

2D materials and chalcogenides: elaboration and applications

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OUTLINE

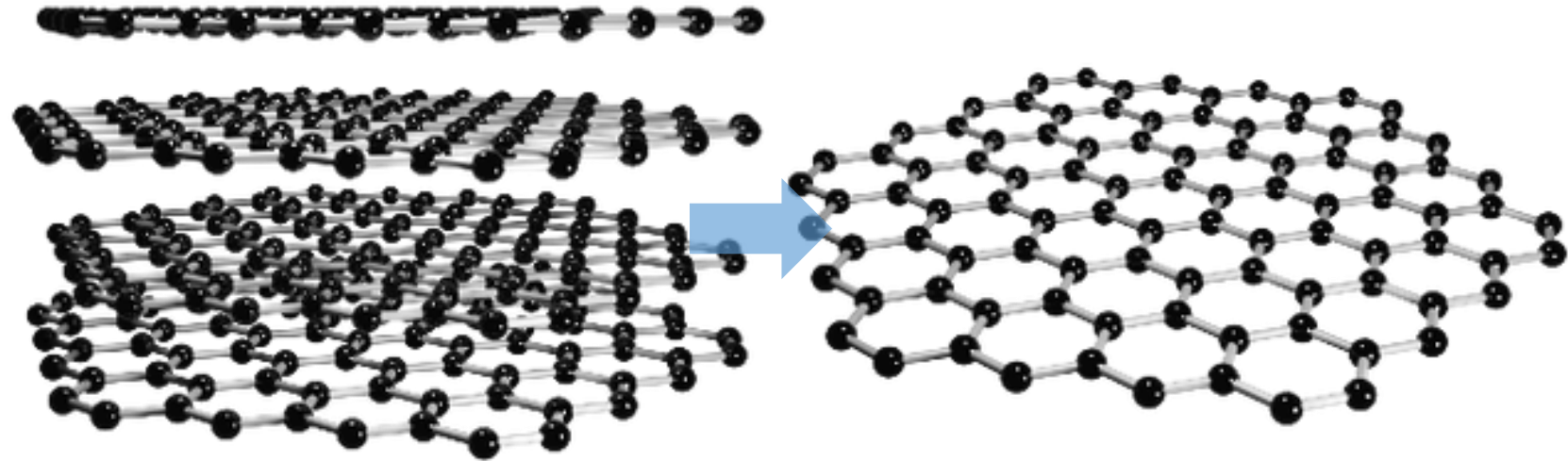
1. Introduction to 2D and van der Waals materials
2. Growth of 2D materials and chalcogenides: from exfoliation to molecular beam epitaxy
3. Recent achievements in MBE-grown 2D materials: narrow excitonic lines, doping, alloys, superconductivity, ferroelectricity, ferromagnetism
4. 2D magnets for spintronics: $\text{Cr}_{1+\delta}\text{Te}_2$, $\text{Fe}_{3-5}\text{GeTe}_2$
5. Conclusion and perspectives

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Superlative material



A. Geim

NOBEL PRIZE IN 2010

graphite

- 200 times stronger than steel
- 1.000.000 times thinner than a single human hair
- The world's lightest material (1 m² weighs about 0,77 milligram)
- Flexible
- Transparent
- Impenetrable for molecules
- Excellent electrical and heat conduction

graphene

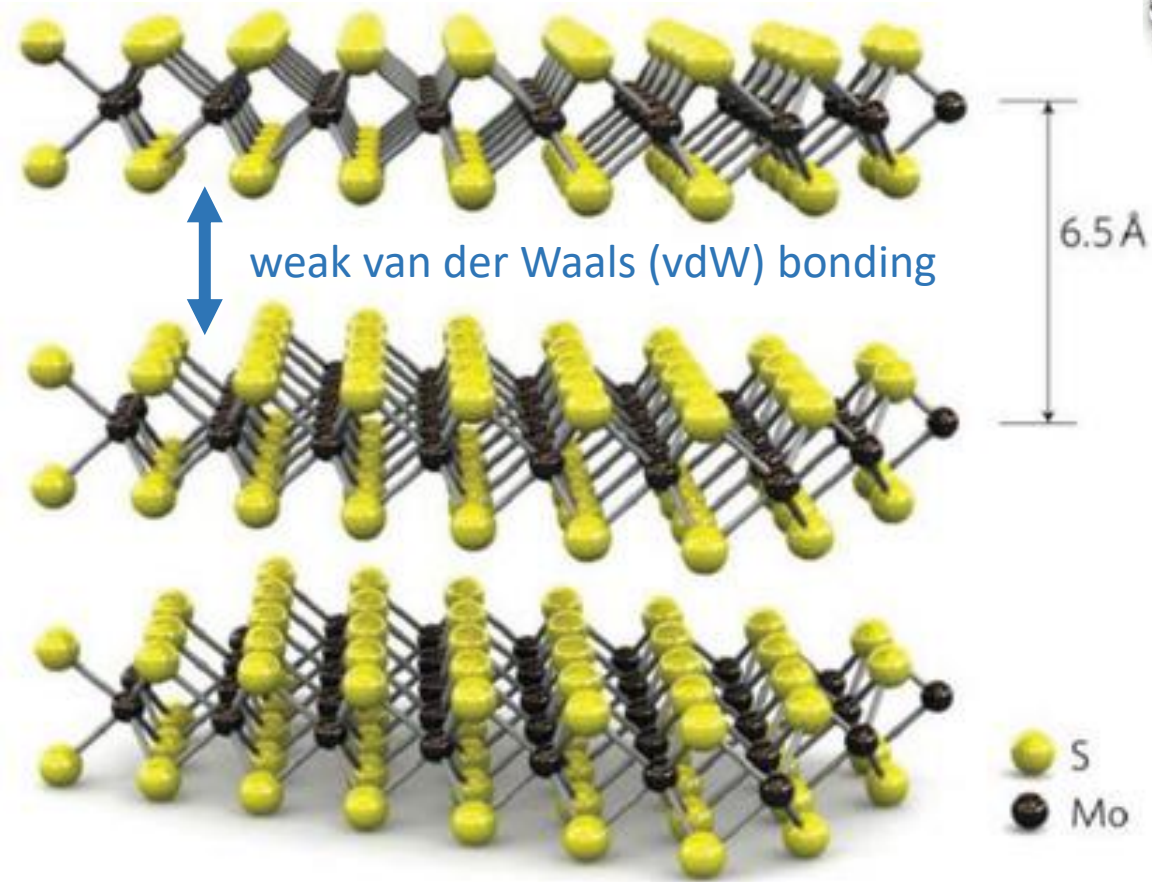


K. Novoselov

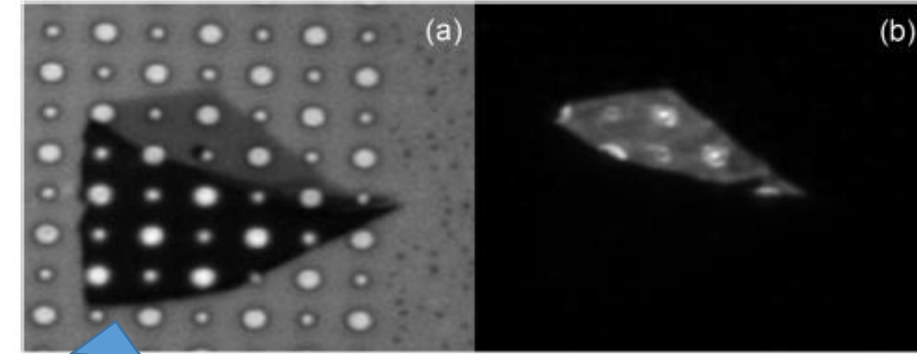
NOBEL PRIZE IN 2010

K. Novoselov and A. Geim, Nature **438**, 197 (2005)

2010, TRANSITION METAL DICHALCOGENIDES (TMD)



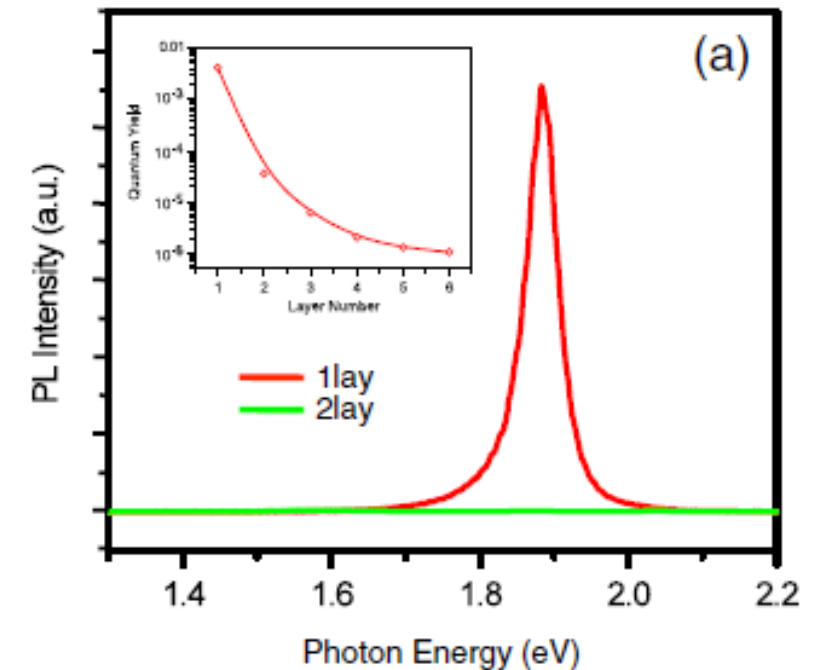
MoS₂



from the mine...to a single layer flake

MoS₂ becomes direct bandgap semiconductor in 1 monolayer

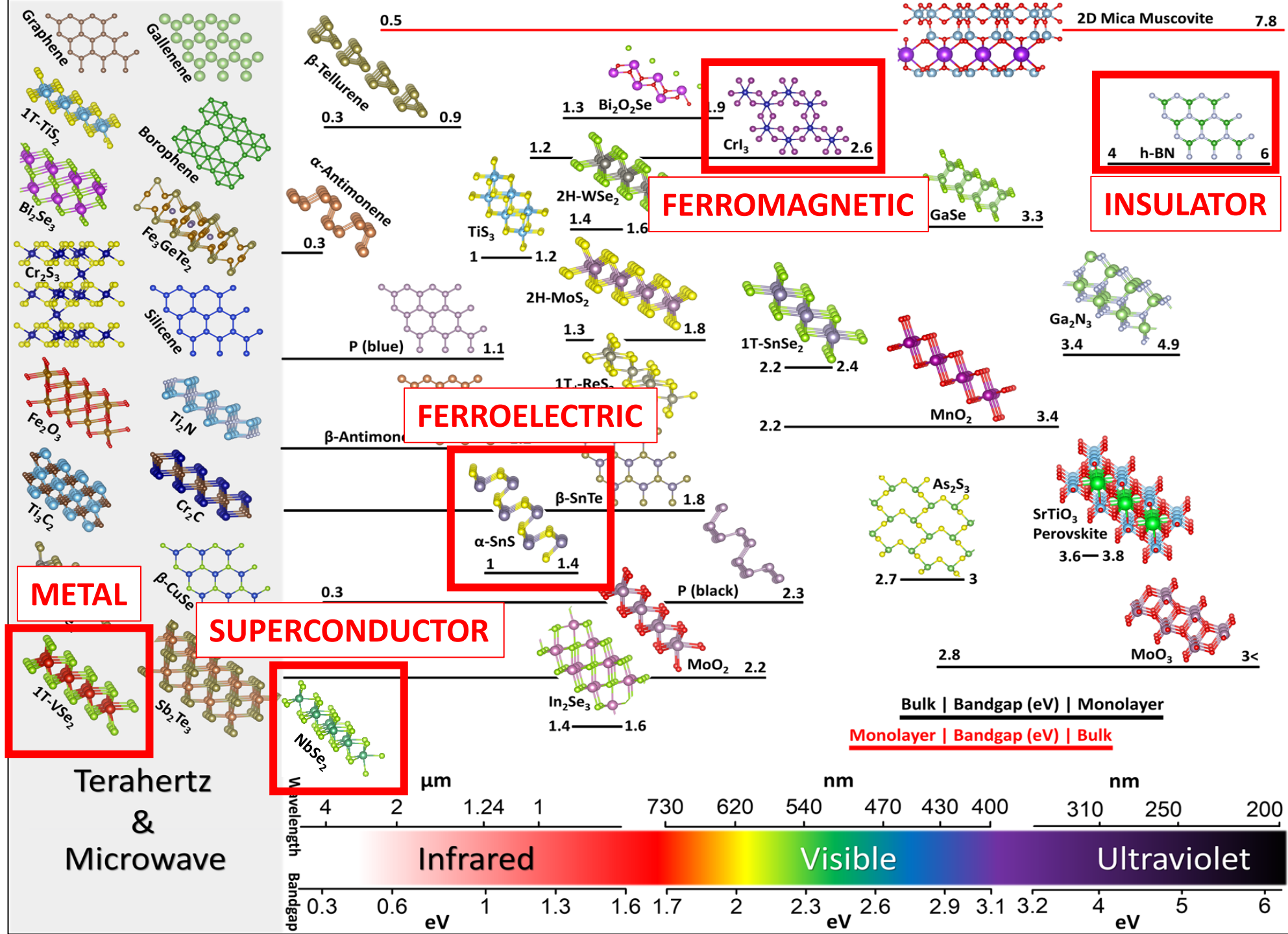
exceptional
light absorber/emitter



2004-2021

Boom in the number
of 2D materials

2D constellation



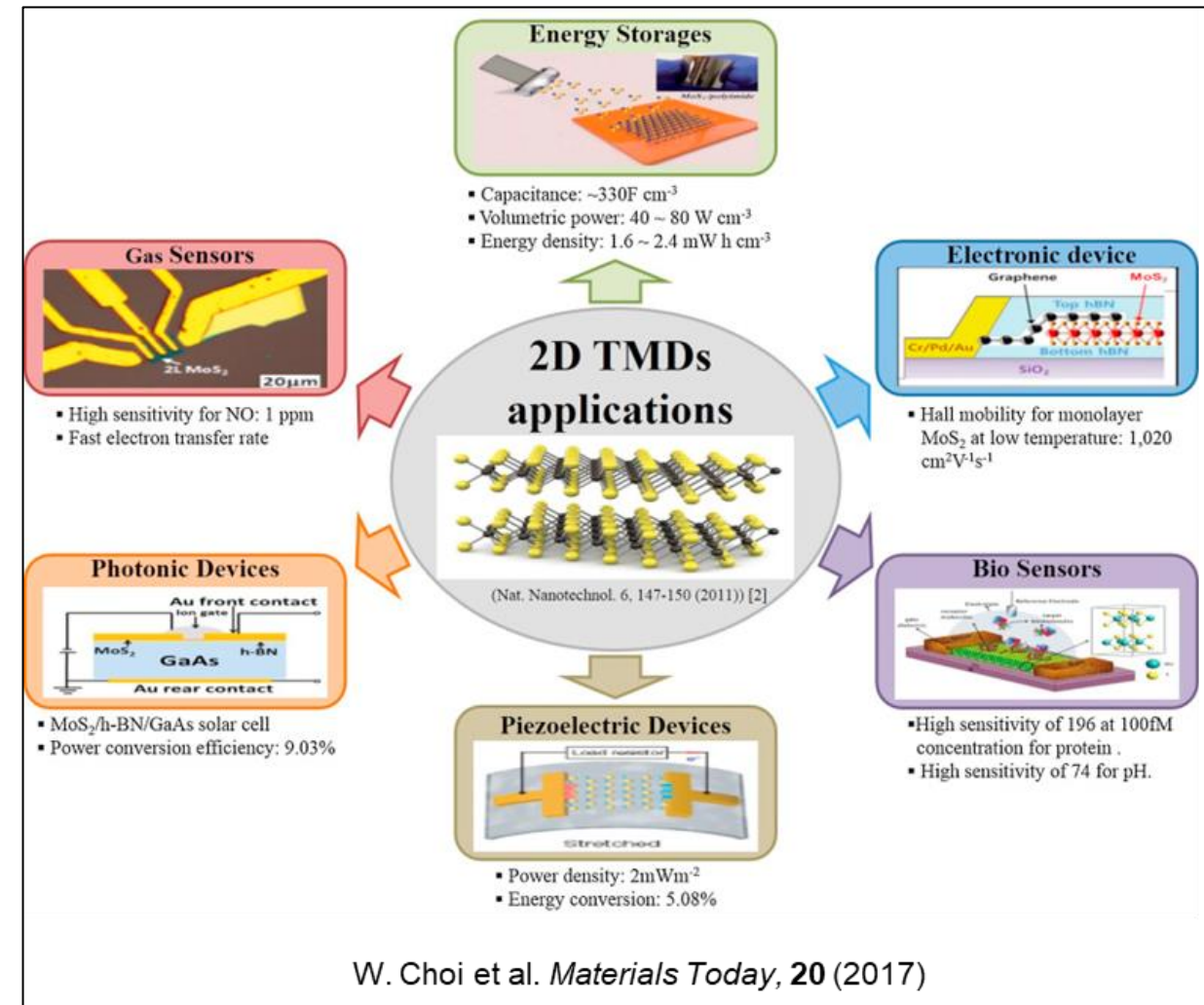
Why so much success ?

□ atomically thin layers: quantum confinement effects (indirect-to-direct bandgap, high carrier mobility, excitonic effects, quantum light emitters...), high sensitivity to their environment and any stimulus (electric field, chemicals, light, stress...) + flexibility

HIGHLY TUNABLE ELECTRONIC
PROPERTIES WITH LOW ENERGY COST

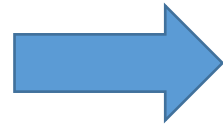
LESS MATERIAL FOR SUSTAINABLE
ELECTRONICS

EASY TO ETCH

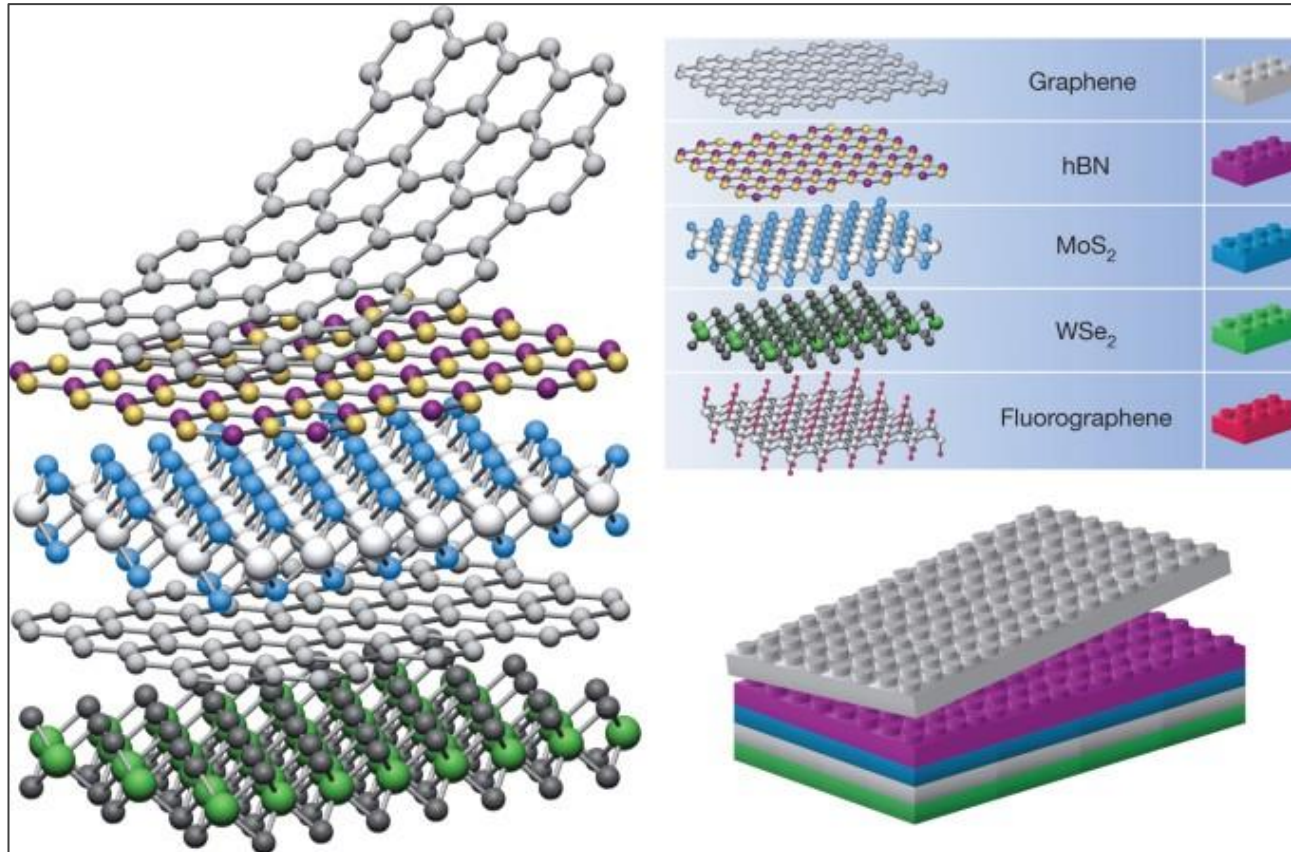


Why so much success ?

