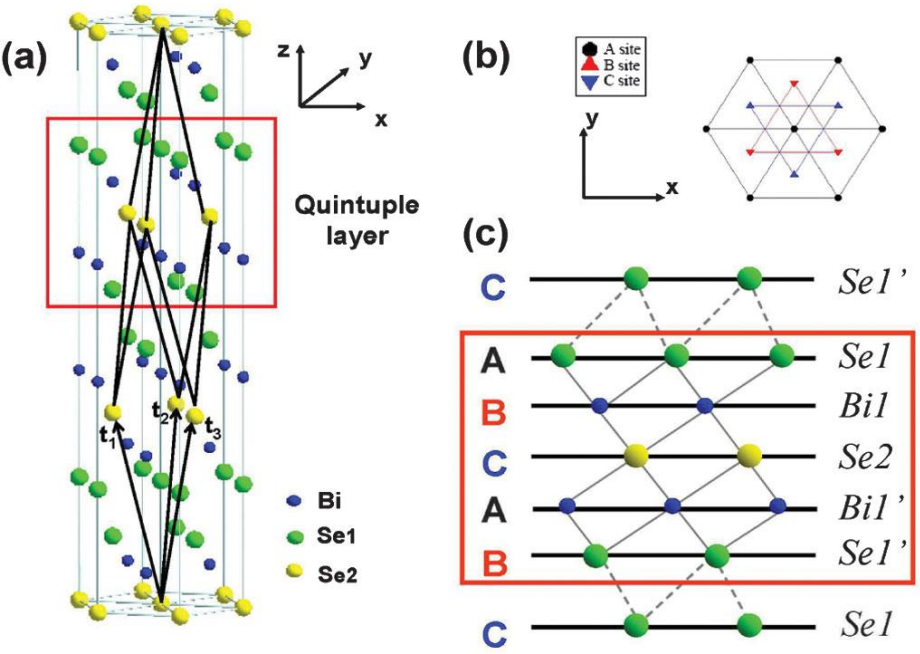


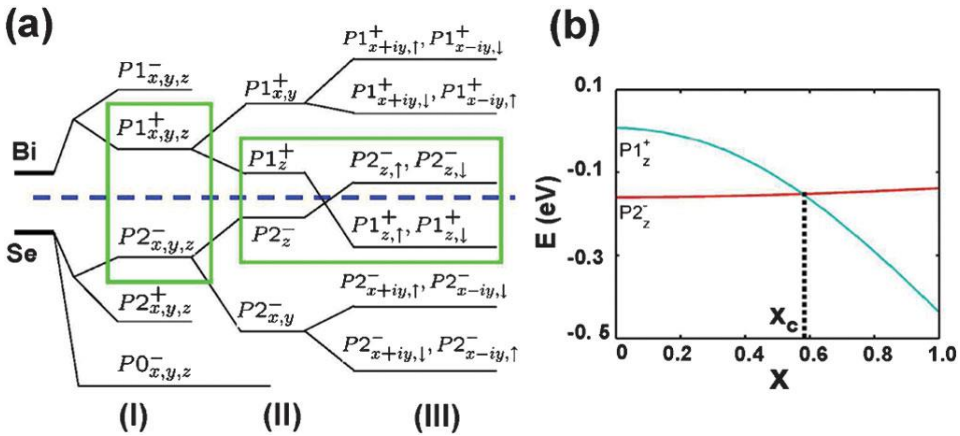

A
Max.
Min.
Energy (eV)
Γ_4^-
Γ_2^+
E_F
−0.4
−0.8
0.5
k_x (Å^{-1})
0.0
0.2
0.4
0.6
Dopant density N (ML)
B
4.8
2.8
d (Å)
Band gap (eV)
0.6
0.4
0.2
0.0
−0.2
Critical point
N_c
Γ_4^-
Γ_2^+
Inverted
gap at Γ
Γ_2^+
Γ_4^-
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Dopant density N (ML)
C
Armchair
Zigzag
−0.2
−0.4
−0.6
−0.8
−1.0
Energy (eV)
CB
VB
0.2 Å^{-1}
k
k
D
CB min.
VB max.



Topological insulator and related materials

3D topological insulators

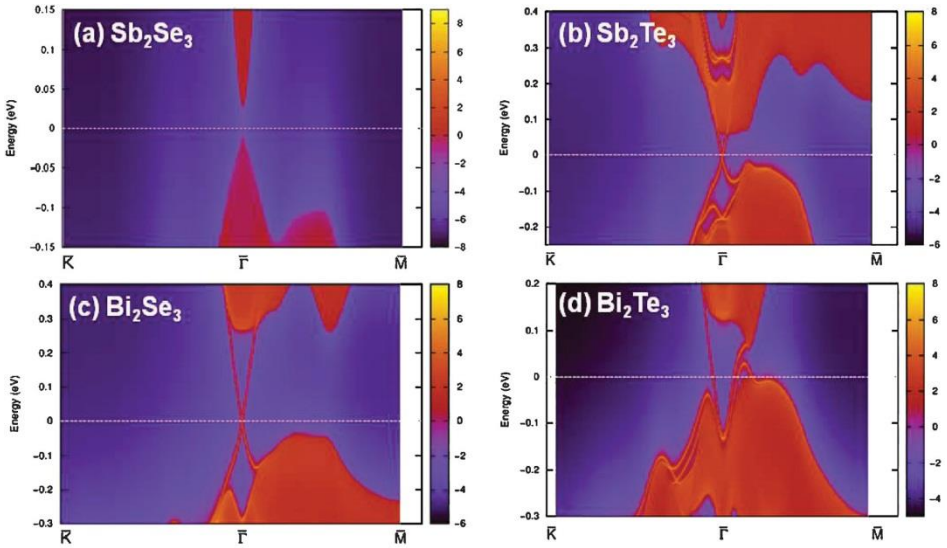


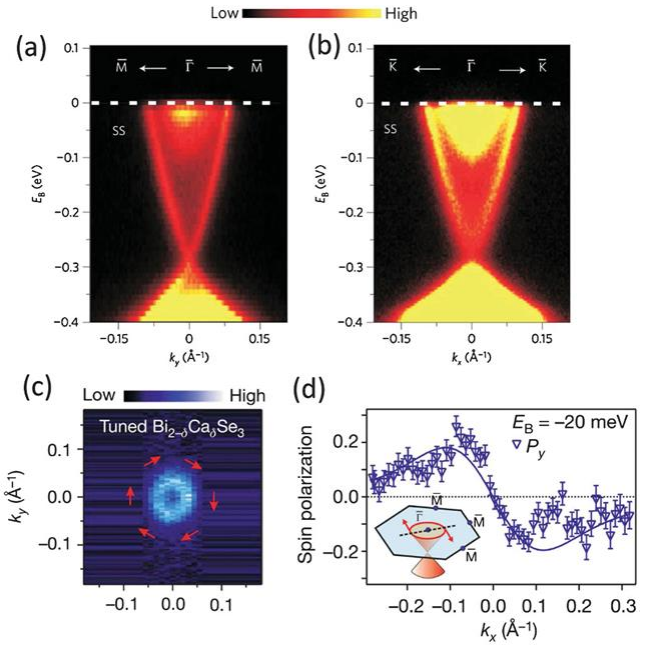


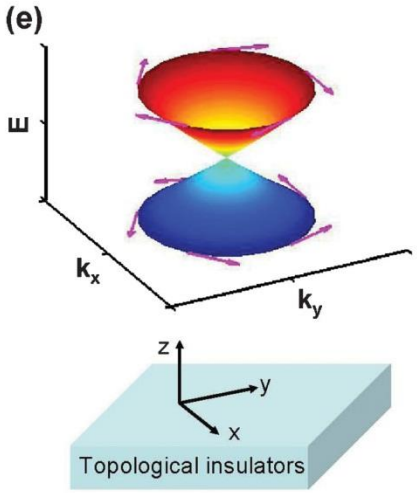
Strong spin-orbit coupling
Induce the band inversion

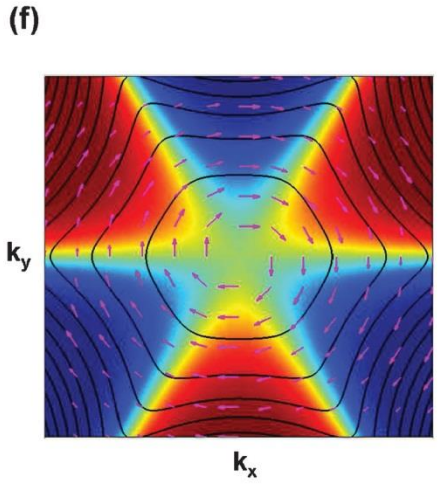
Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

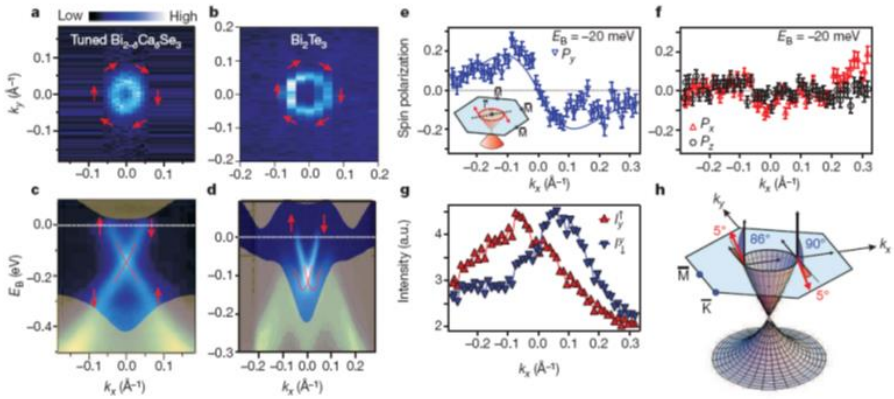
Predictions of 3D topological insulators









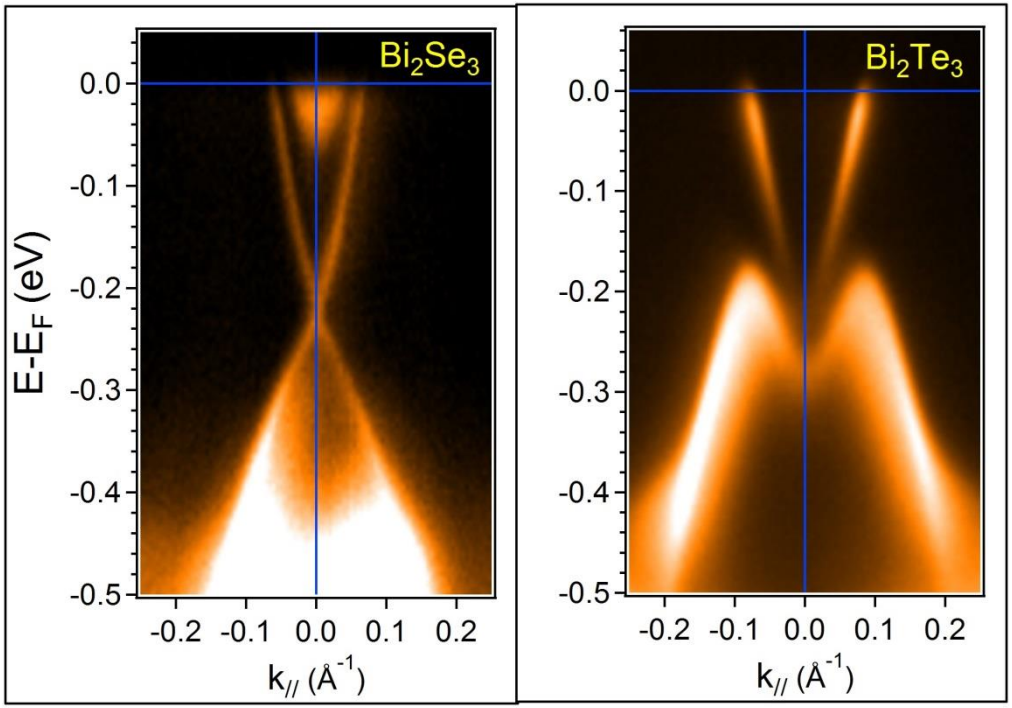


Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

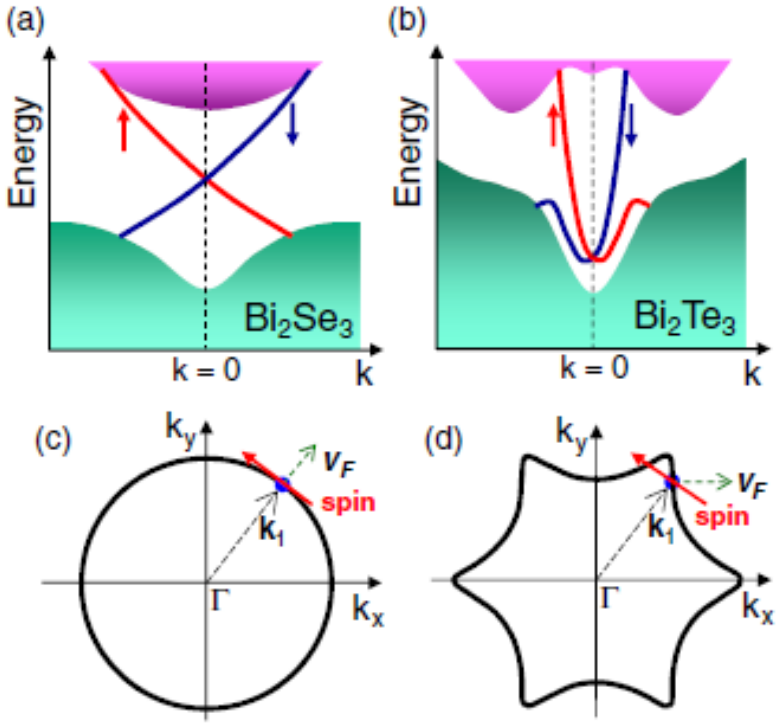
Xia et al., Nature Physics (2009)
Hsieh et al., Nature (2009)

Chen et al, Science (2009)

