2D materials beyond graphene: synthesis, properties and applications from the single layer toward the heterostructure

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Centre de Nanosciences et de Nanotechnologies (C2N)

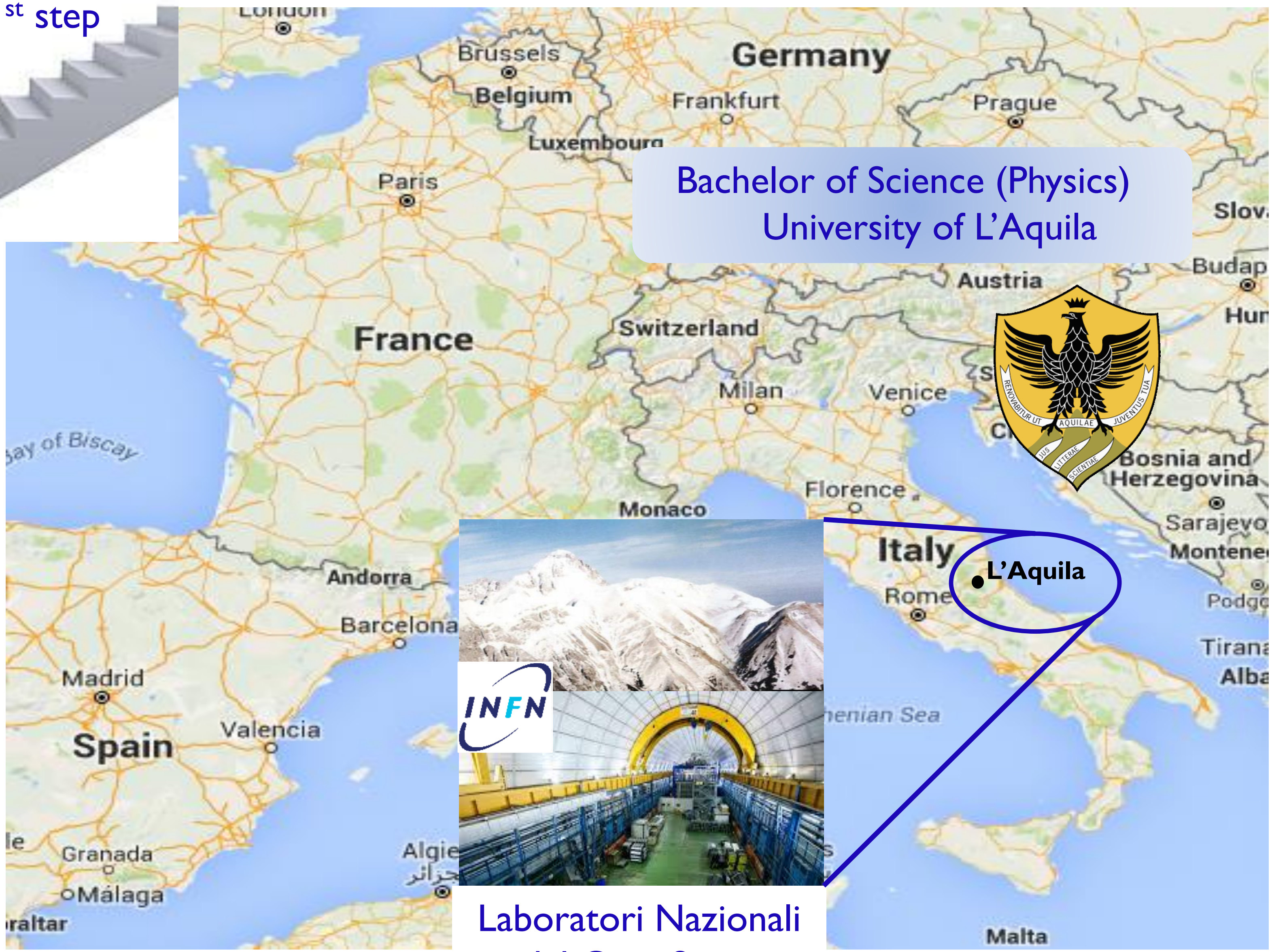
cnrs dépasser les frontières

université PARIS-SACLAY

Outlines

- Introduction to my scientific career
- Introduction on 2D materials:
  - Transition metal dichalcogenides (MX_2) family
  - MX_2/ferroelectric oxide vdW heterostructure
  - Conclusions and perspectives

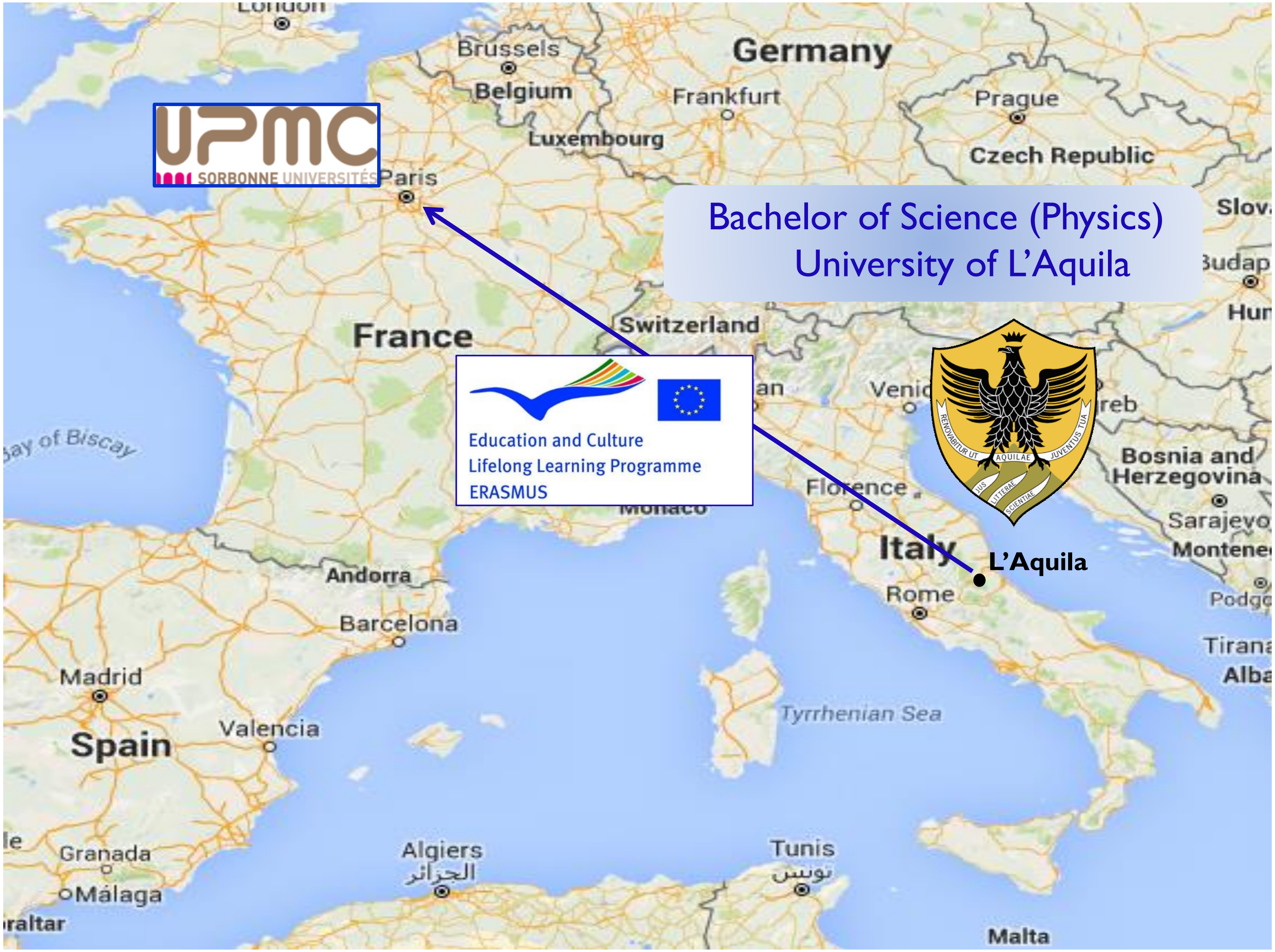
Scientific career path: Bachelor



Bachelor of Science (Physics)
University of L'Aquila

Laboratori Nazionali
del Gran Sasso

Scientific career path: Erasmus Program (2009)



Scientific career path: Master degree (2010)

Scientific career path: Ph.D (2010-2013)

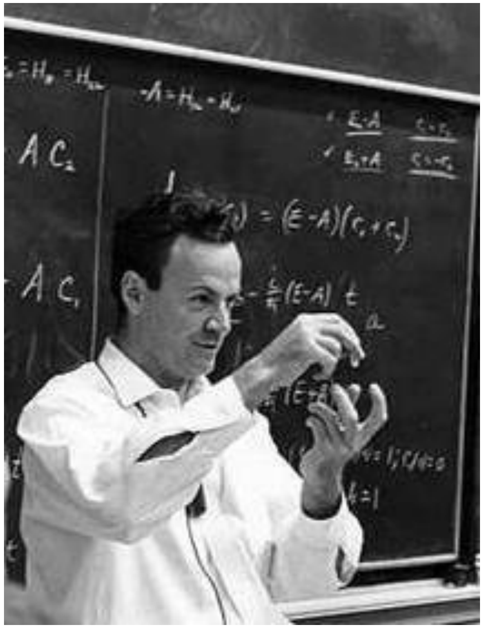
Scientific career path: post Doc (2014-2016)

2D materials “world”

Scientific career path: post Doc (2016-2017)

Scientific career path: Beamline Scientist (2017-2020)

Scientific career path: CNRS researcher (CR) from 2021



“What could we do with layered structures with just the right layer? What would the properties of materials be if we could really arrange the atoms the way we want them…”

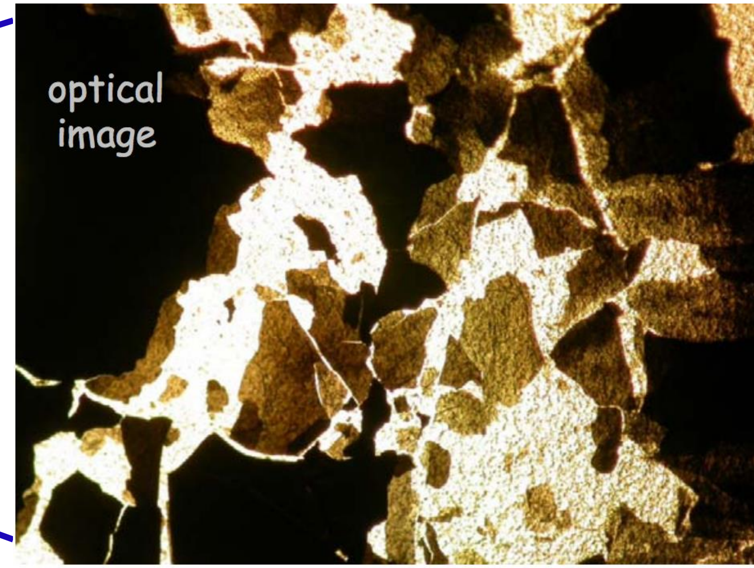
Richard P. Feyman – Lecture “There`s Plenty of Room at the Bottom” 1959

Isolation of graphene

2004 Novoselow and Geim

MANCHESTER 1824
The University of Manchester

Thin film of graphite



Geim A.,K. Nobel Lecture 2010

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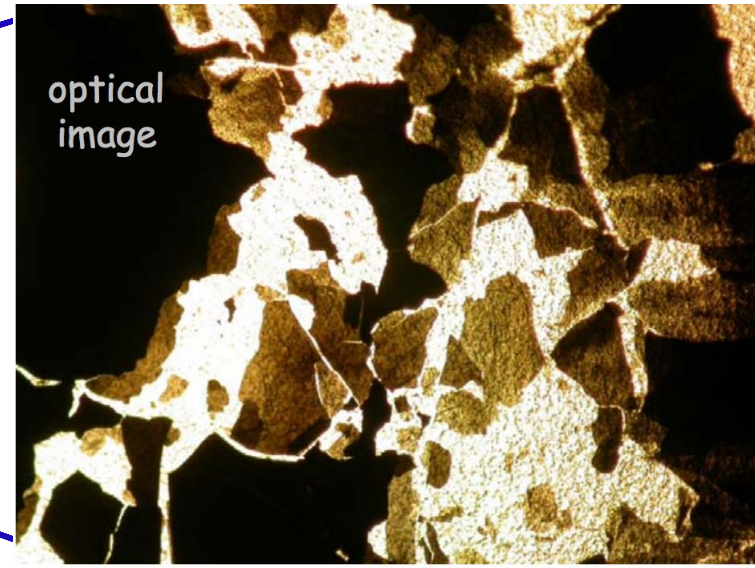

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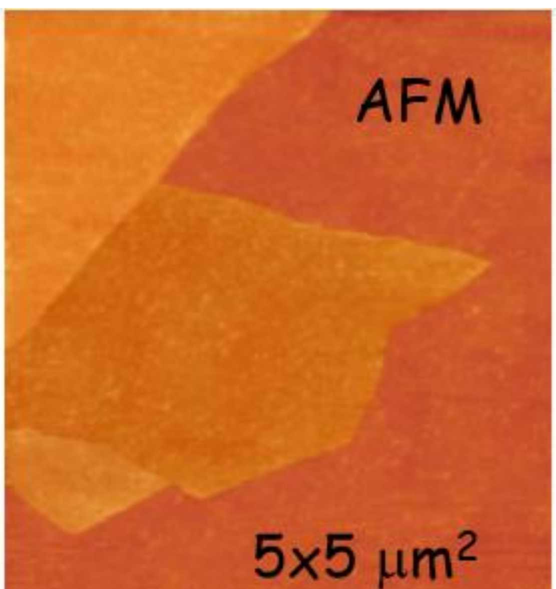
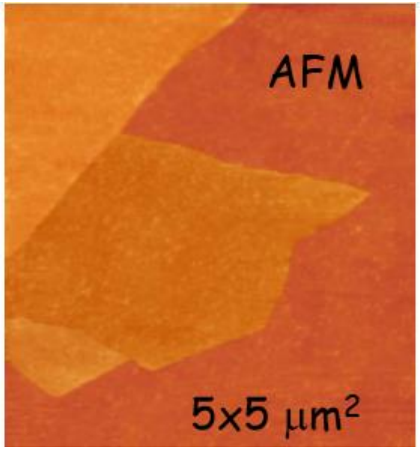
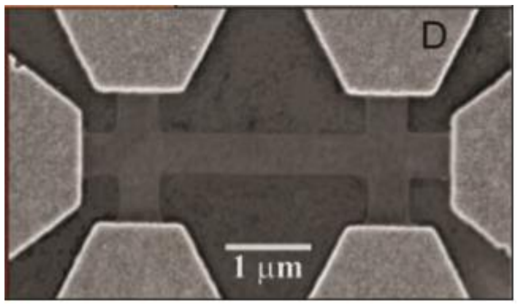


UNTIL A SINGLE LAYER FOUND

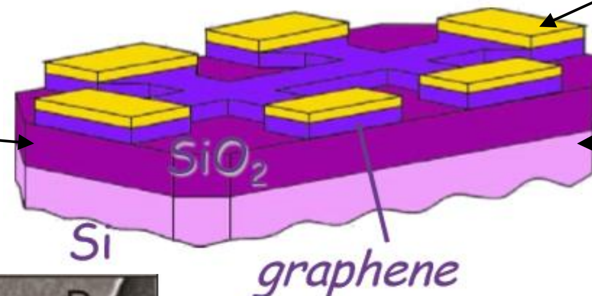
Not just observation of graphene





Source Drain Electrodes

SiO_2 dielectric



Doped Si Gate

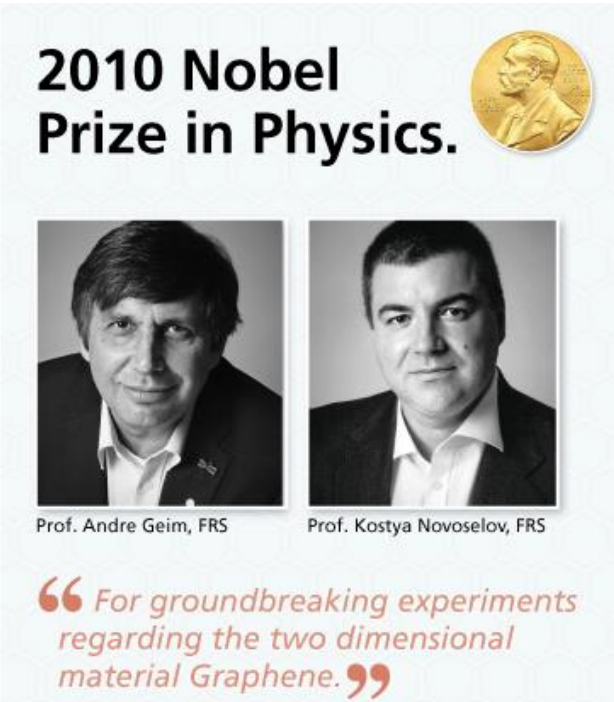
First device !