□ vdW interfaces: perfectly clean and sharp interfaces with no chemical reaction or atomic intermixing. Perfect control of interface effects: proximity effects (magnetism, superconductivity...), band engineering with well defined band offsets

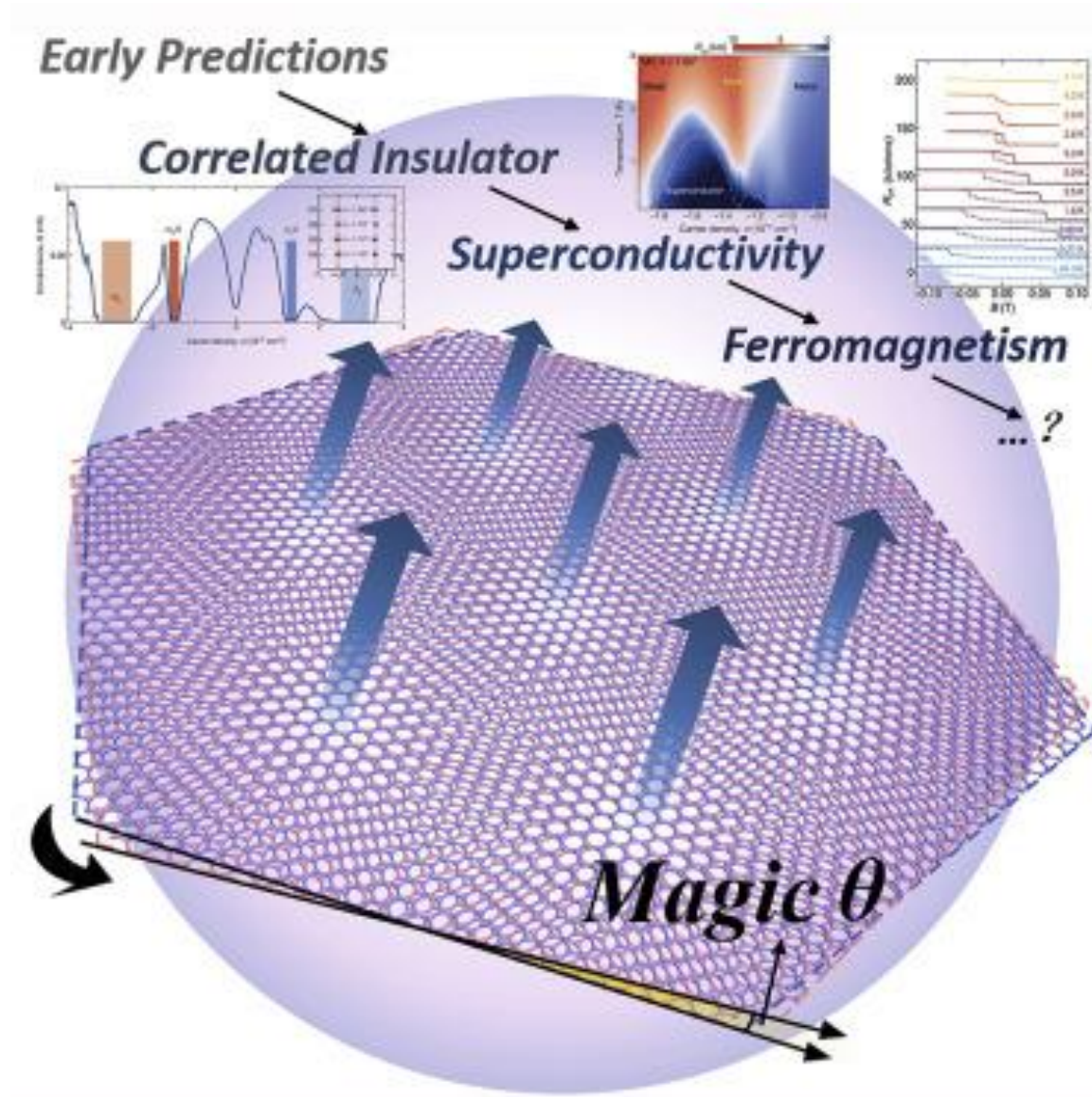


NEW PHYSICS AND VERTICAL DEVICES



A. K. Geim et al., Nature **499**, 419 (2013)

the case of bilayer graphene at the magic twist angle 1.1°



Superconductivity up to $T = 1.7$ K,
Y. Cao et al., Nature **556**, 43 (2018)

Ferromagnetism up to $T = 3.5$ K,
G. Chen et al., Nature **549**, 56 (2020)

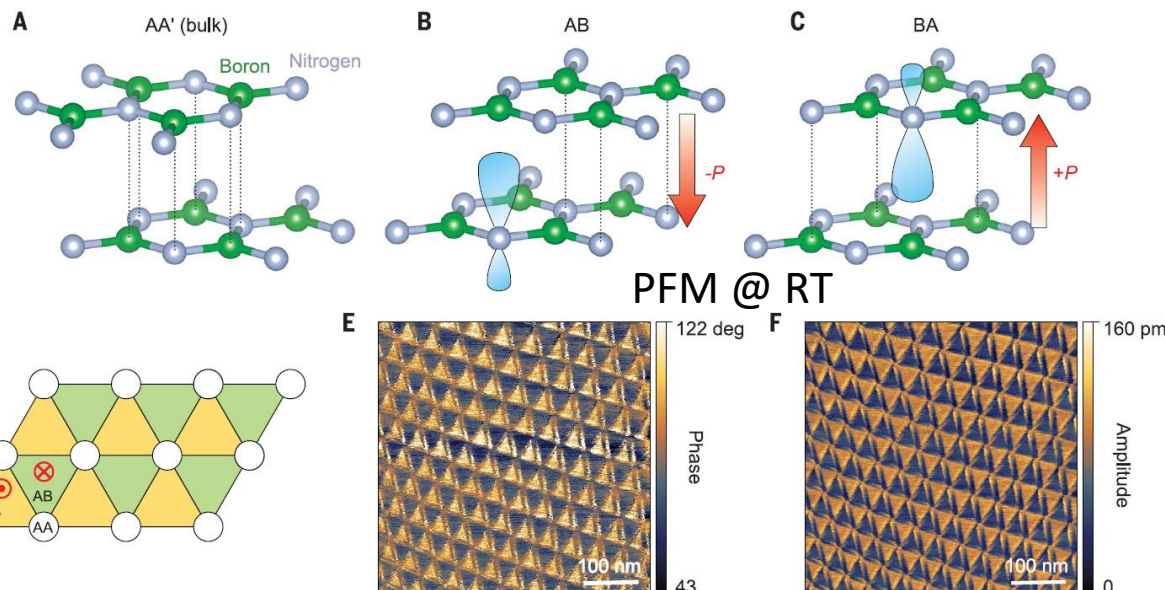
Z. Sun et al., Matter **2**, 1106 (2020)

FERROELECTRICITY IN BILAYERS hBN & MoSe₂

tear-and-stack fabrication method

hBN

MoSe₂

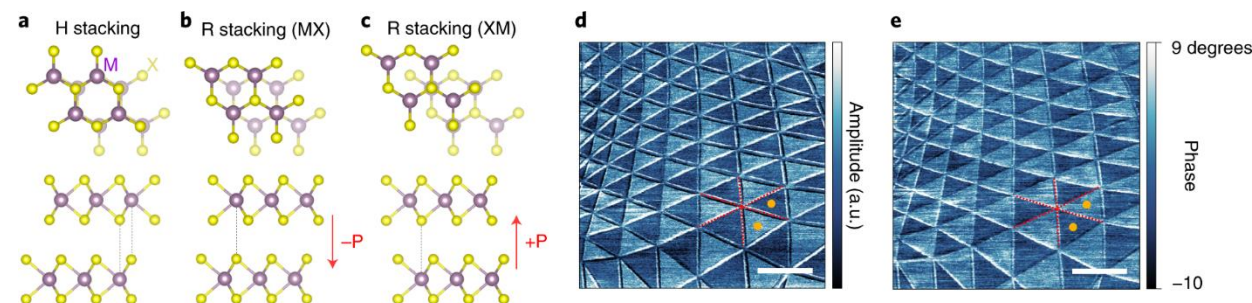
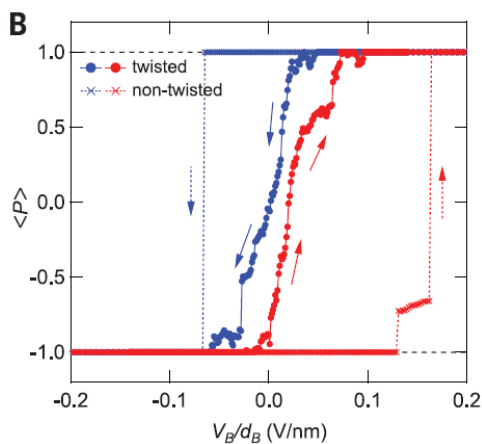


PFM @ RT

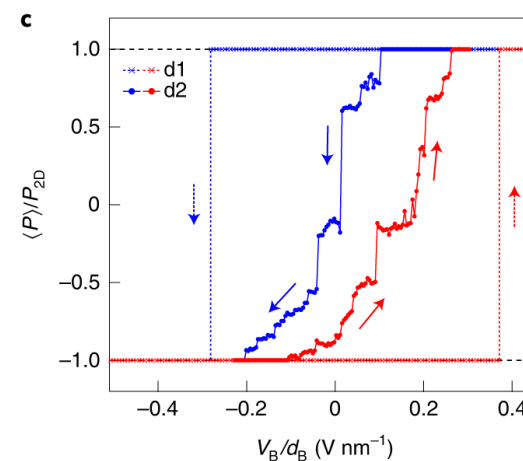
PFM @ RT

Yasuda et al., Science 372, 1458 (2021)

Hysteresis curves from electrical meas. @ 4.2K



X. Wang et al., Nat. Nanotechnol. 17, 367 (2022)



Hysteresis curves from electrical meas. @ 4.2K

Same with WSe₂, MoS₂, WS₂

Also WTe₂: Z. Fei et al., Nature 560, 336 (2018) and MoTe₂: A. Jindal et al., Nature 613, 48 (2023)

TMDs: a very specific band structure

Courtesy Xavier Marie, LPCNO, INSA Toulouse, France

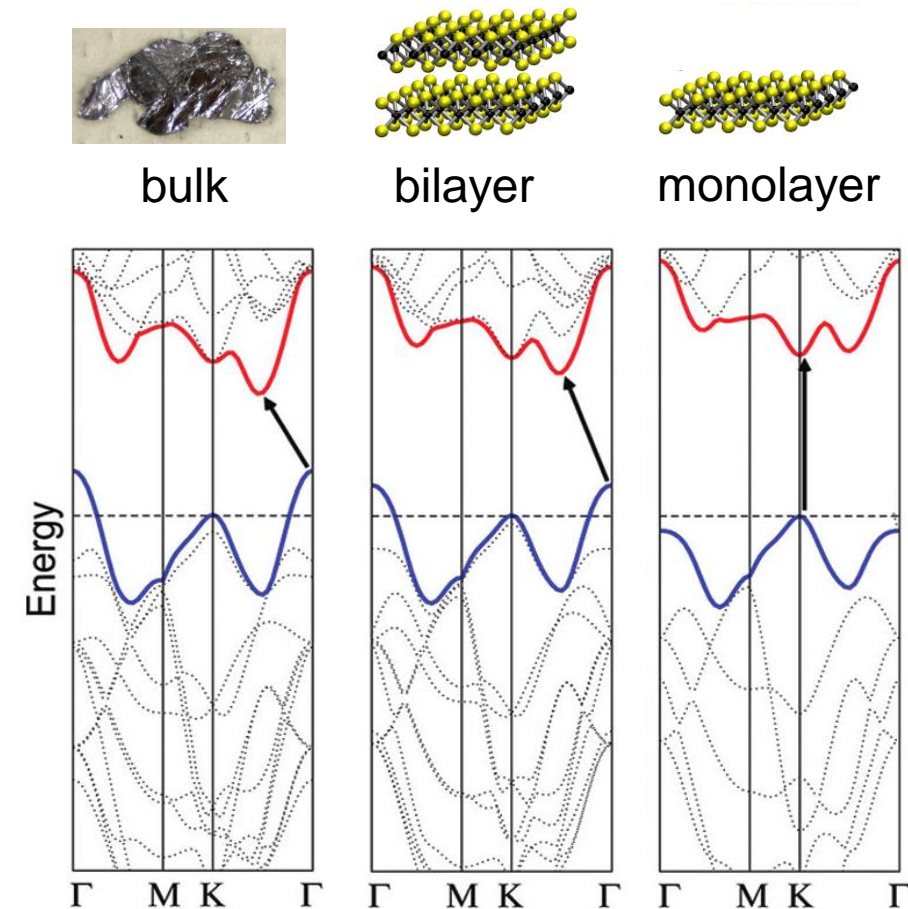
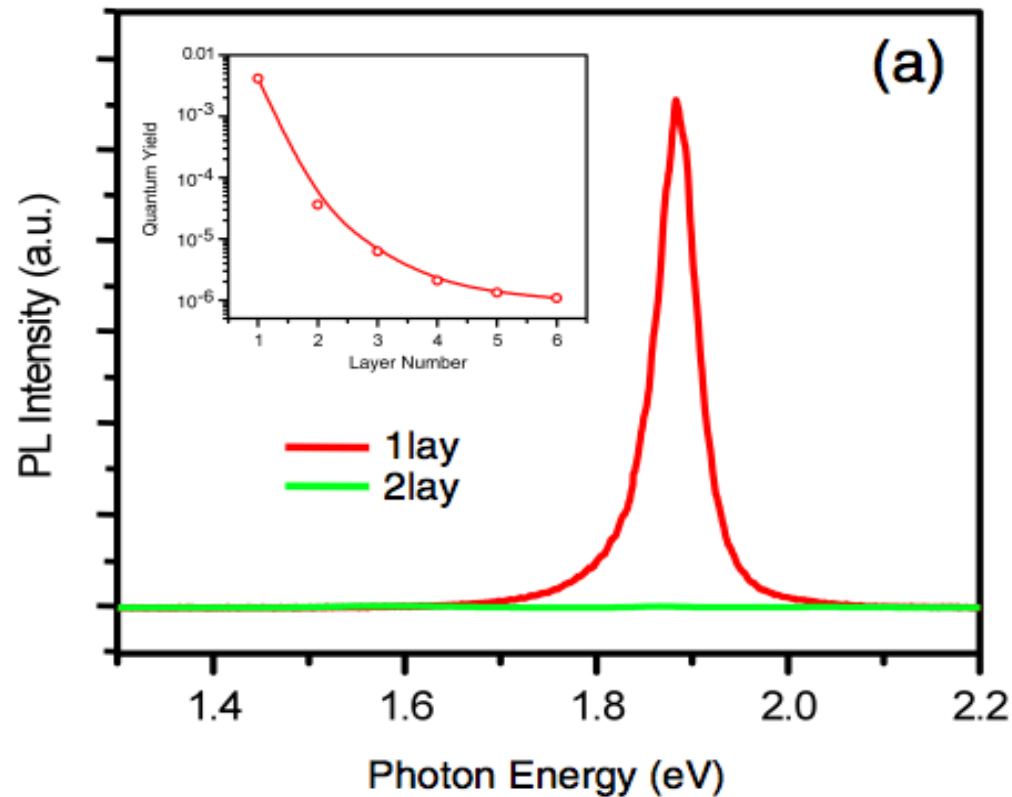
MoS₂ : Optical properties

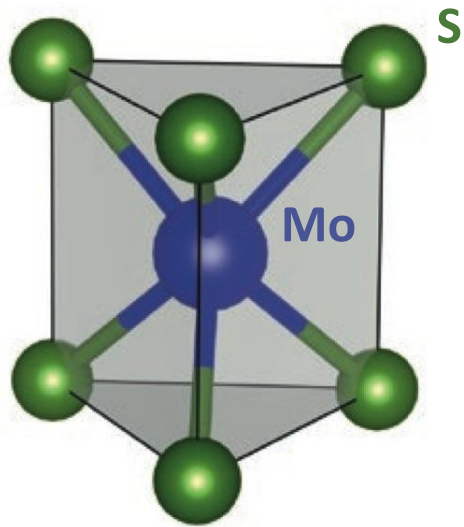
Bulk MoS₂ : indirect bandgap



1 Monolayer: **direct** bandgap

J. Phys.C : Solid State Phys. 5, 759 (1972)





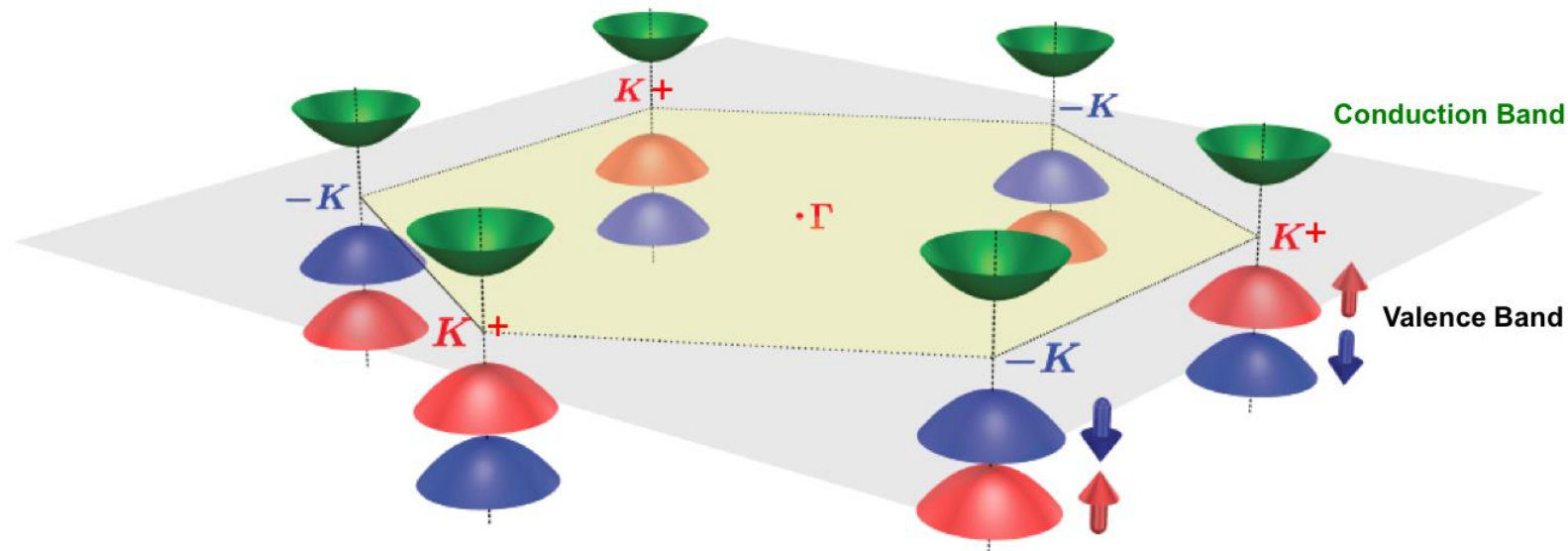
Monolayer MoS₂ band structure

Main difference to Graphene:

- direct bandgap
- broken Inversion symmetry
- strong spin-orbit coupling

} *Spin splitting in
Valence band*

CB and VB edges located at the corners (K points) of the 2D hexagonal Brillouin zone :

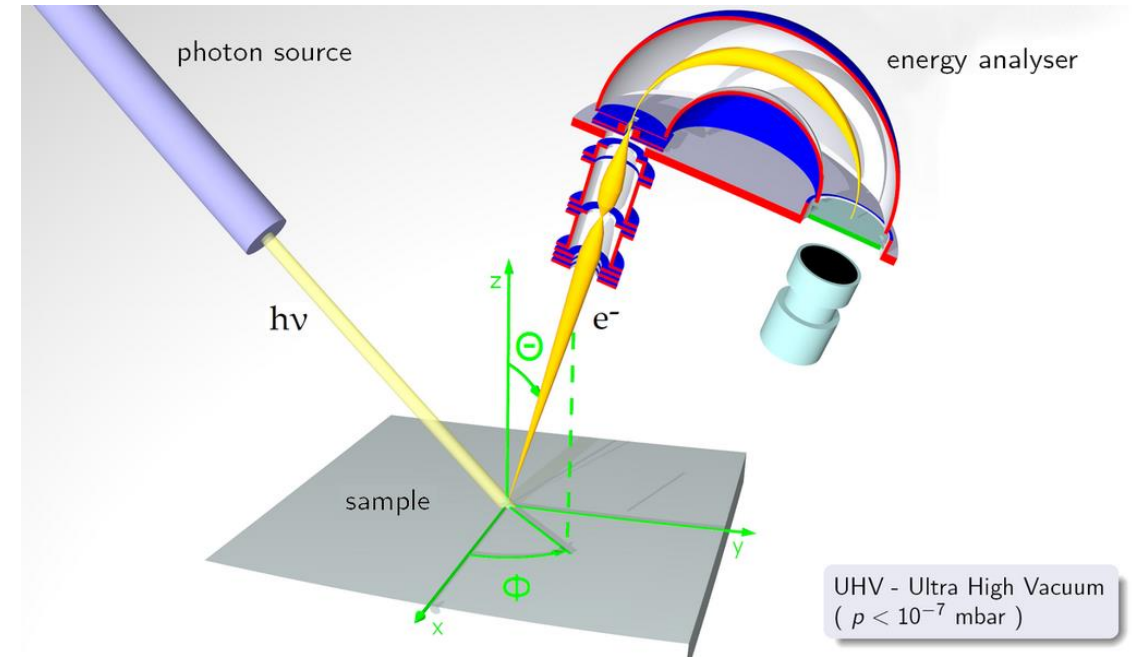
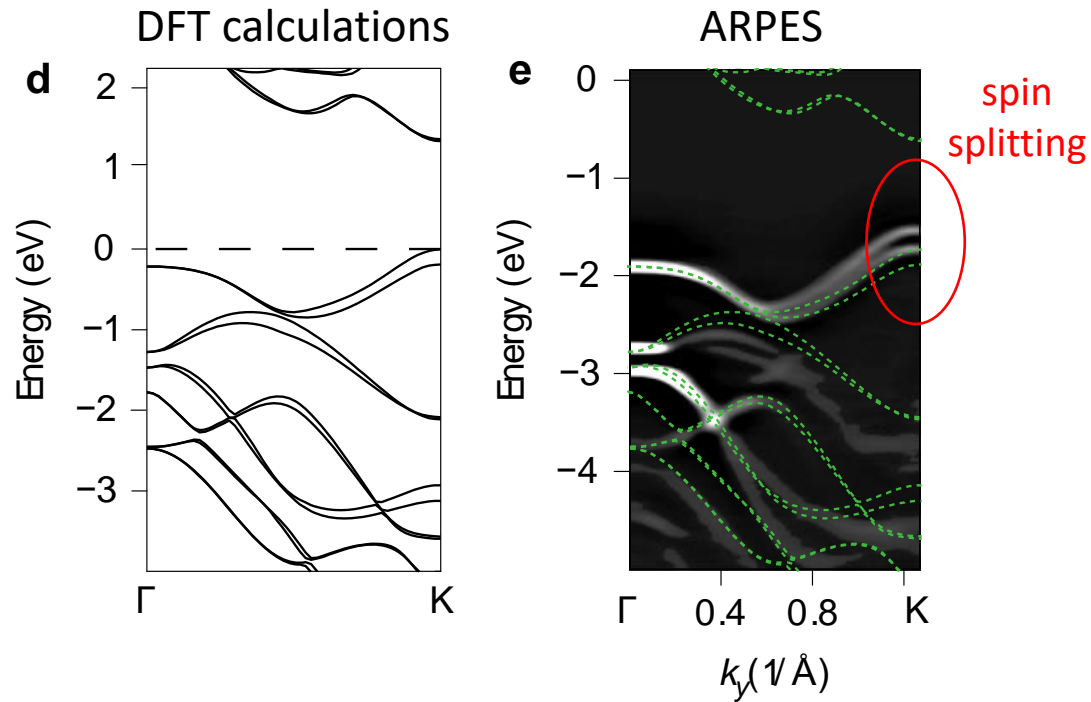


Valleytronics
(addressing $-K$ or K^+
by light, magnetism
or electrically)

Time reversal symmetry \rightarrow *Spin splitting at different valleys is opposite*

Angle-Resolved Photoemission Spectroscopy (ARPES)

MoSe₂-monolayer



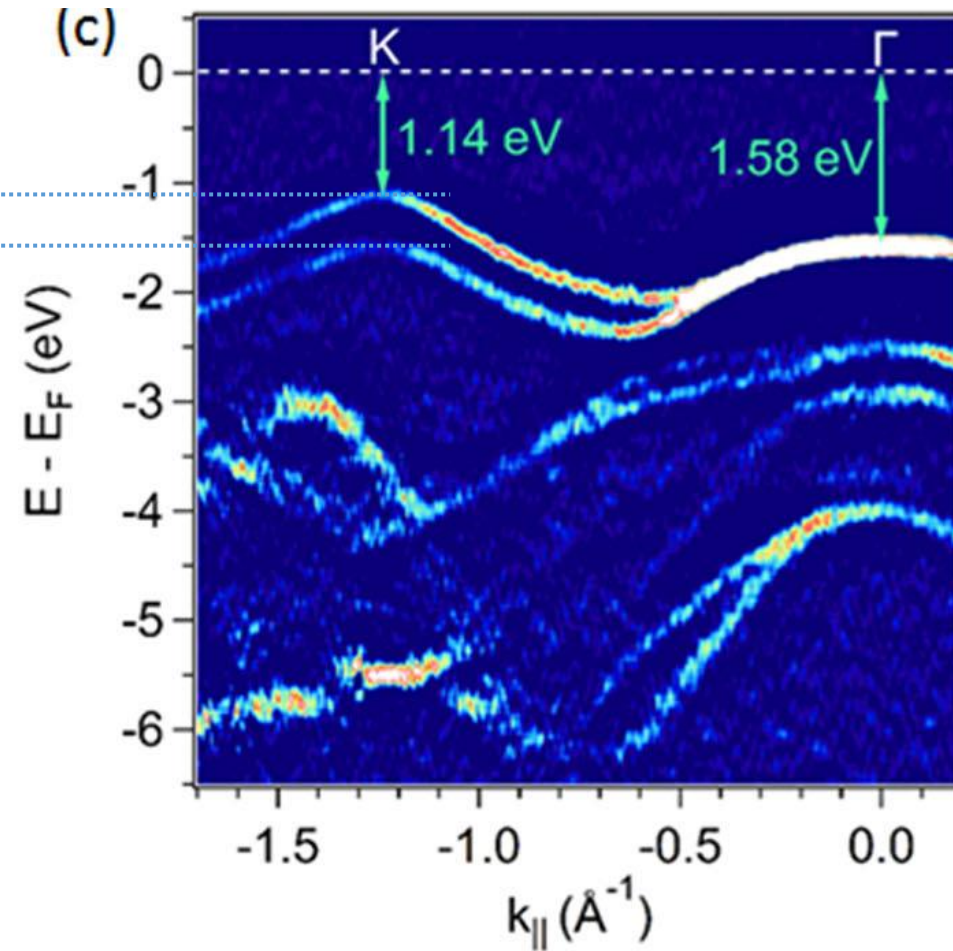
Nature Nano. **9**, 111. (2013)

PRL **111**, 106801 (2013)

Angle-Resolved Photoemission Spectroscopy (ARPES)

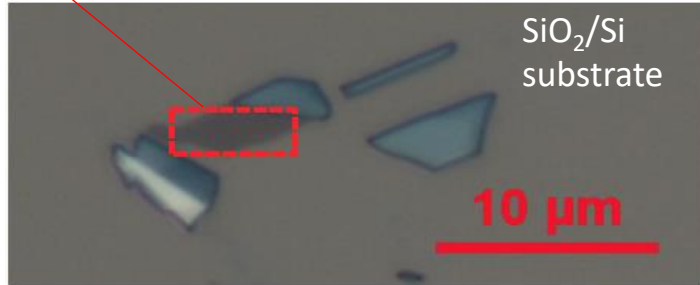
WSe₂-monolayer

spin splitting by SOC
 $\Delta_{\text{SO}} = 480 \text{ meV}$



1 ML WSe₂ sample

Courtesy Xavier Marie, LPCNO, INSA Toulouse, France

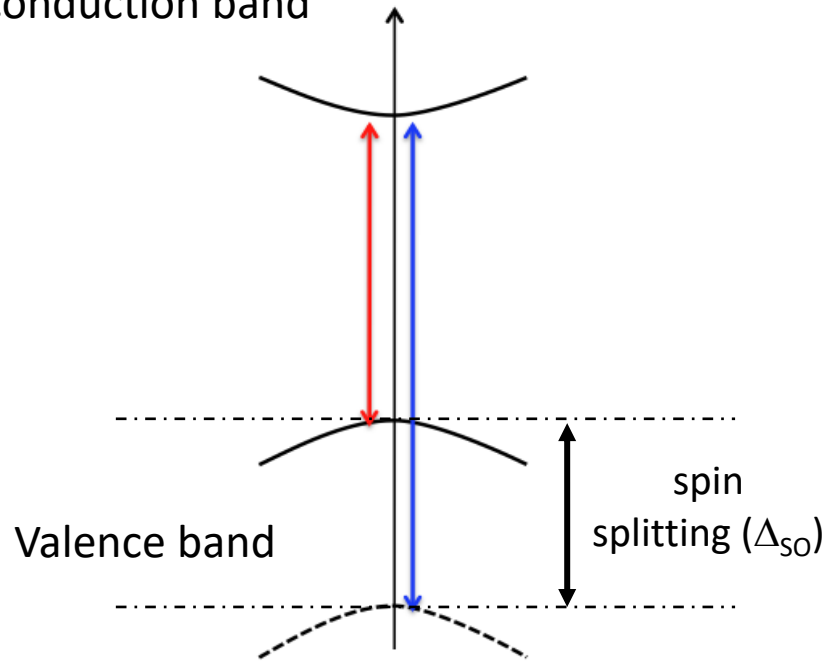


Optical detection

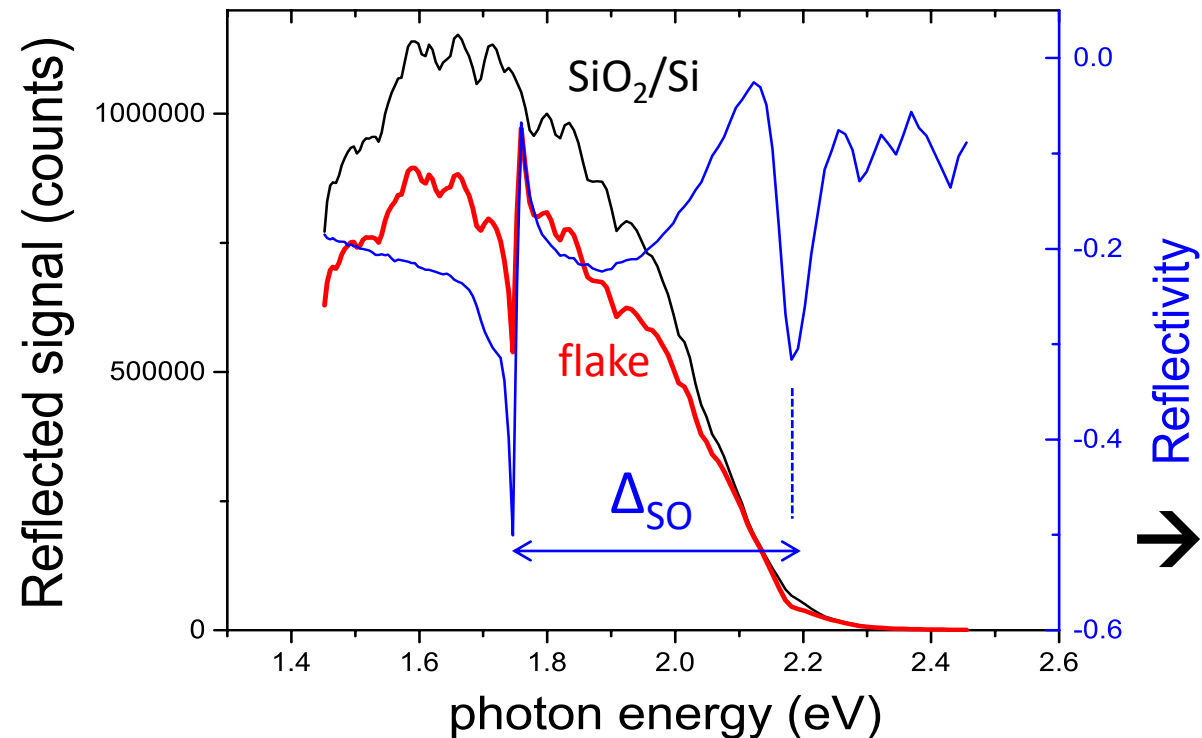
Excitation: *White Light source*

Detection: *reflected Light*

Conduction band



Strong Light ↔ Matter Interaction



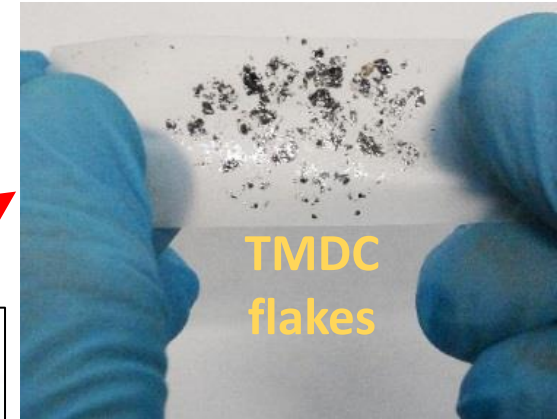
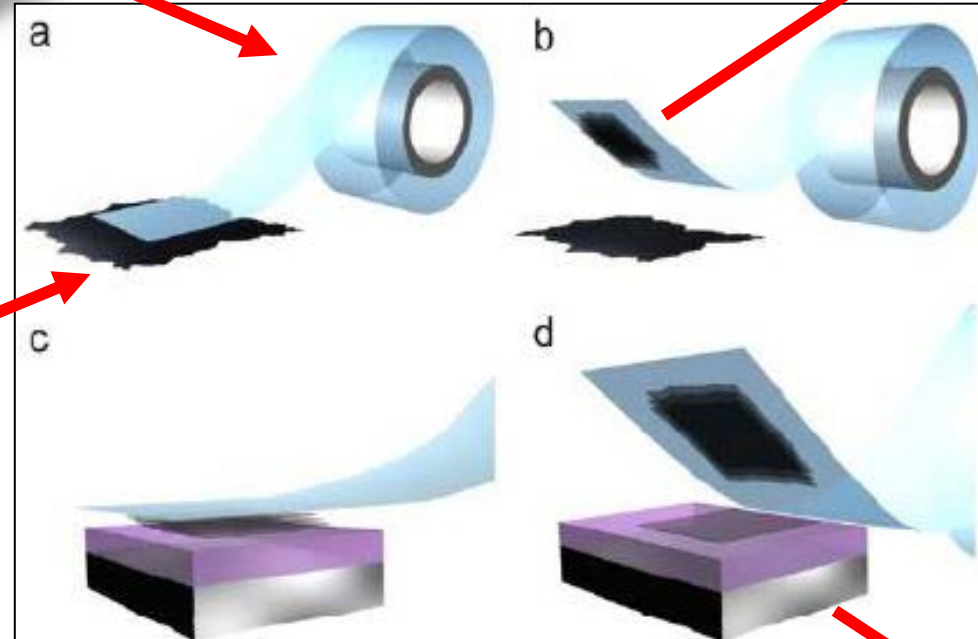
→ Δ_{SO} energy
: 410 meV

OUTLINE

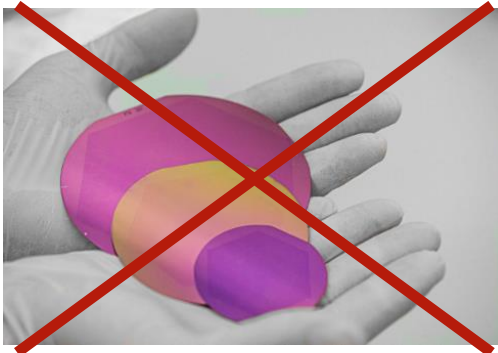
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■ Mechanical exfoliation

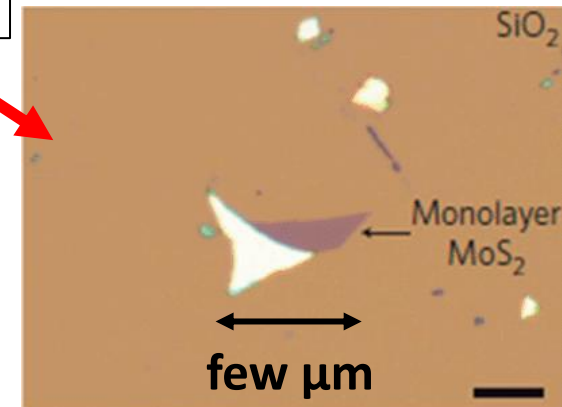
(starting in 2010 with MoS₂)