Predictions of 3D topological insulators

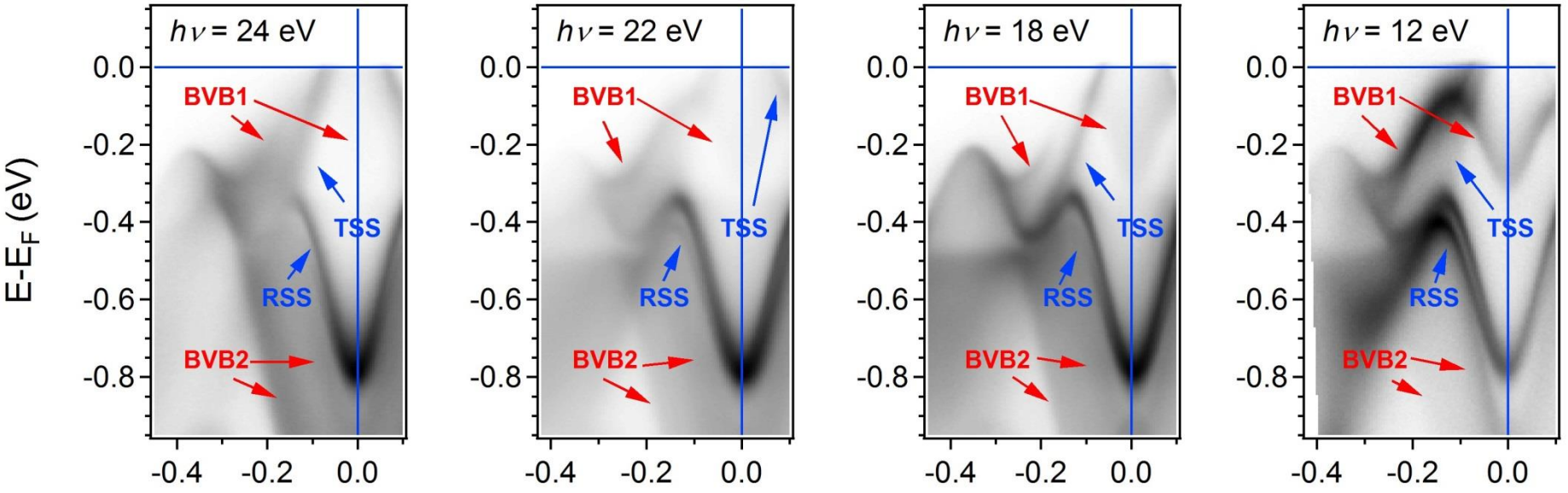


Spectra taken at BL21B1, NSRRC



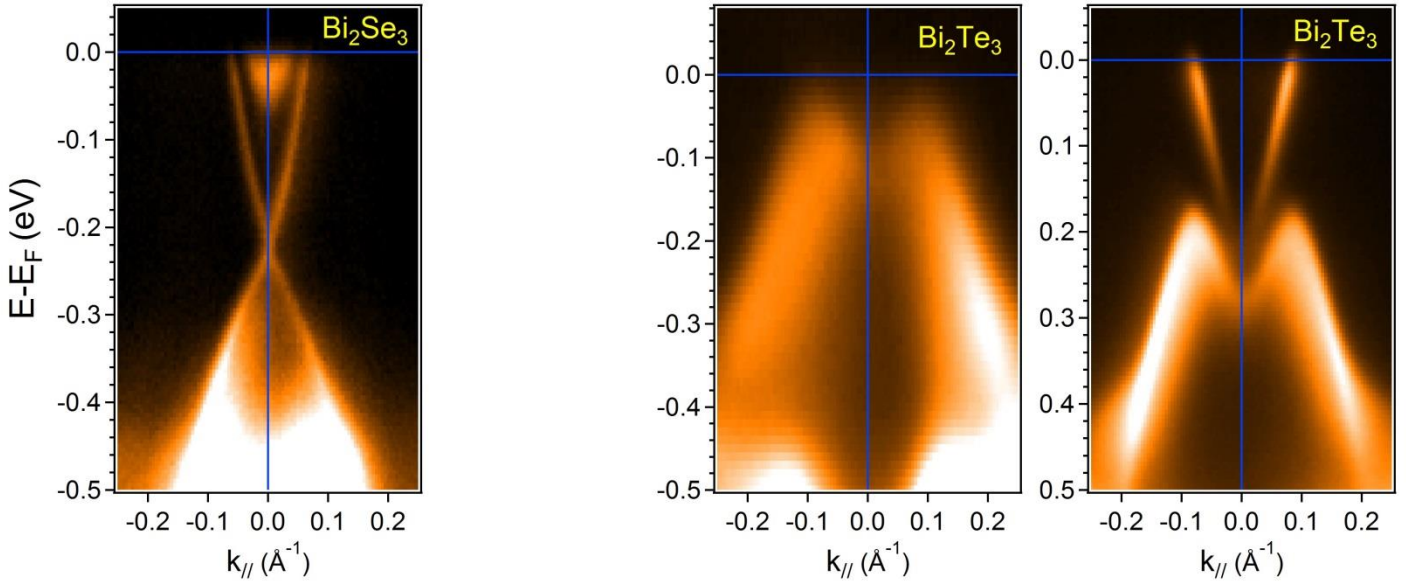
Y. Ando, J. Phys. Soc. Japan (2013)

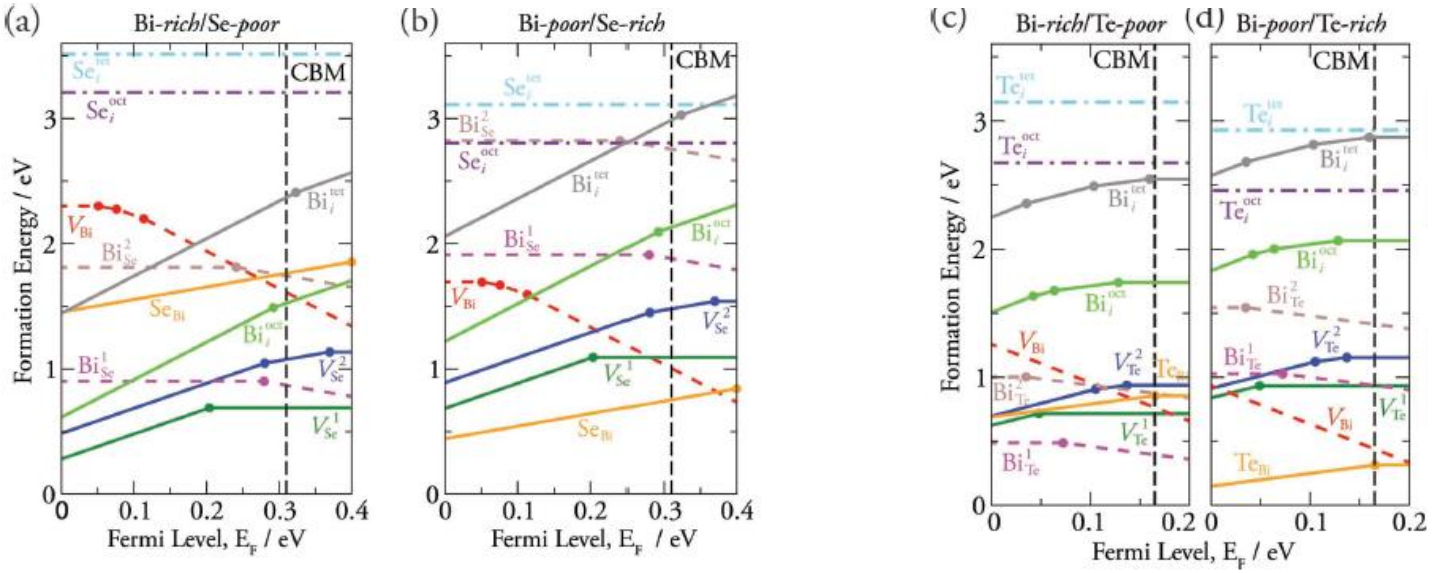
The electronic structure of Sb_2Te_3 insulators



Cheng et al., submitted to Sci. Rep.

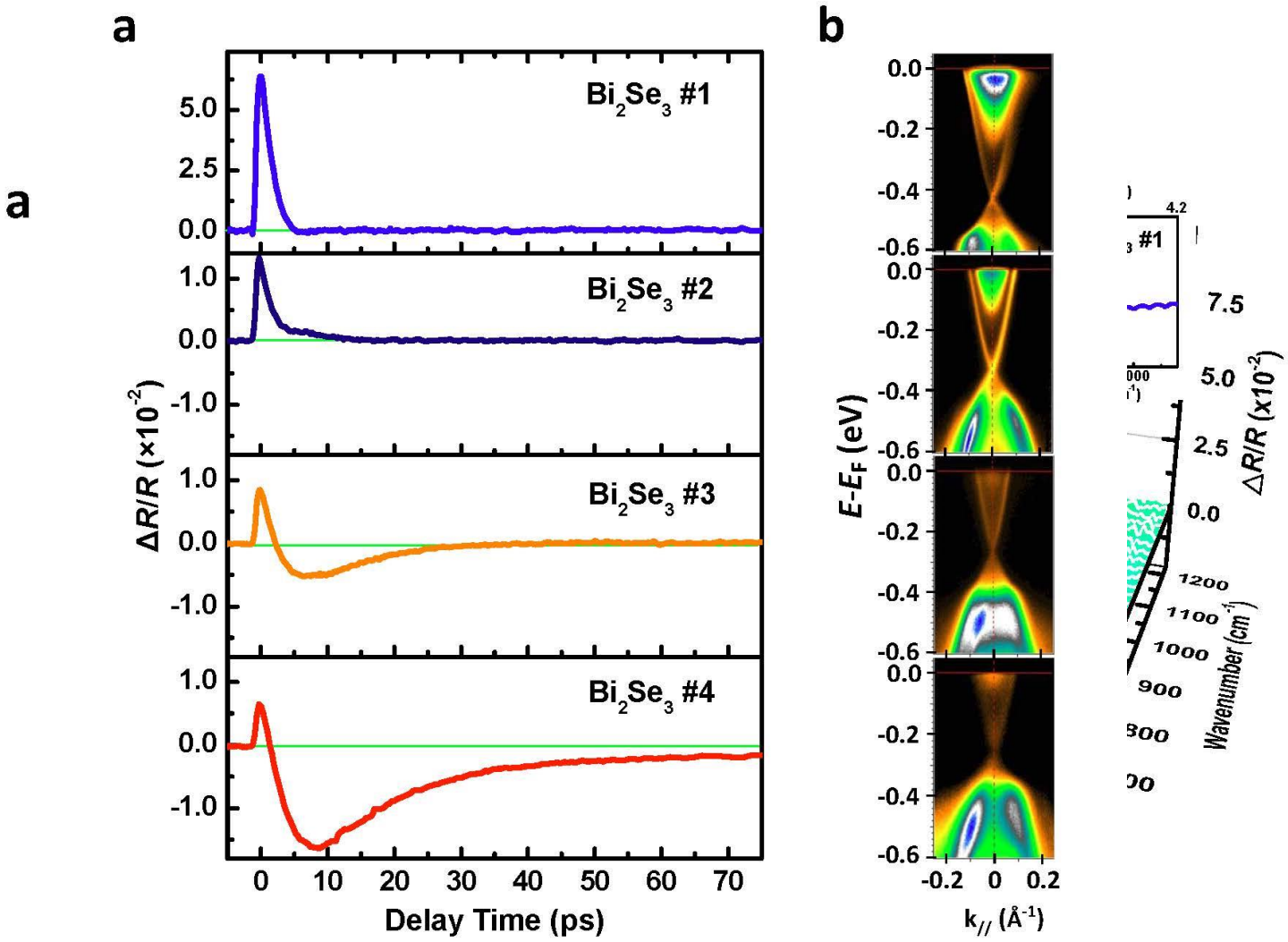
Initial growth condition of Bi family TIs





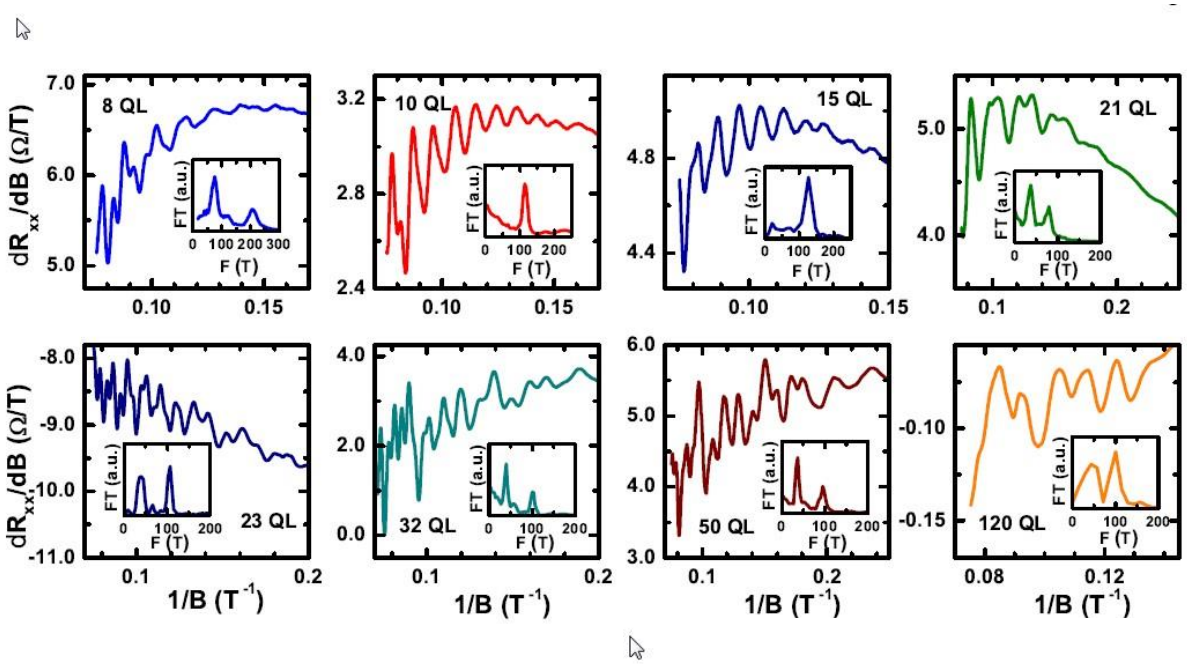
D.O. Scanlon, Adv. Mat. (2012)

Ultrafast Dynamics of Dirac Fermion in Topological Insulators

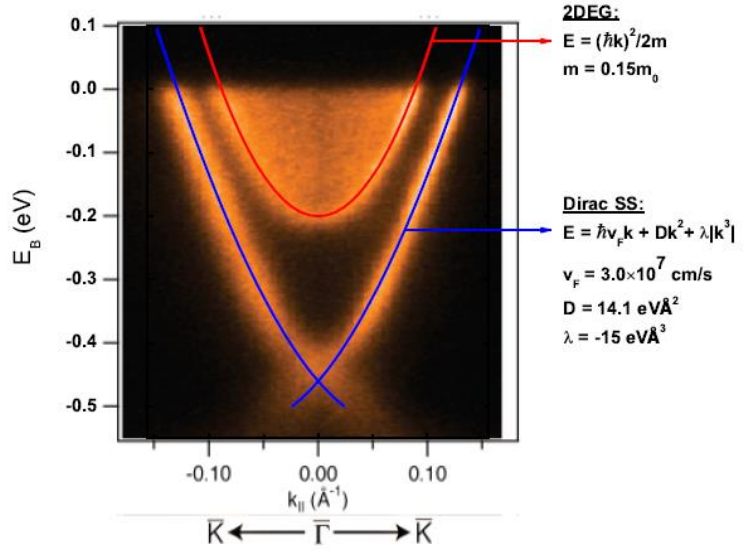


Luo et al., Nano Lett. (2013)

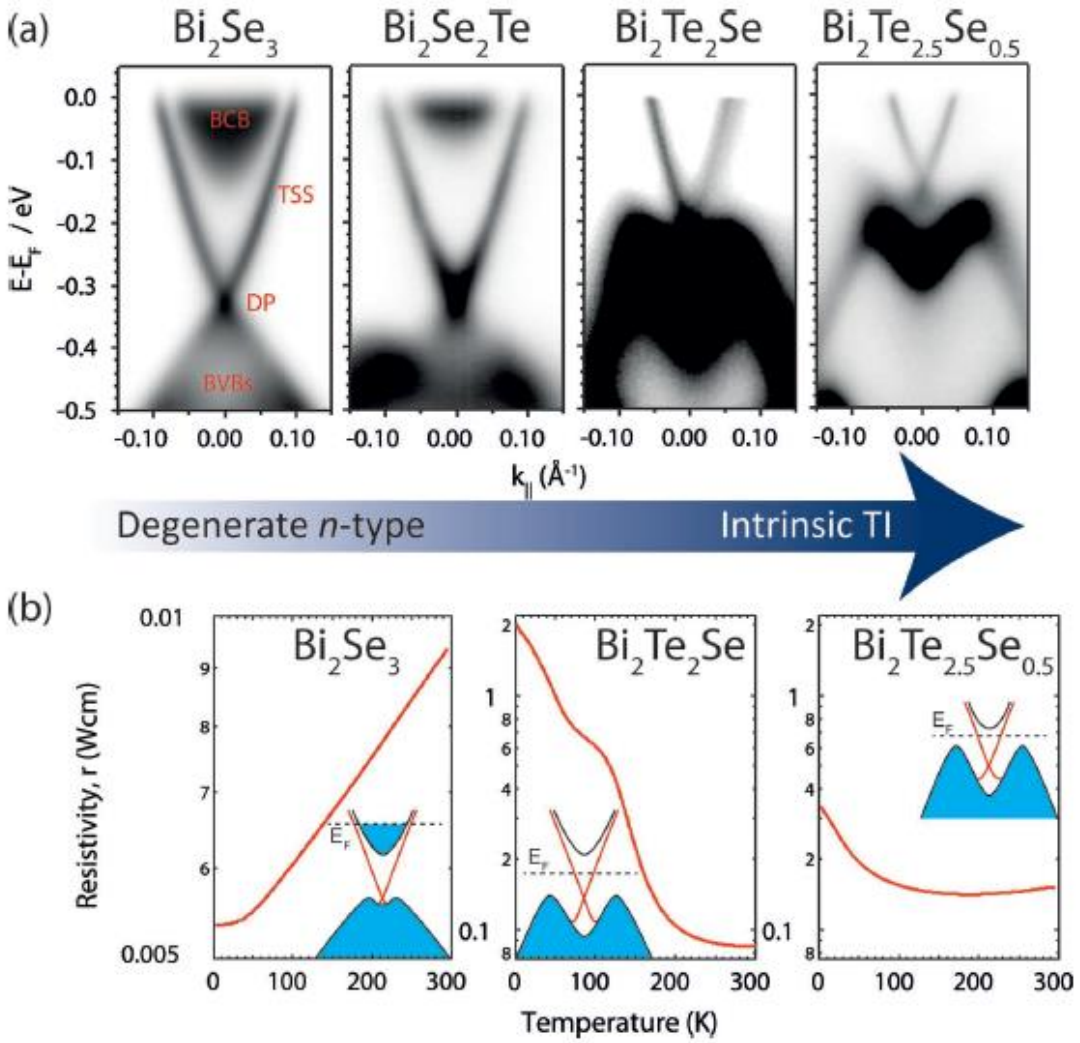
Estimate the surface charge carrier density : *SdH* oscillations ($n_s = \frac{{k_F}^2}{4\pi}$)