22 OCTOBER 2004 VOL 306 SCIENCE www.sciencemag.org

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

Not just observation of graphene



"Birth" of a field:
2D materials

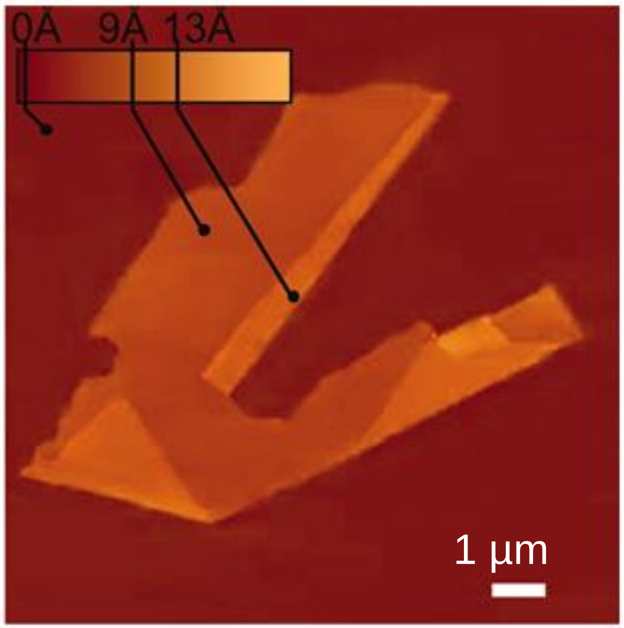
22 OCTOBER 2004 VOL 306 SCIENCE www.sciencemag.org

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

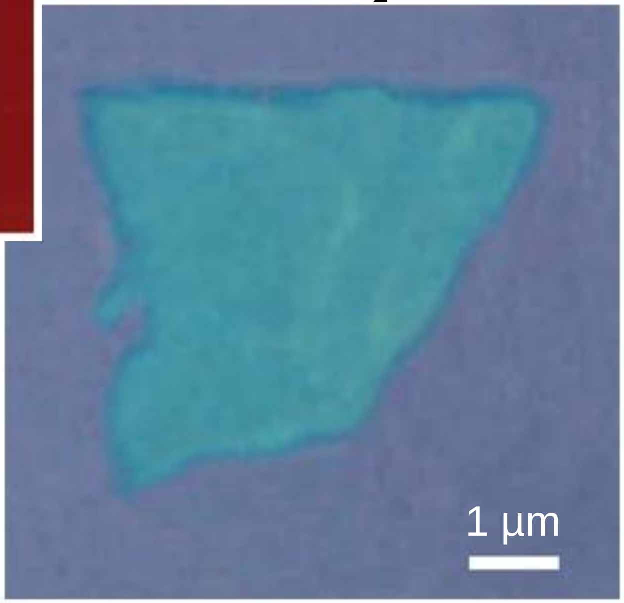
… only one year later in 2005

2D boron nitride



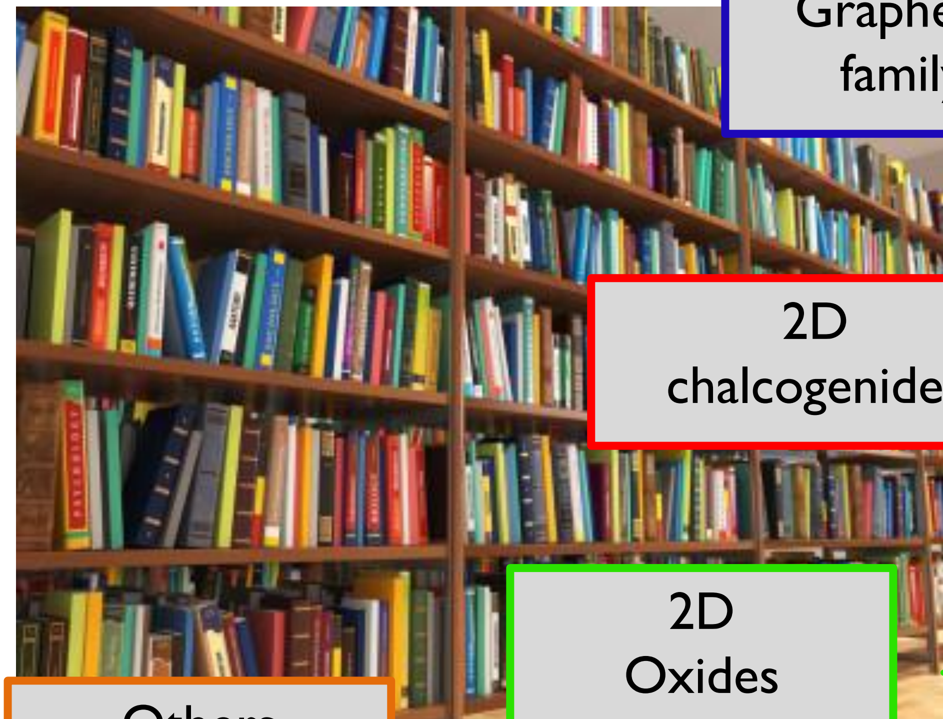
Graphene 2.0 age has begun

2D MoS_2



Novoselov et al. , PNAS 2005

Large library of 2D Crystals



Graphene family

- Graphene
- h- BN
- Silicene
- Germanene

2D chalcogenides

- MX : GaSe, GaTe, InSe and so on
- MX_2 : MoS_2, $MoSe_2$, WS_2, WSe_2 and so on

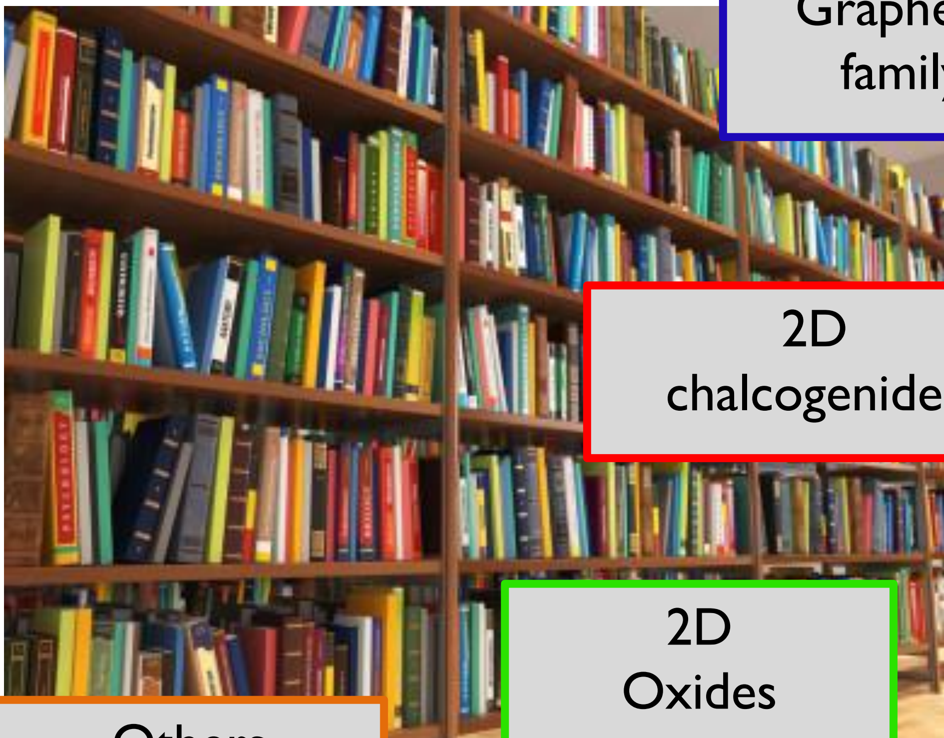
2D Oxides

- Micas
- Layered Cu oxides
- Perovskite-type
- MoO_3, WO_3
- and so on

Others

Not only monolayer but also bi-, tri-, few layers

Large library of 2D Crystals



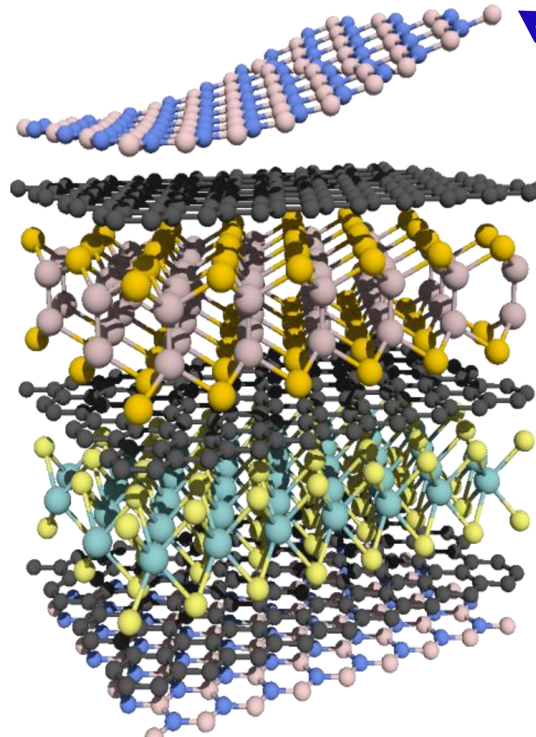
Graphene family

2D chalcogenides

2D Oxides

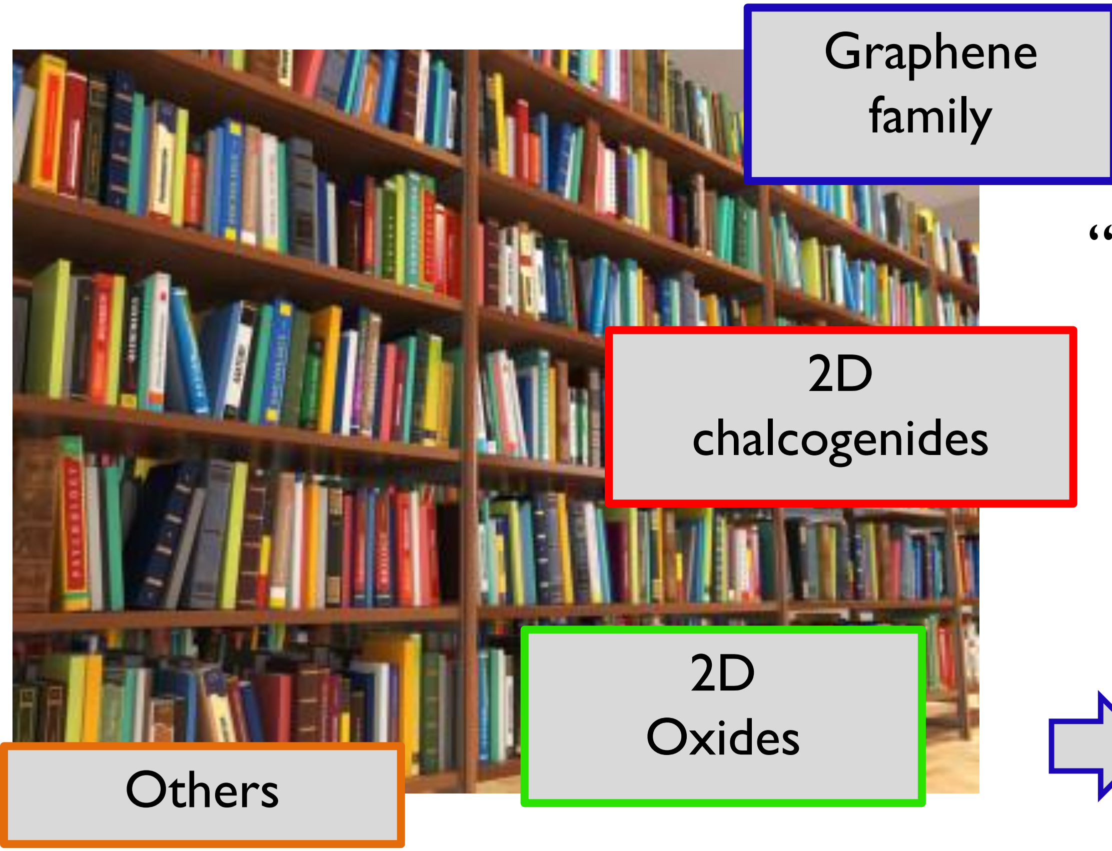
Others

van der Waals interactions



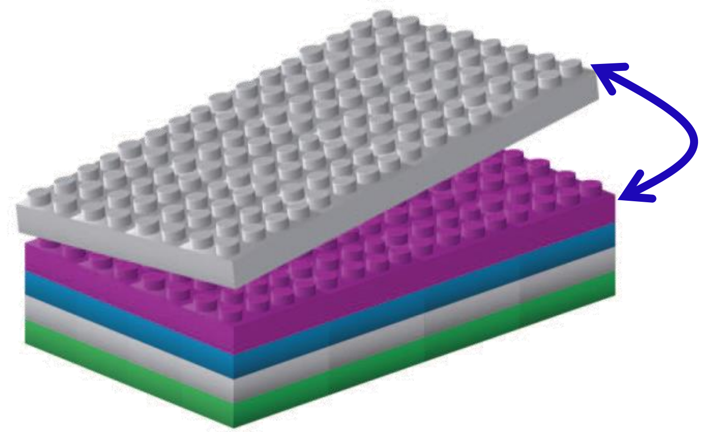
Geim A. K. & Grigorieva I.V, Nature (2013)

New Material on demand: Graphene 3.0



"Lego-game" on atomic scale

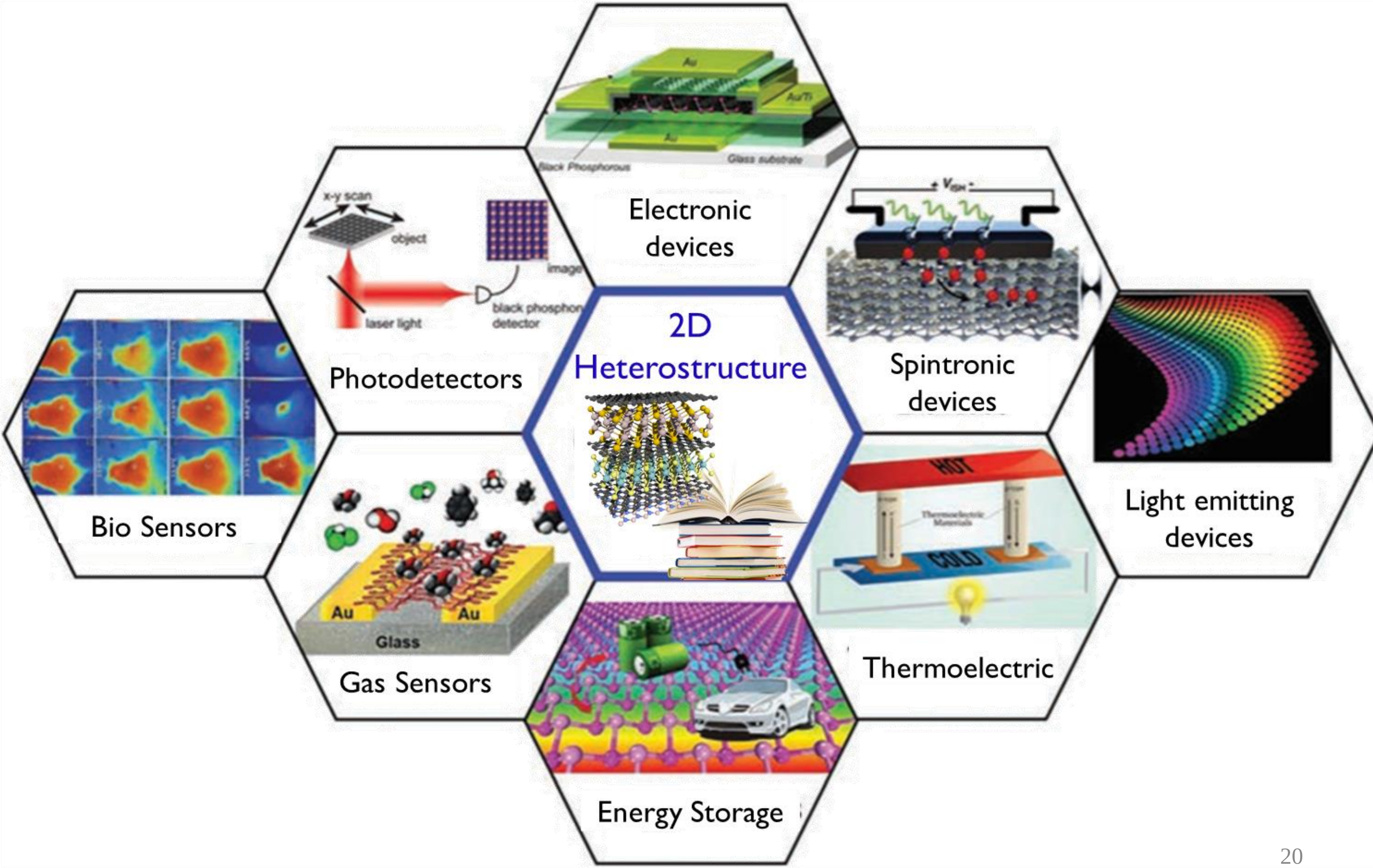
van der Waals interactions



Geim A. K. & Grigorieva I.V, Nature (2013)

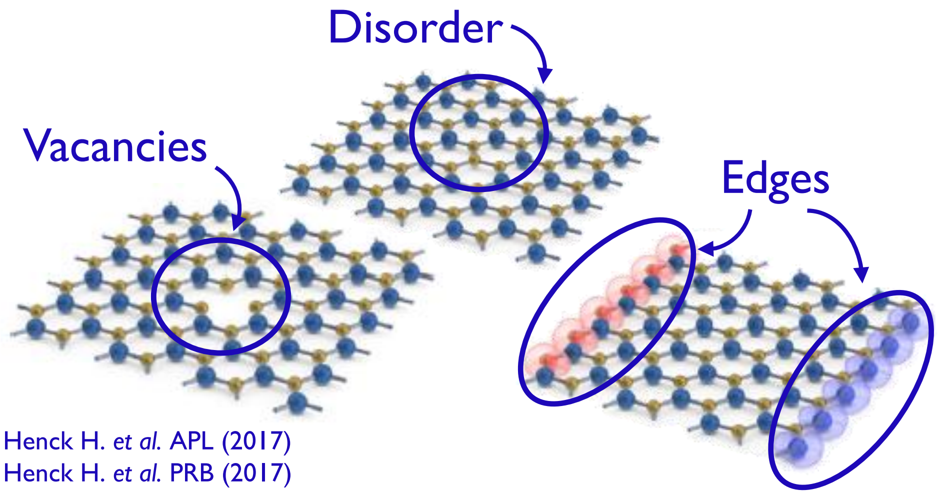
What their properties would be ?