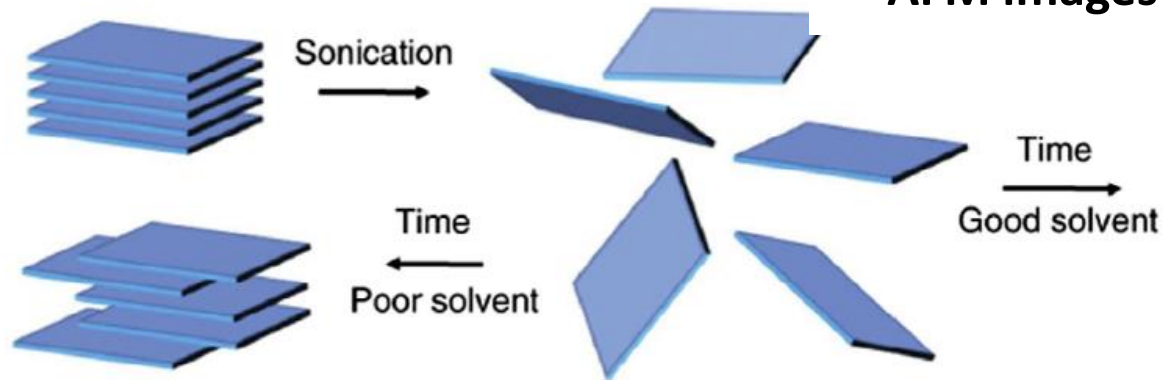
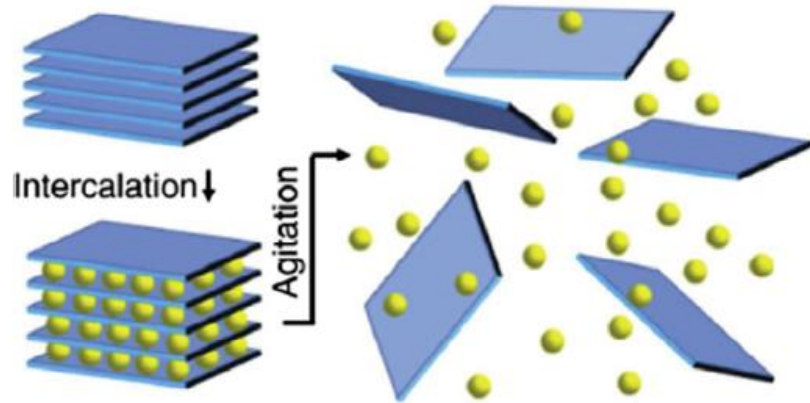
transfer to substrate



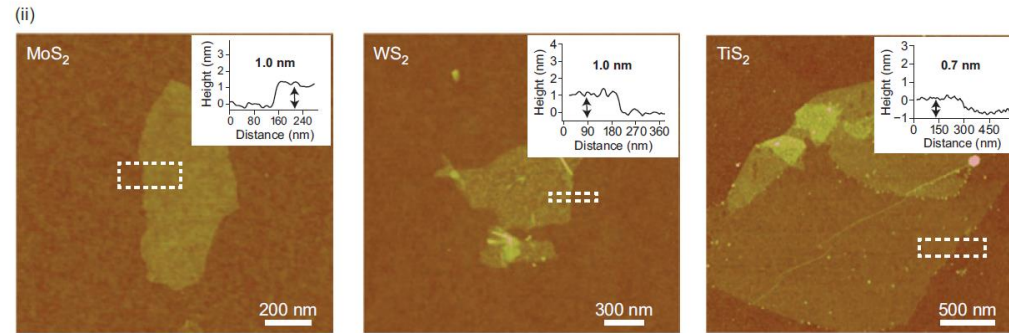
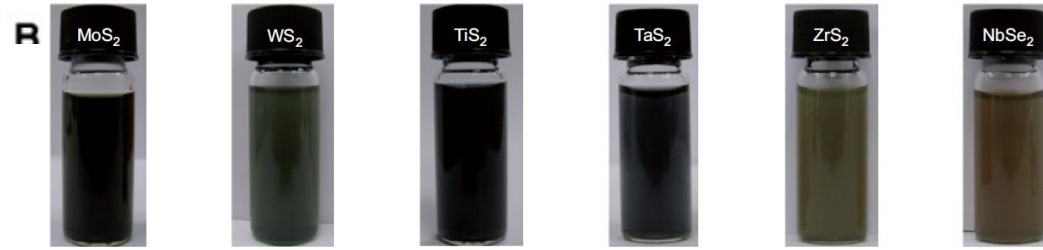
No possible upscaling



Chemical exfoliation



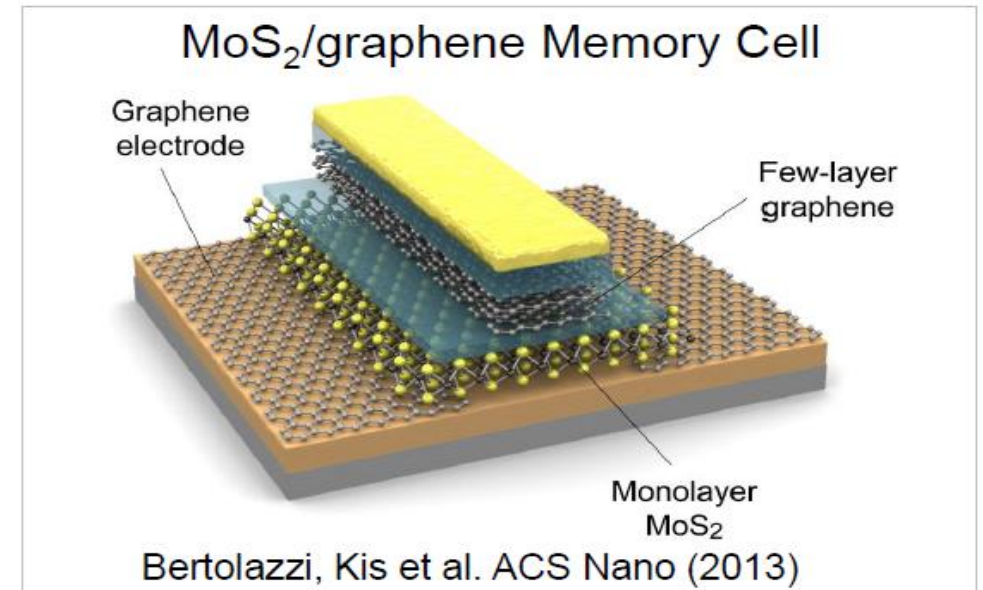
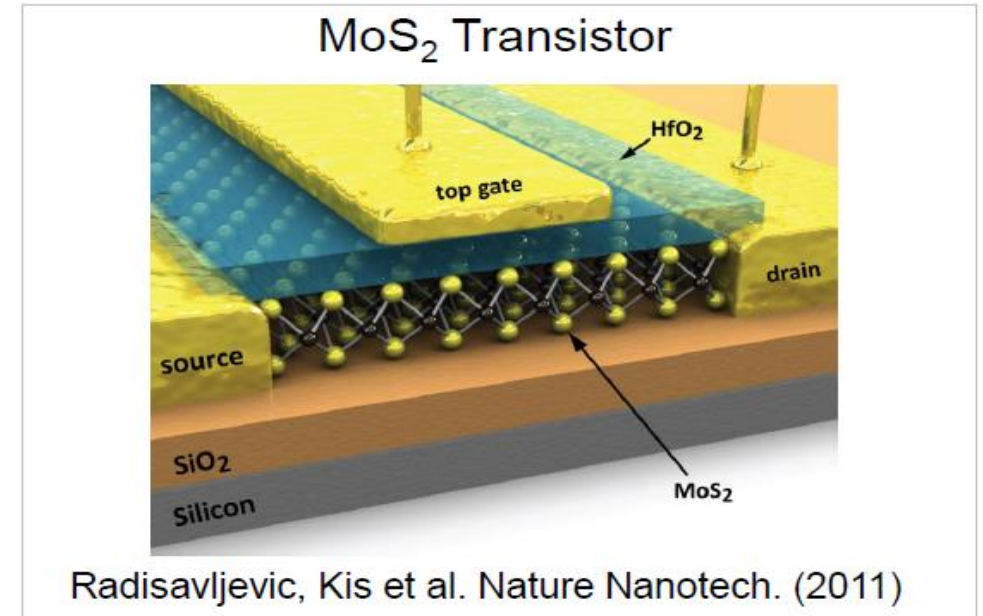
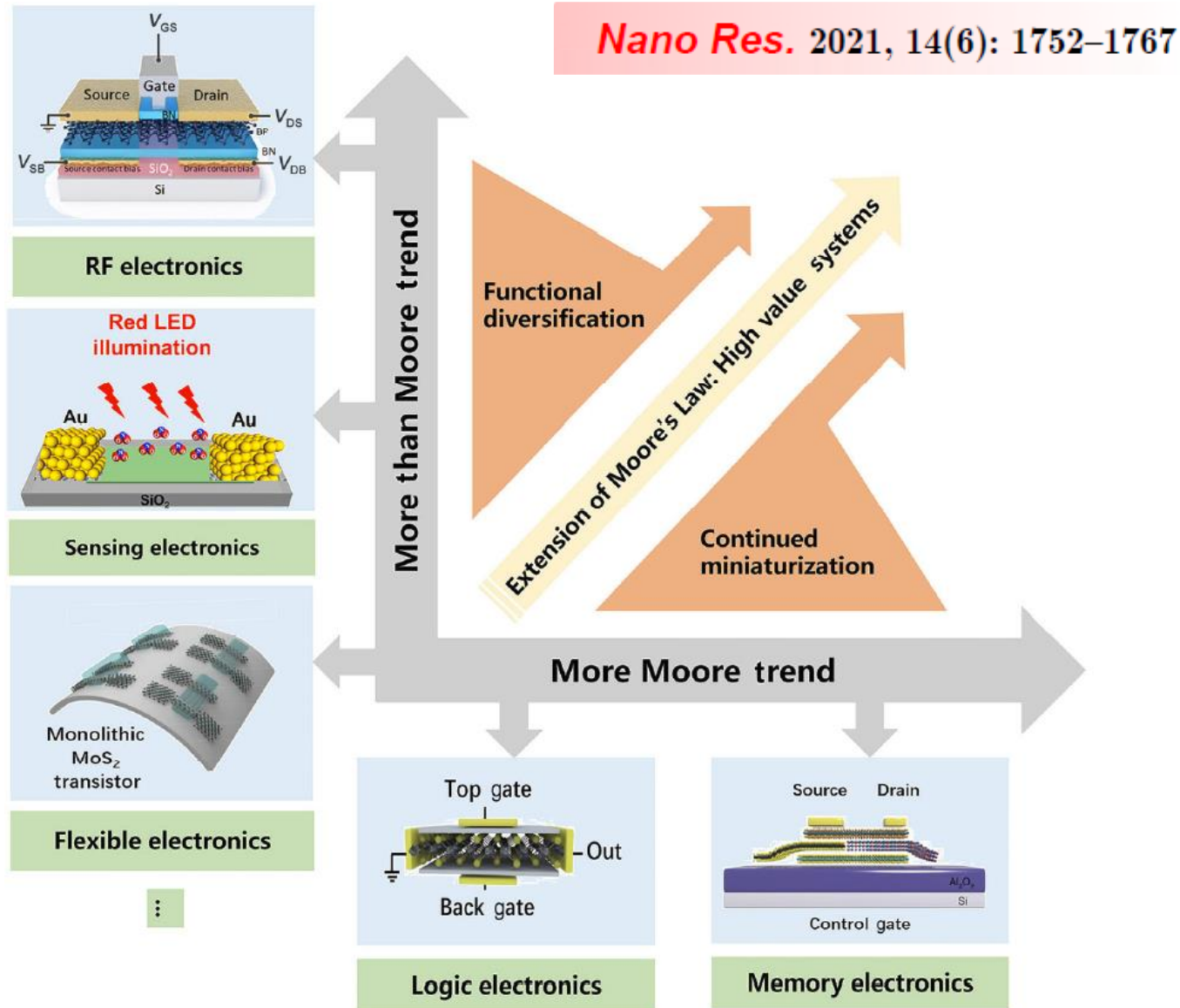
flakes in solution



AFM images

Science **340**, 1226419 (2013)
Angew. Chem. Int. Ed. **50**, 11093 (2011)

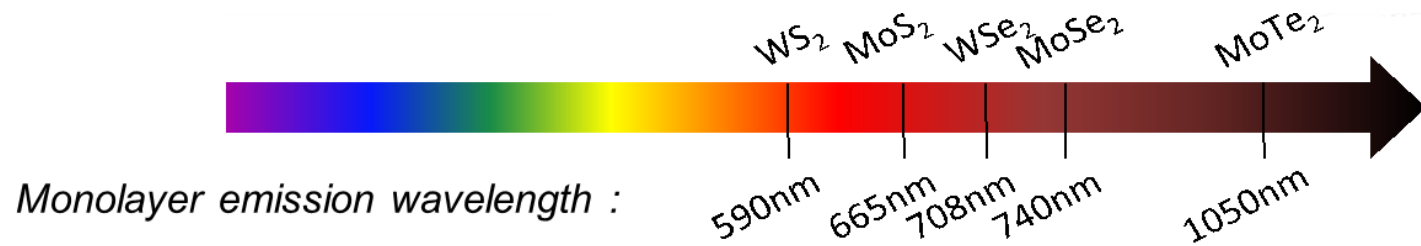
Electronics based on Single Layer TMD flake



Photodetectors based on Single Layer MoS₂ flake

MX₂ monolayers – common properties : strong interaction with light

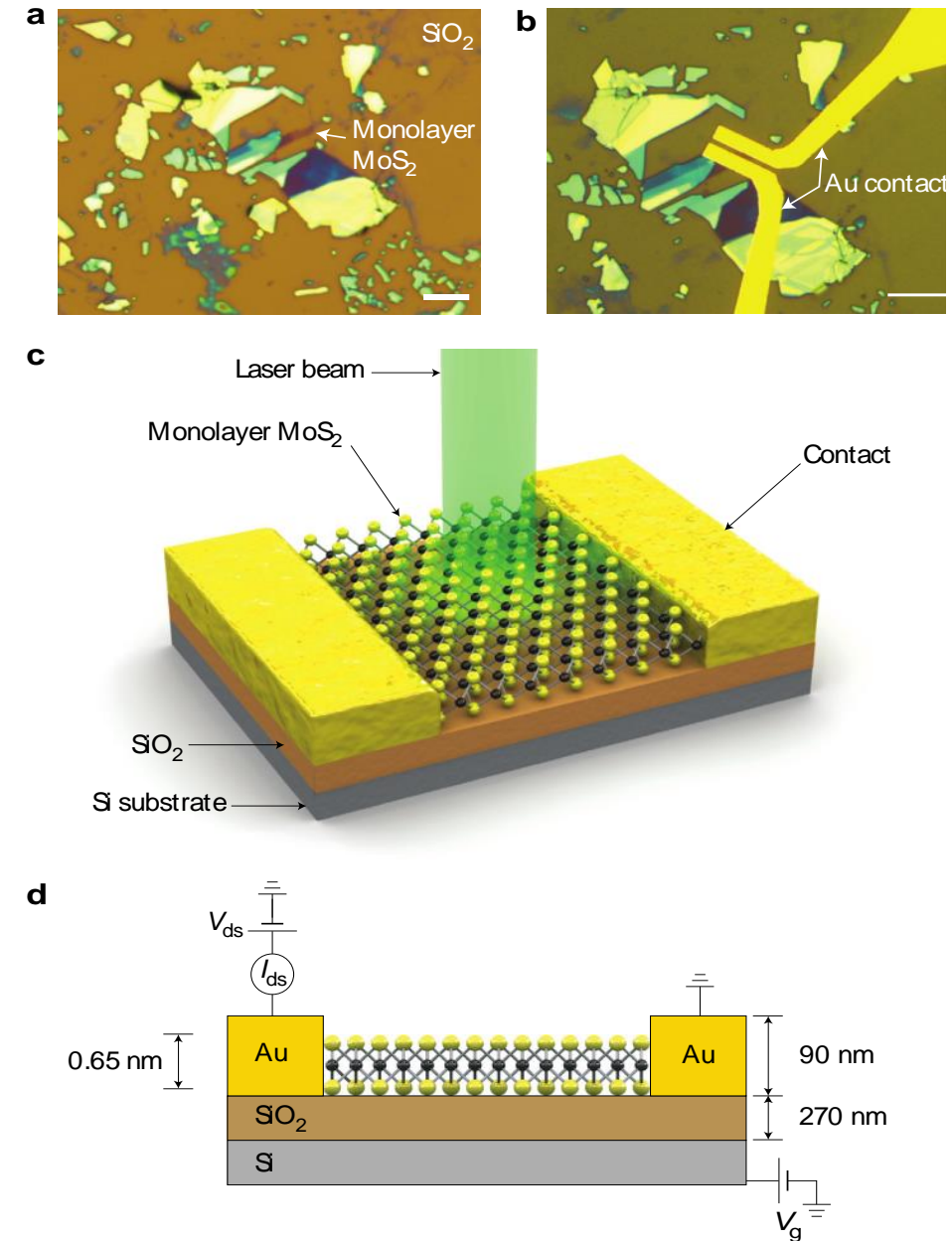
~10-15 % absorption of light for a monolayer



- Very sensitive
- maximum external photoresponsivity of 880 A/W at a wavelength of 561 nm and a photoresponse in the 400–680 nm range

(100 mA/W silicon-based photodetectors)

NanoLett. 12, 3695 (2012)
Nature Nanotec 8, 497 (2013)
Scientific Report 4, 3826 (2014)
Sensors 21, 2758 (2021) –Review

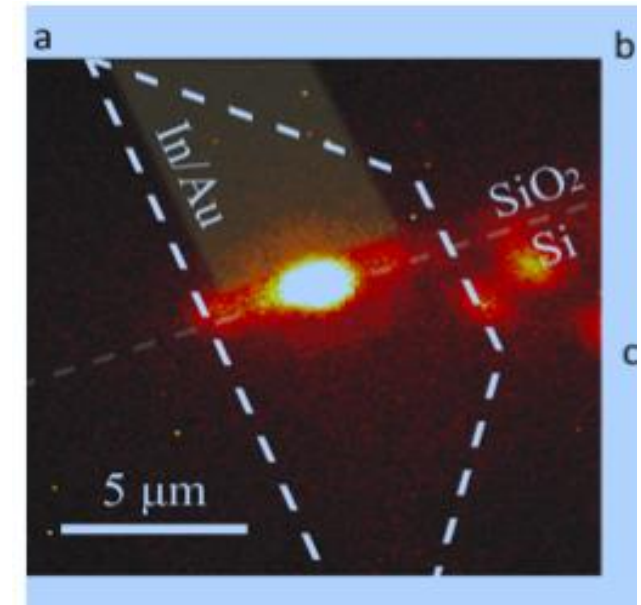
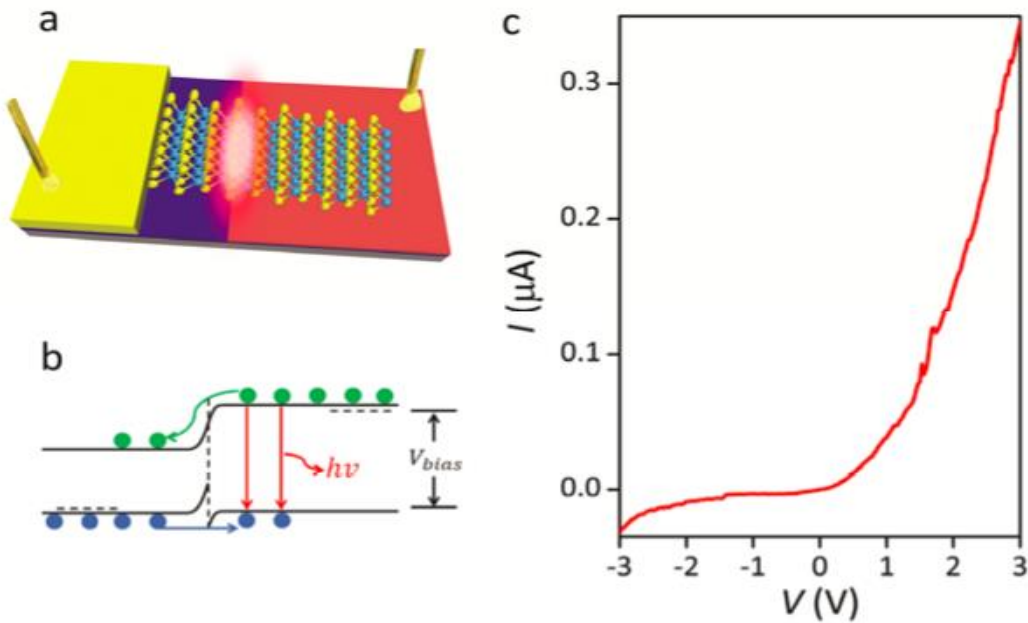