Estimate the surface charge carrier density : ARPES

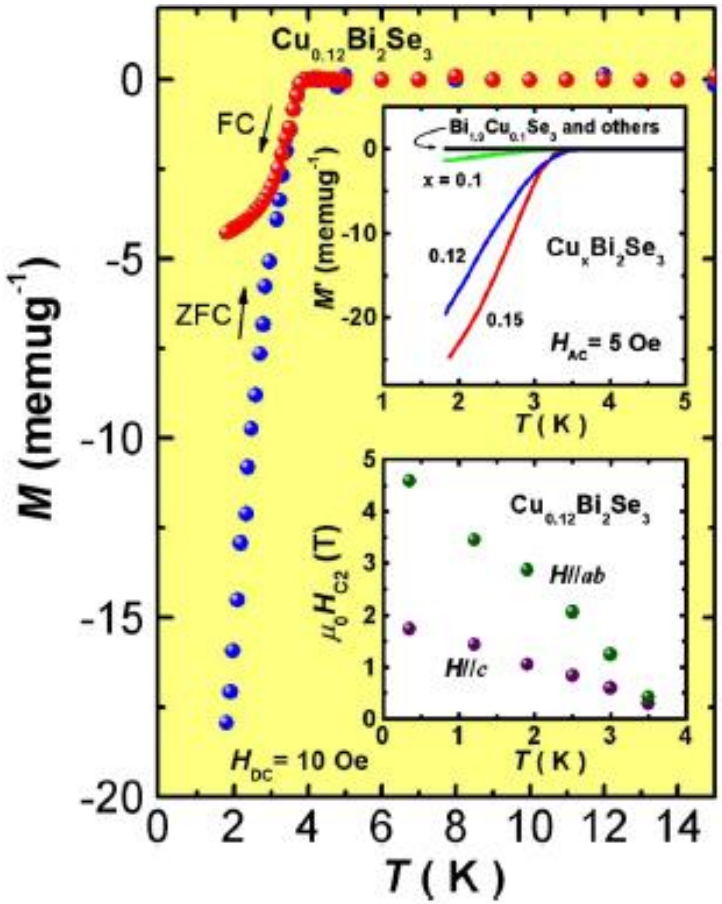


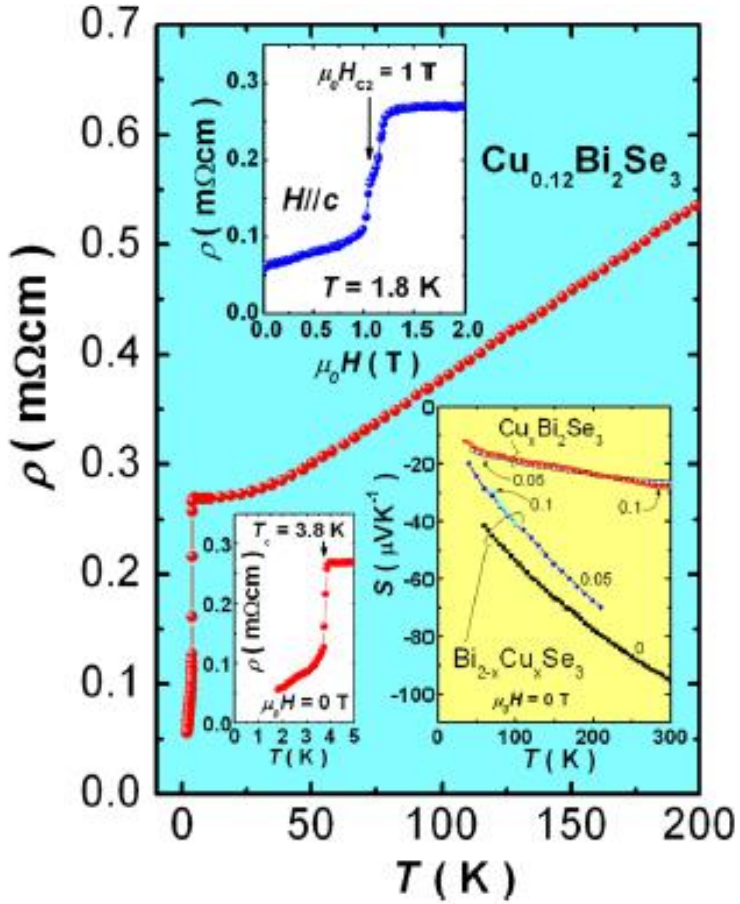
Tuning the position of the Dirac point in ternary topological insulators



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

Superconductivity in Cu doped Bi_2Se_3 compound

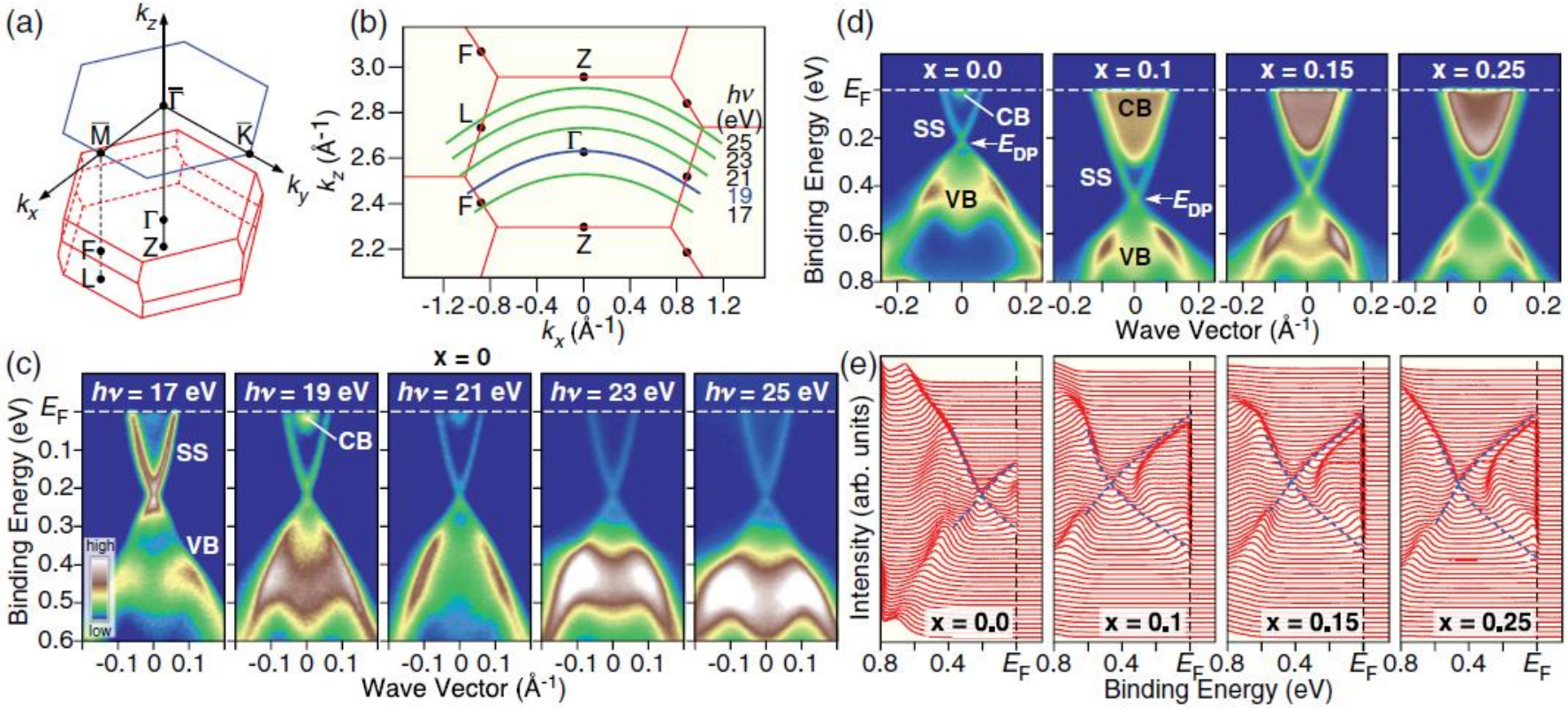




Hor et al., PRL (2010)

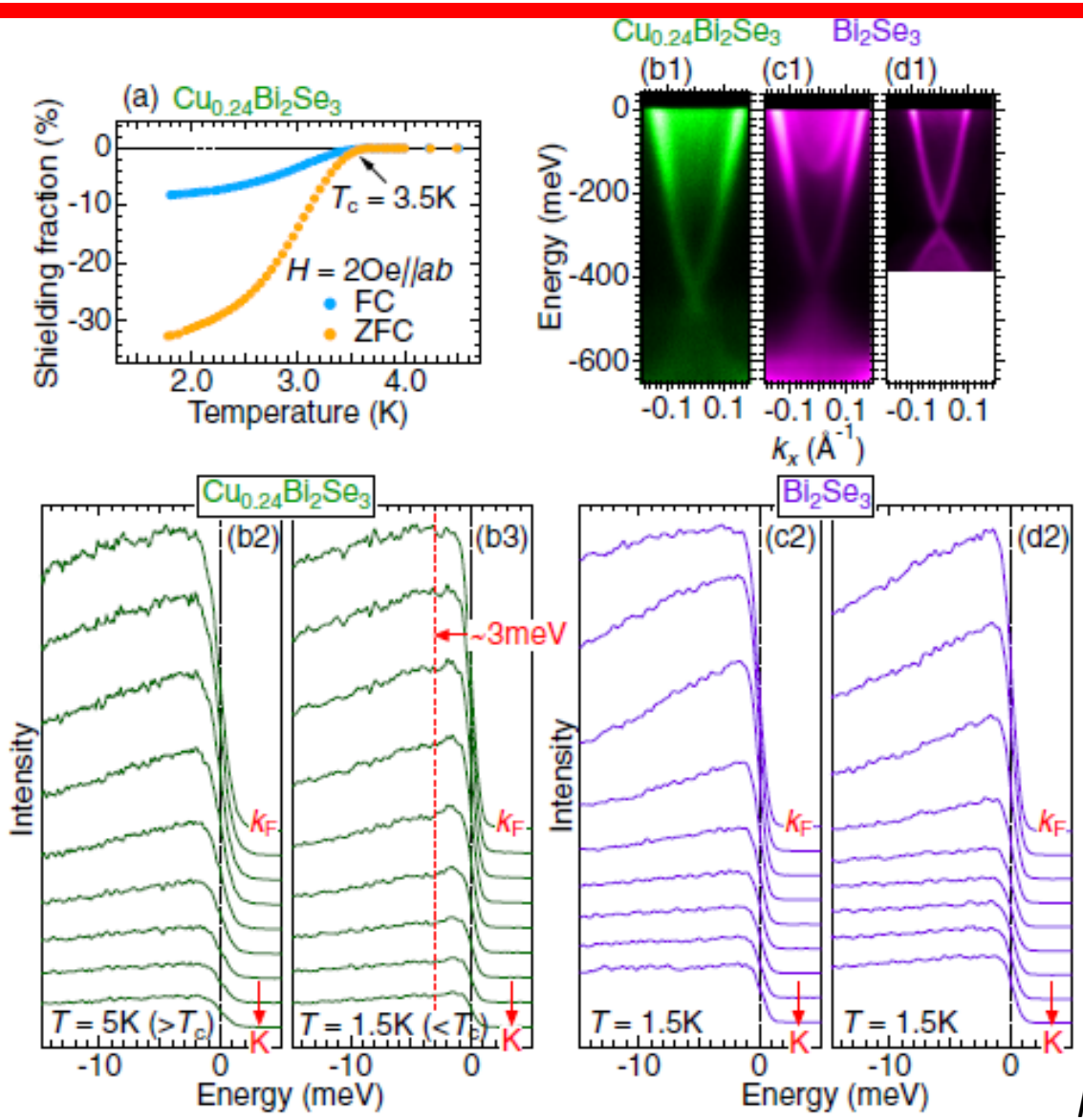
$Cu_xBi_2Se_3$ for 0.1<x<0.15

Superconductivity in Cu doped Bi_2Se_3 compound



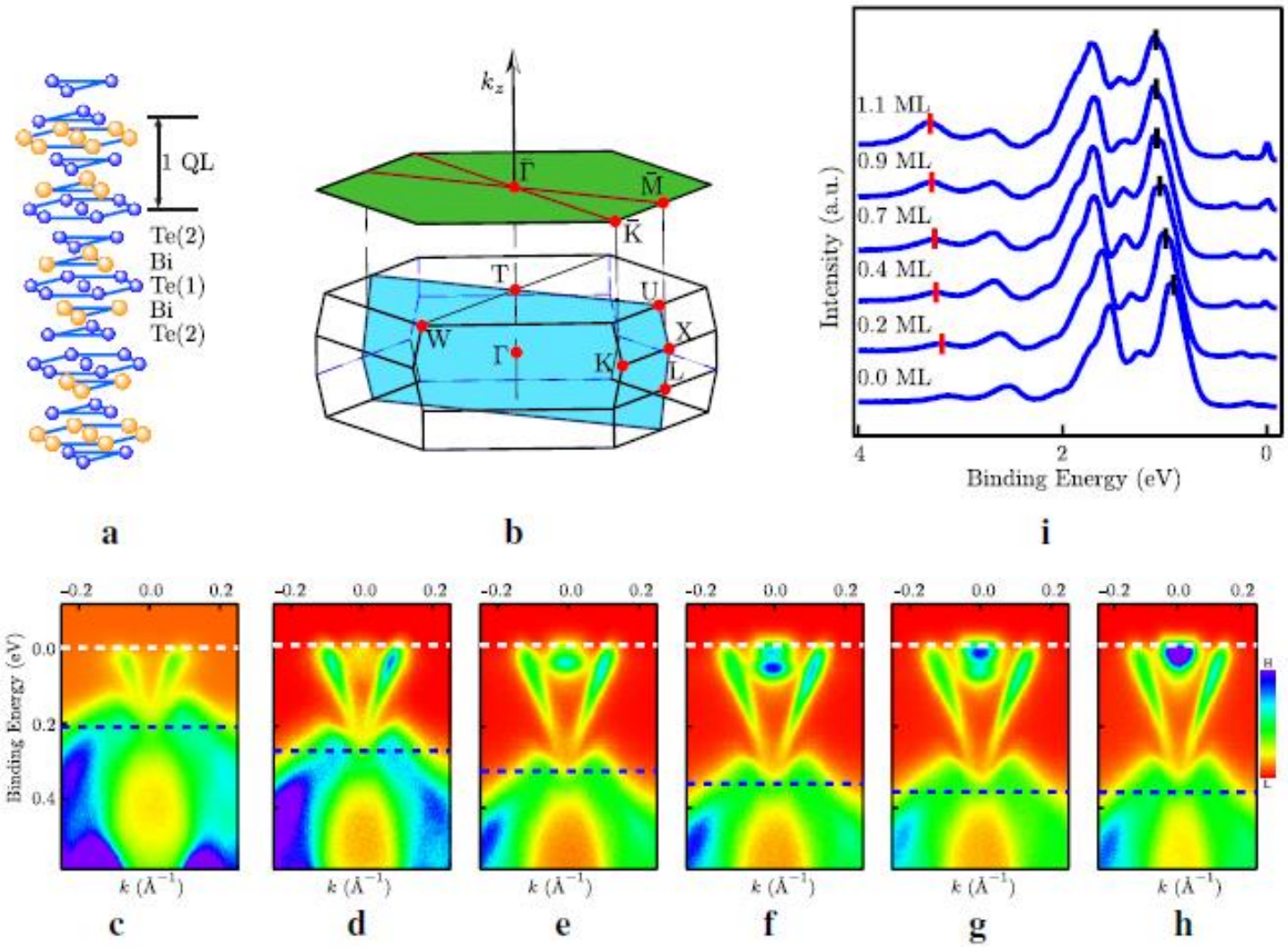
Tanaka et al., PRB (2012)

Superconductivity in Cu doped Bi_2Se_3 compound



Kondo et al., PRL (2013)