Heterostructure based on 2D crystals



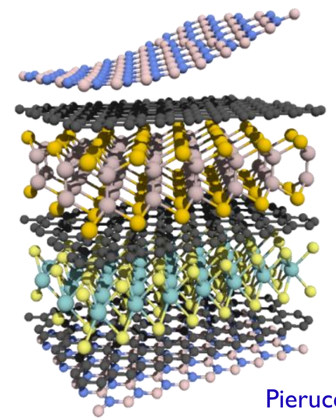
Towards the device integration

Defect characterization and engineering



Henck H. *et al.* APL (2017)
Henck H. *et al.* PRB (2017)
Sediri H. *et al.* Scientific Reports (2015)
Pierucci D. *et al.* ACS nano (2017)
Pierucci D. *et al.* *APL (2018)*

Interface engineering: vdW heterostructure



2D/2D heterostrucutre:

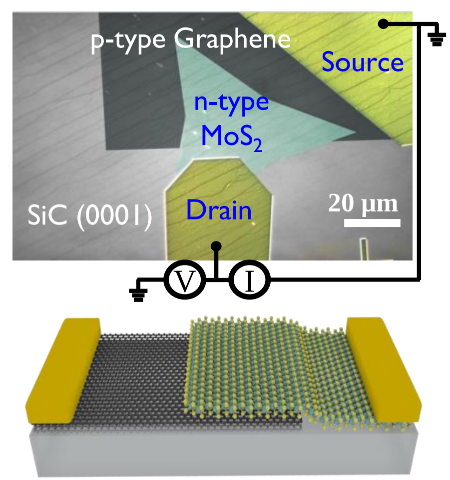
- ➔ h-BN/ graphene
- ➔ GaSe/graphene
- ➔ MoS_2/graphene
- ➔ WS_2/graphene
- ➔ MoSé$_2$/WSe_2
- ➔ SnS_2/WSe_2

2D/3D heterostrucutre:

- ➔ MoS_2/GaN
- ➔ WS_2/BTO

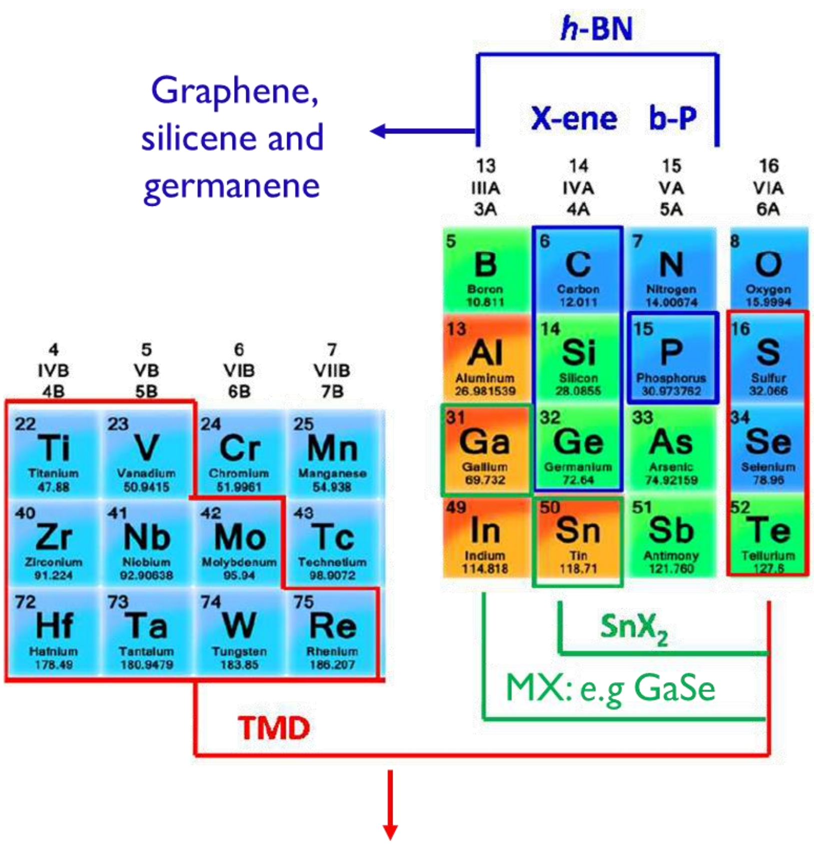
Pierucci D. *et al.* Scientific Reports (2016)
Pierucci D. *et al.* Nano Letters (2016)
Ben Aziza Z. *et al.* Carbon (2016)
Ben Aziza Z, . *et al.* PRB (2018)
Zribi J., *et al.* npj 2D Materials and Applications (2019)
C Ernandes *et al.* npj 2D Materials and Applications (2021)

Device fabrication



Henck H. et al. APL (2016)

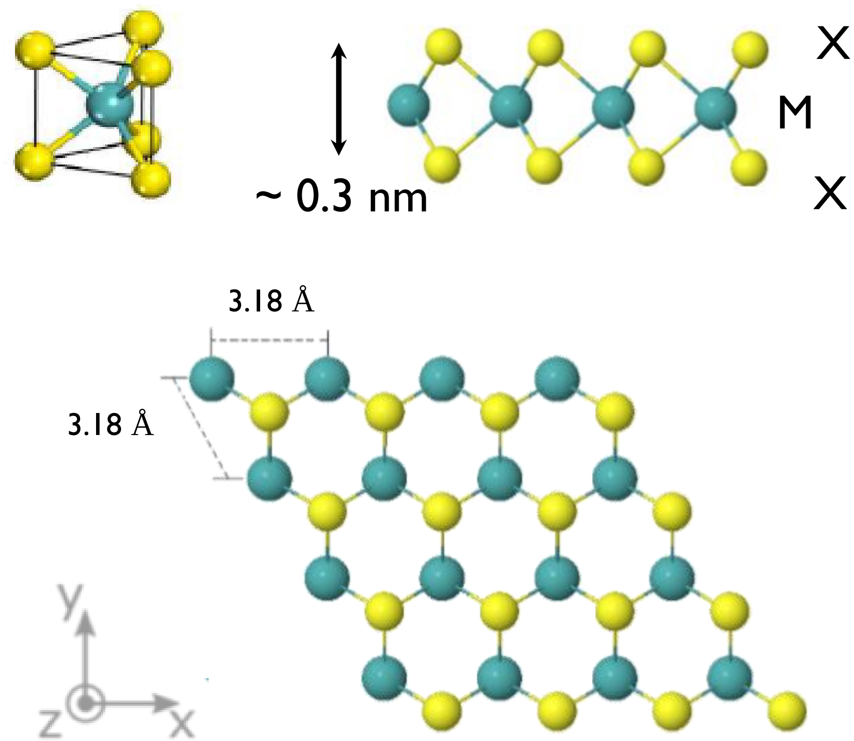
MX_2: Fundamental Properties



MX_2: MoS_2, $MoSe_2$, WS_2, WSe_2 etc..

Group VI dichalcogenide MX_2

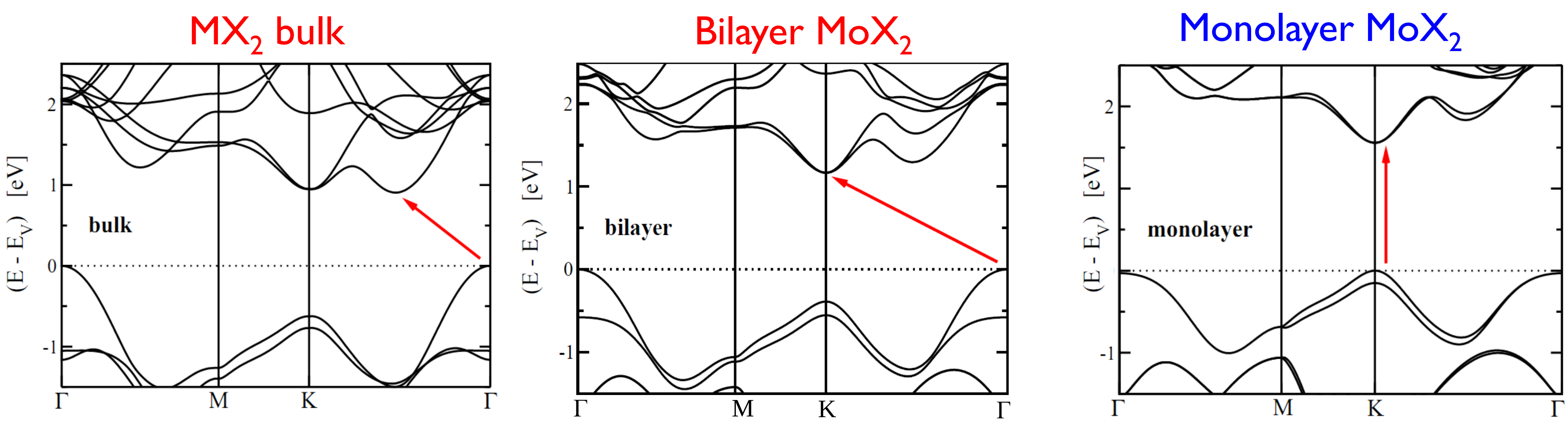
1H -Trigonal prismatic phase



MX_2: Fundamental Properties

Layer-dependent properties

Indirect → direct band gap

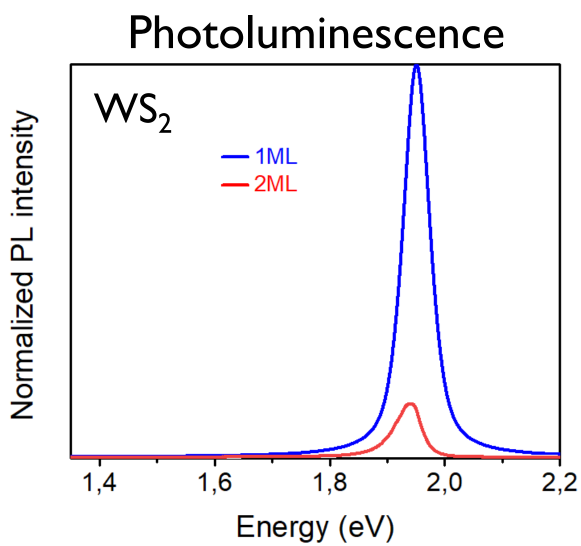


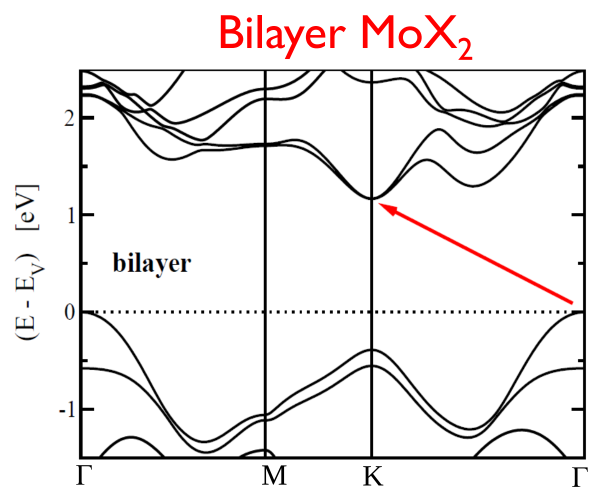
T. Brumme et al. PRB (2015)

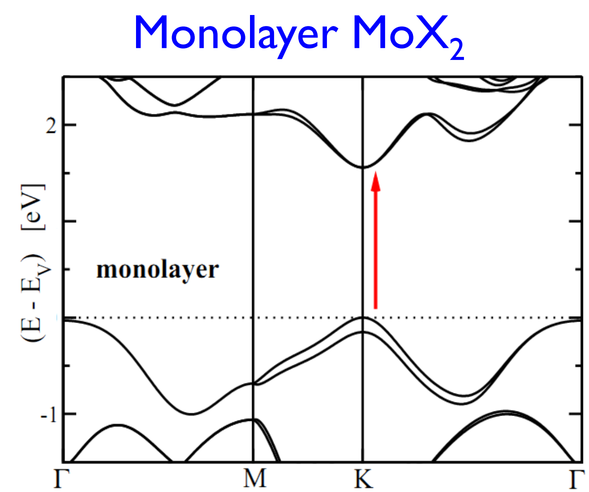
MX_2: Fundamental Properties

Layer-dependent properties

Indirect → direct band gap



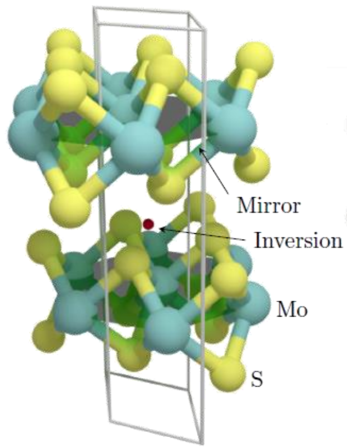


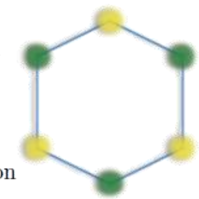


Direct gap in the visible spectrum (from 1.6 eV up to 2 eV)

T. Brumme et al. PRB (2015)
C. Ernandes, D.Pierucci. *et al.*, 2D Materials and Applications (2021)

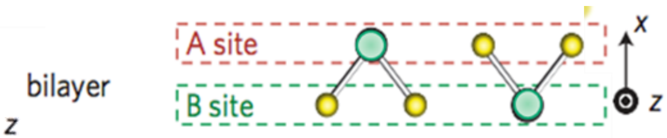
MX_2: Fundamental Properties



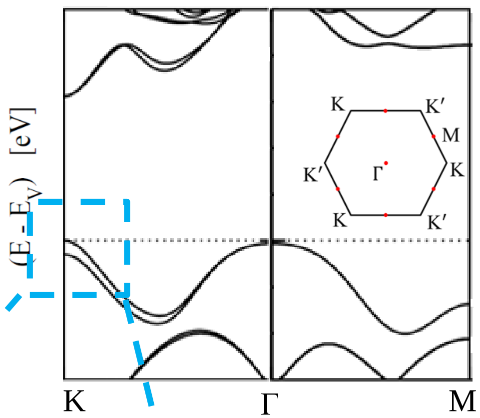


Inversion asymmetry

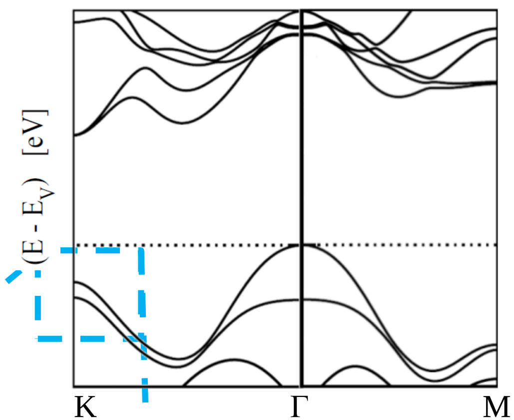
Inversion symmetry



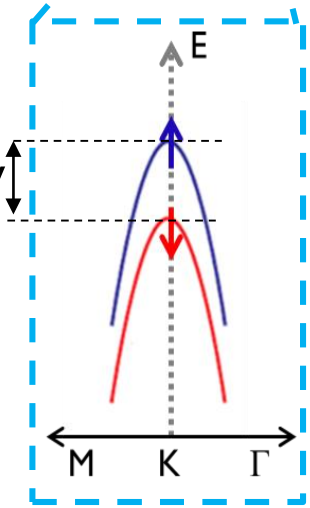
Monolayer MoX_2

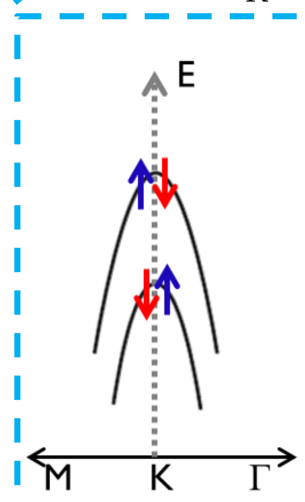


Bilayer MoX_2



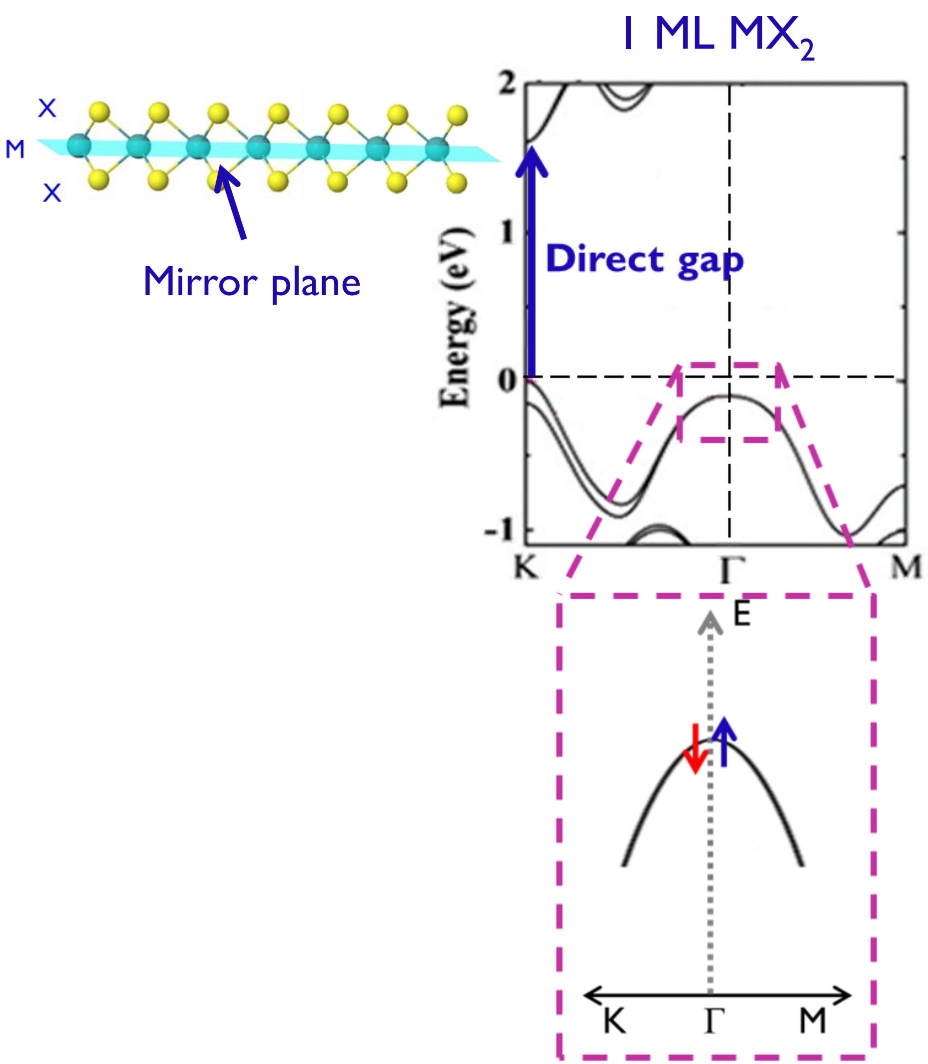
ΔE_{SO} ~ 150-500 meV





Spin degeneracy

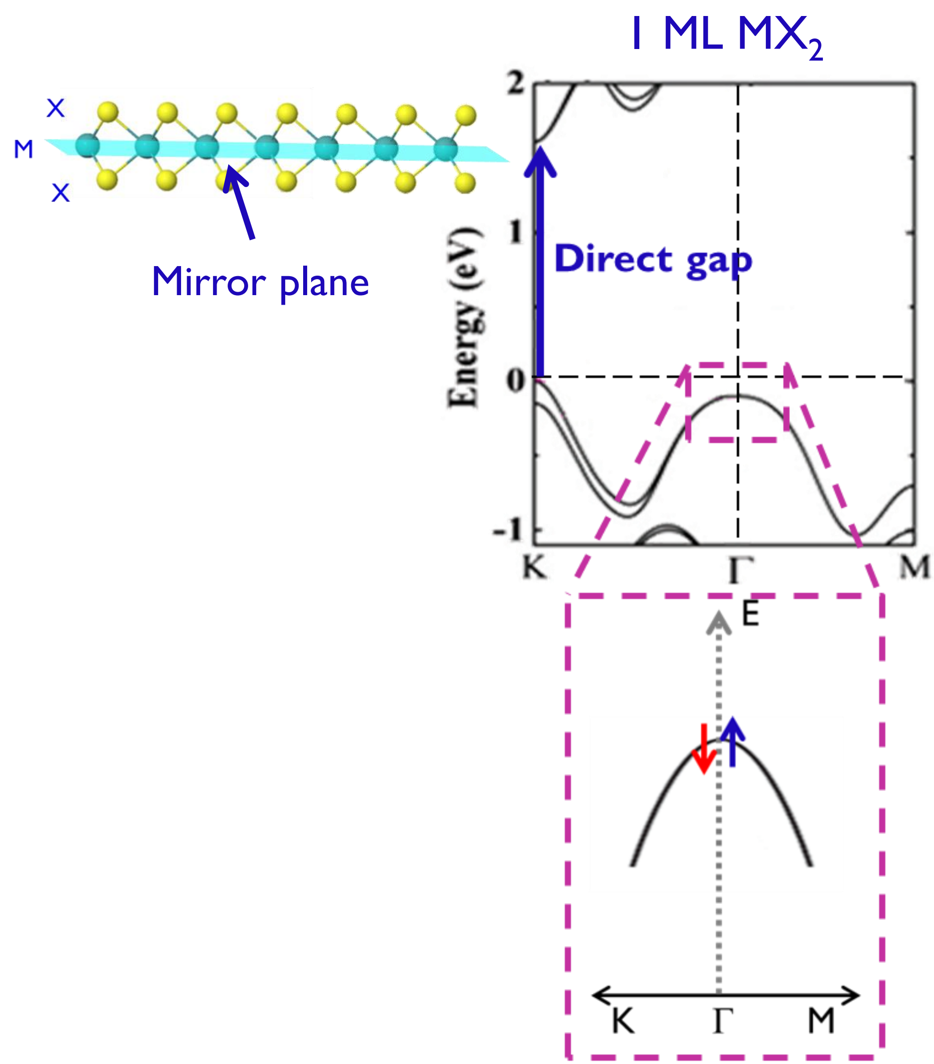
MX_2: Fundamental Properties



Spin degeneracy

Hu et al. PRB 97,235404 (2018)