MoS₂ LED Prototypes

Electroluminescence in Single Layer MoS₂

NanoLett **13**, 1416 (2013)

APL **104**, 193508 (2014)



MoS₂ ML fabricated on a heavily p-type doped silicon substrate

WSe₂ (WS₂) monolayer laser ? : Nature **520**, 69 (2015)
Nature Phot. **9**, 733 (2015)

Second Harmonic Generation

MoS₂ : PRB **87**, 161403(R) (2013)

WSe₂ : PRL 114, 097403 (2015)

Second harmonic microscopy of monolayer MoS₂

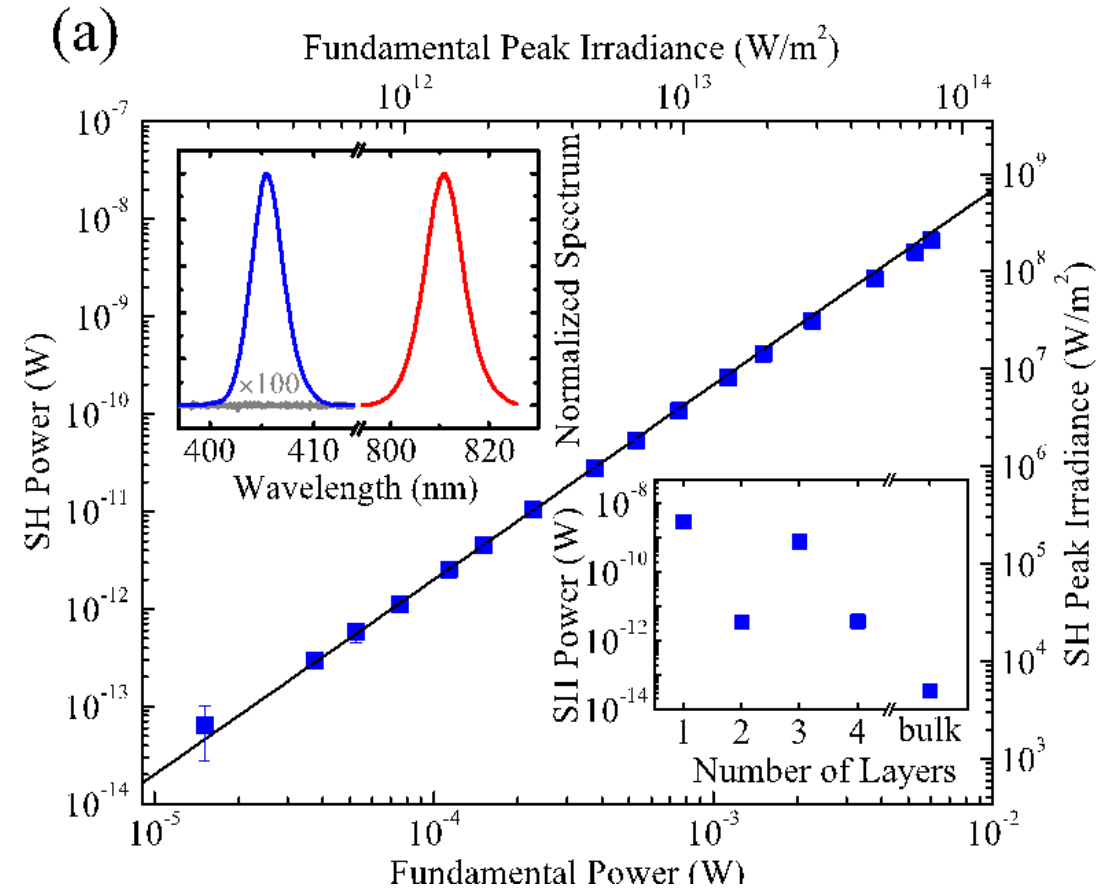
Nardeep Kumar,¹ Sina Najmaei,² Qiannan Cui,¹ Frank Ceballos,¹ Pulickel M. Ajayan,² Jun Lou,² and Hui Zhao^{1,*}

¹Department of Physics and Astronomy, The University of Kansas, Lawrence, Kansas 66045, USA

²Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, USA

(Dated: April 9, 2013)

We show that the lack of inversion symmetry in monolayer MoS₂ allows strong optical second harmonic generation. Second harmonic of an 810-nm pulse is generated in a mechanically exfoliated monolayer, with a nonlinear susceptibility on the order of 10^{-7} m/V. The susceptibility reduces by a factor of seven in trilayers, and by about two orders of magnitude in even layers. A proof-of-principle second harmonic microscopy measurement is performed on samples grown by chemical vapor deposition, which illustrates potential applications of this effect in fast and non-invasive detection of crystalline orientation, thickness uniformity, layer stacking, and single-crystal domain size of atomically thin films of MoS₂ and similar materials.



→ Lack of inversion symmetry in monolayer MoS₂ allows optical second harmonic generation

The different growth methods

❑ Large scale growth of synthetic TMDCs

Chemical routes

Based on chemical reactions in the gas phase or on a substrate

- ❑ Chemical Vapor Deposition (CVD)
- ❑ Metal Organic Chemical Vapor Deposition (MOCVD)
- ❑ Atomic Layer Deposition (ALD)

VLS, plasma assisted...

Physical routes

Based on the condensation of atomic species on a substrate under vacuum or ultrahigh vacuum

- ❑ Molecular beam epitaxy in the van der Waals regime
- ❑ Sputtering: Phase Change Materials

❑ chalcogenization

The different growth methods

Objectives

- ❑ Growth on **centimeter scale** single crystal of TMDC monolayer (low density of defects, high mobility, electronic properties approaching the ones of flakes...)
- ❑ **Doping and Alloys** (*n*-type, *p*-type and magnetic doping, alloys for lattice parameter and bandgap tuning...)
- ❑ Vertical or lateral **heterostructures** (Band alignment tuning, heterojunctions, contacting, proximity effects...)

Criteria to assess TMDC quality

- ❑ Peak intensity and width of PL and Raman spectroscopy
 - ❑ Carrier mobility
 - ❑ ON/OFF ratio in a Field Effect Transistor (FET)
- Depend on: film continuity, grain size and orientation (given by TEM and x-ray diffraction), grain boundaries, density of point or extended defects, substrate, contamination, oxidation/pollution

For each growth technique

- ❑ Basic principle
- ❑ Key parameters
- ❑ Review of recent advances

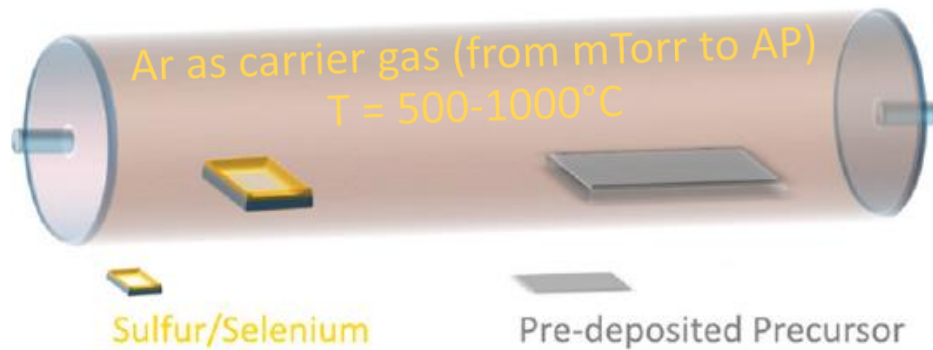
The different growth methods: CVD

Review of reviews on Chemical Vapor Deposition:

- ❑ Materials Today 20, 116 (2017)
- ❑ Small 13, 1700098 (2017)
- ❑ Crystals 8, 35 (2018)
- ❑ Chem. Soc. Rev. 44, 2587 (2015) and 2744 (2015)
- ❑ RSC Adv. 5, 75500 (2015)
- ❑ Chem. Rev.: DOI: 10.1021/acs.chemrev.7b00212 and 7b00536 (2017)
- ❑ Electronics 4, 1033 (2015)
- ❑ Nature Chem. 5, 263 (2013)
- ❑ Nature Nanotech. 7, 699 (2012)

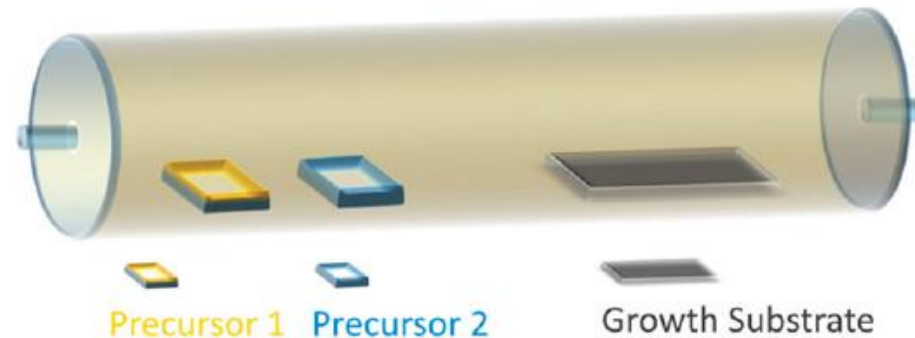
The different growth methods: CVD

■ SOLID PRECURSORS



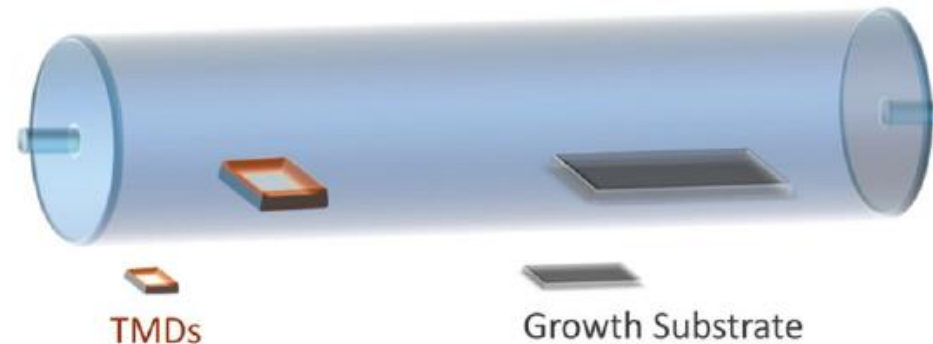
Two-step method:

- Deposition of the TM (Mo , MoO_3 , W , WO_3)
- Sulfurization/selenization in the CVD reactor



One-step method:

Both the TM (MoO_3 , MoCl_5 , WO_3 , WCl_5) and S, Se powders are evaporated in the CVD reactor



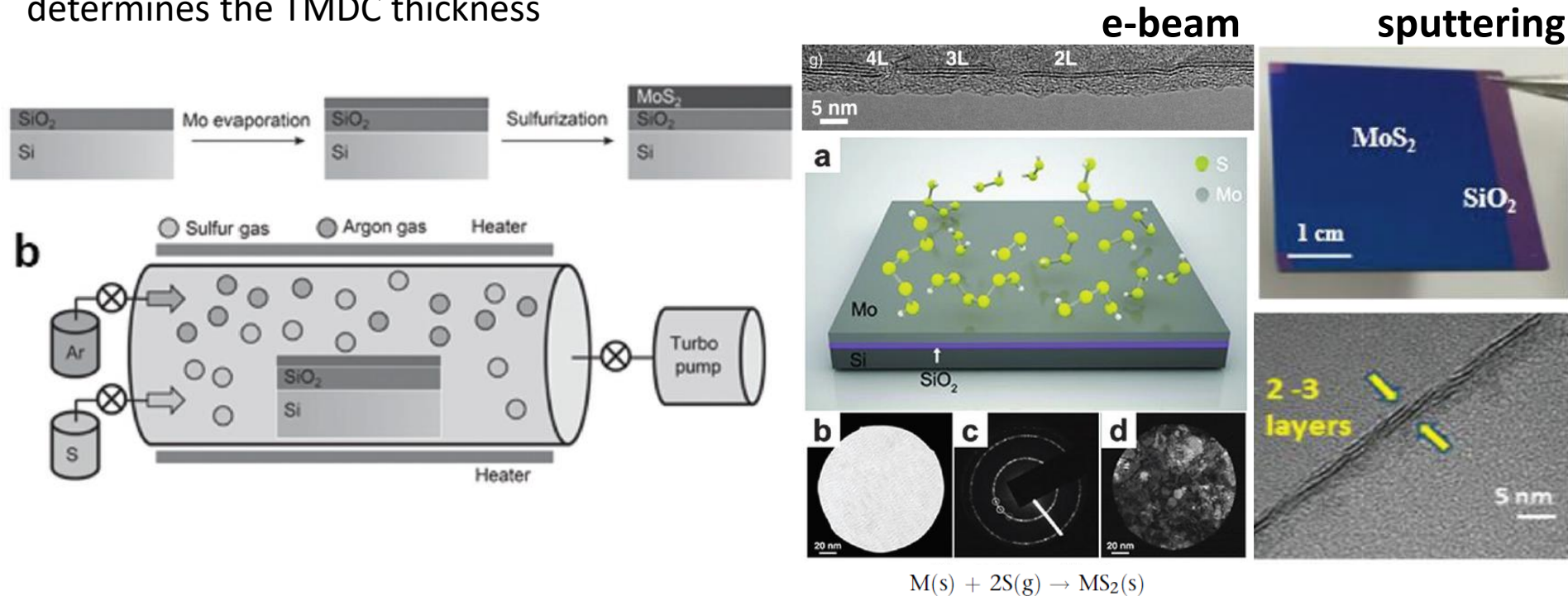
Direct evaporation of the TMDC

Adjusting parameters: T, p, carrier gas (Ar, H_2/Ar), substrate (single crystal, presence of defects, patterning, functionalization, liquid substrate...)

The different growth methods: CVD

Two-step CVD method

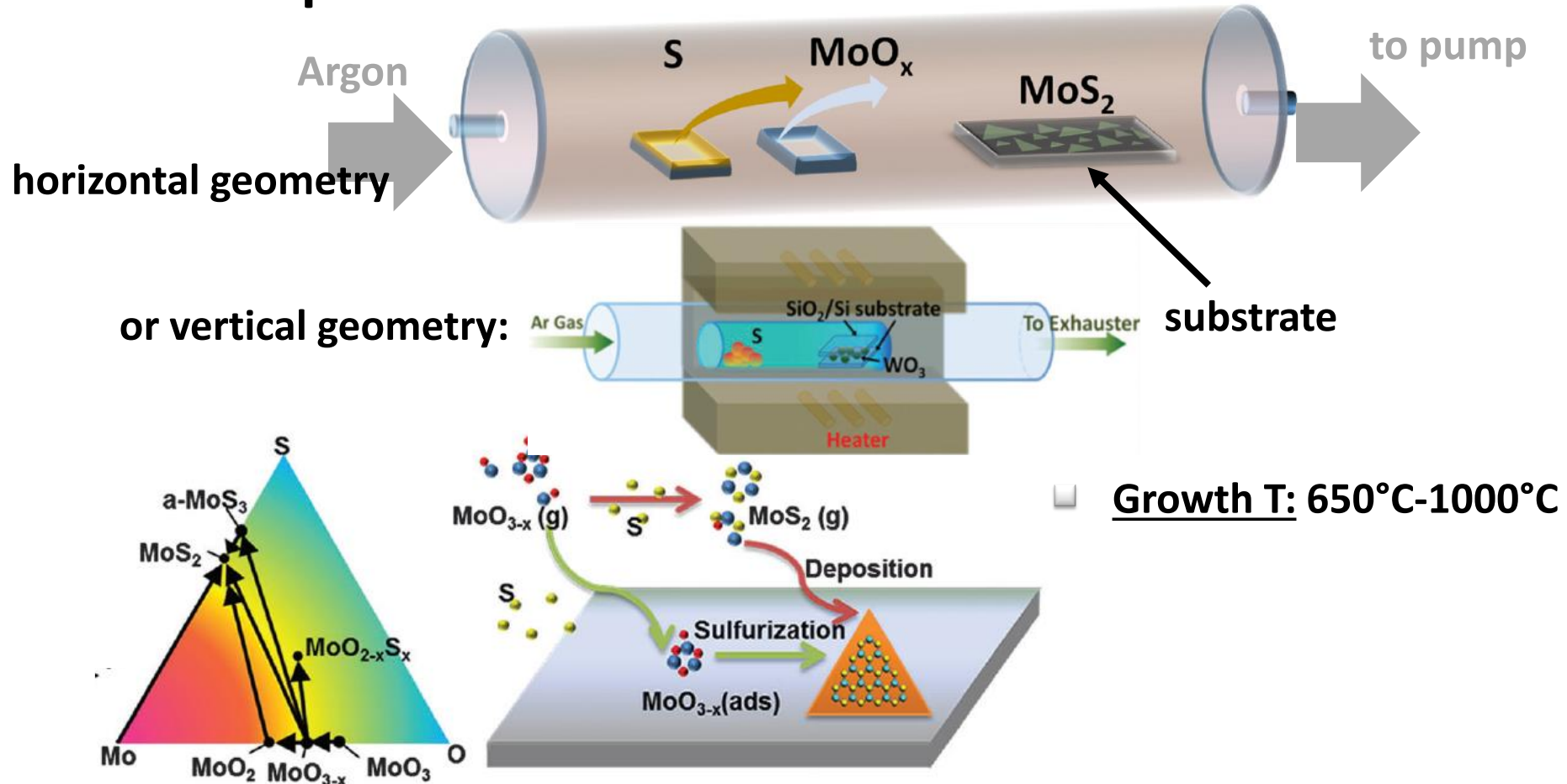
The thickness of pre-deposited Mo, MoO₂ or MoO₃ (by e-beam, sputtering, ALD for WO₃) determines the TMDC thickness



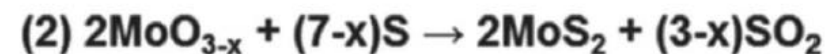
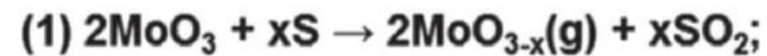
Continuous films on large area **BUT** very small randomly oriented grains (10 nm), metallic character for Mo (low ON/OFF ratios), semiconducting character for MoO₃ (ON/OFF ratio 10⁴), distribution of thicknesses (1-20 ML), defective layers. Mobility ≤ 1 cm²/(V.s), (max exp. 100; theory 300).