Cu doped epitaxial Bi_2Te_3 thin films

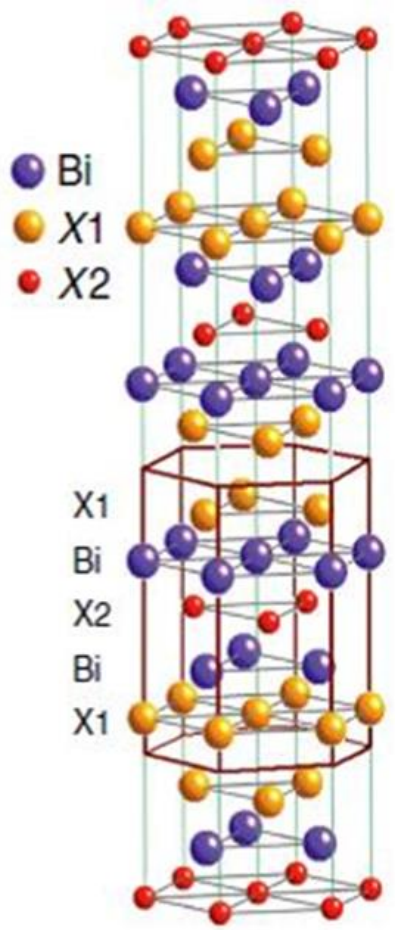


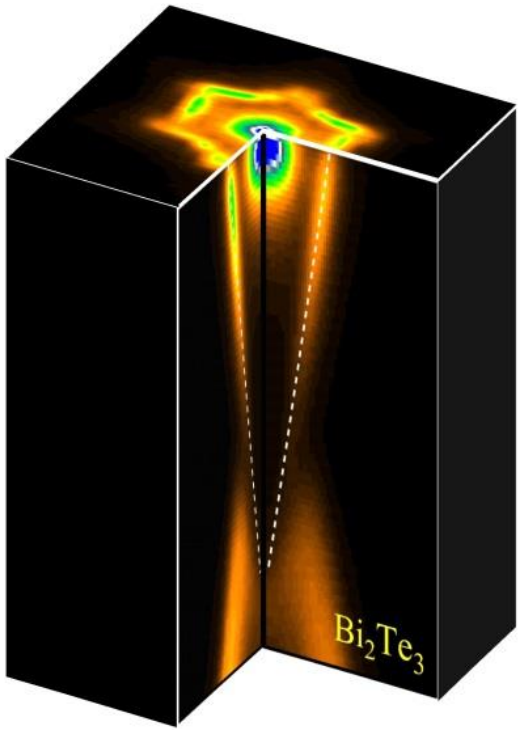
Zhu et al., Surf. Sci. (2013)

The crystal structure of Bi family TIs

Bi_2X1_2X2

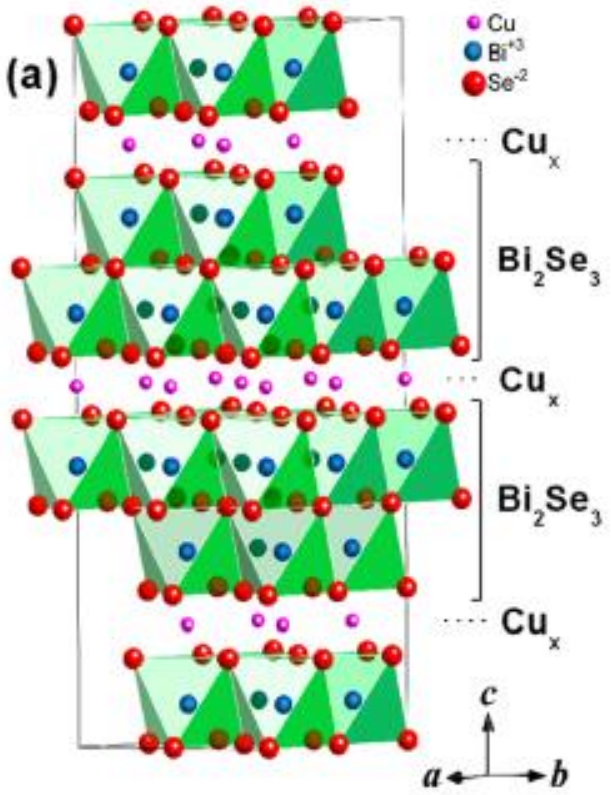
- Bi_2Te_2Se
- Bi_2Se_3
- Bi_2Te_3





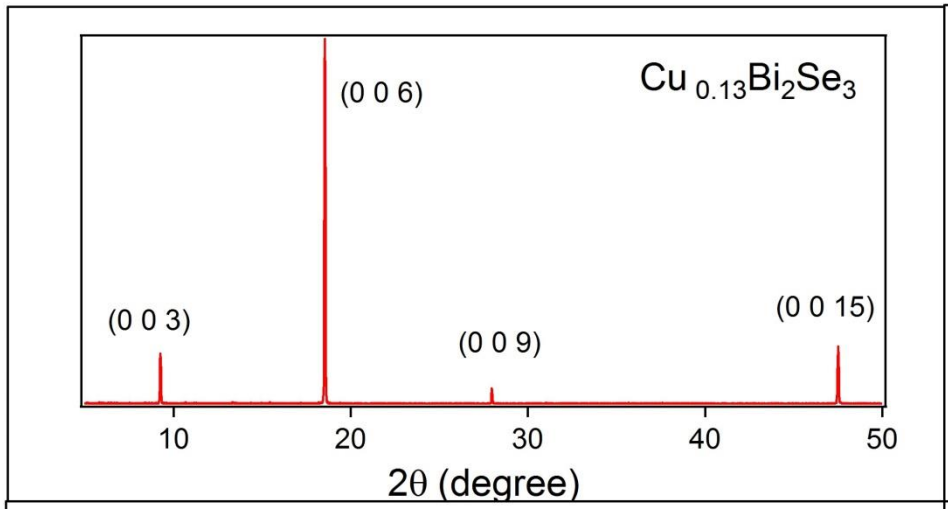
The role of Cu atoms in Cu doped Bi_2Se_3 and Bi_2Te_3 topological insulators

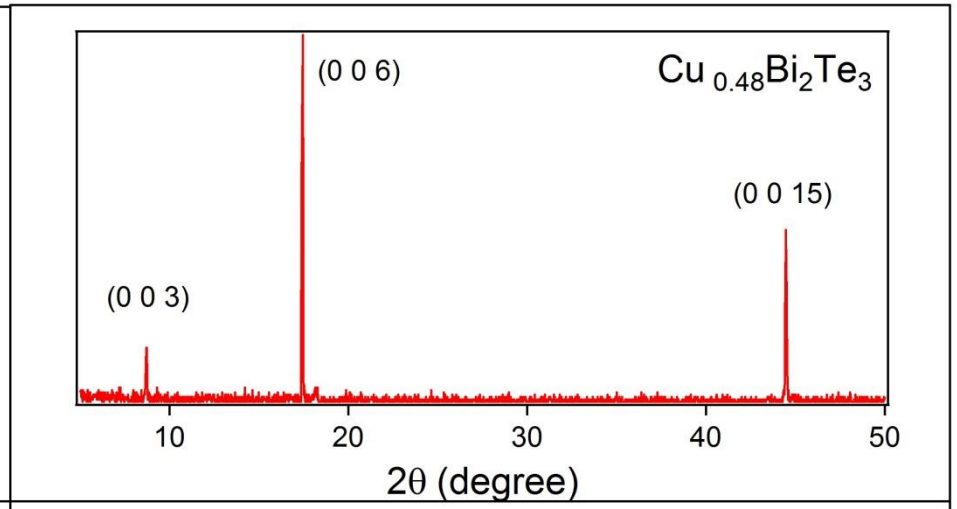
$Cu_xBi_2Se_3$ or $Bi_{2-x}Cu_xSe_3$?

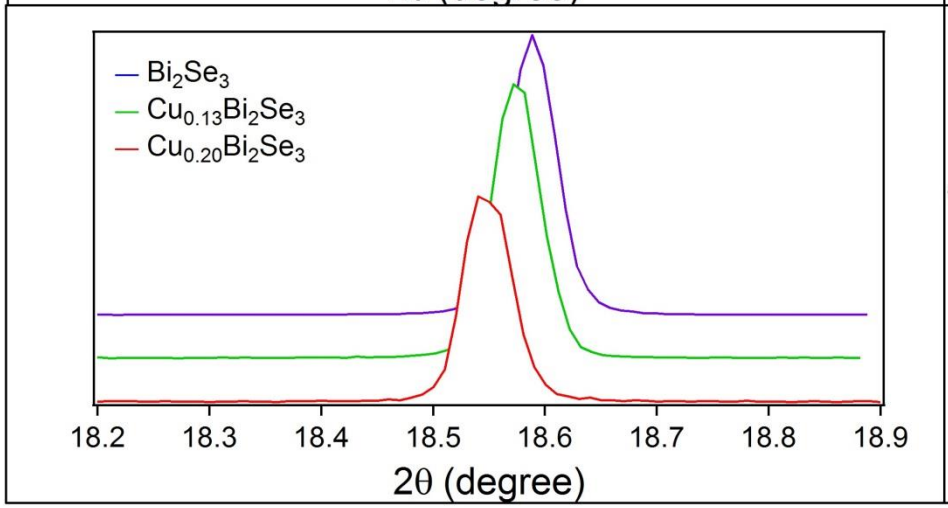


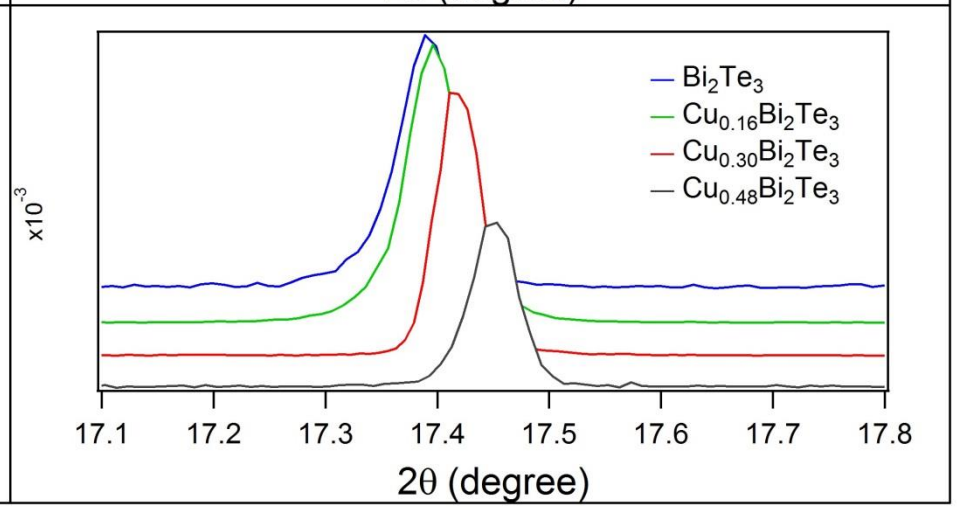
Hor et al., PRL (2010)

XRD results of Cu doped Bi_2Se_3 and Bi_2Te_3 TIs





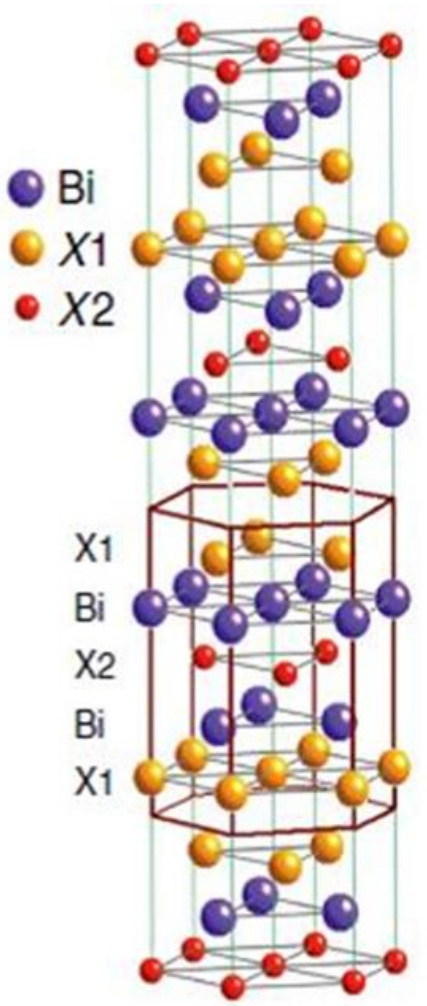




Lattice constant of Cu doped Bi_2Se_3 and Bi_2Te_3

Bi_2X1_2X2

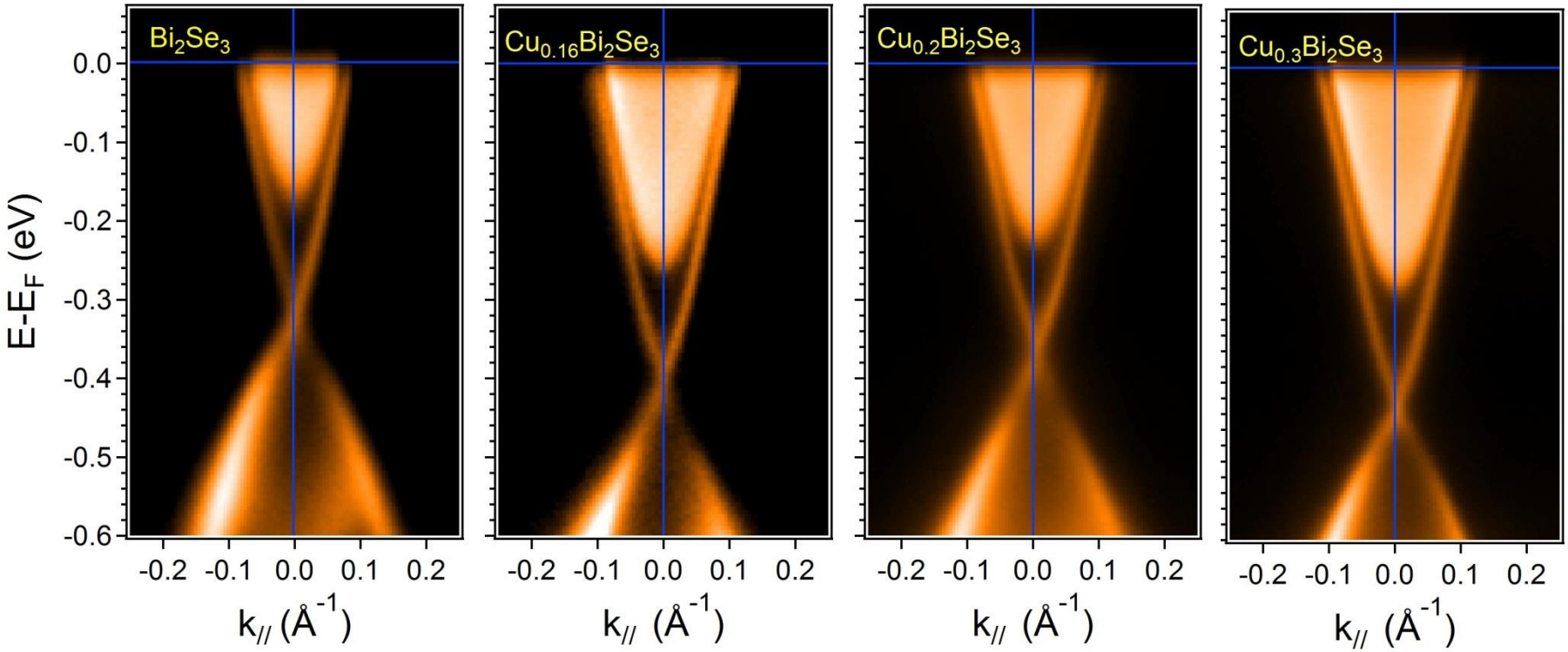
$\begin{bmatrix} Bi_2Te_2Se \\ Bi_2Se_3 \\ Bi_2Te_3 \end{bmatrix}$



Concentration of Cu doped in Bi_2Se_3	Lattice constant along c-axis (Å)
undoped	28.620
0.16	28.642
0.2	28.660