MX_2: Fundamental Properties



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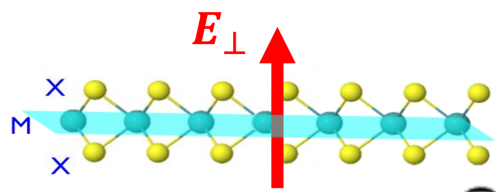
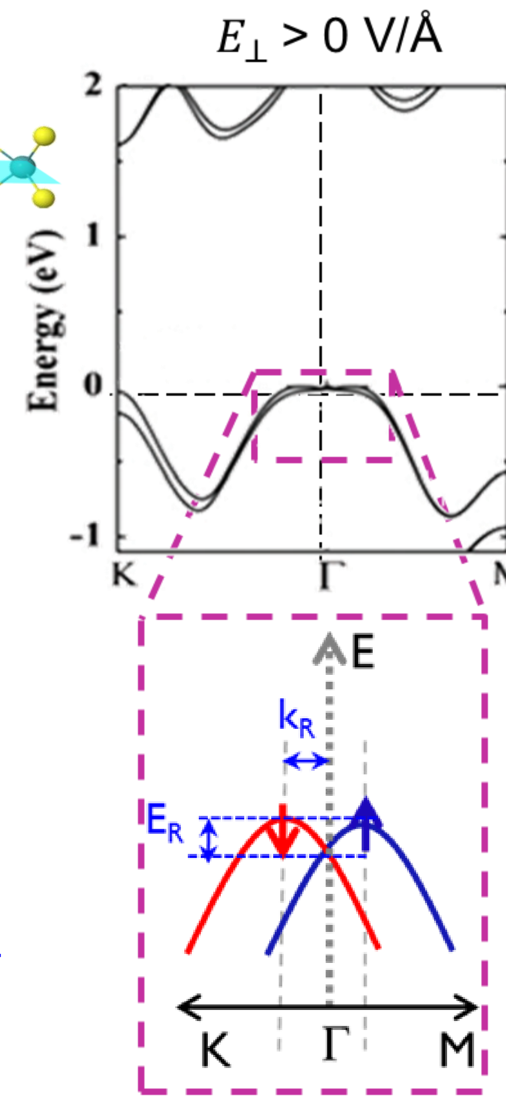


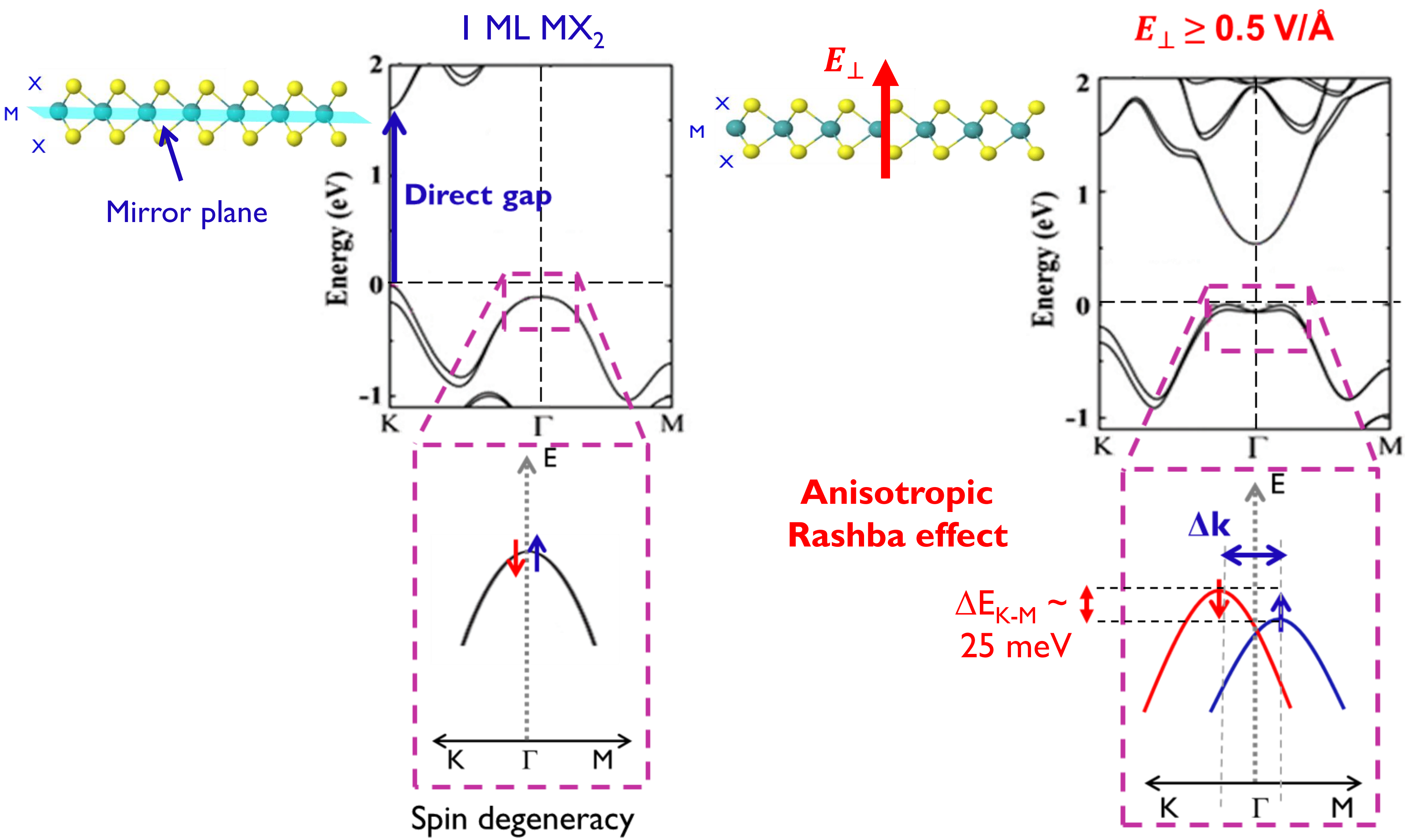


Rashba effect

$$\alpha_R = \frac{2E_R}{k_R}$$

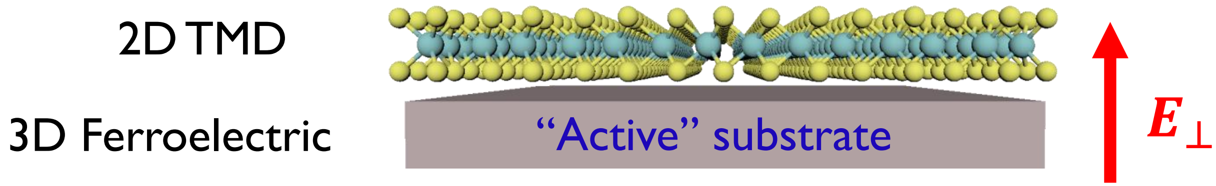
Hu et al. PRB 97,235404 (2018)

MX_2: Fundamental Properties

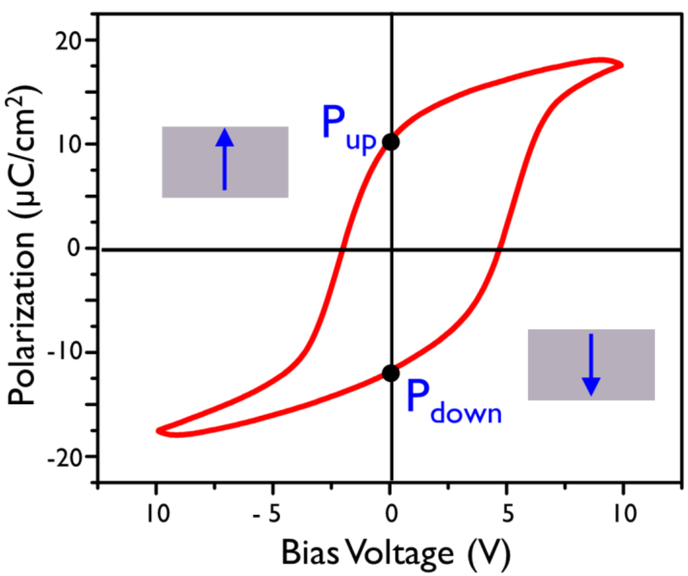


Hu et al. PRB 97,235404 (2018)

MX_2/ ferroelectric oxide vdW heterostructure



Integrated electric modulation



C2N (OXIDE group)

Spontaneous reversible polarization

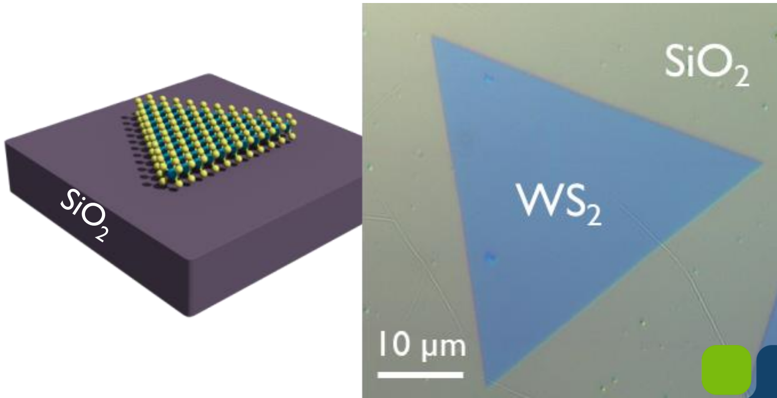
=

Induced high electric field

(0.1 up to 3 V/Å)

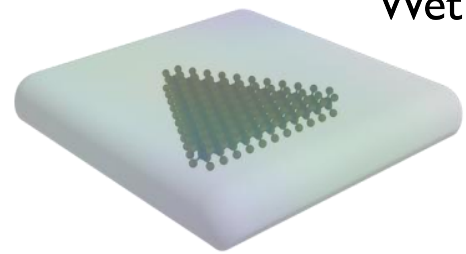
How obtain a vdW heterostructure?

CVD growth of MX_2



Transfer

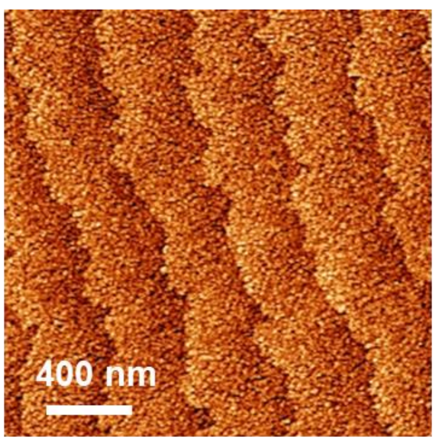
"Wet transfer"



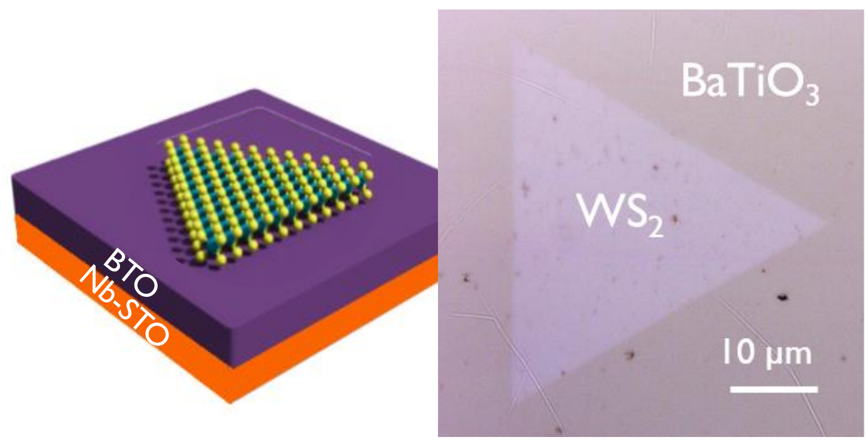
PMMA coating +
KOH etching

PLD growth of FE substrate

AFM topography



$BaTiO_3$ on Nb-doped $SrTiO_3$
30 nm-thick film
R_{rms} = 0.3 nm

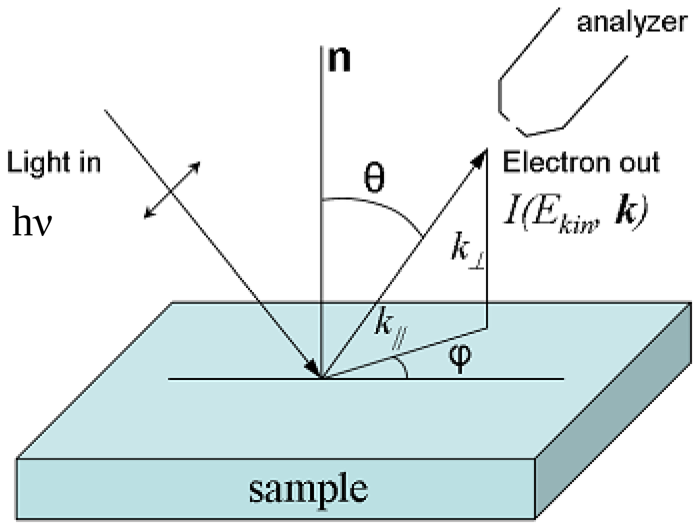


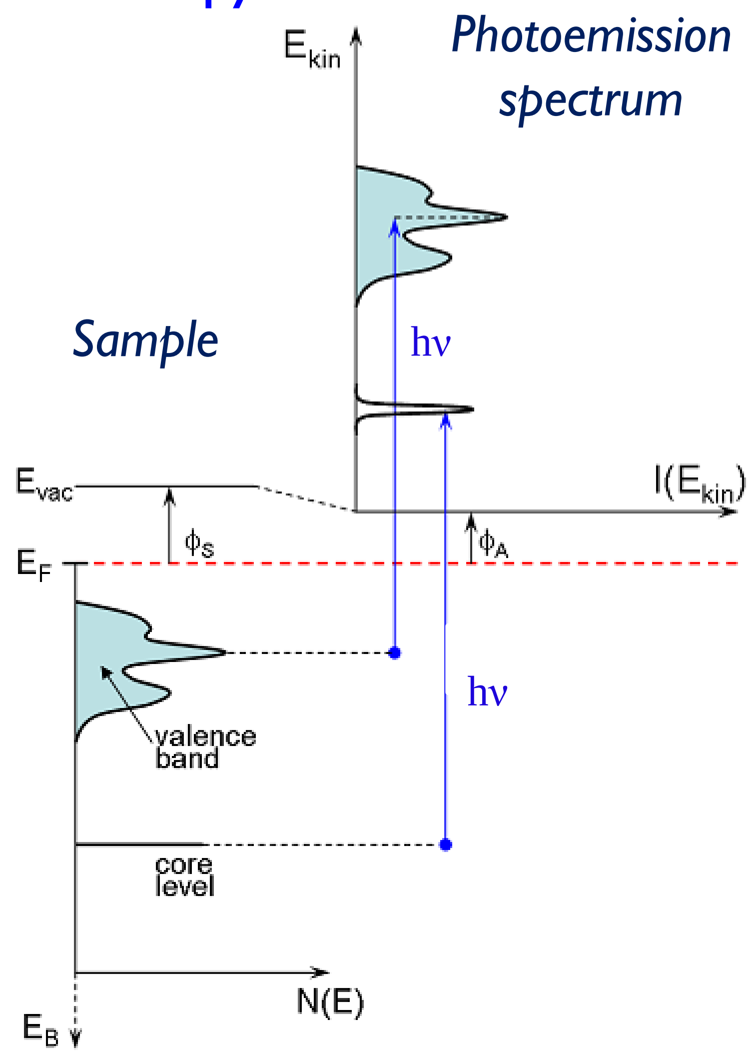
How obtain a direct access to the band structure?