The different growth methods: CVD

One-step CVD method



Gas phase and surface reactions:

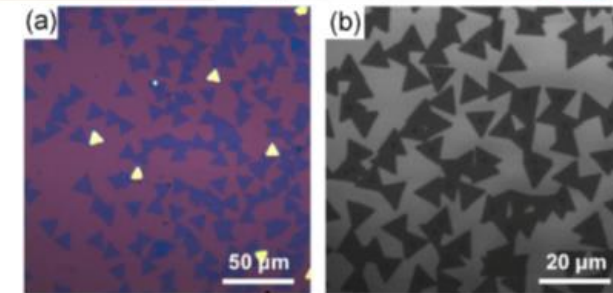
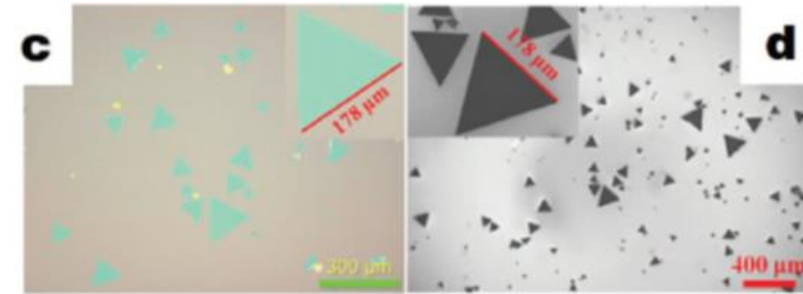
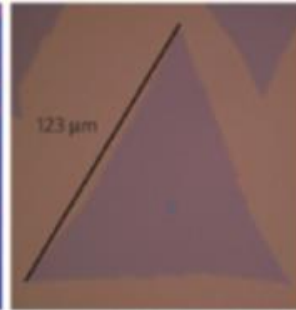


The different growth methods: CVD

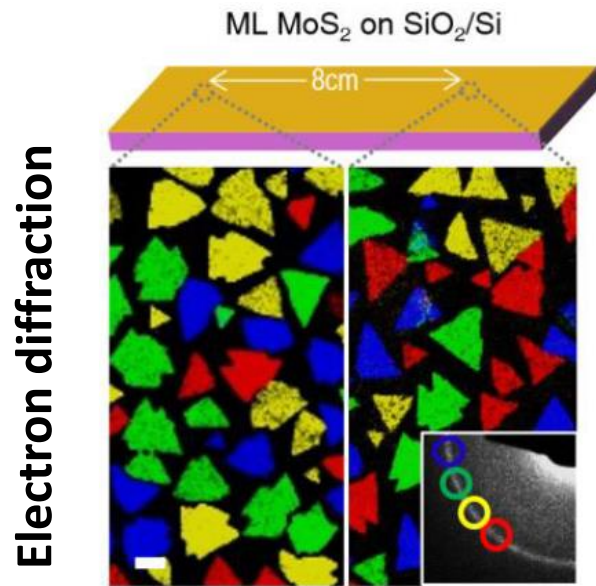
Some examples



MoS₂/SiO₂/Si



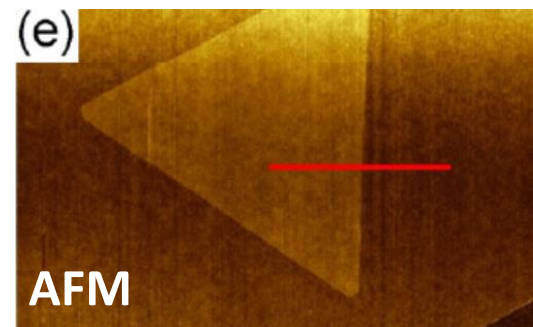
WS₂/SiO₂/Si



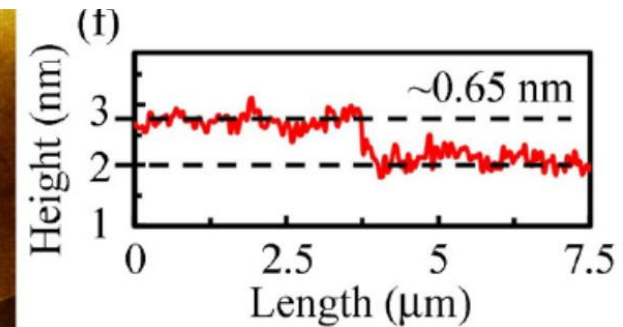
Electron diffraction

Randomly oriented flakes

≈100 μm triangles



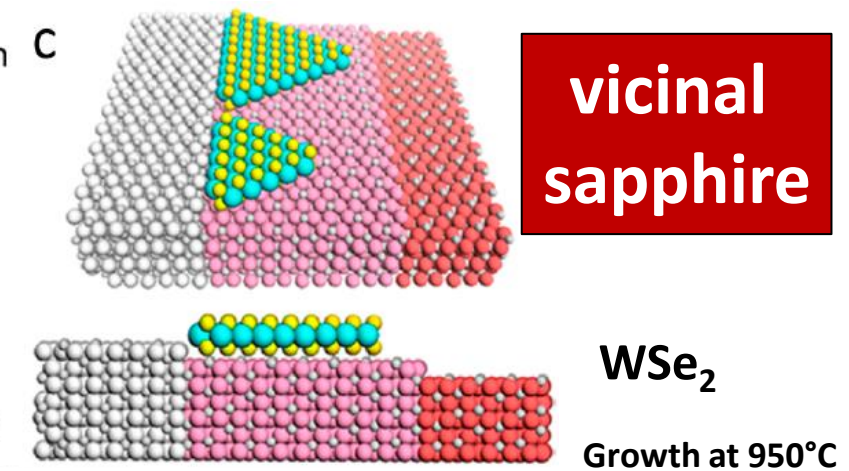
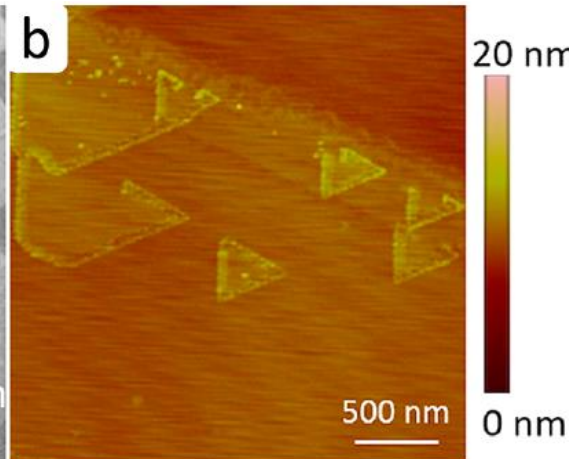
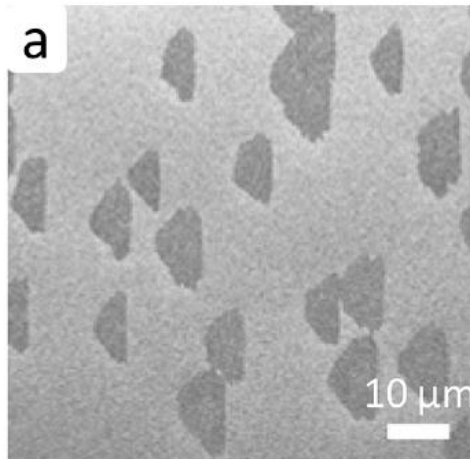
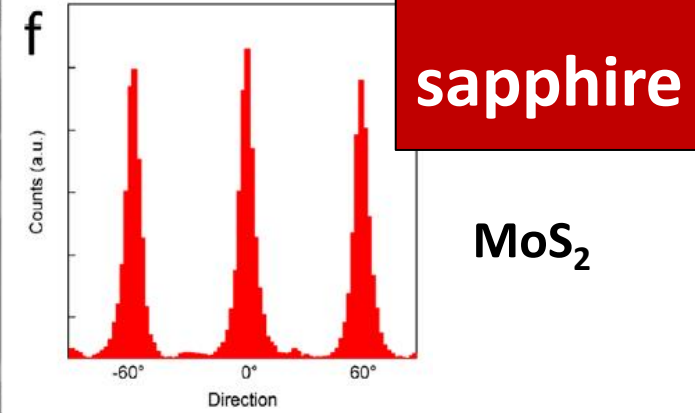
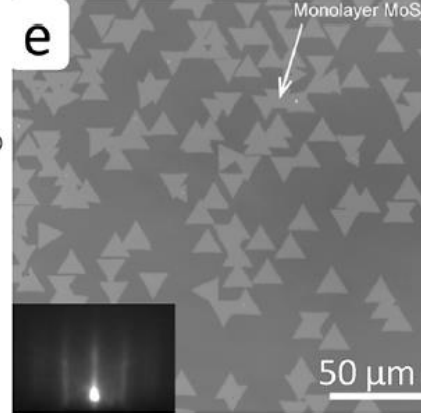
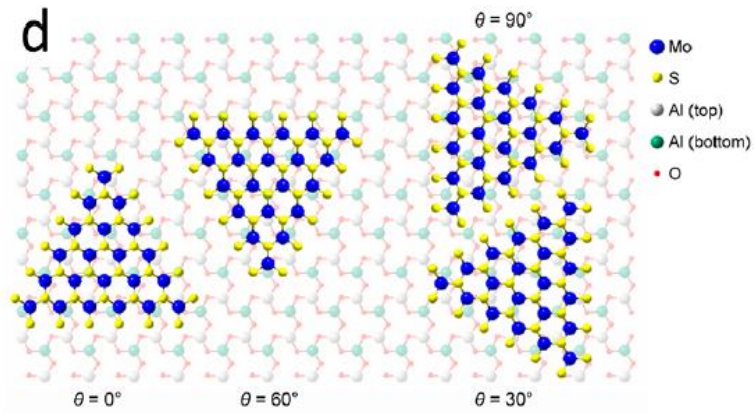
AFM



VdW gap

The different growth methods: CVD

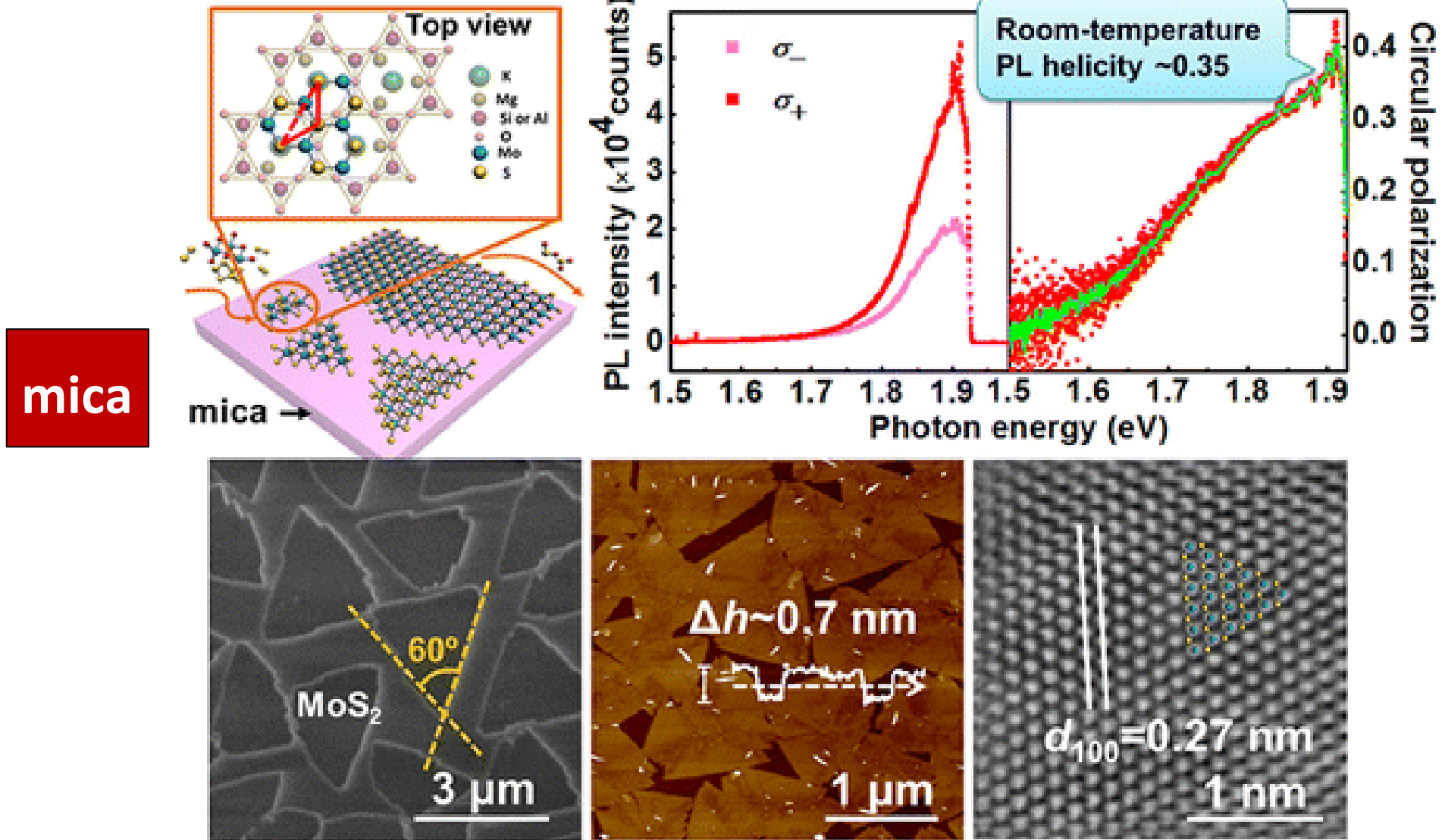
Grain orientation



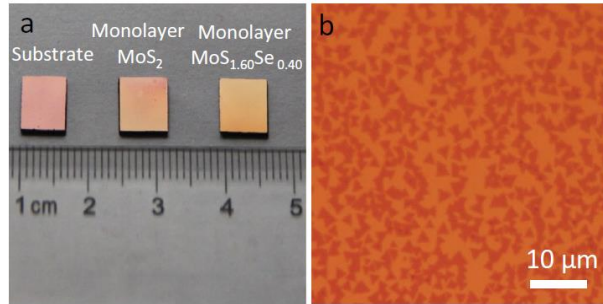
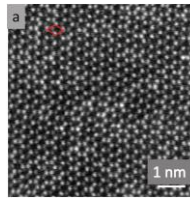
The different growth methods: CVD

Grain orientation

LPCVD: 30 Pa; 50 sccm; 530°C; 1 hour



The different growth methods: CVD

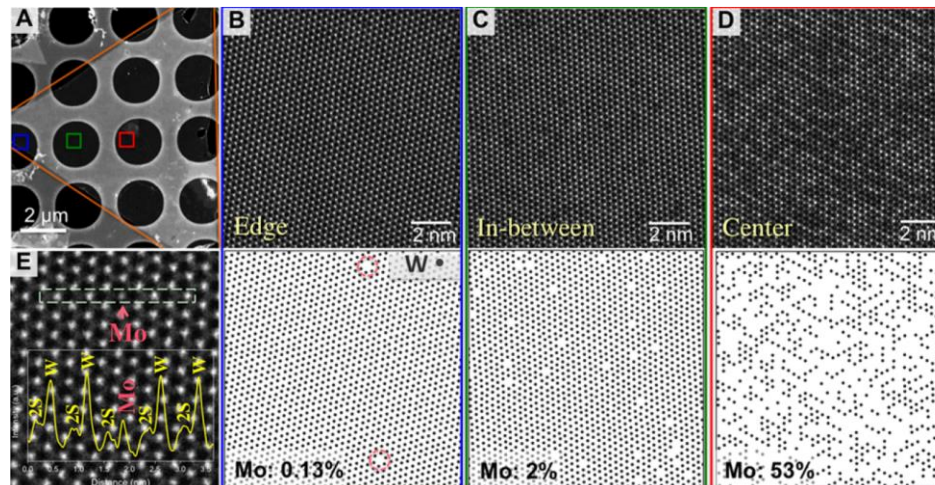
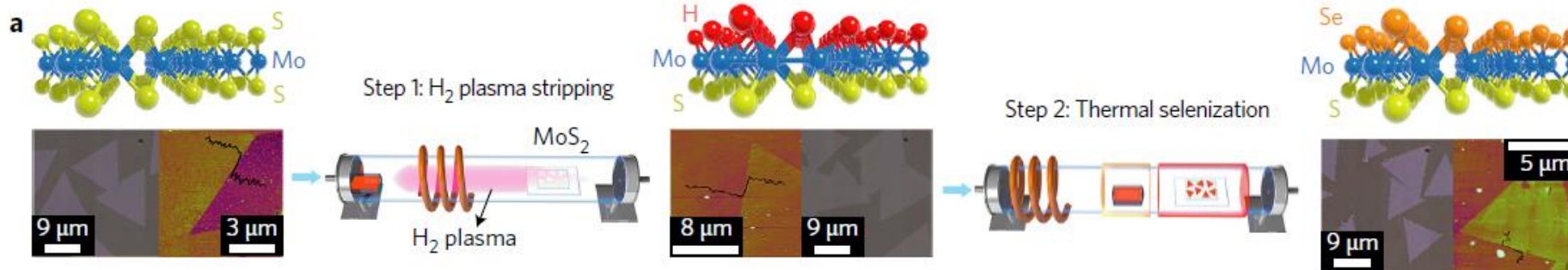


Alloys MoSeS (random)

Adv. Mater. **26**, 2648 (2014)

Alloys MoSeS (Janus)

Nature Nanotech. **12**, 744 (2017)



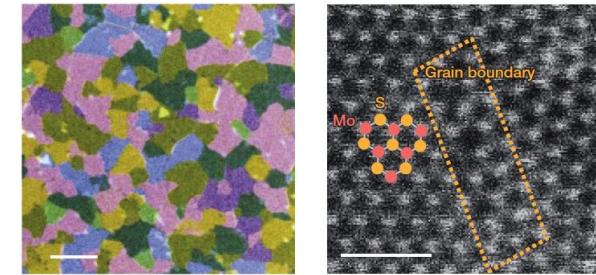
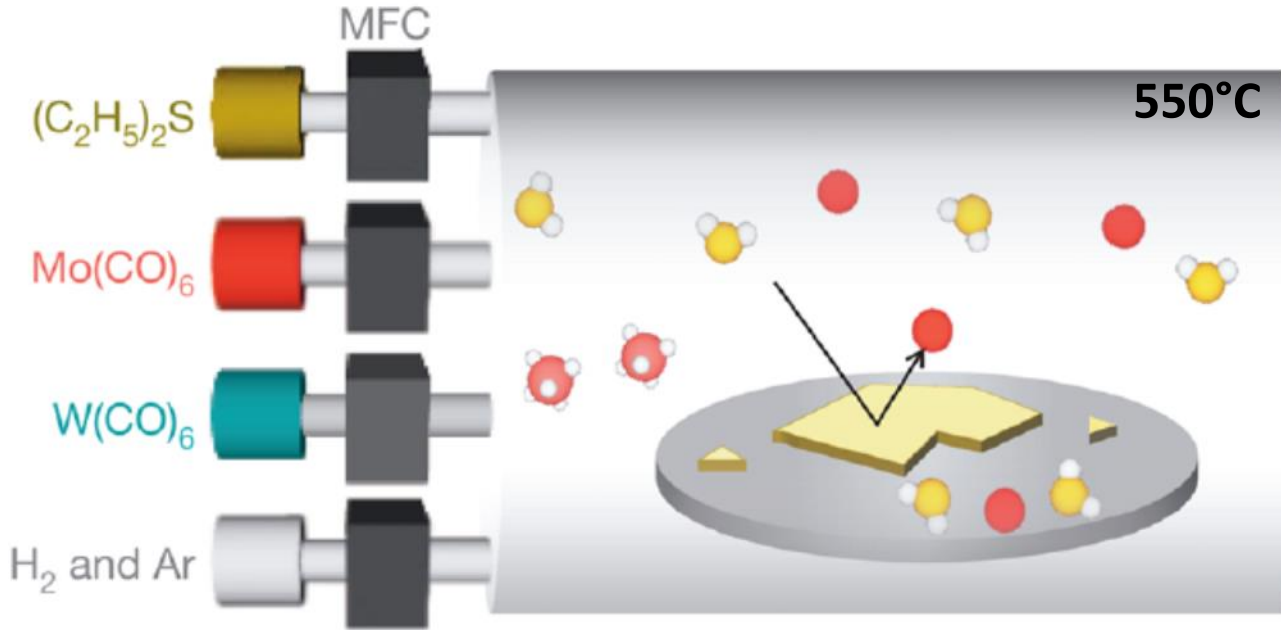
Alloys MoWS₂

Nano Lett. **16**, 6982 (2016)

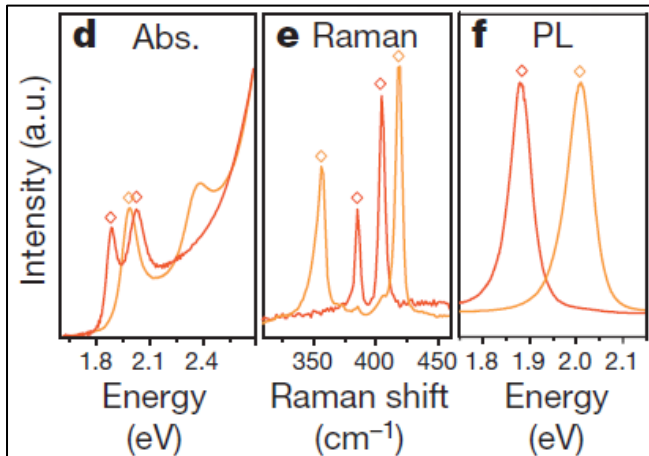
Nano Lett. **17**, 2802 (2017)