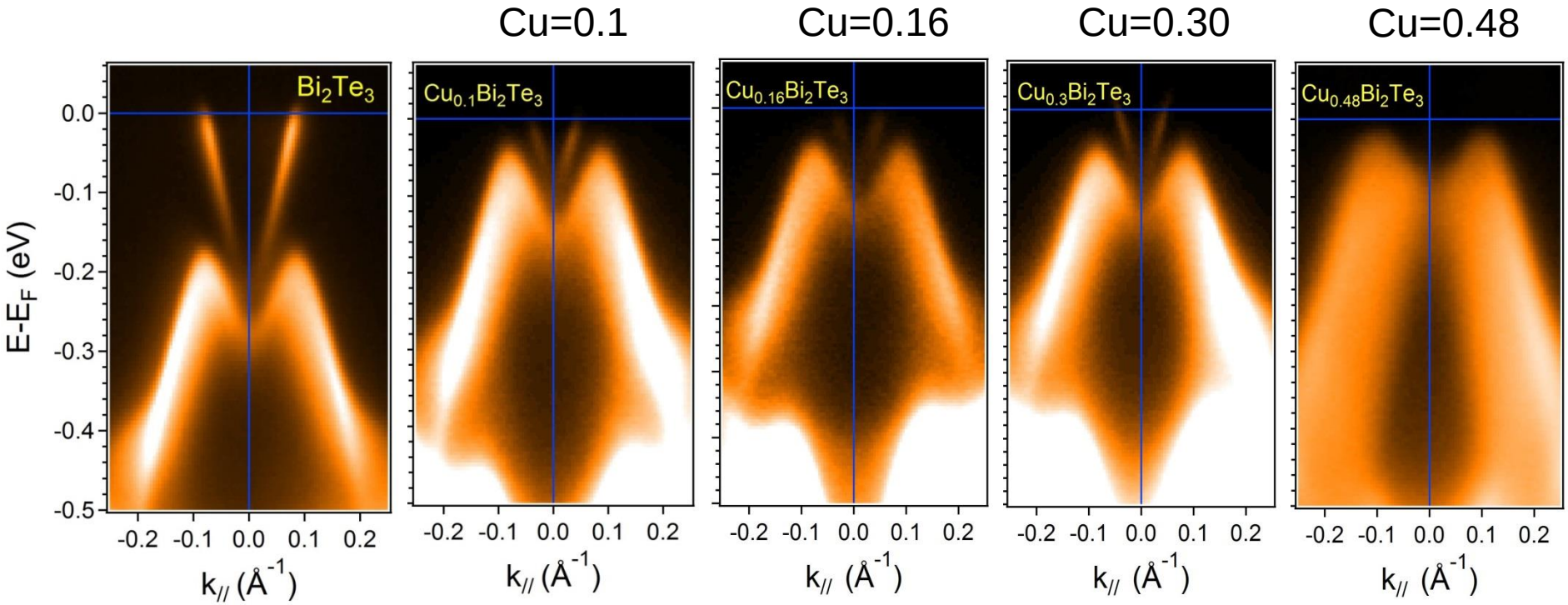
Concentration of Cu doped in Bi_2Te_3	Lattice constant along c-axis (Å)
undoped	30.574
0.16	30.562
0.30	30.522
0.48	30.463

ARPES results of Cu doped Bi_2Se_3 TIs

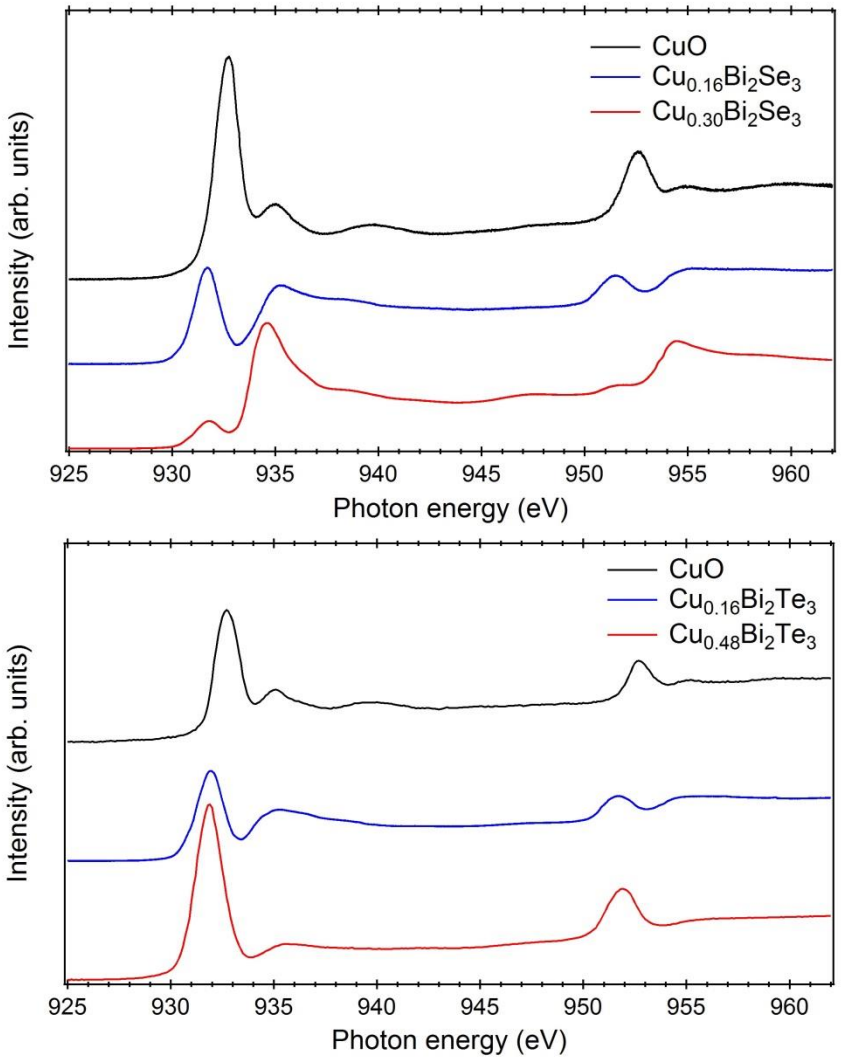


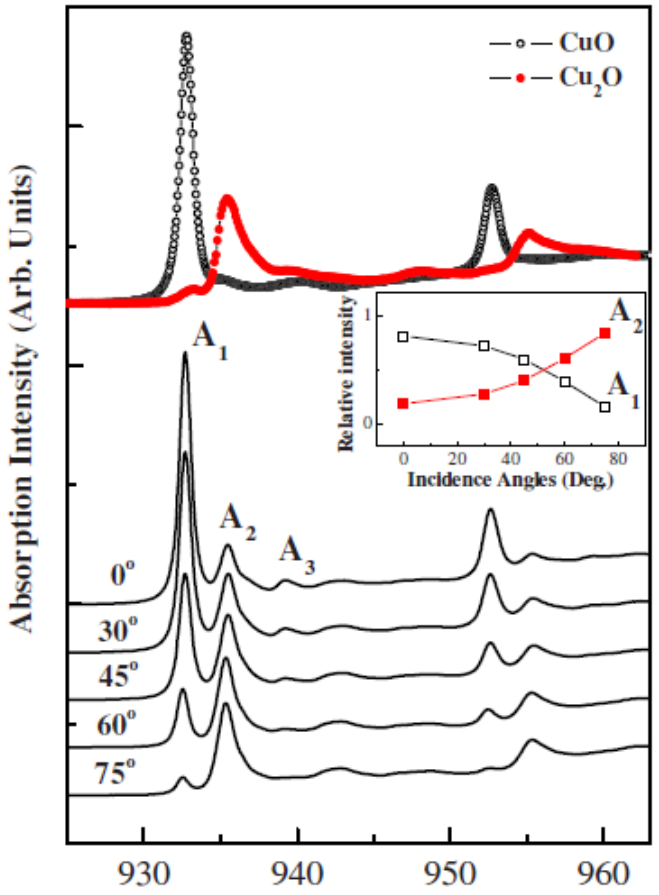
Cheng et al., submitted to PRB

ARPES results of Cu doped Bi_2Se_3 TIs



XAS results of Cu doped Bi_2Se_3 and Bi_2Te_3 TIs

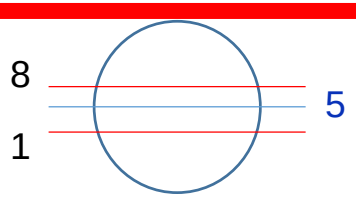




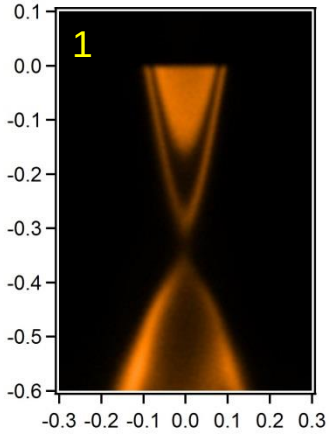
Chen et al., PRB 78, 214105 (2008)