Photoemission Spectroscopy

Photoelectric Effect:

photon in – electron out





➔ **Energy conservation:**

$$E_{kin}=h\nu-E_B-\phi_A$$

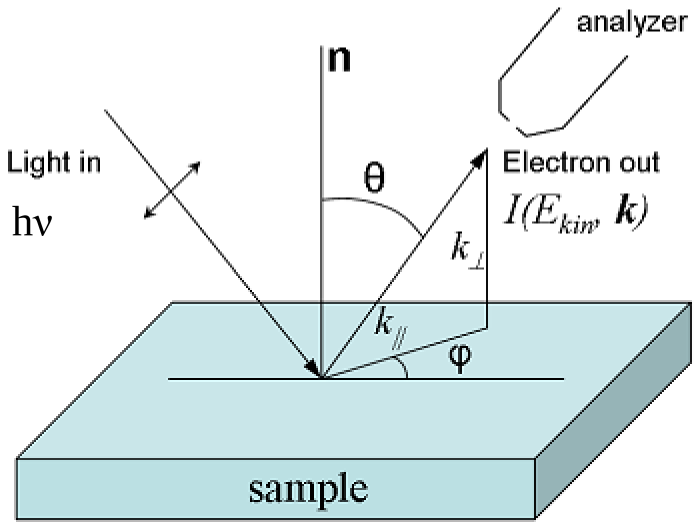
→ Work function analyzer

Chemical properties and band offset (interface dipole)

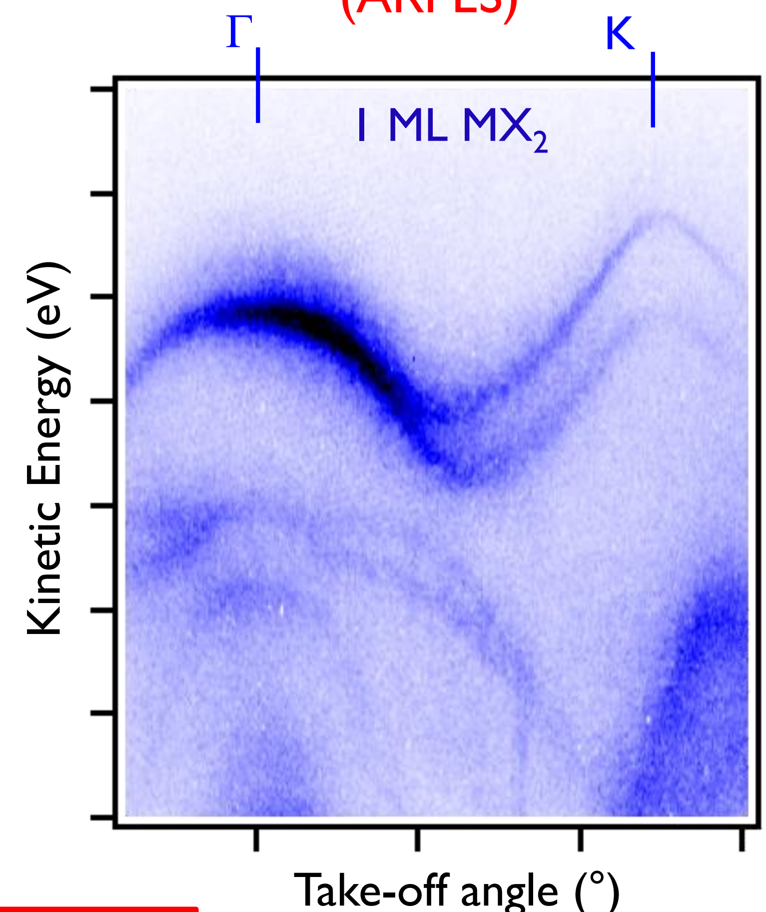
How obtain a direct access to the band structure?

Photoemission Spectroscopy

Photoelectric Effect:
photon in – electron out



Angle resolved photoemission spectroscopy (ARPES)



→ **Energy conservation:**

$$E_{kin} = h\nu - E_B - \phi_A$$

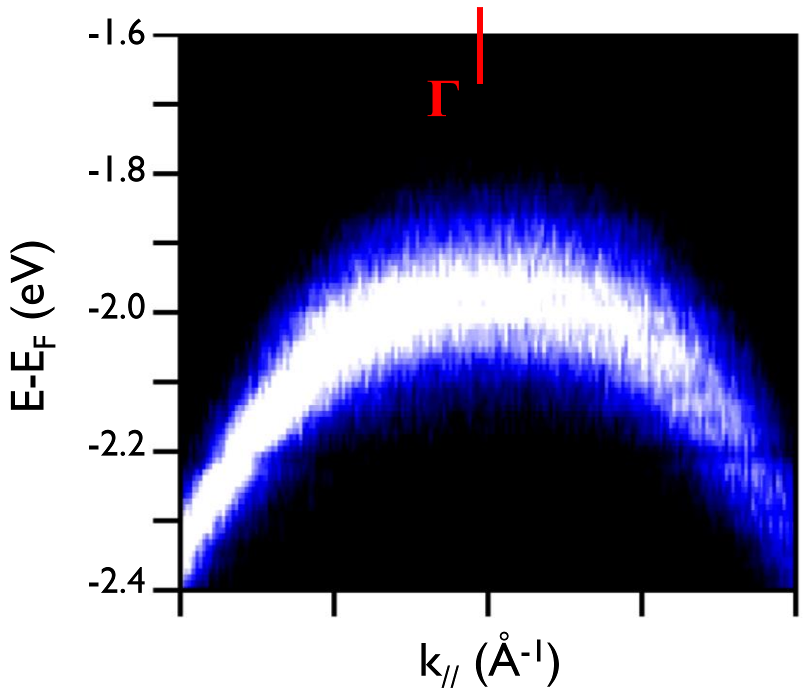
→ **Momentum conservation:**

$$\hbar k_{\parallel} = \sqrt{2mE_{kin}} \cdot \sin\theta$$

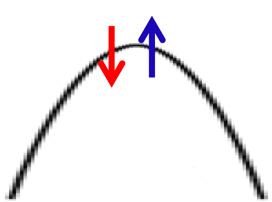
Band Structure

WS_2 / ferroelectric oxide: electronic structure

$WS_2/BaTiO_3$: before annealing



No splitting

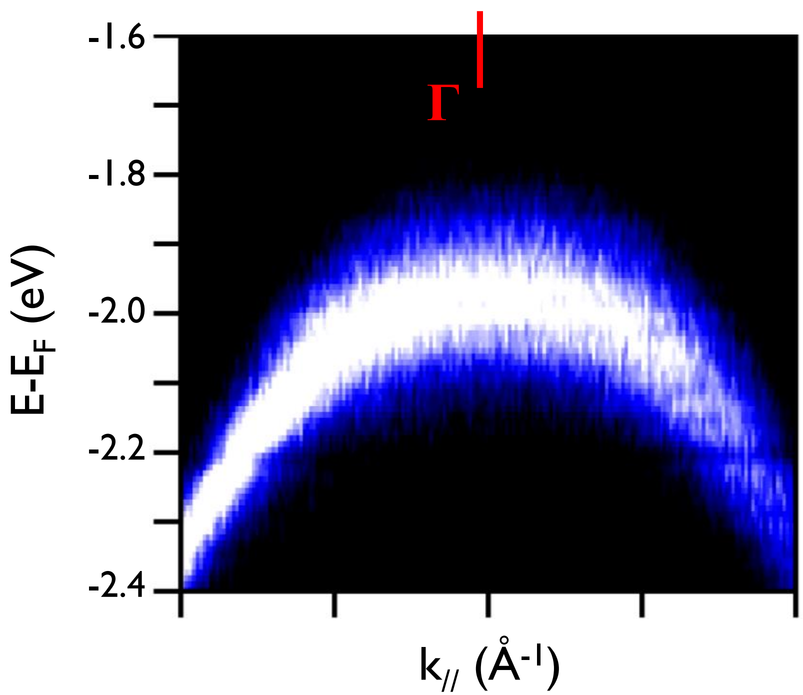


➔ **Presence of interface screening = no electric field**

D. Pierucci et *al.* to be submitted

WS_2 / ferroelectric oxide: electronic structure

$WS_2/BaTiO_3$: before annealing



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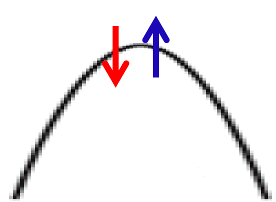
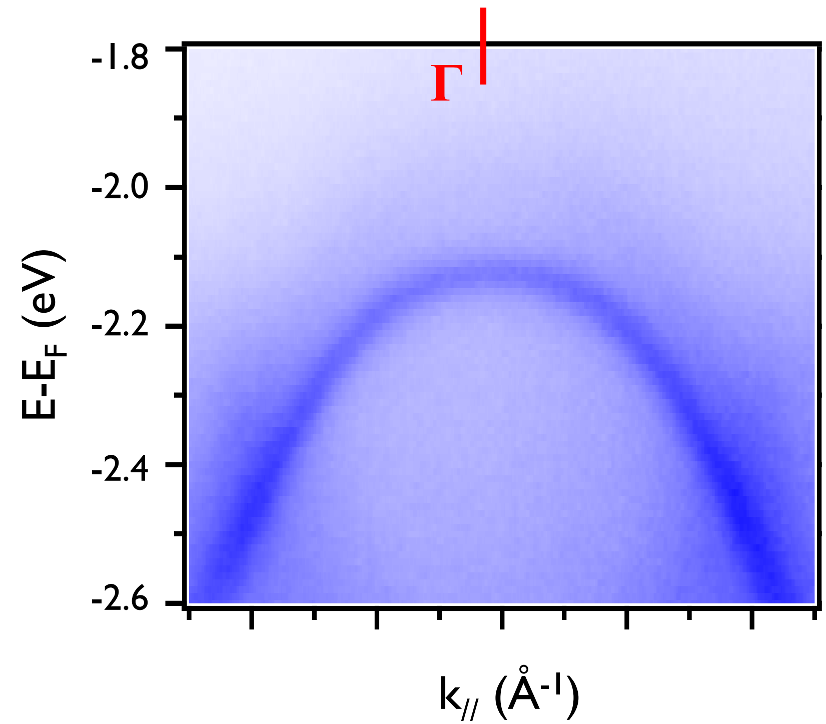


WS_2/Gr



Henck H., Pierucci D. *et al.* PRB (2018)

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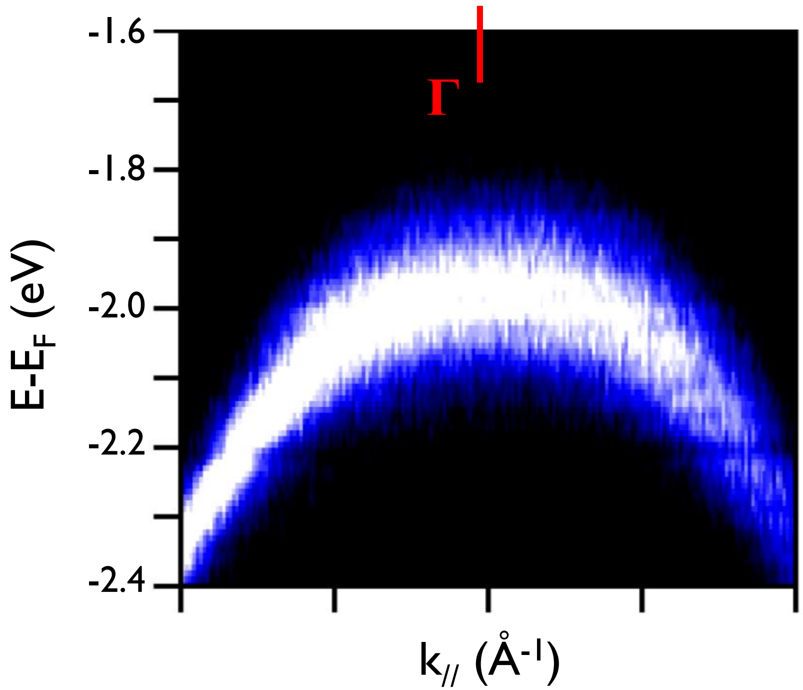
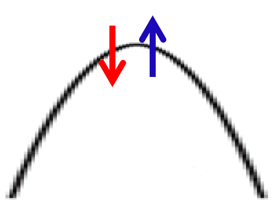
WS_2 / ferroelectric oxide: electronic structure

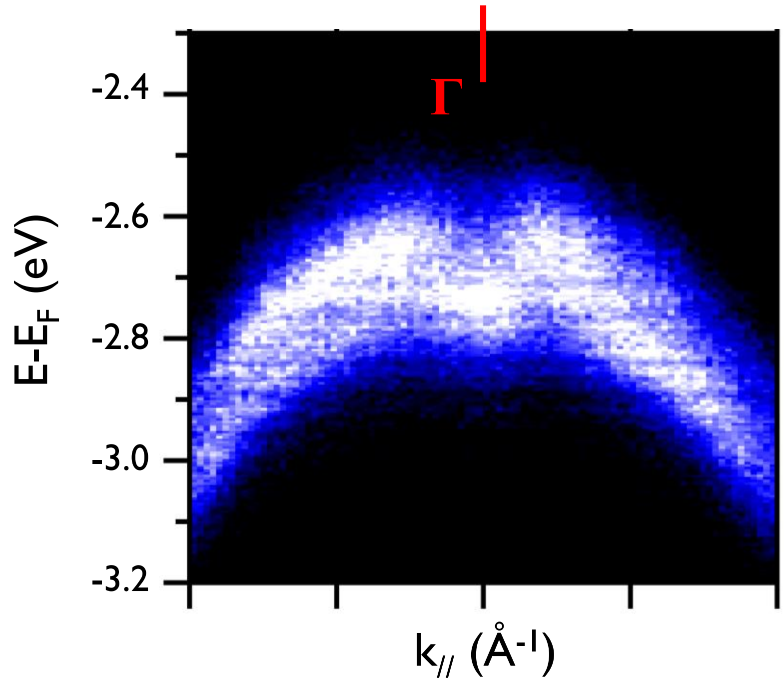
$WS_2/BaTiO_3$: before annealing



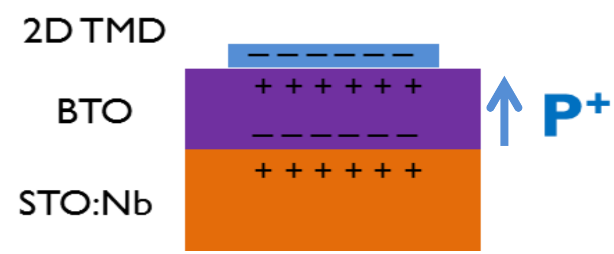
No splitting



$WS_2/BaTiO_3$: after annealing



- VBM is shifted = high *n*-type doping



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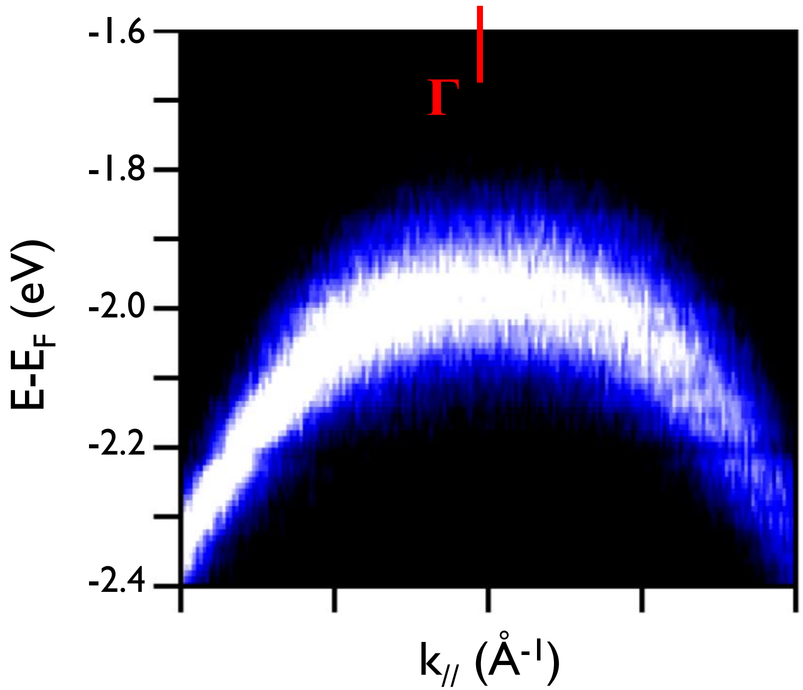
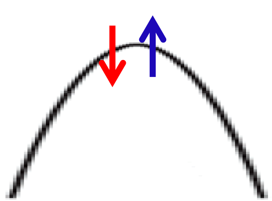
WS_2 / ferroelectric oxide: electronic structure

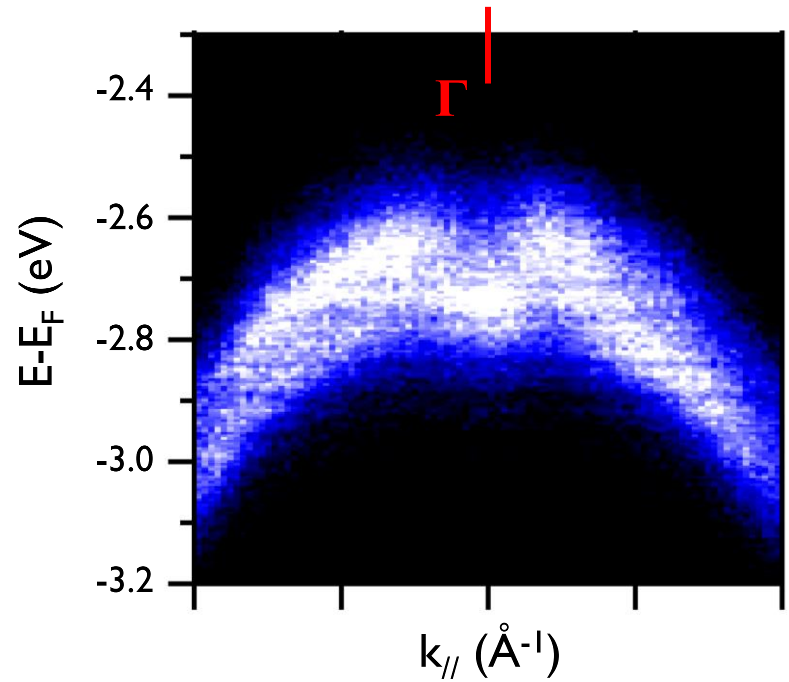
$WS_2/BaTiO_3$: before annealing



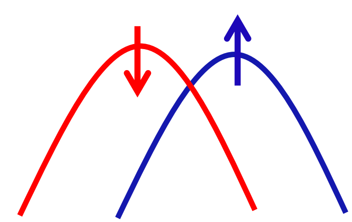
No splitting



$WS_2/BaTiO_3$: after annealing



Rashba splitting



Integrated electric modulation *via* herostructure

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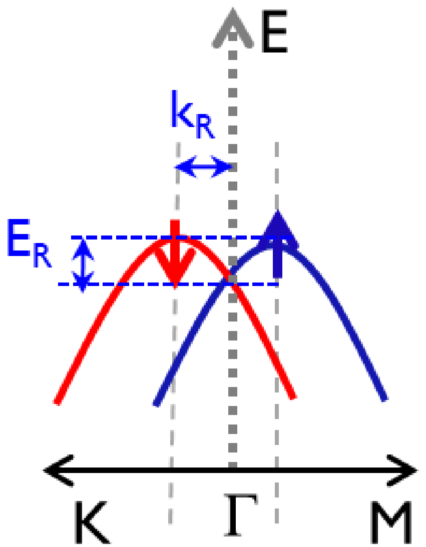
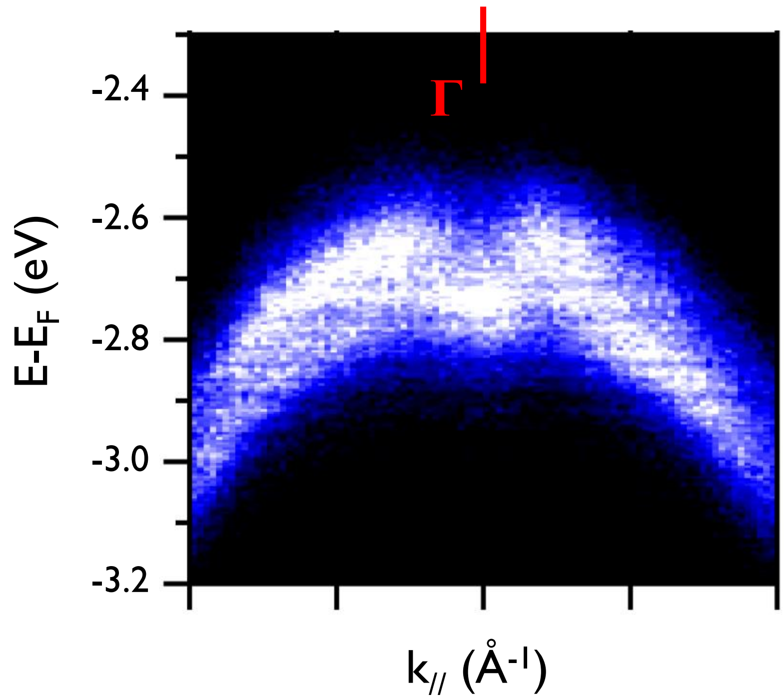
WS_2 / ferroelectric oxide: electronic structure



$WS_2/BaTiO_3$: after annealing



Giant
Rashba splitting

$$\alpha_R = \frac{2E_R}{k_R} = 3.6 \text{ eV}\cdot\text{Å} \quad >>$$

- InGaAs/GaAs 0.08-0.12 eV·Å
- InGaAs/InAlAs = 0.07 eV·Å
- Au(111) = 0.33 eV·Å
- Au/W(110) = 0.16 eV·Å

D. Pierucci et *al.* to be submitted

Take home messages

→ Integrated electric modulation via herostructure is possible!