The different growth methods: MOCVD

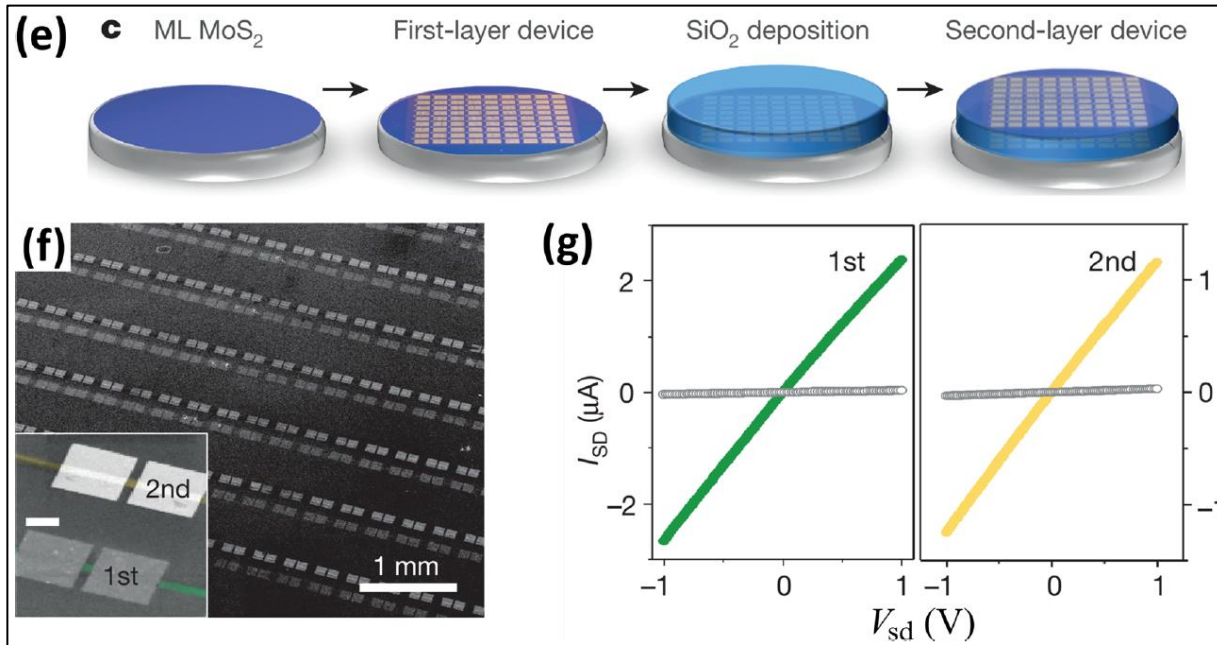
■ MOCVD



100% coverage, randomly oriented small grains 10-20 nm, 26 hours growth for 1 ML

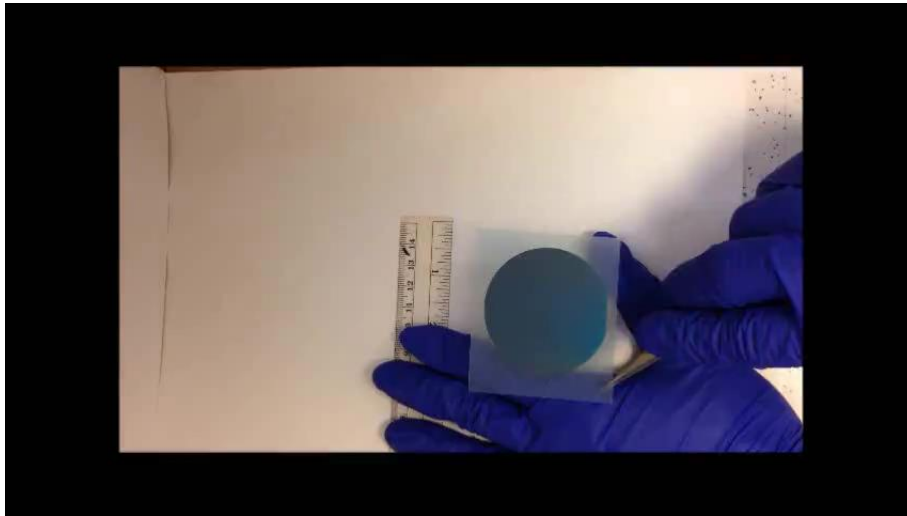


$\mu = 114 \text{ cm}^2/(\text{Vs}) @ 90 \text{ K}$

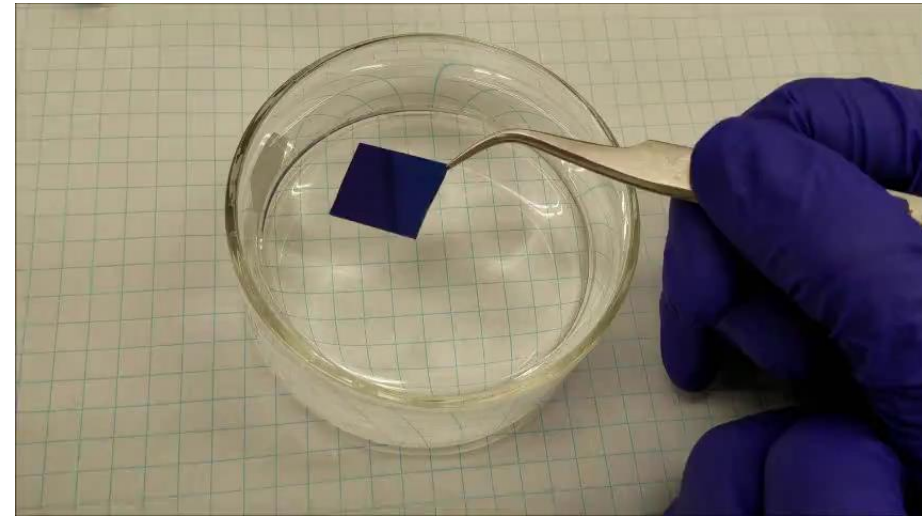


The different growth methods: MOCVD

■ Layer transfer



Kang et al., Nature **520**, 656 (2015)



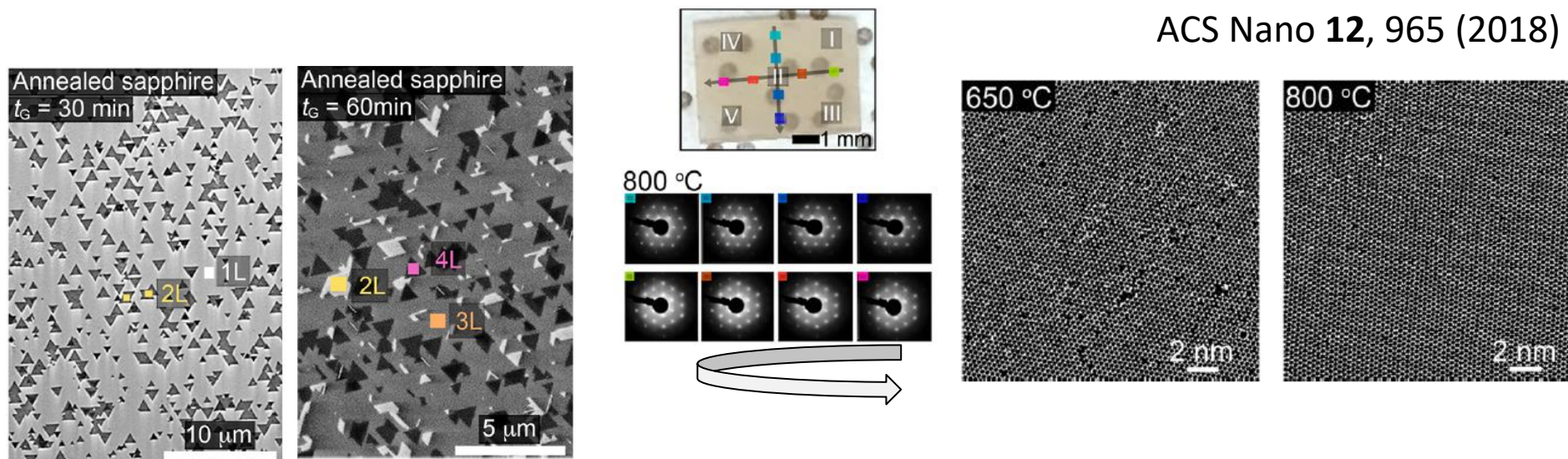
Also:

J. Cryst. Growth **464**, 100 (2017)

ACS Nano **9**, 2080 (2015)

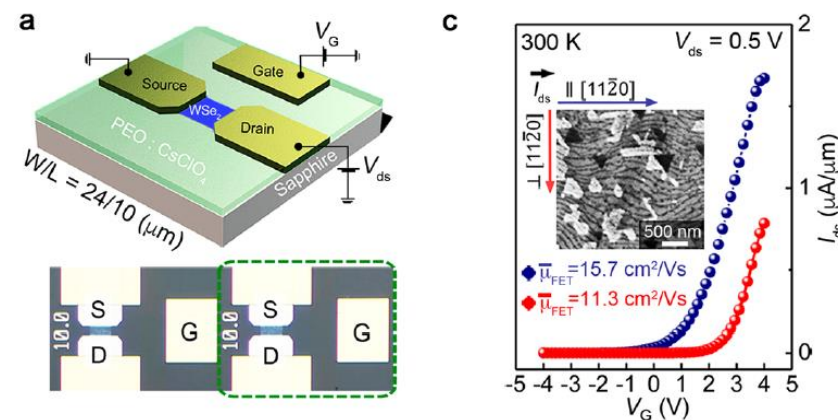
The different growth methods: MOCVD

- **Last achievement by MOCVD:** single crystalline WSe₂/Sapphire (Aixtron: WS₂/sapphire)

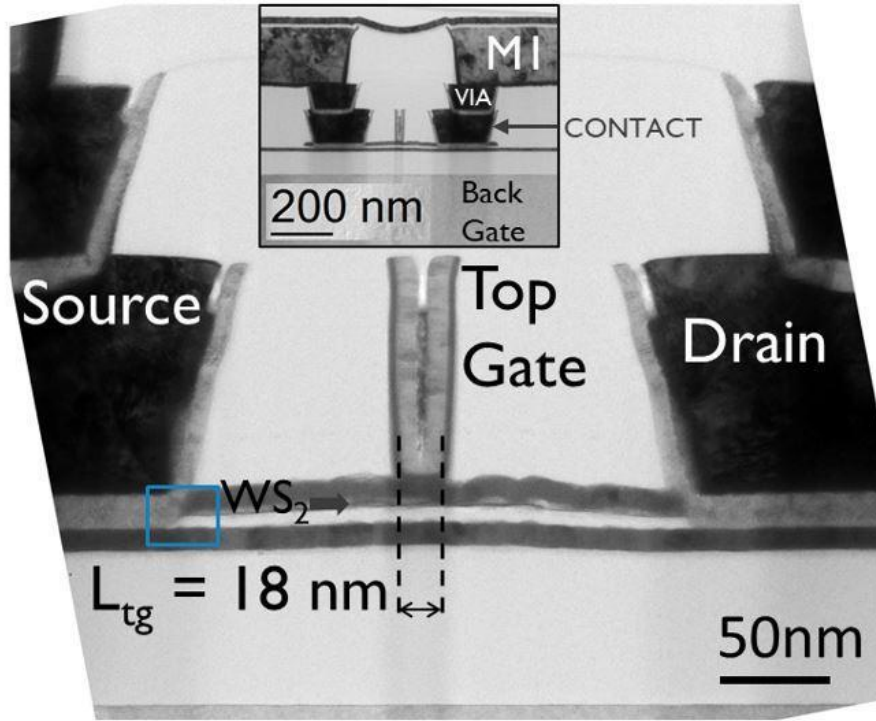


3-step process

- (1) Single crystalline, flat substrate with high surface energy (Sapphire)
- (2) Short nucleation step with high flow rates of precursors (W and Se)
- (3) Postgrowth annealing at 800°C under H₂Se



FETs (TMDs for digital electronics)



300 mm WS₂ integration @ IMEC (MOCVD)
IEDM 2020

+ INTEL
(MoS₂ CVD
growth and
transfer)

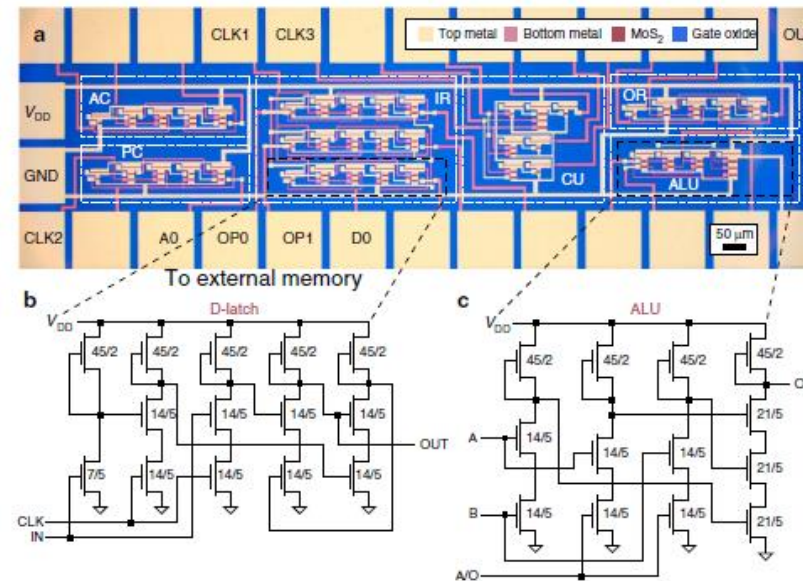
ON/OFF ratios > Silicon
MoS₂ n-channel 10⁸, WS₂ p-channel 10⁶

SS ≤ Silicon
MoS₂ 74 mV/dec, WS₂ 60 mV/dec

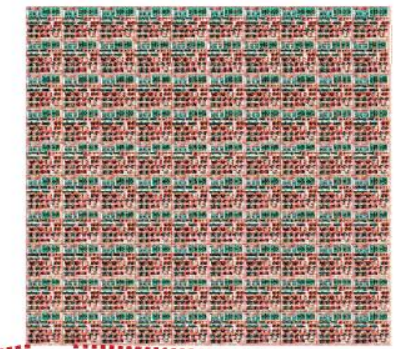
Better scalability (down to 0.7nm channel)

Cadence < Silicon (to improve: reduce
channel length, improve carrier mobility,
electrical doping, contacts)

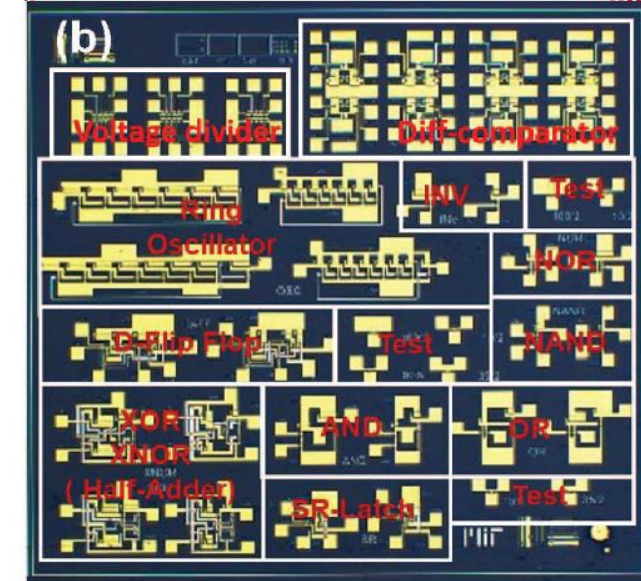
115 transistors processor (2017)



(a)



(b)

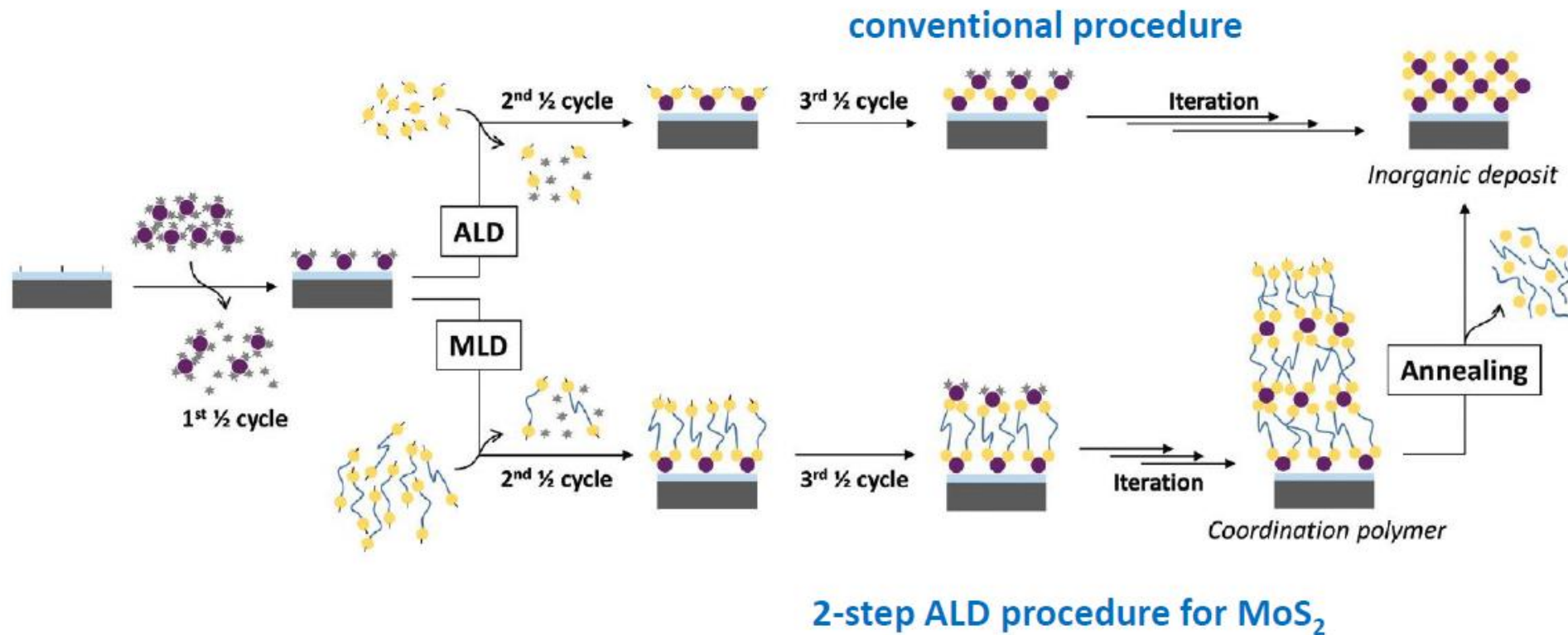


MIT, IEDM2015

The different growth methods: ALD

■ ALD or « pulsed MOCVD »

■ Principle of Atomic Layer Deposition and Molecular Layer Deposition



The different growth methods: ALD

State of the art Atomic Layer Deposition of MoS₂

- **Metal-halides as metal precursor (MoCl₅, WF₆)**

- Well known issue with **byproducts** (HCl, HF)
 - **Substrate etching**
 - Protective layer required on SiO₂ (e.g. ZnS)

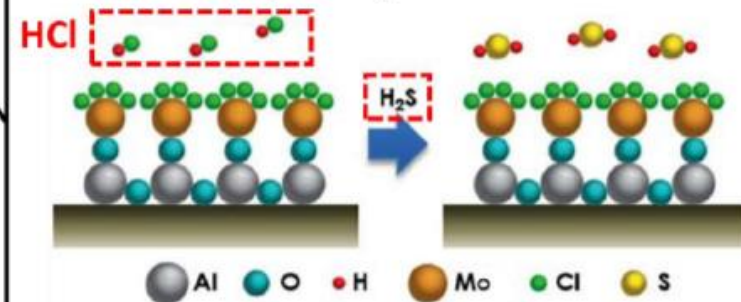
- Monolayer MoS₂ target = high uniformity

→ **Alternative to molybdenum halides ?**

- **H₂S as sulfur precursor**

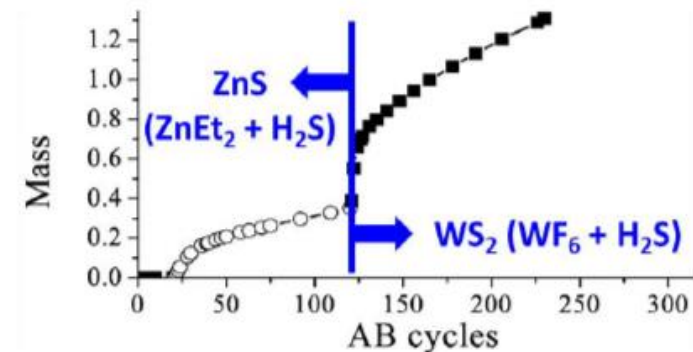
- Highly **toxic** and **flammable** gas (bp = -60°C)
- Handling and storage issues...