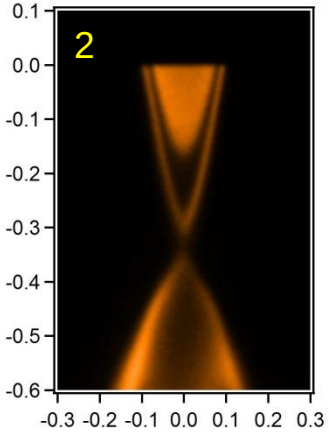
Light element doped TIs

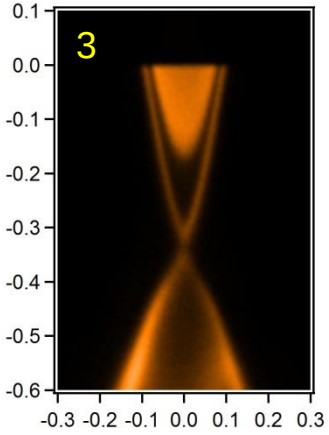
#C4/第一批/C=0.08

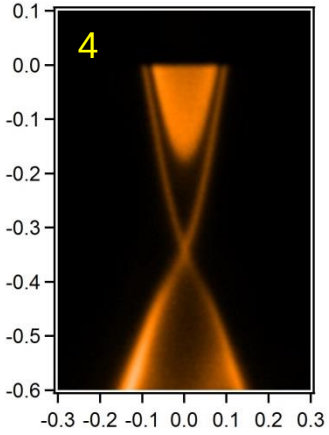


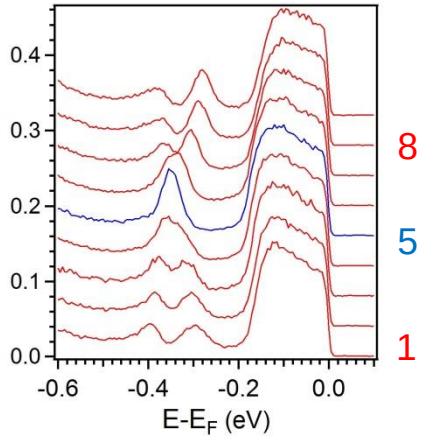
EDC at Γ with varied tilting ang

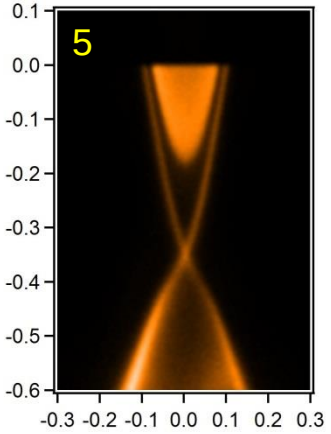


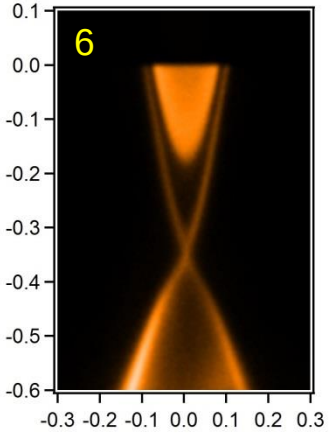


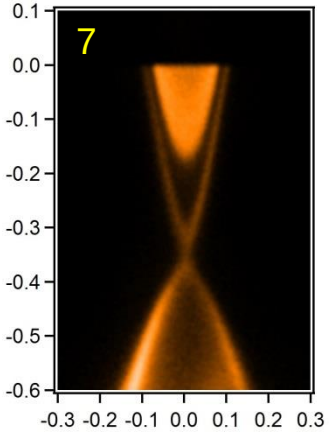


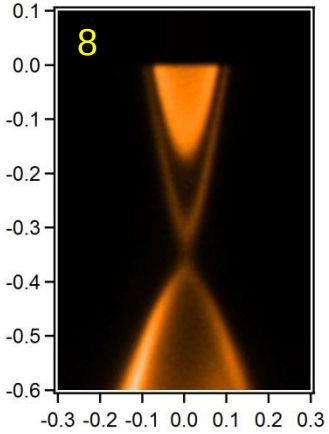


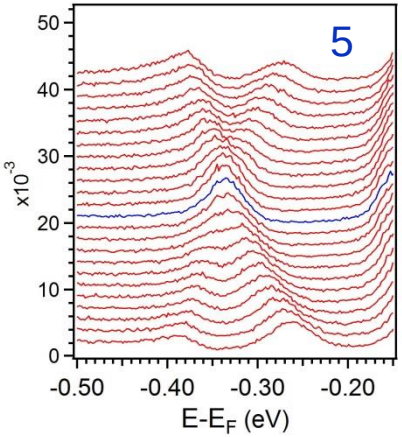




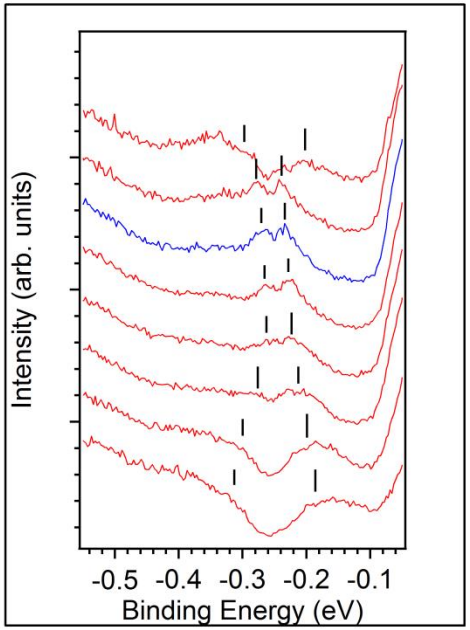


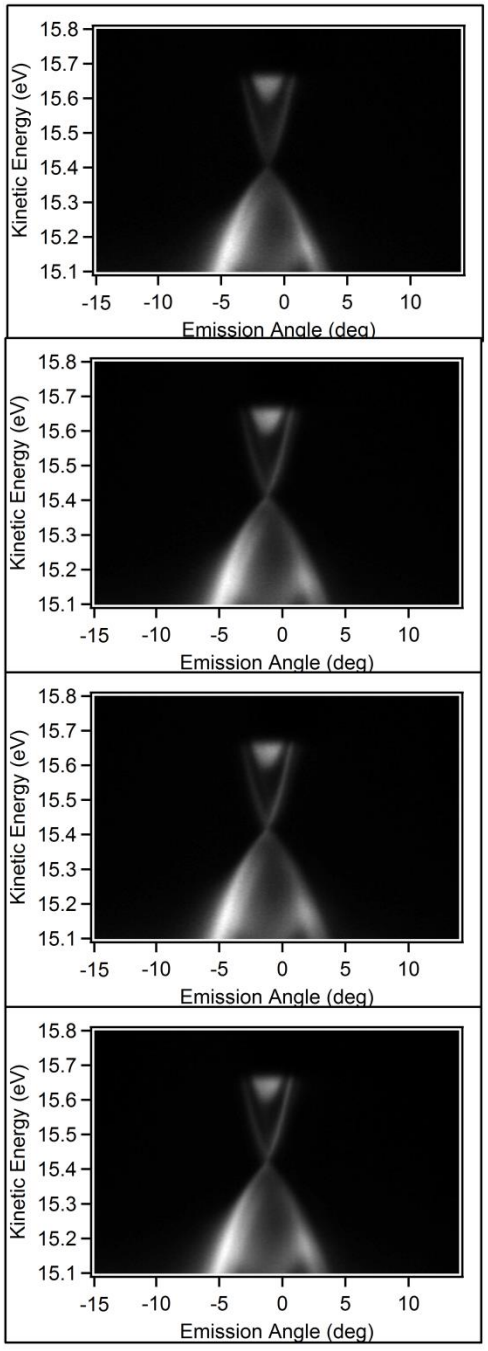


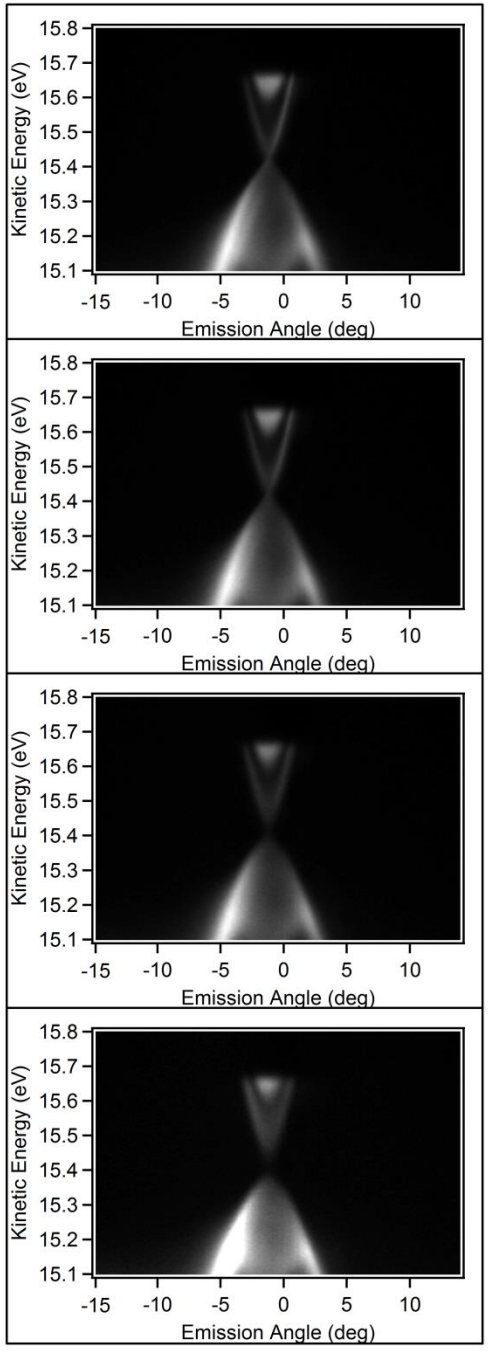


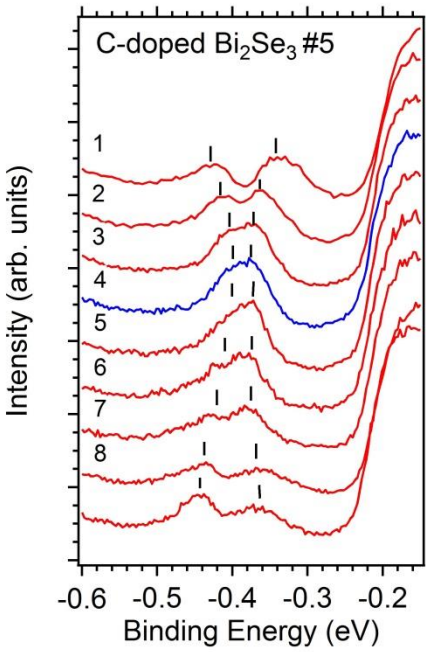


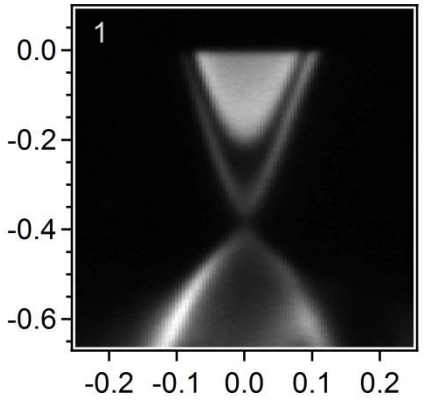
C-doped Bi_2Se_3 #3
Possible gap ~ 48 meV

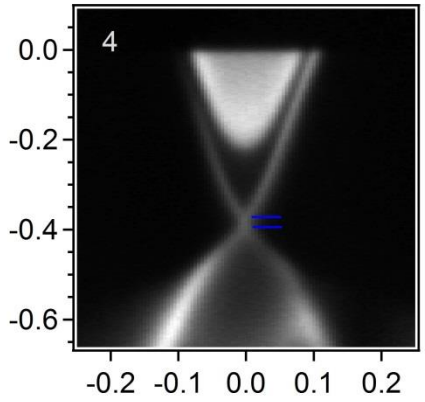


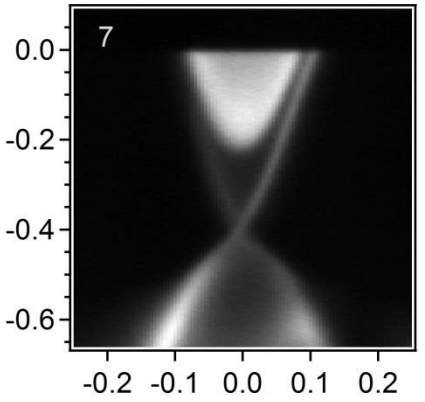


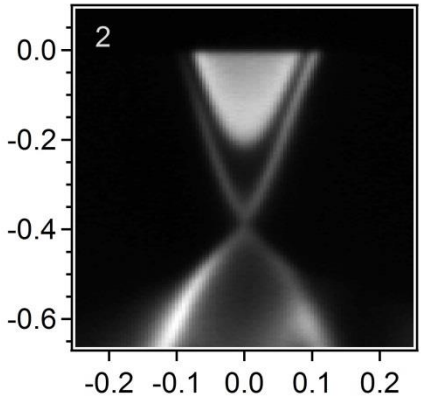


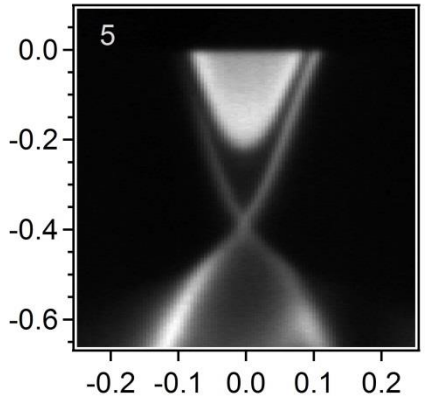




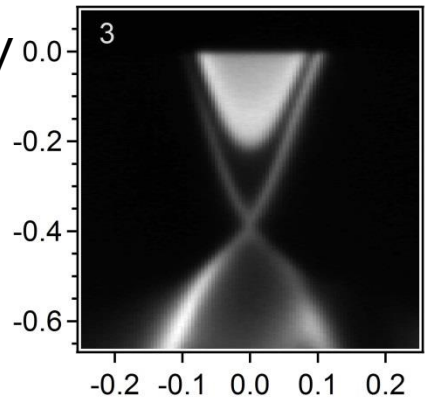


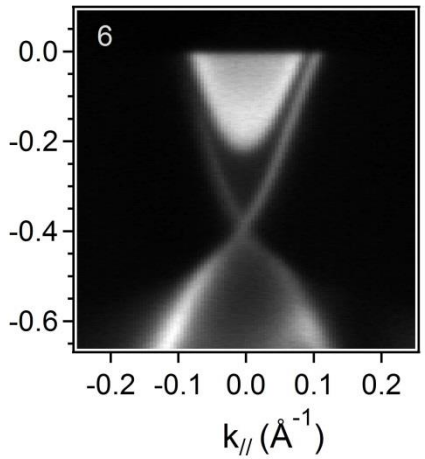






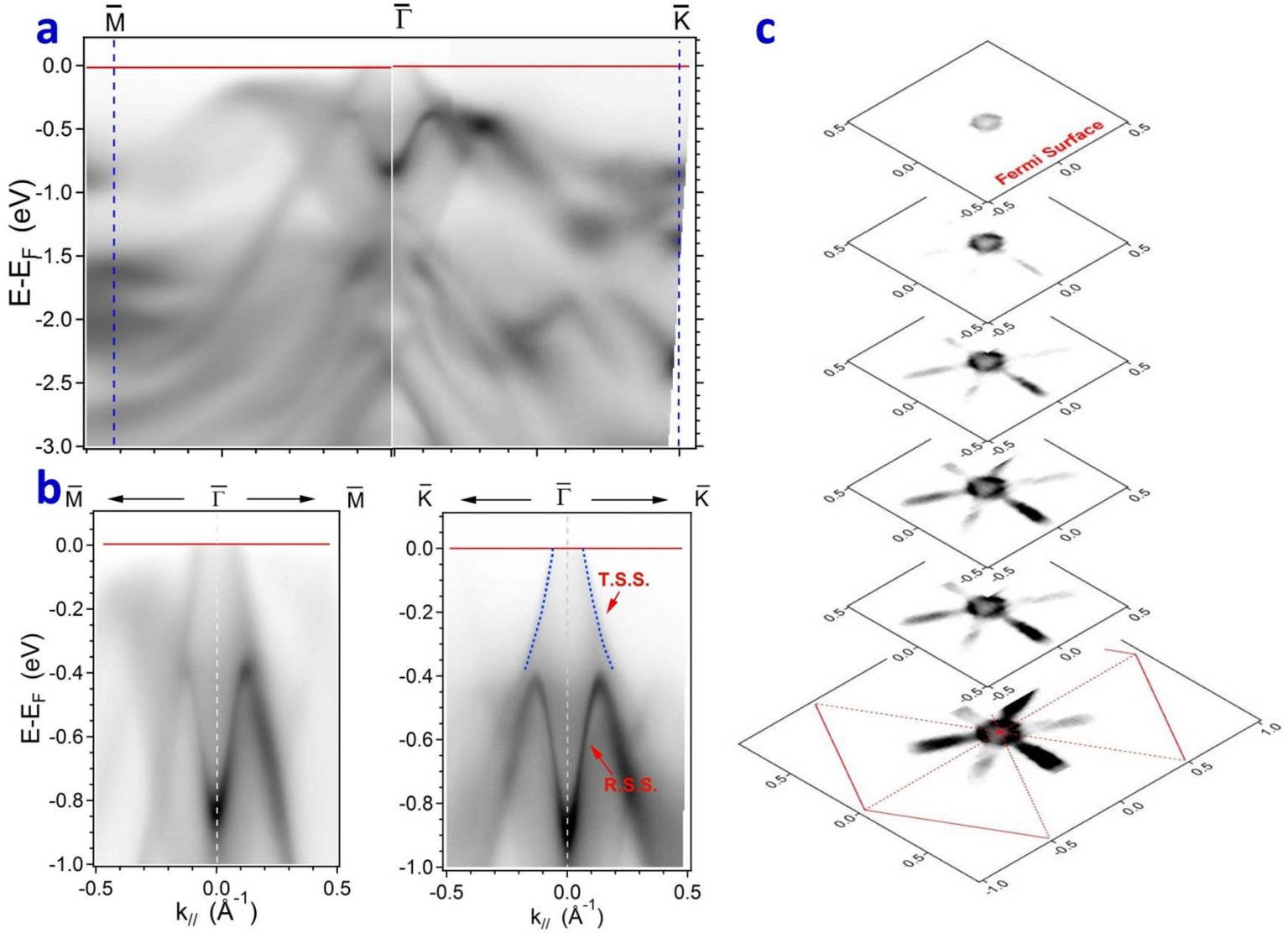
C-doped Bi2Se3 #5
Possible gap ~ 24 meV



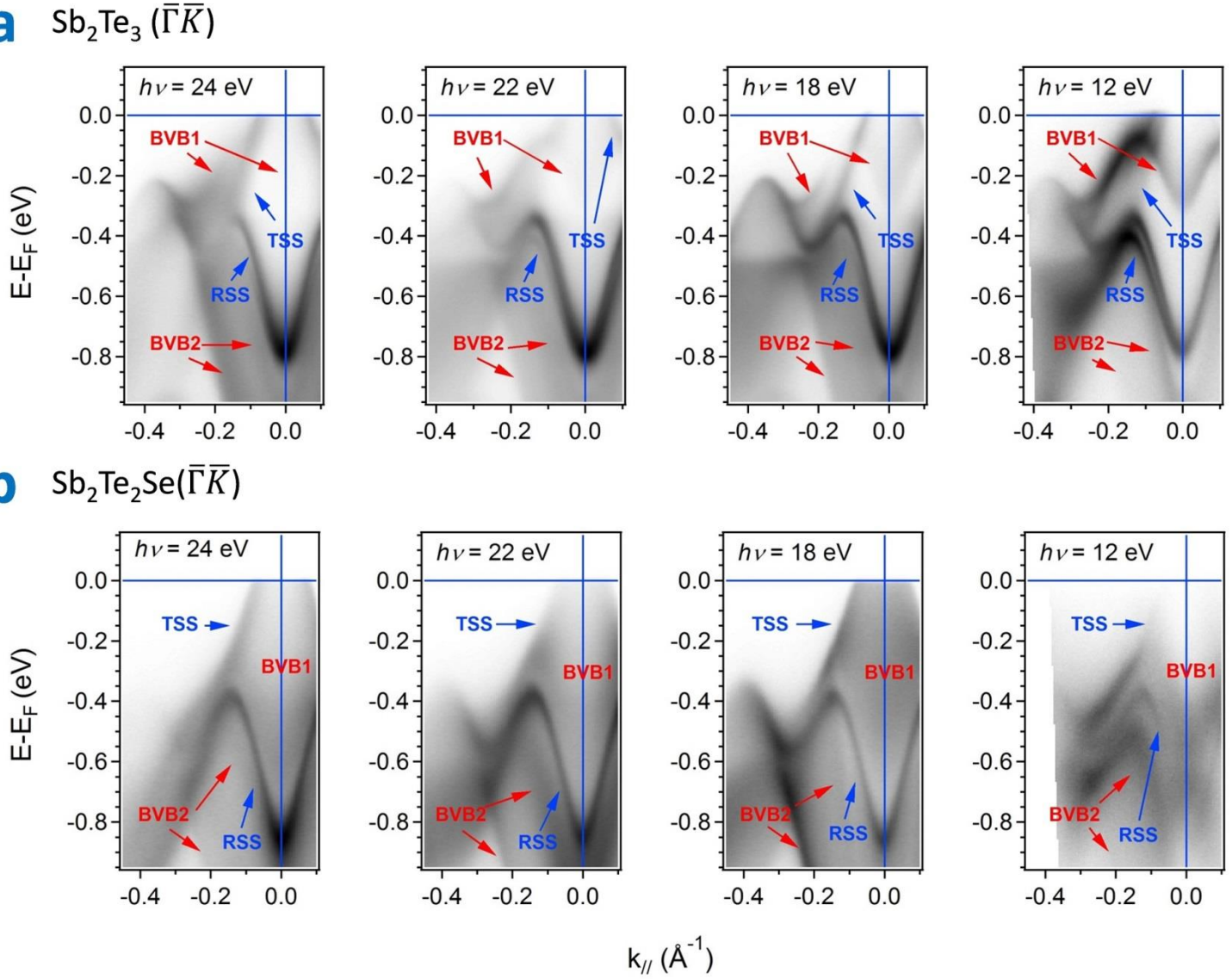


Carbon site?
Se site 1 or Se site 2?