→ The interface is crucial: contaminations = screening effects

→ ARPES is a very powerful techniques to uncover the electronic structure of the heterostructure

Take home messages

➔ Integrated electric modulation via herostructure is possible!

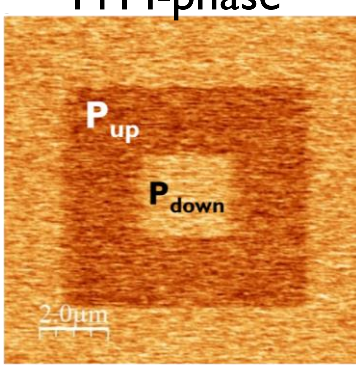
➔ The interface is crucial: contaminations = screening effects

➔ ARPES is a very powerful techniques to uncover the electronic structure of the heterostructure

TO GO FURTHER:

➔ Polarization switching = up and down domains

PFM-phase

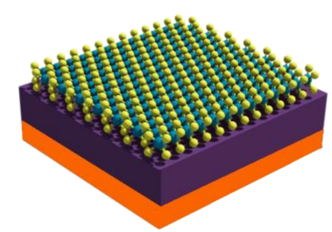


C2N (OXIDE group)

➔ 2D TMDs Direct growth via MBE

Thales MBE set-up at C2N

- Precise control of the number of layers on a large scale
- Sharp interface = higher induced electric field



Acknowledgements

2D Materials team

- ✓ A. Ouerghi
- ✓ J. Chaste
- ✓ F. Oehler

Ph.D students & Post Docs:

- ✓ H. Henck
- ✓ Z. Ben Aziza
- ✓ J. Zribi
- ✓ C. Ernandes
- ✓ L. Khalil

Oxide team

- ✓ P. Lecoeur
- ✓ T. Maroutian
- ✓ S. Matzen

Collaborations:

- ✓ P. Dudin & J. Avila (ANTARES)
- ✓ F. Bertran & P. Lefevre (Cassiopée)

Thank you for your attention

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80
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TECHNICIANS AND
ADMNISTRATIVE STAFF

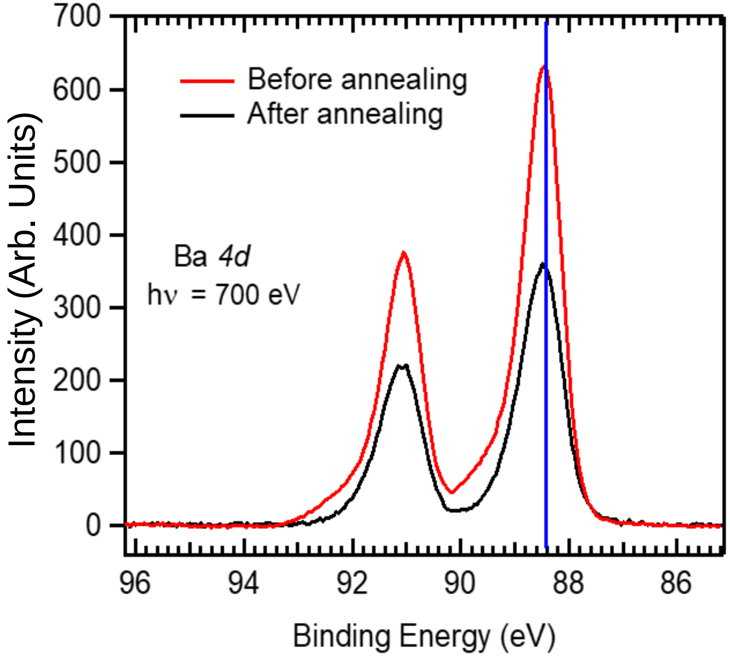
18 000 sqm
INCL. 2 800 SQM OF
CLEANROOM FACILITY

4
RESEARCH
DEPARTMENTS

WS_2 / ferroelectric oxide: electronic structure

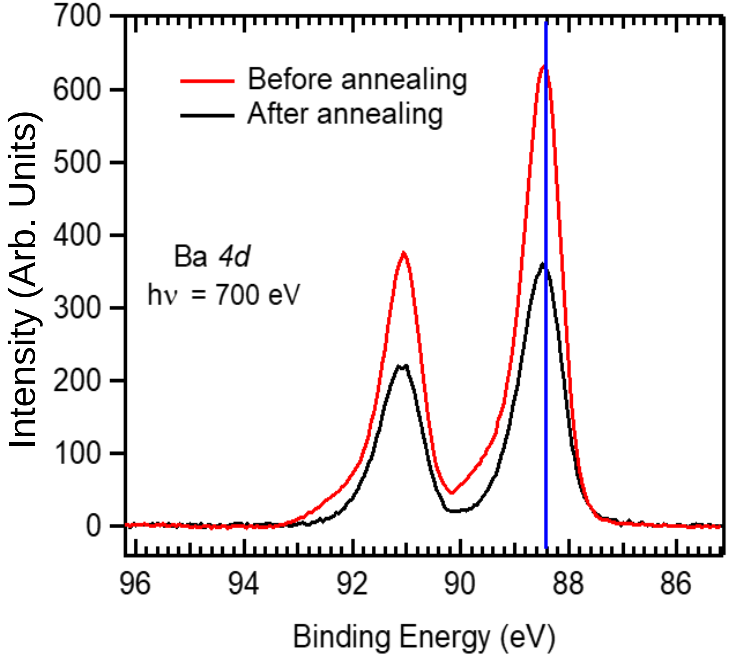
XPS spectra

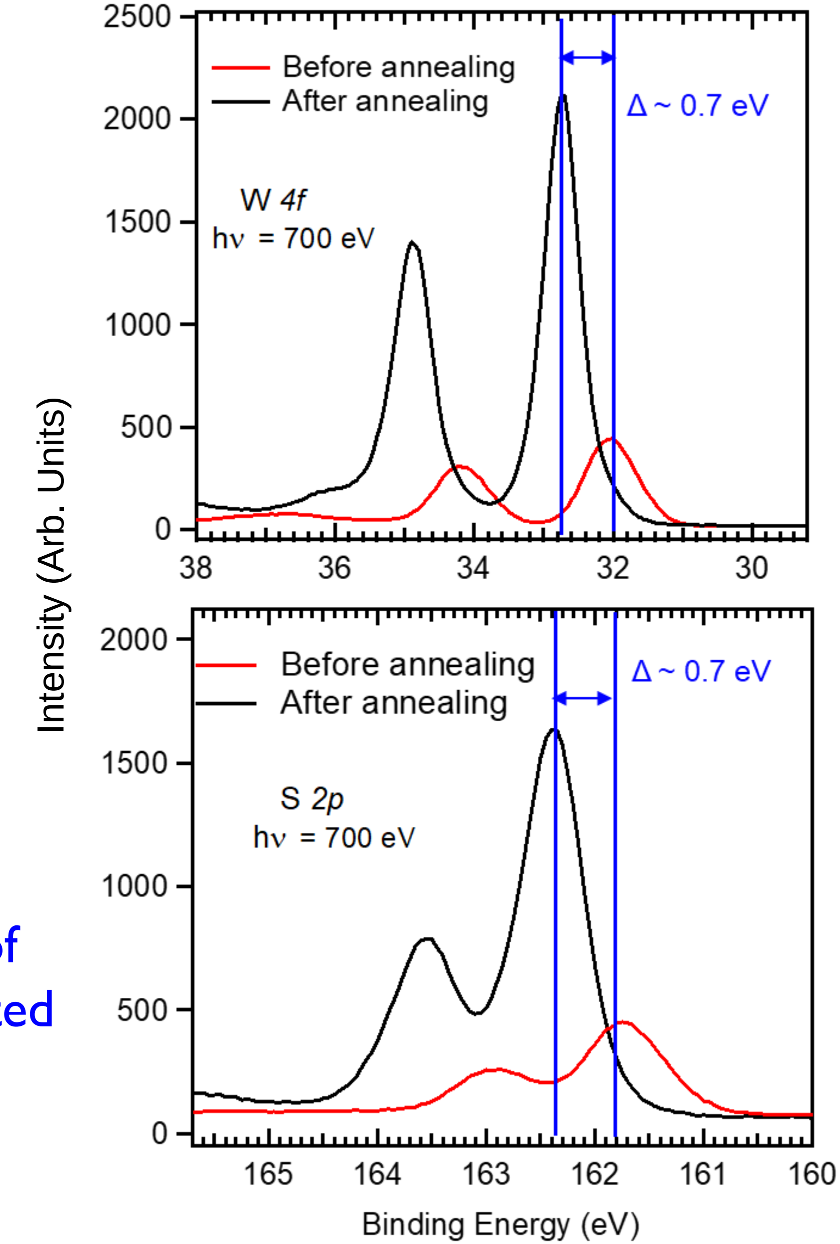
No shift



WS_2 / ferroelectric oxide: electronic structure

No shift

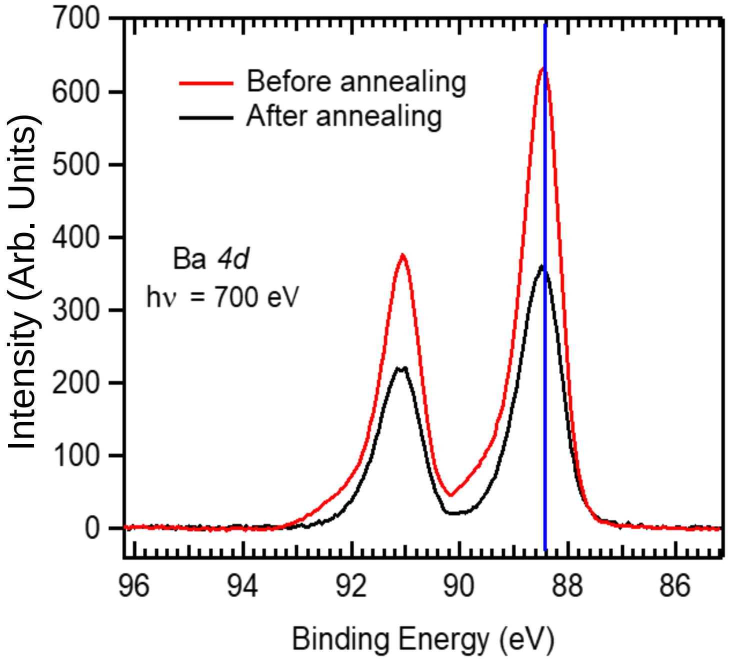


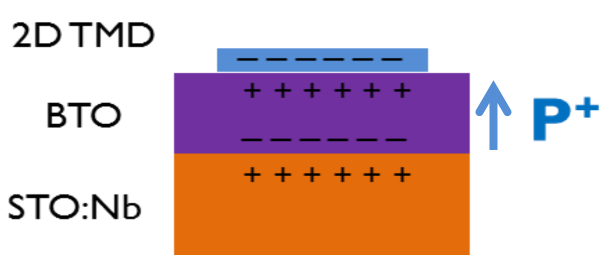


Core levels of WS_2 are shifted

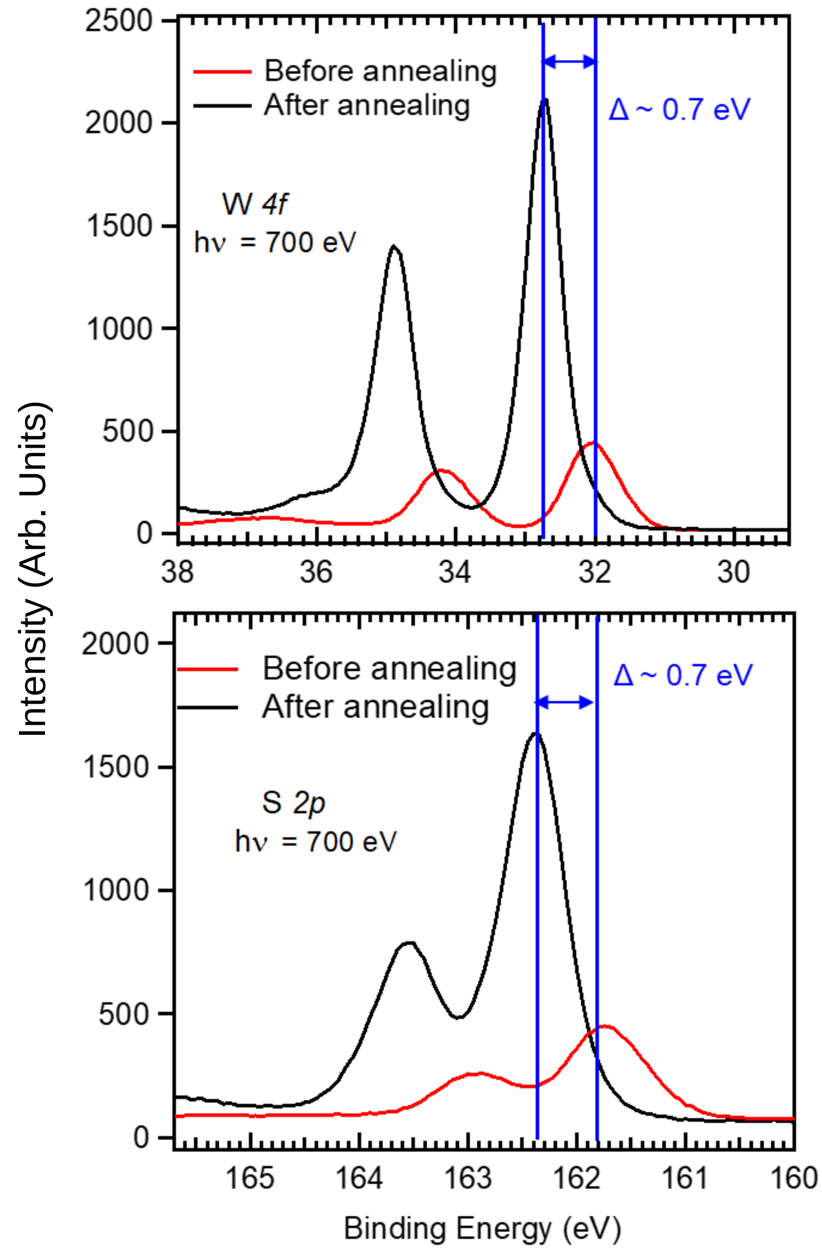
WS_2 / ferroelectric oxide: electronic structure

No shift



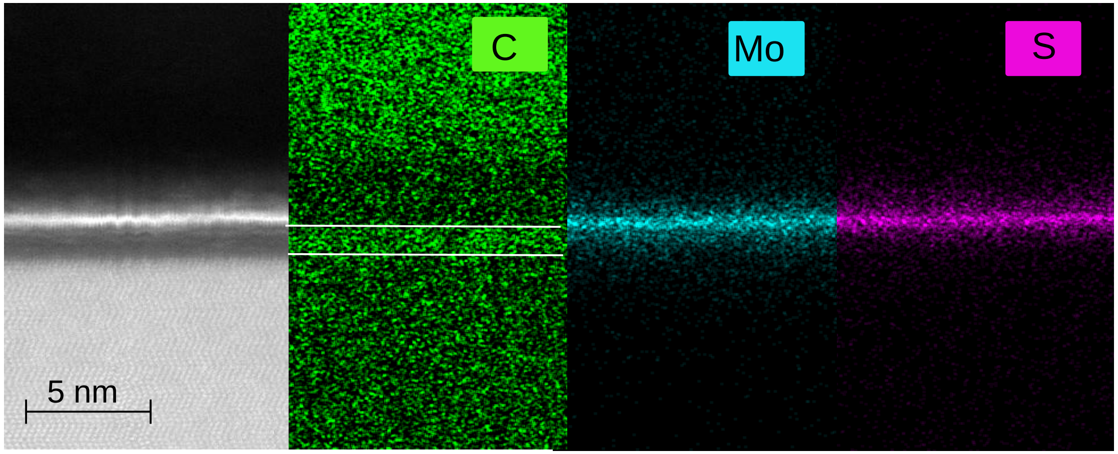


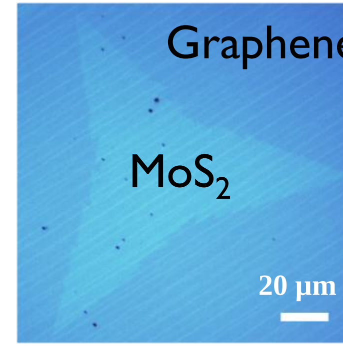
$\vec{E}_{dep} \sim 0$

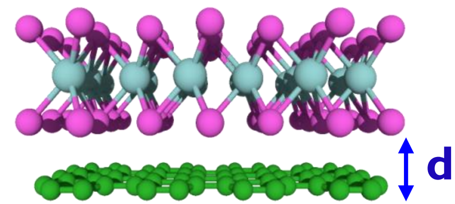


MoS_2/Graphene: Interface quality

HR-TEM/EDX

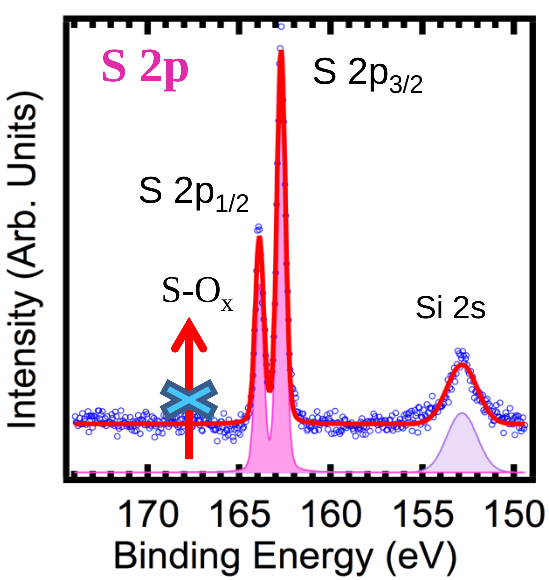


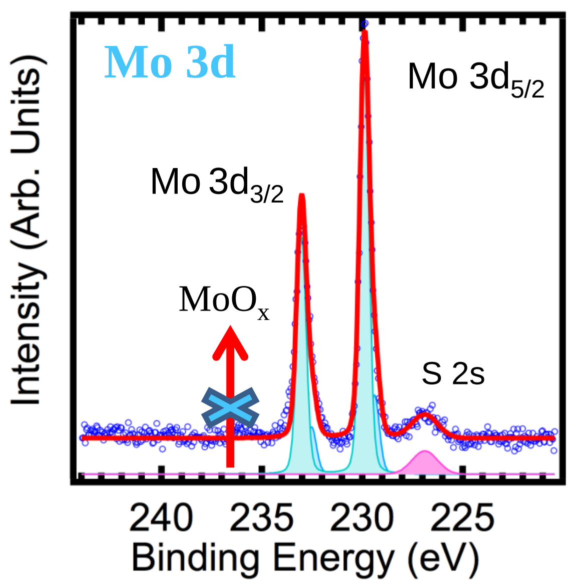




d = 3.4 ± 0.1 Å

HR-XPS



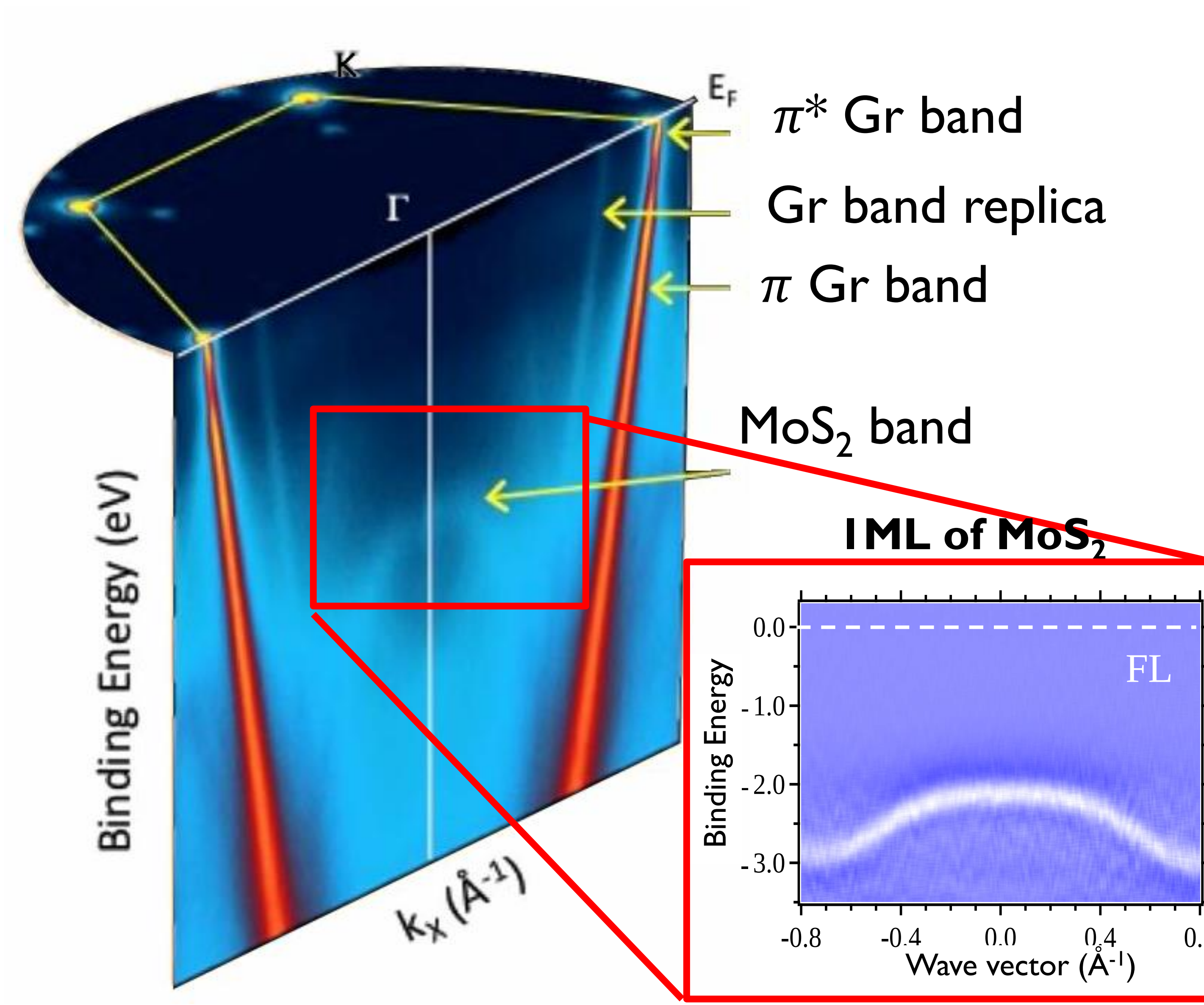


Sharp vertical interface between the MoS_2 and graphene

Real vdW heterostructure

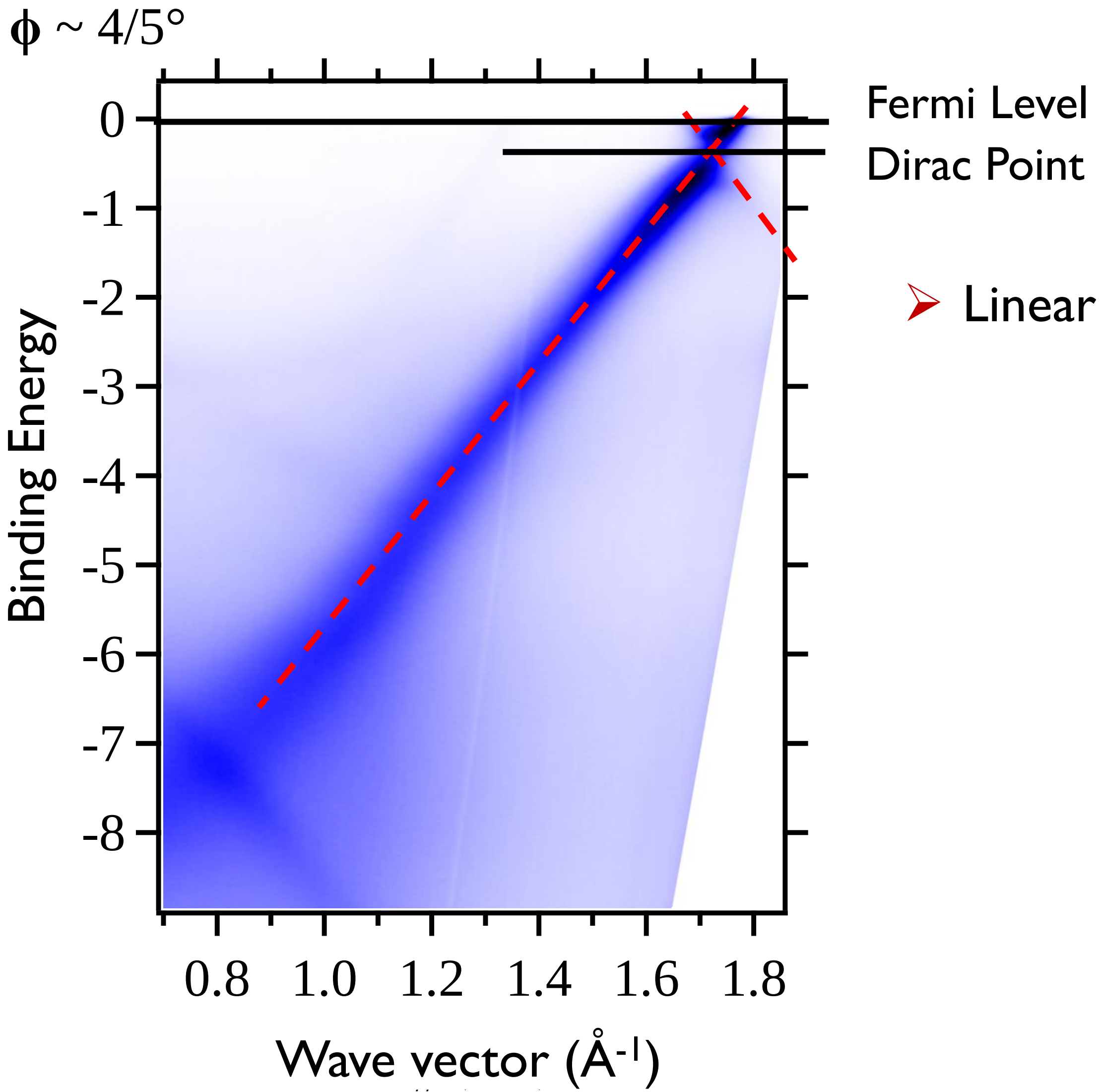
Pierucci D. et al. Scientific Report (2016)
Pierucci D. et al. Nano Letters (2016)

MoS_2/Graphene : electronic structure



Pierucci D. *et al.* Nano Letters (2016)

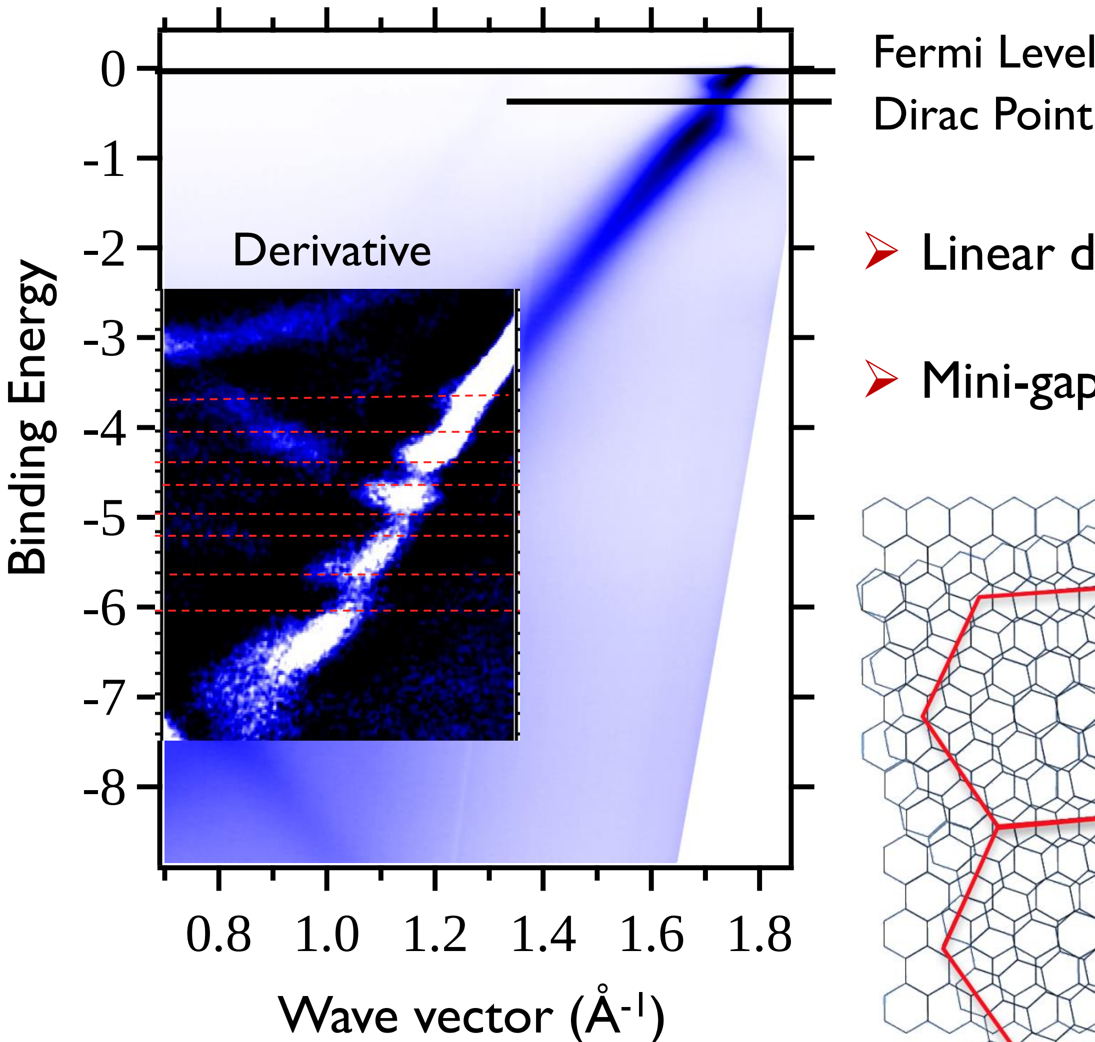
MoS_2/Graphene : interlayer interaction



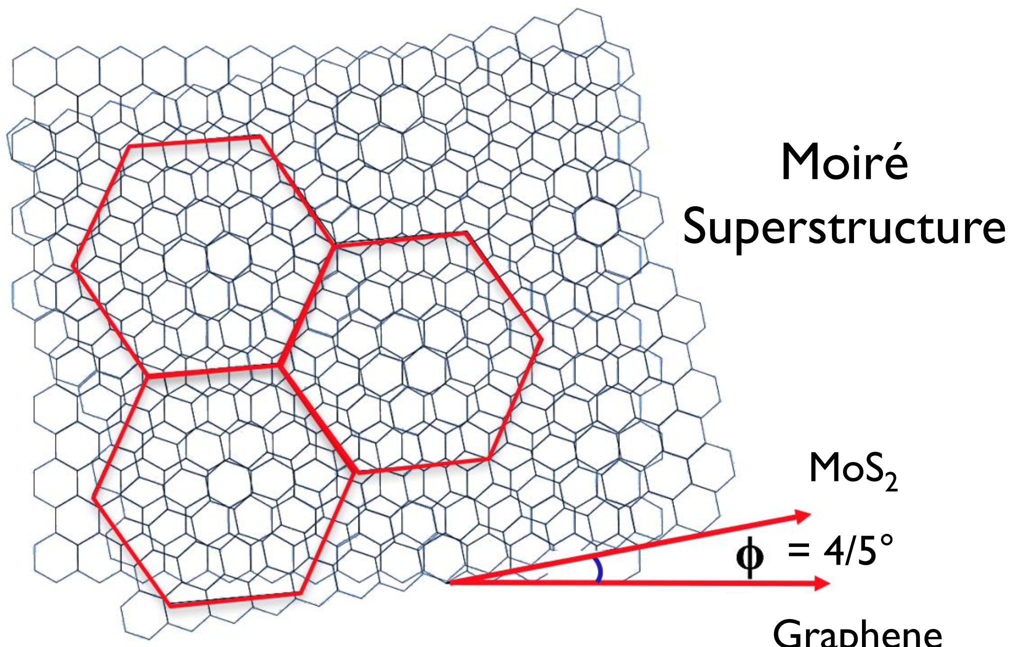
- Linear dispersion typical of graphene

Pierucci D. et al. Nano Letters (2016)