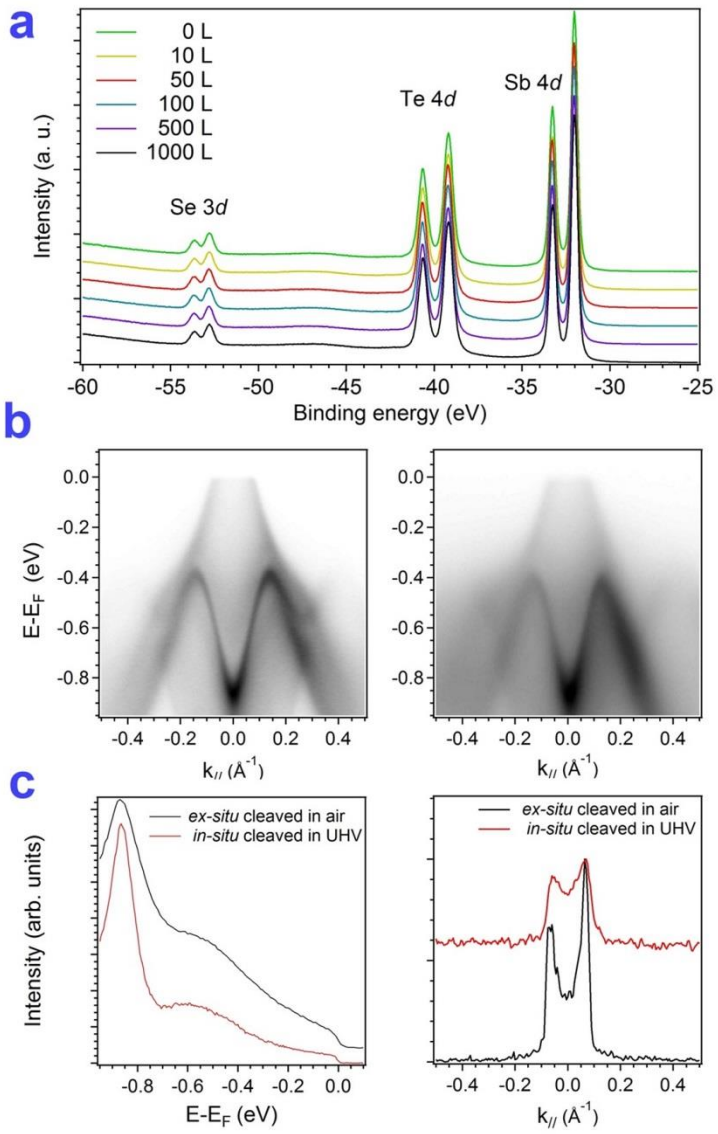
The electronic structure of Sb_2Te_2Se

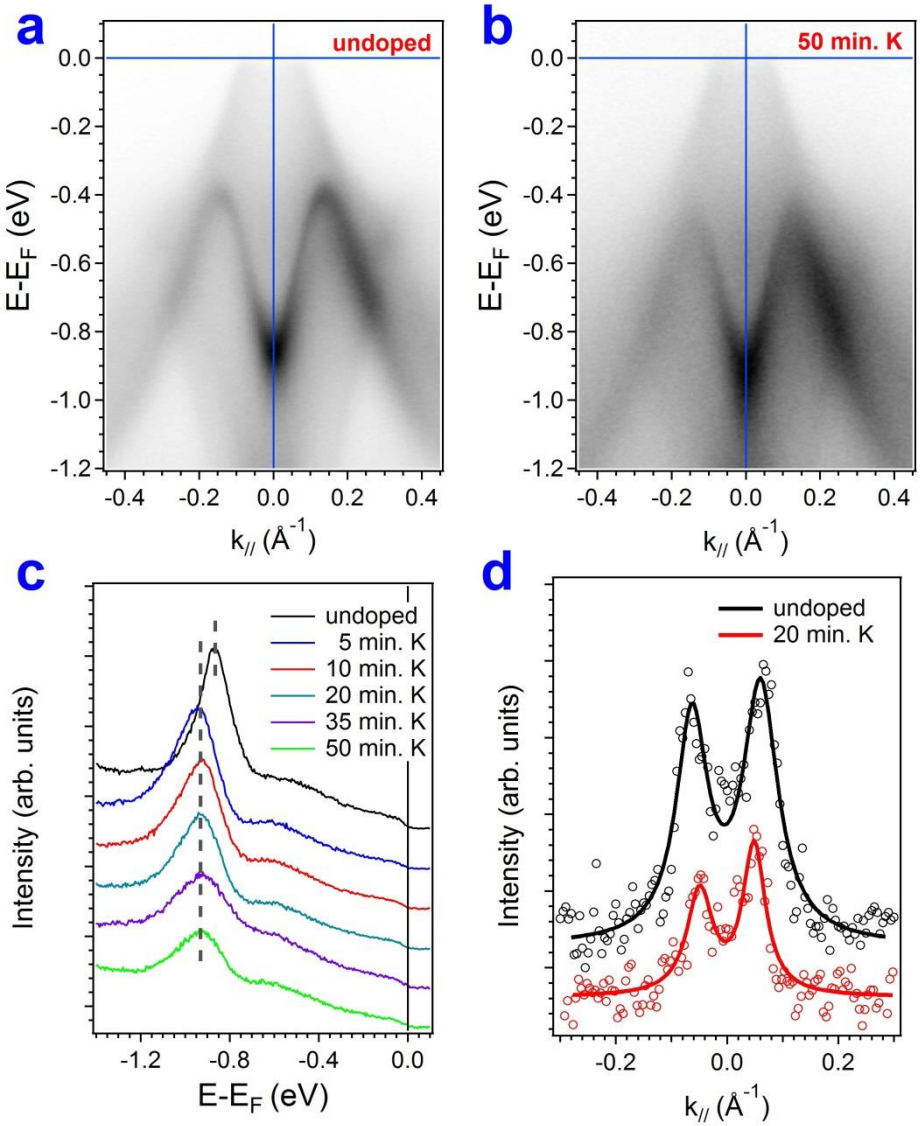


Comparison of Sb_2Te_3 and a Sb_2Te_2Se



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

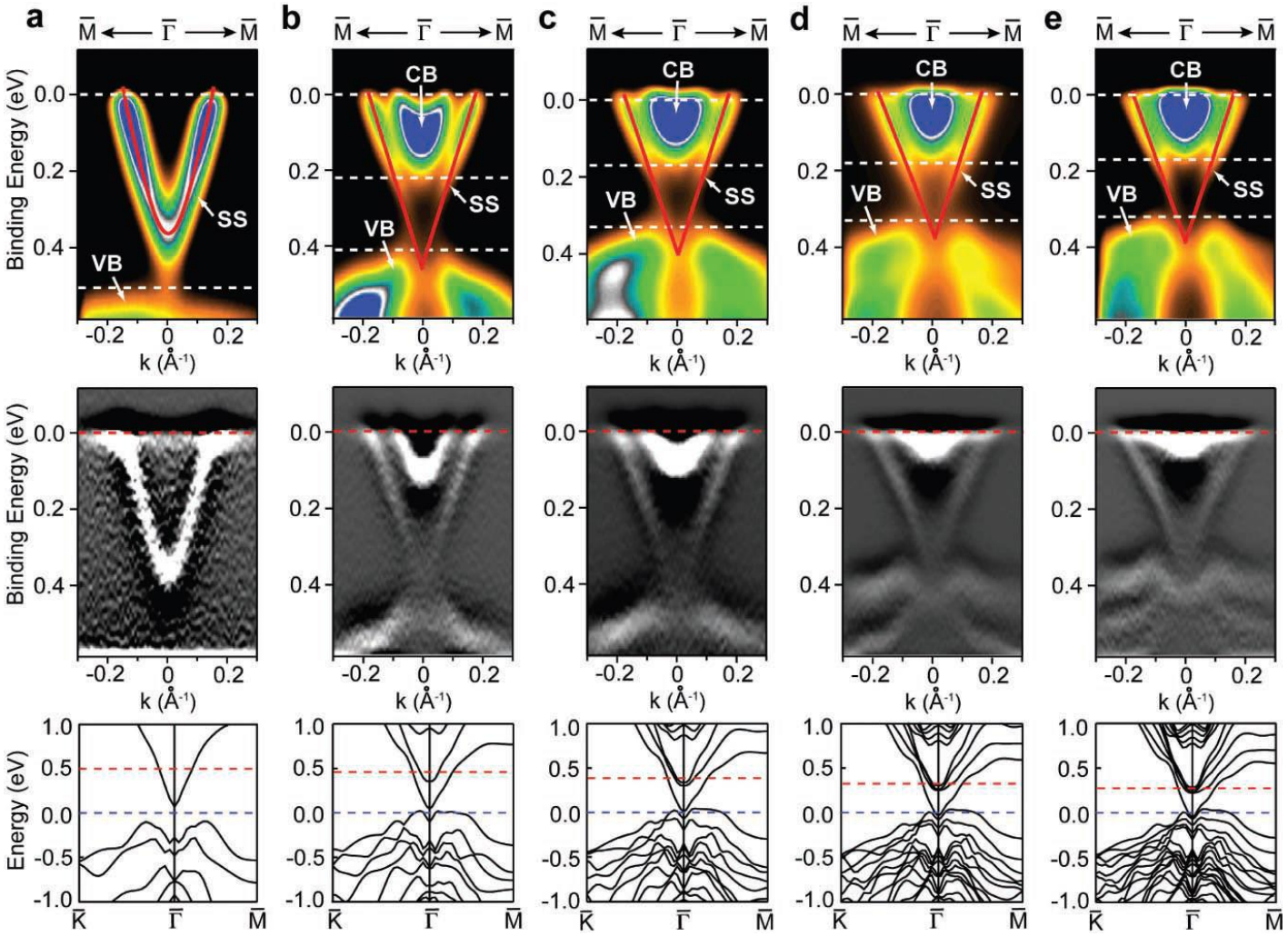




Toward future electronic devices

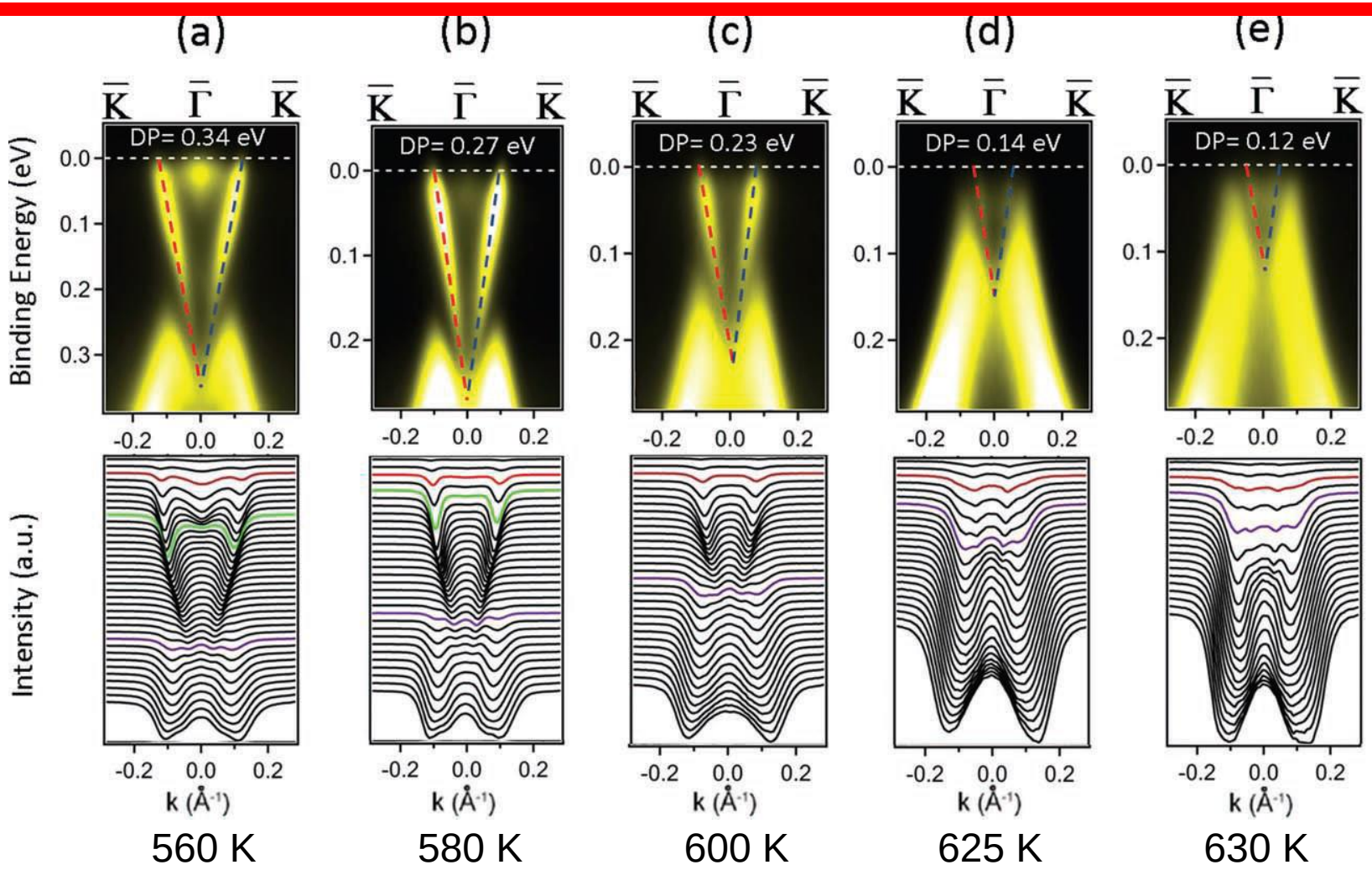
MBE growth topological insulators (Bi_2Te_3)

Bi_2Te_3/Si



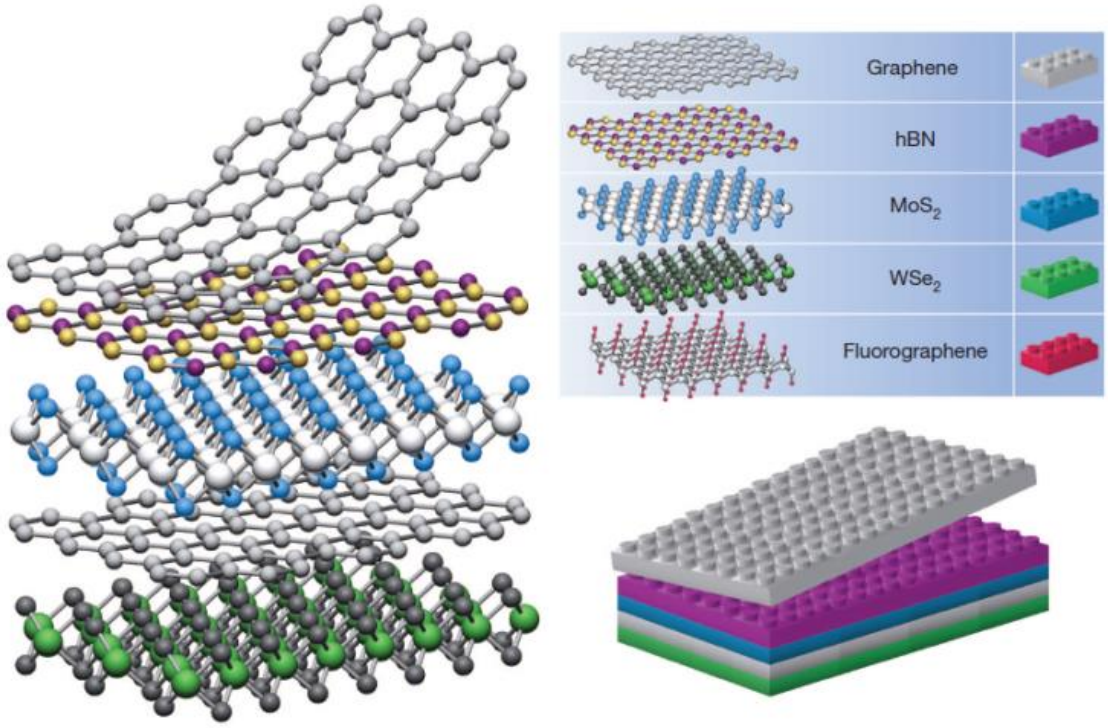
Li et al., Adv. Mat. (2010)

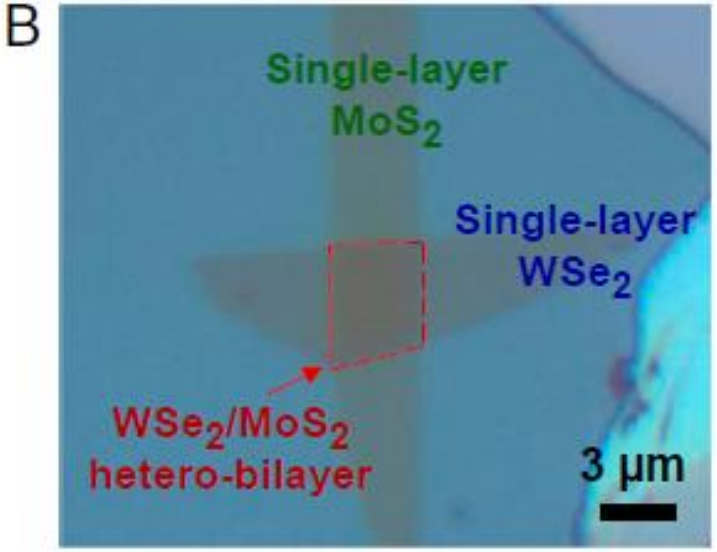
Temperature effect on MBE growth TIs



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

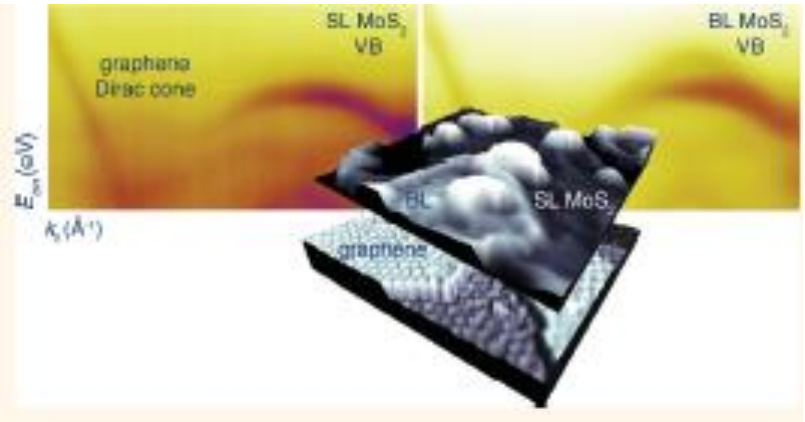
Van der Waals heterostructure

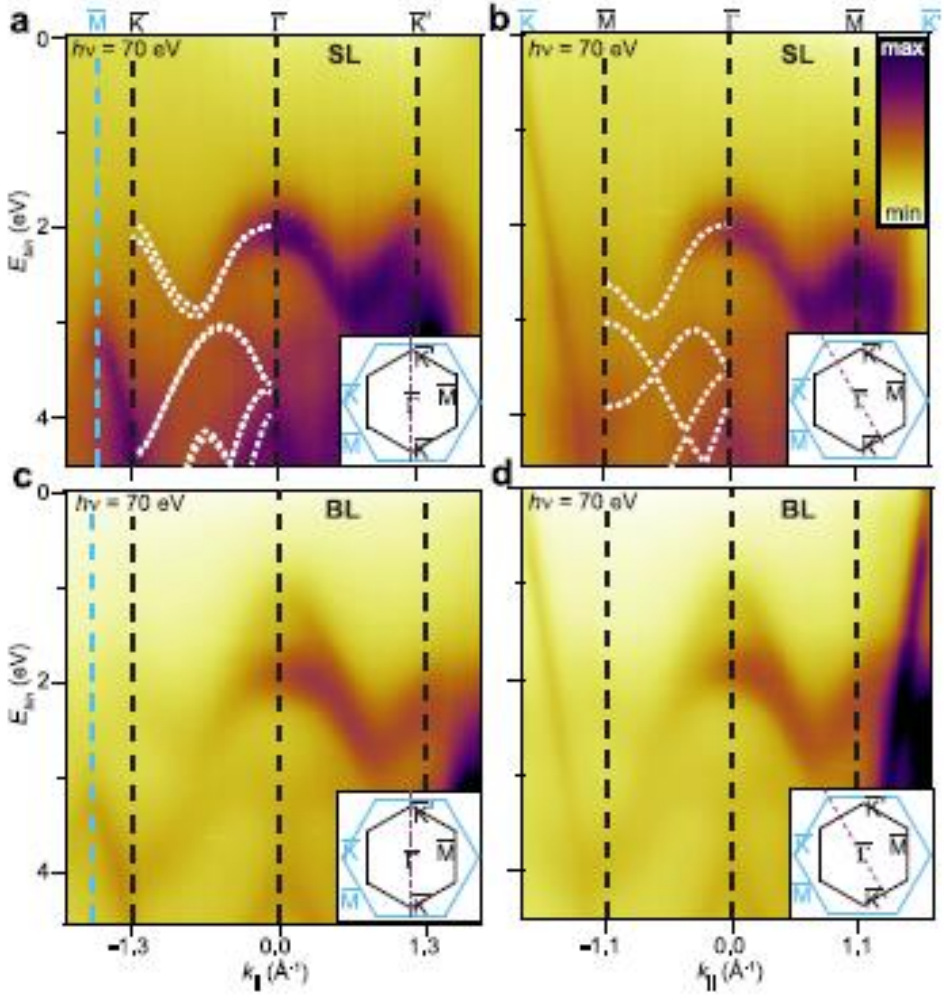




Ref : Geim, Nature (2013)