MoS_2/Graphene : interlayer interaction

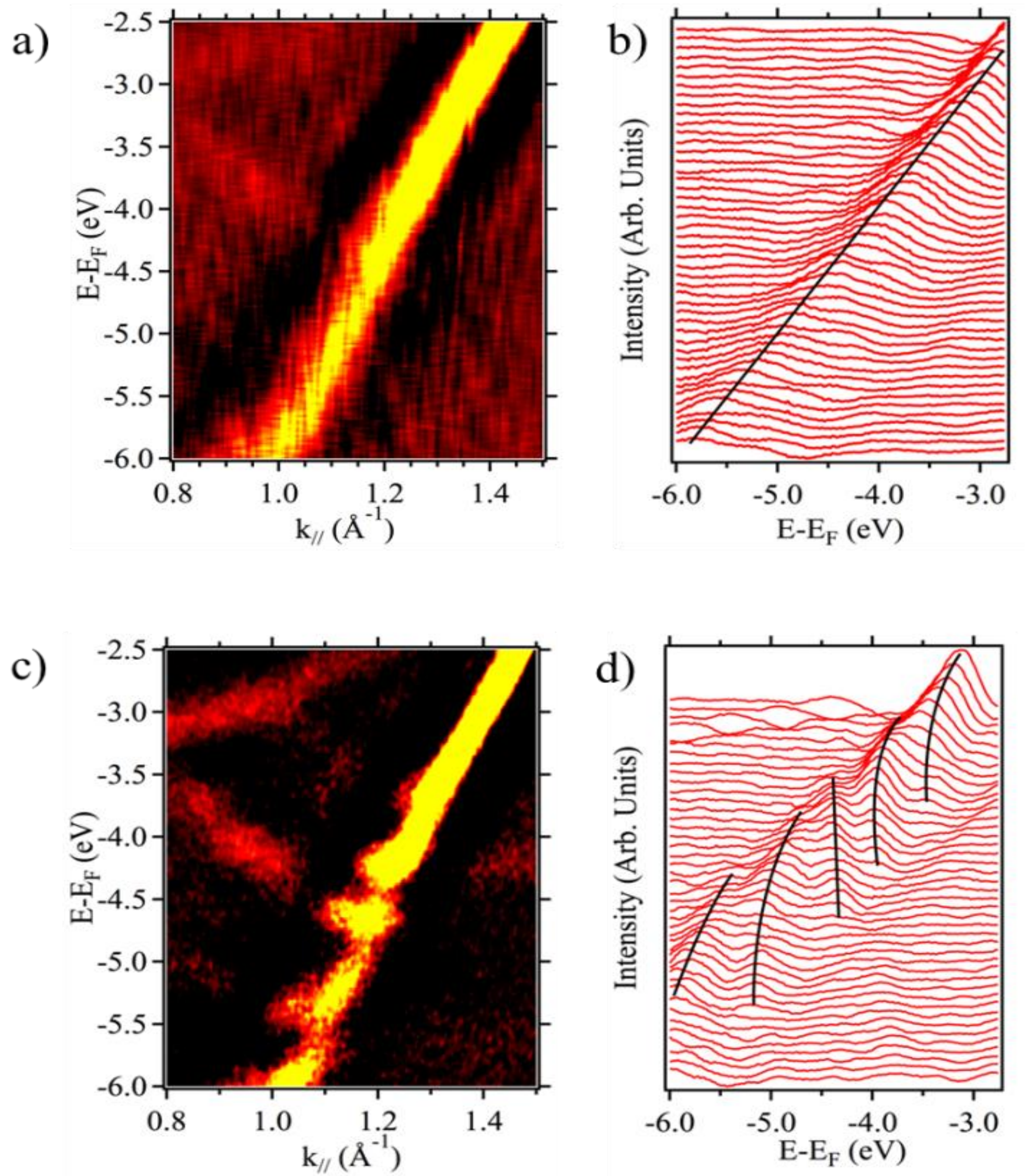


- Linear dispersion typical of graphene
- Mini-gaps induced by a superpotential



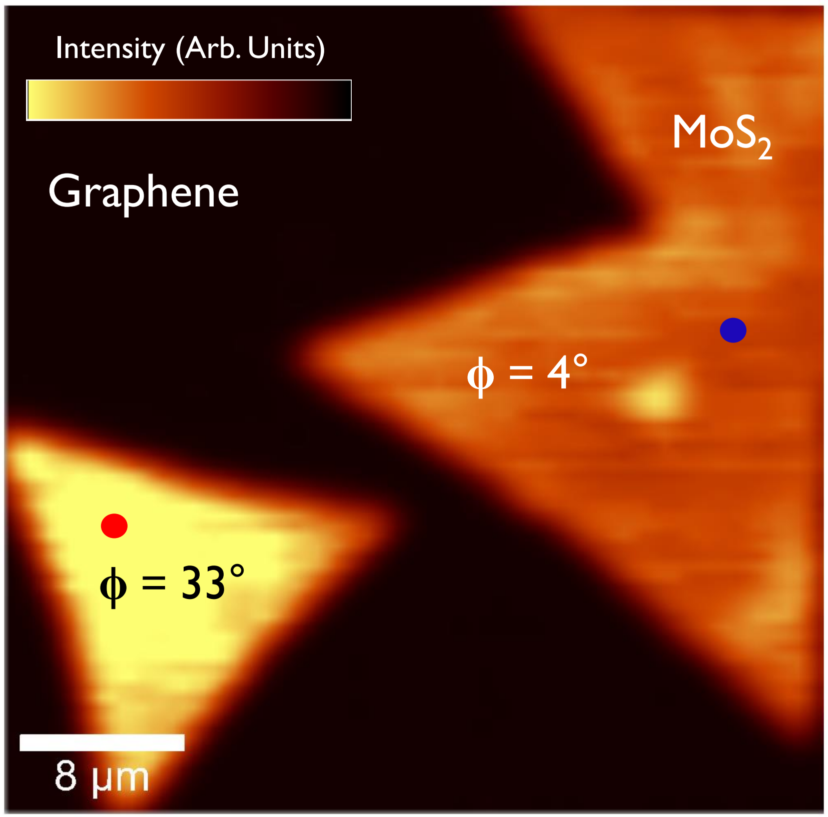
Pierucci D. et al. Nano Letters (2016)

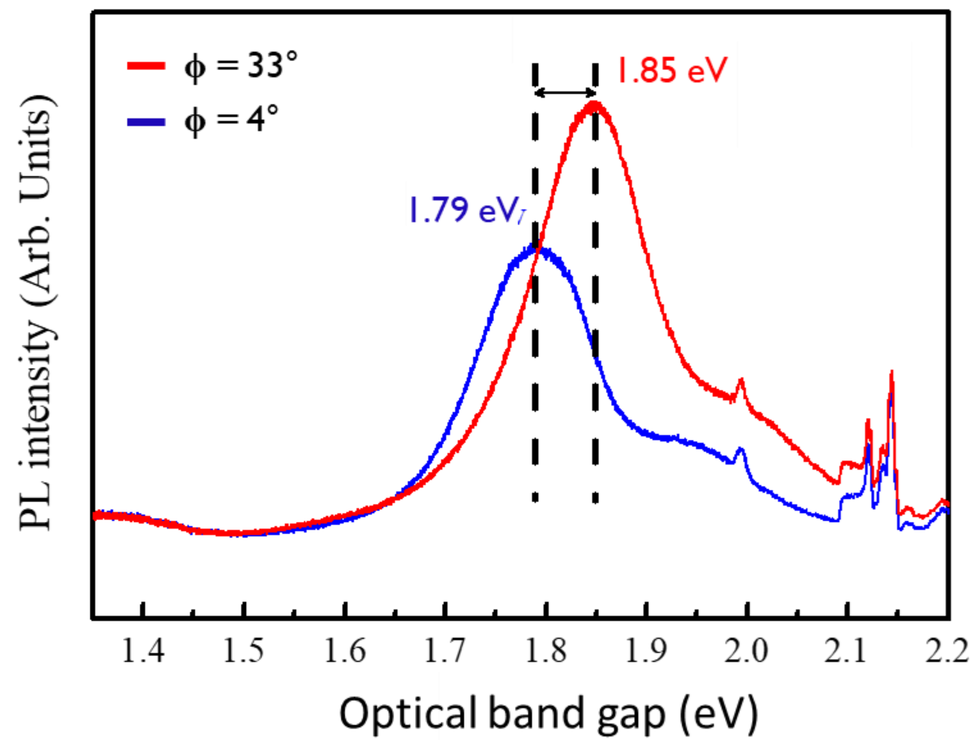
MoS_2/Graphene : mini gaps



MoS_2/Graphene : interlayer interaction

Photoluminiscence Map

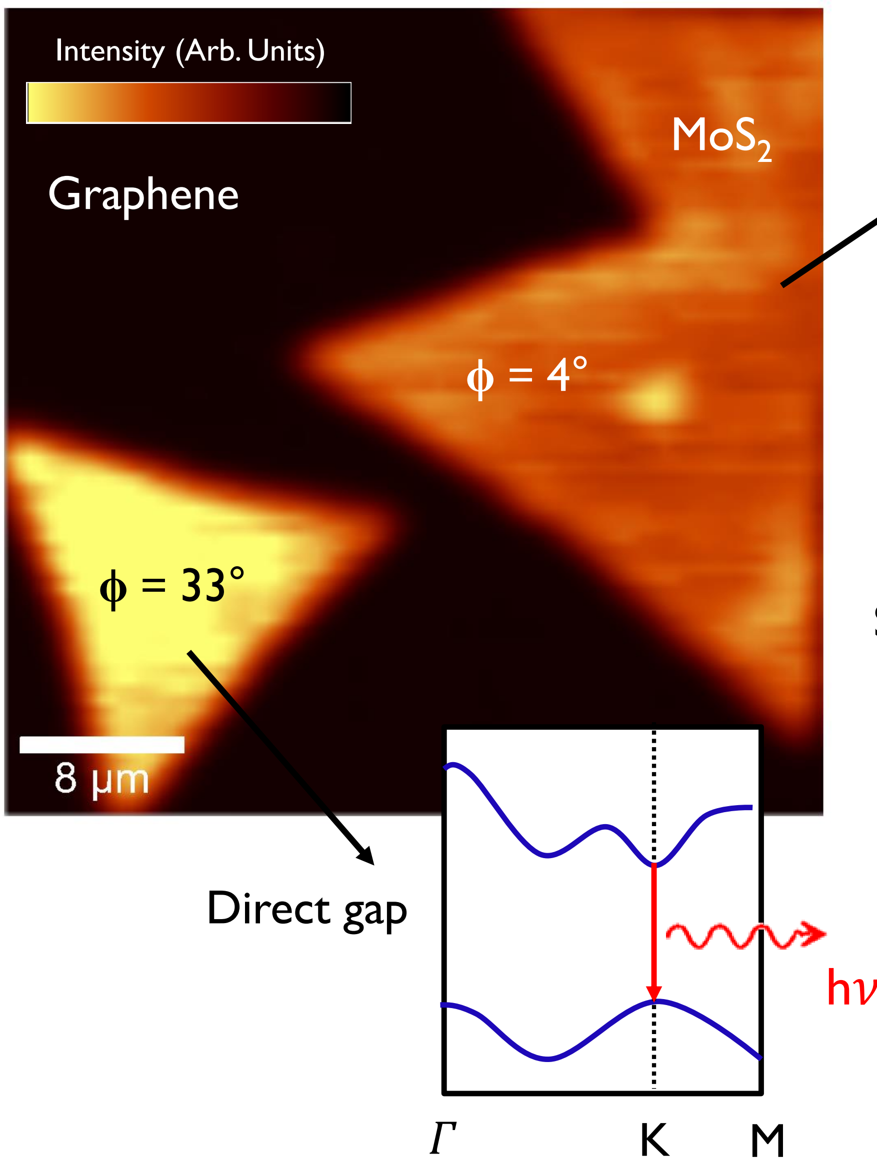


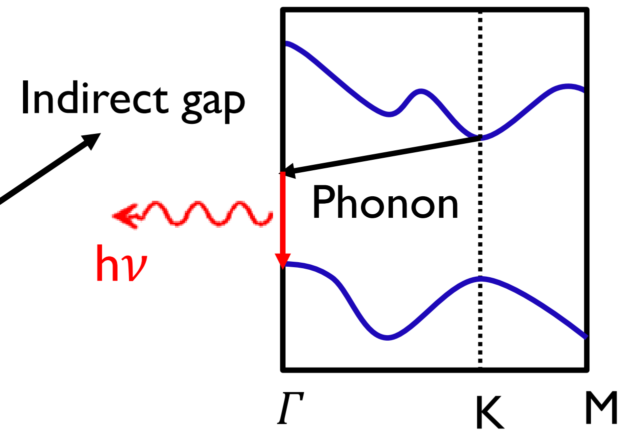


Ben Aziza Z., Pierucci D. et al. Carbon (2016)

MoS_2/Graphene : interlayer interaction

Photoluminiscence Map



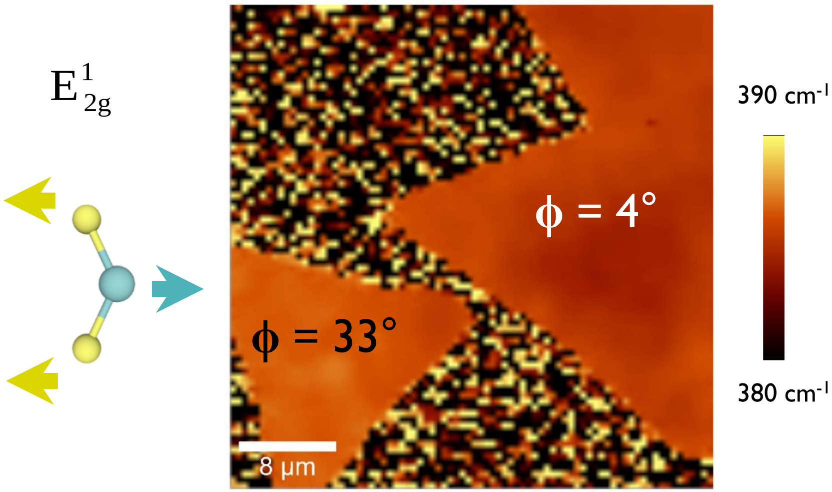


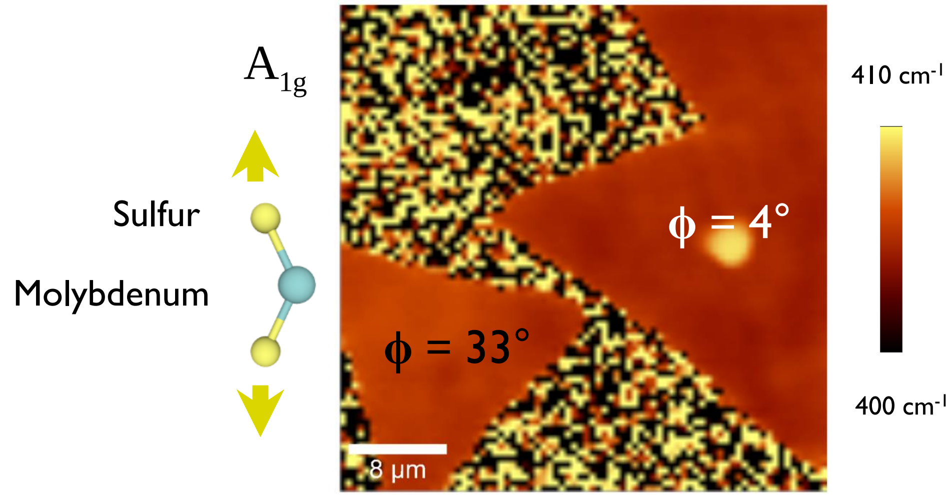
Stacking ⇒ Direct → indirect band gap ⇒ Radiative → non radiative process

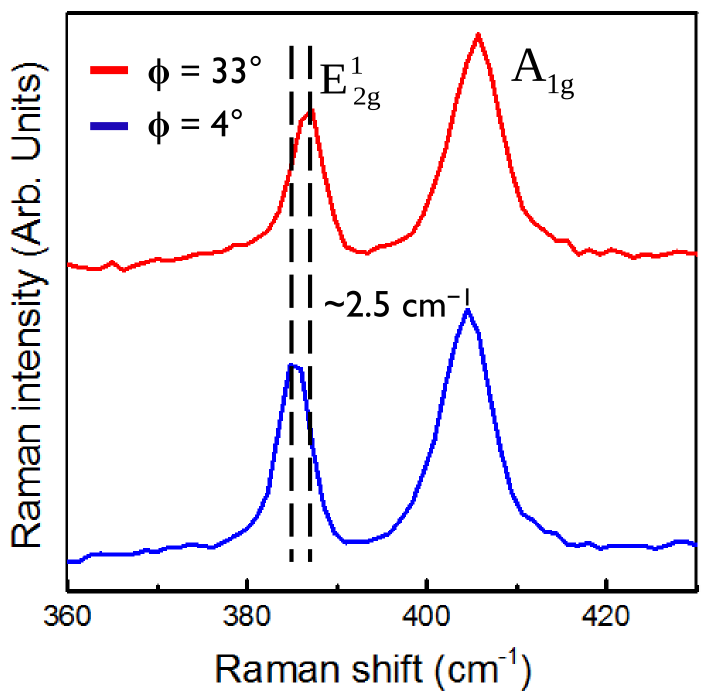
Ben Aziza Z., Pierucci D. et al. Carbon (2016)

MoS_2/Graphene : interlayer interaction

Micro-Raman Map







Biaxial uniform tensile strain

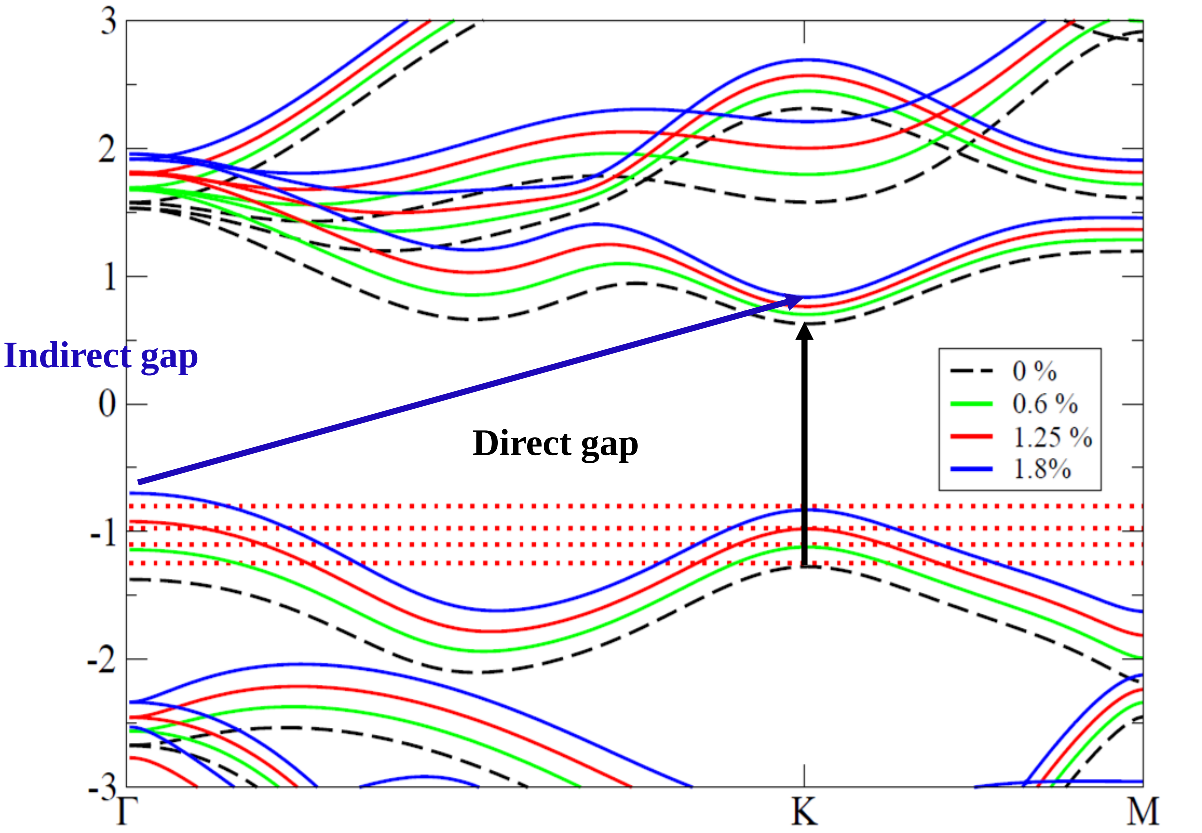
0.6 +/- 0.1%

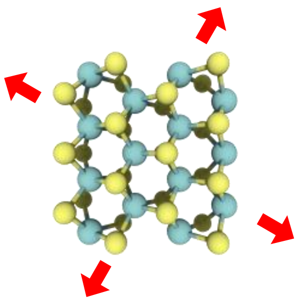
Flake at ϕ = 4° undergoes a more important tensile strain than the flake at ϕ = 33°

Ben Aziza Z., Pierucci D. et al. Carbon (2016)

MoS$_2$/Graphene : interlayer interaction

DFT calculation: effect of strain





Ben Aziza Z., Pierucci D. et al. Carbon (2016)