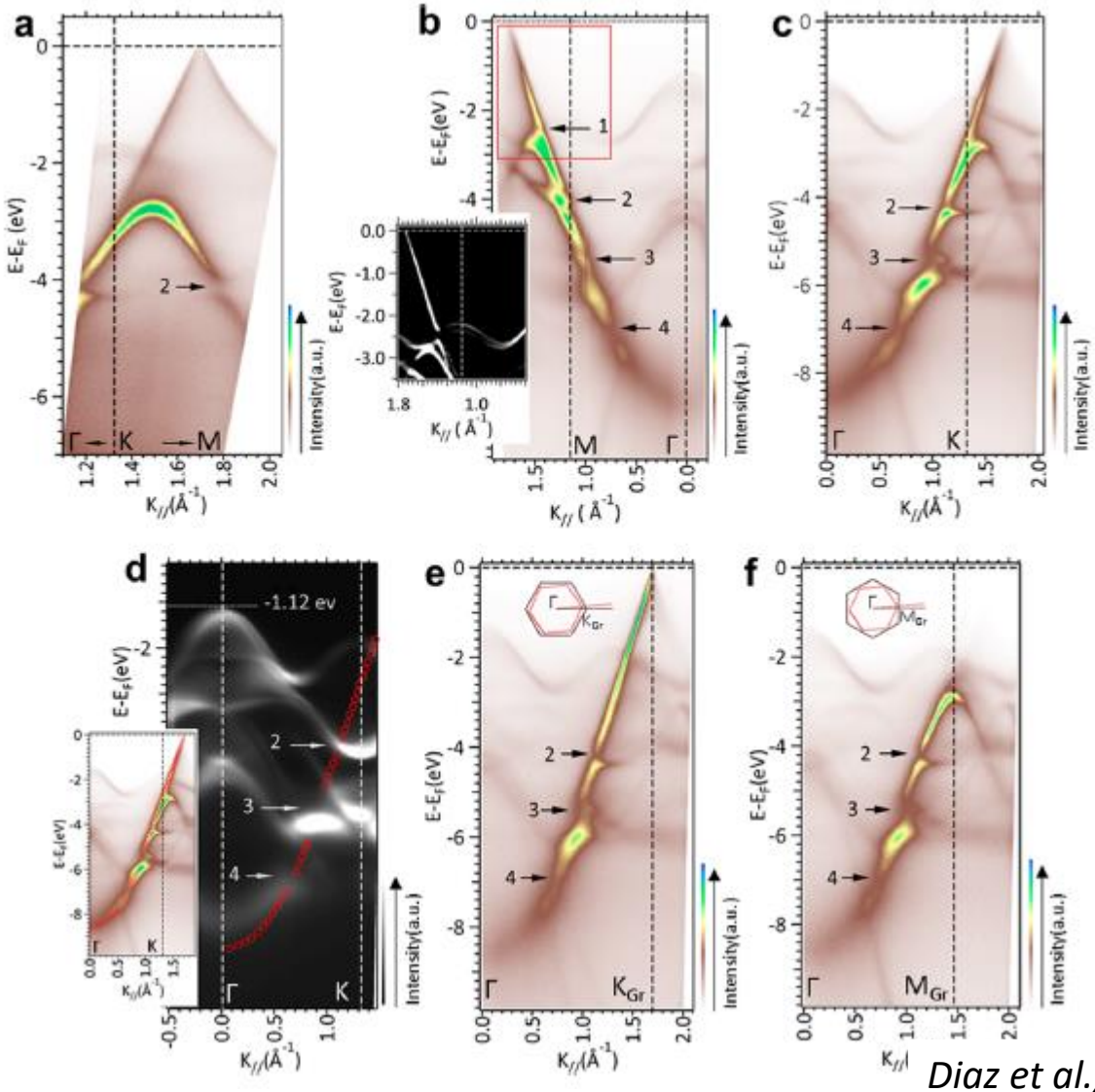
Van der Waals heterostructure : MoS_2/graphene





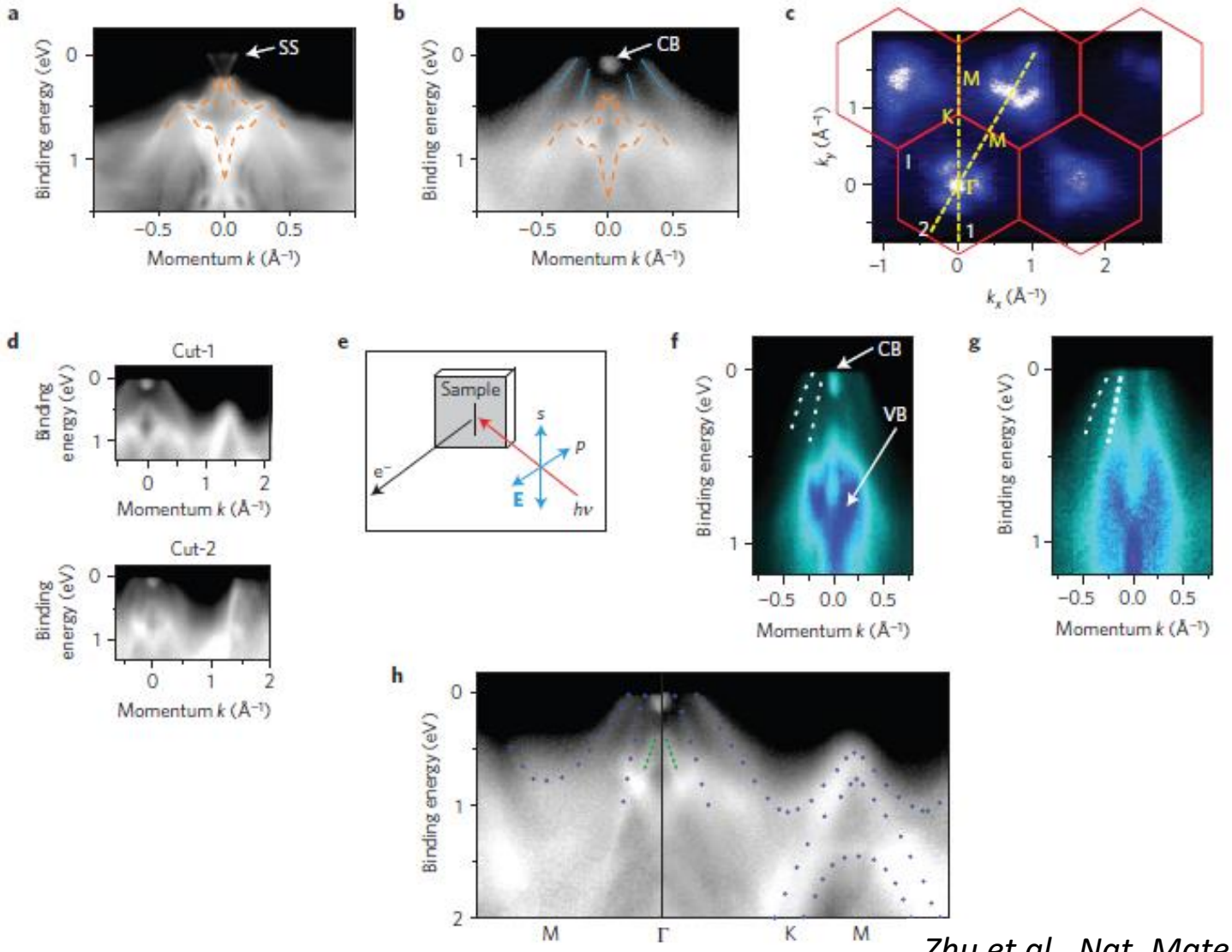
Miwa et al., ACS Nano (2015)

Van der Waals heterostructure : Graphene/MoS_2



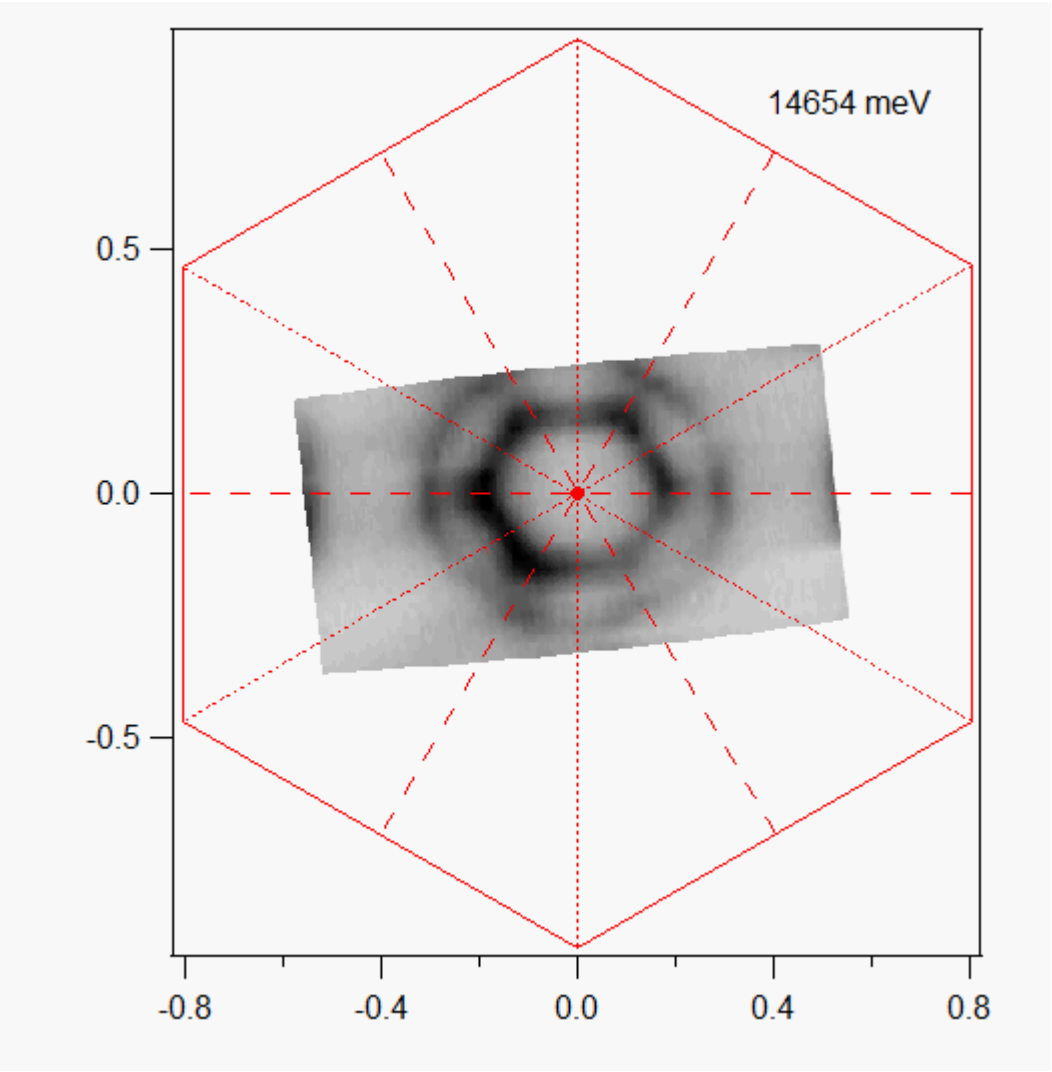
Diaz et al., Nano Lett. 2015

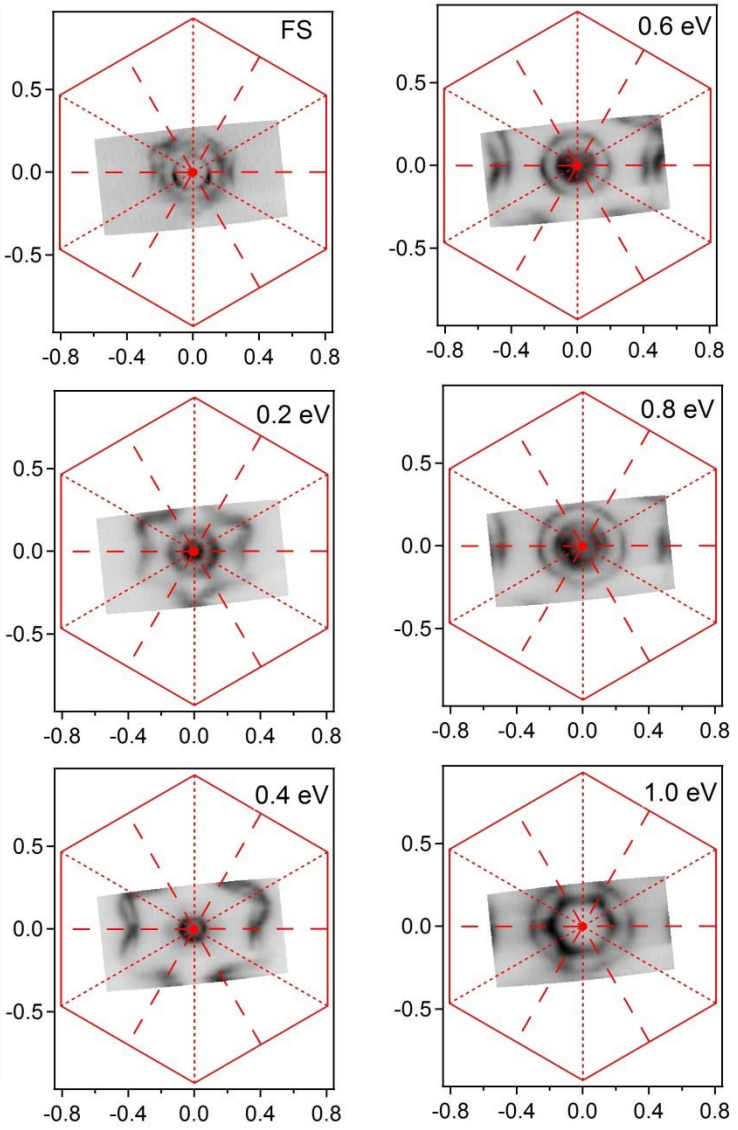
Hybrid nanostructure : Stanene/Bi_2Te_3



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

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Single Crystals

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Prof. Li-Wei Tu (Department of Physics, NSYSU)
Prof. Hung-Duen Yang (*Department of Physics, NSYSU)*

Single Crystals and pump-probe experiments

Prof. Chih-Wei Luo (Department of Electrophysics, NCTU)
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