ALD with MoCl₅ and H₂S



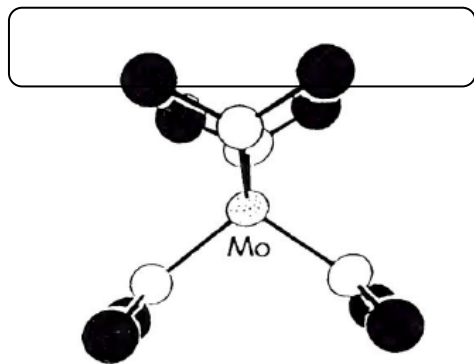
K. P. Loh, *Nanoscale*, 2014, 6, 10584-10588

ALD with WF₆ and H₂S (thick film for tribology)



T.W. Scharf, *J. Mater. Res.*, 2002, 19 (12), 3443-3446

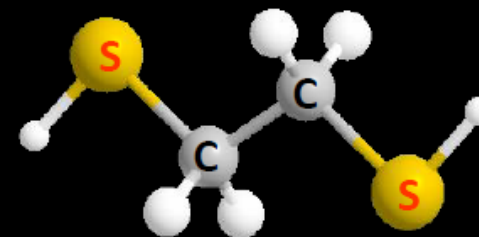
The different growth methods: ALD



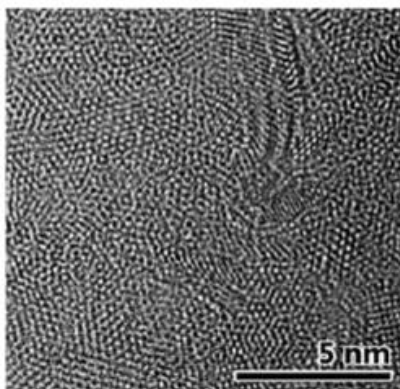
$\text{Mo}(\text{NMe}_2)_4$



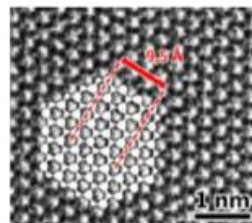
1,2 éthanedithiol



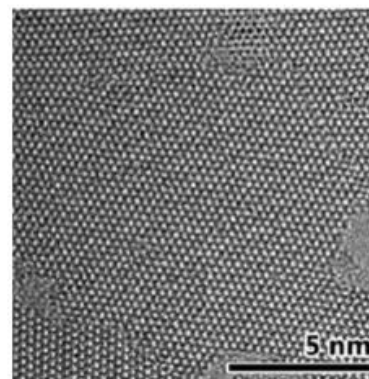
- Evidence of in-plane film organization above 450°C



450°C



2D Monolayer by MLD on SiO₂

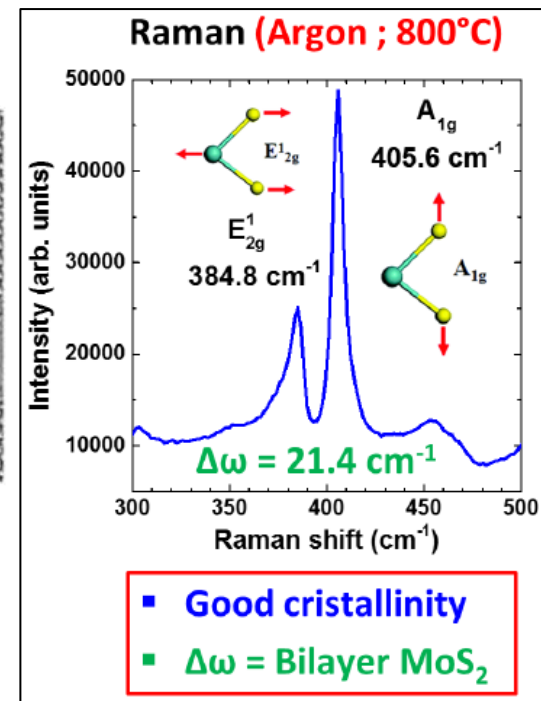


800°C

S. Cadot, H. Okuno et al, Nanoscale 2016

DOI: 10.1039/c6nr06021h

also ACS Nano **7**, 11333 (2013)



The different growth methods: CVD, MOCVD, ALD

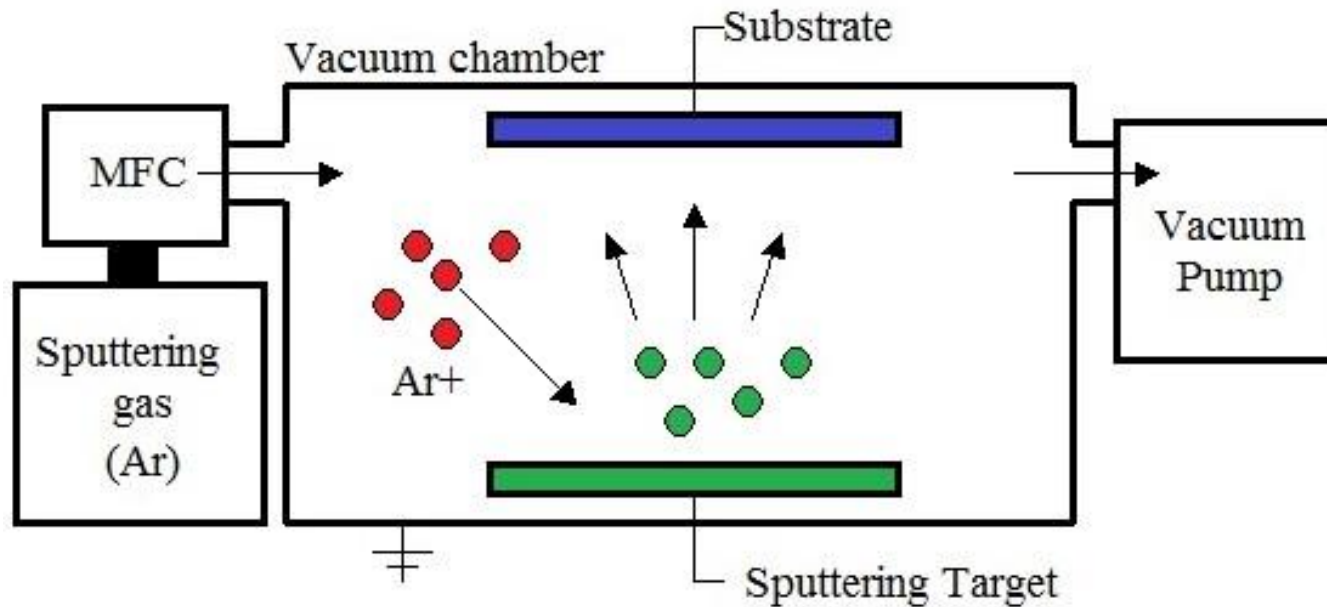
To summarize:

CVD with solid precursors: simple set-up BUT non-uniformity, non-continuous layers, poor control of the number of layers. Poor control of alloys, doping and heterostructures. Good mobility, PL on triangular flakes.

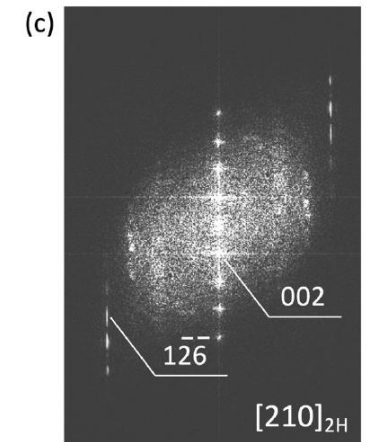
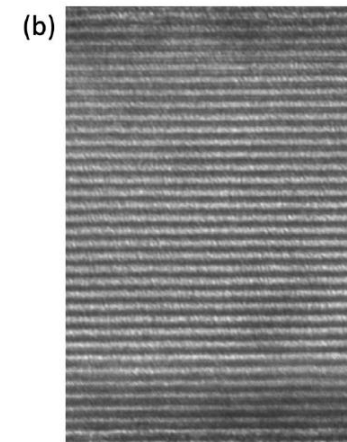
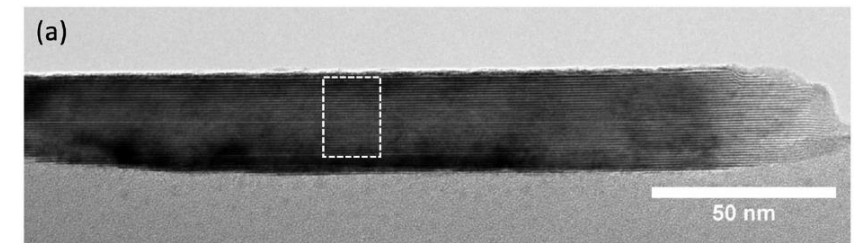
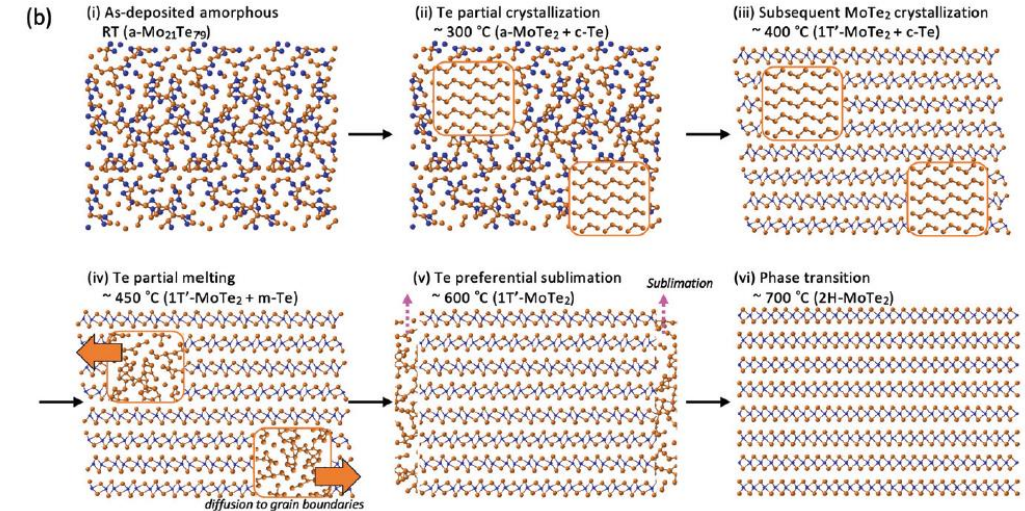
MOCVD including ALD: large area growth, continuity, uniformity, single crystalline on sapphire (2018). Very long growth. To develop: alloying, doping and heterostructures.

The different growth methods: sputtering

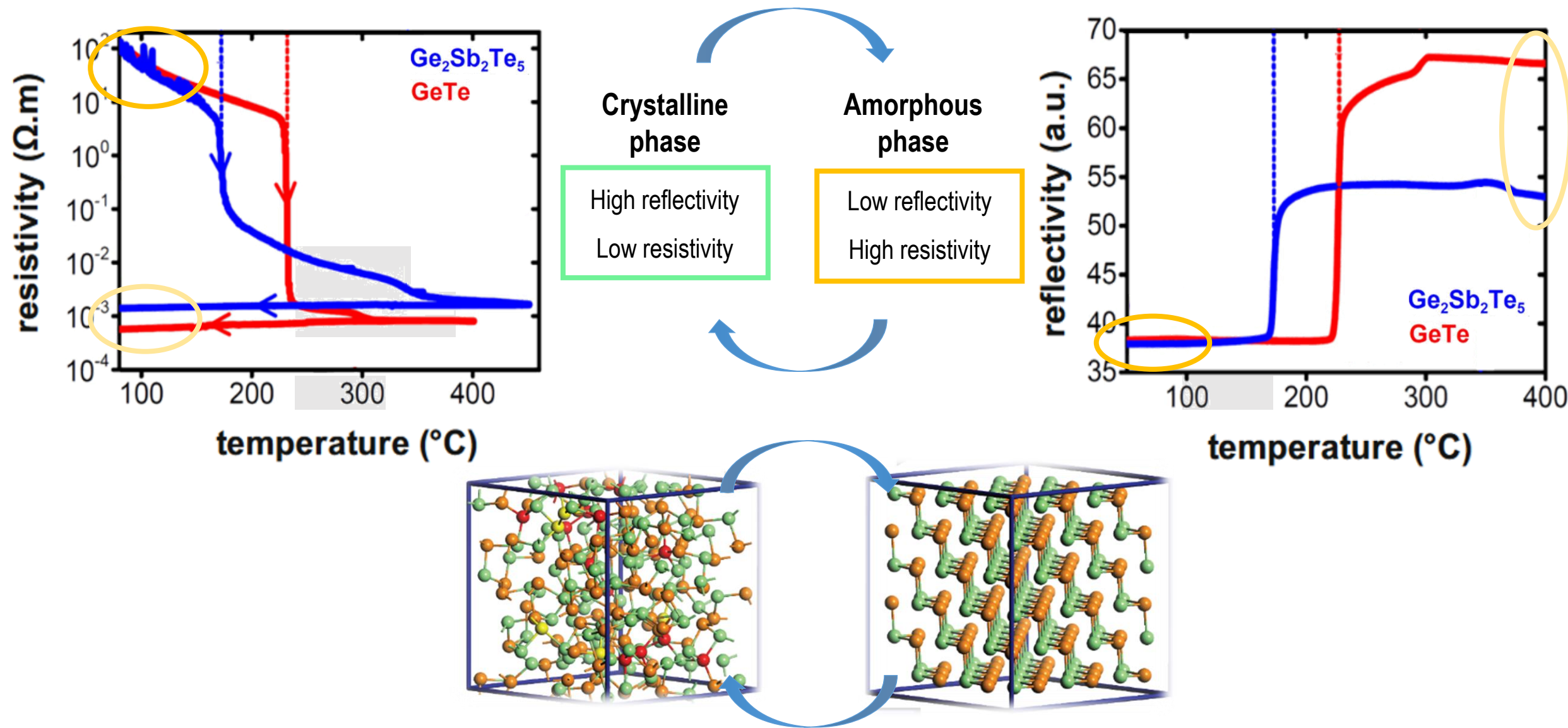
PRINCIPLE



Example: MoTe₂

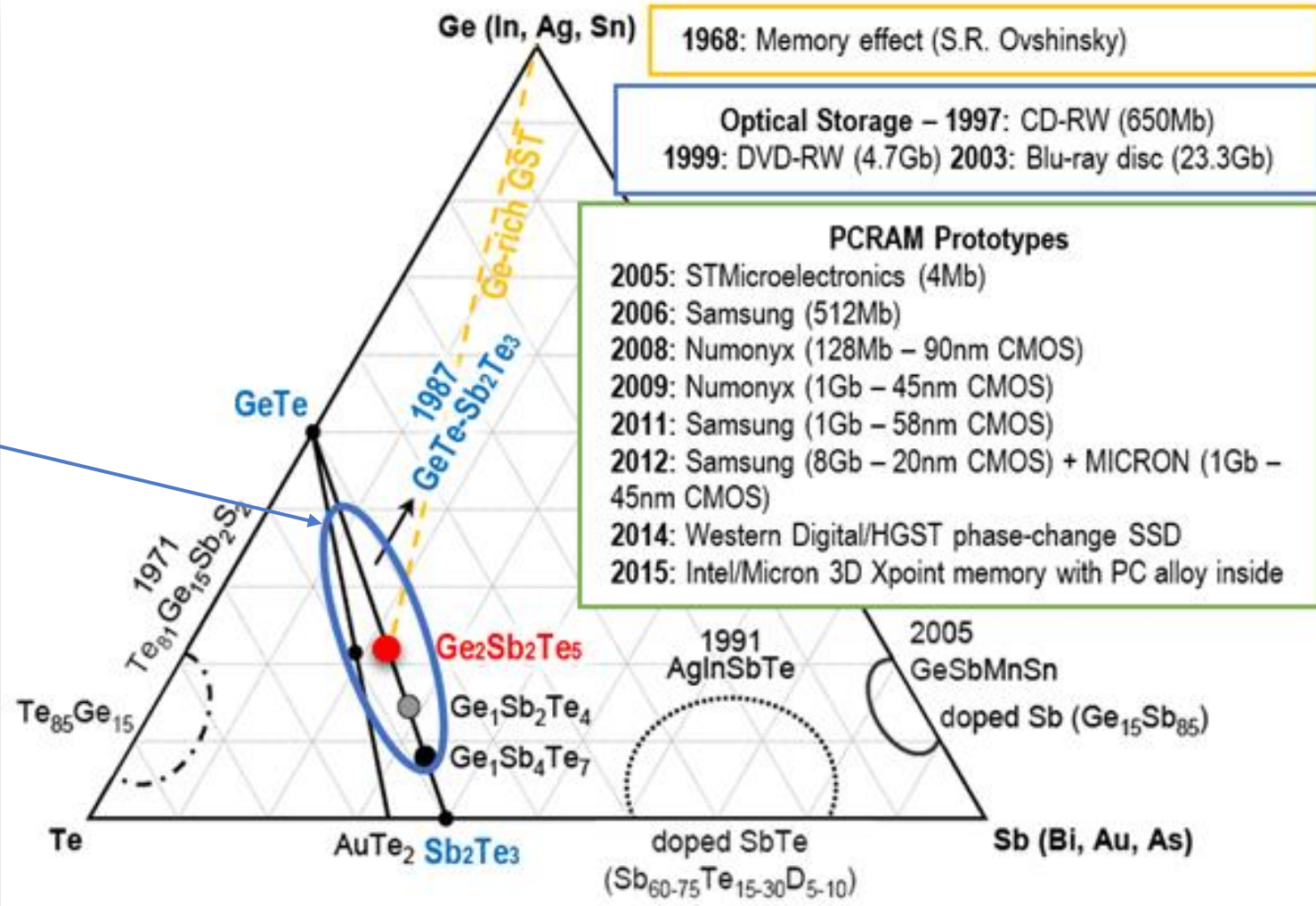


Phase change chalcogenides (PCM)



PHASE CHANGE CHALCOGENIDES (PCM)

IIIA	IVA	VA	VIA	VIIA
13	14	15	16	17
boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998
aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.06	chlorine 17 Cl 35.453
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	seelenium 34 Se 78.96	bromine 35 Br 79.904
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]



Physics of PCM : Metavalent Bonding (MVB) mechanism

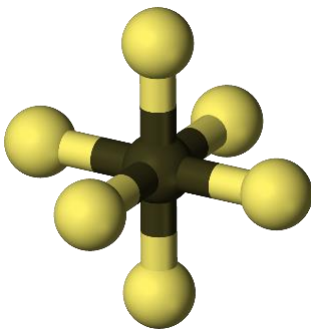
COVALENT

METAVALENT

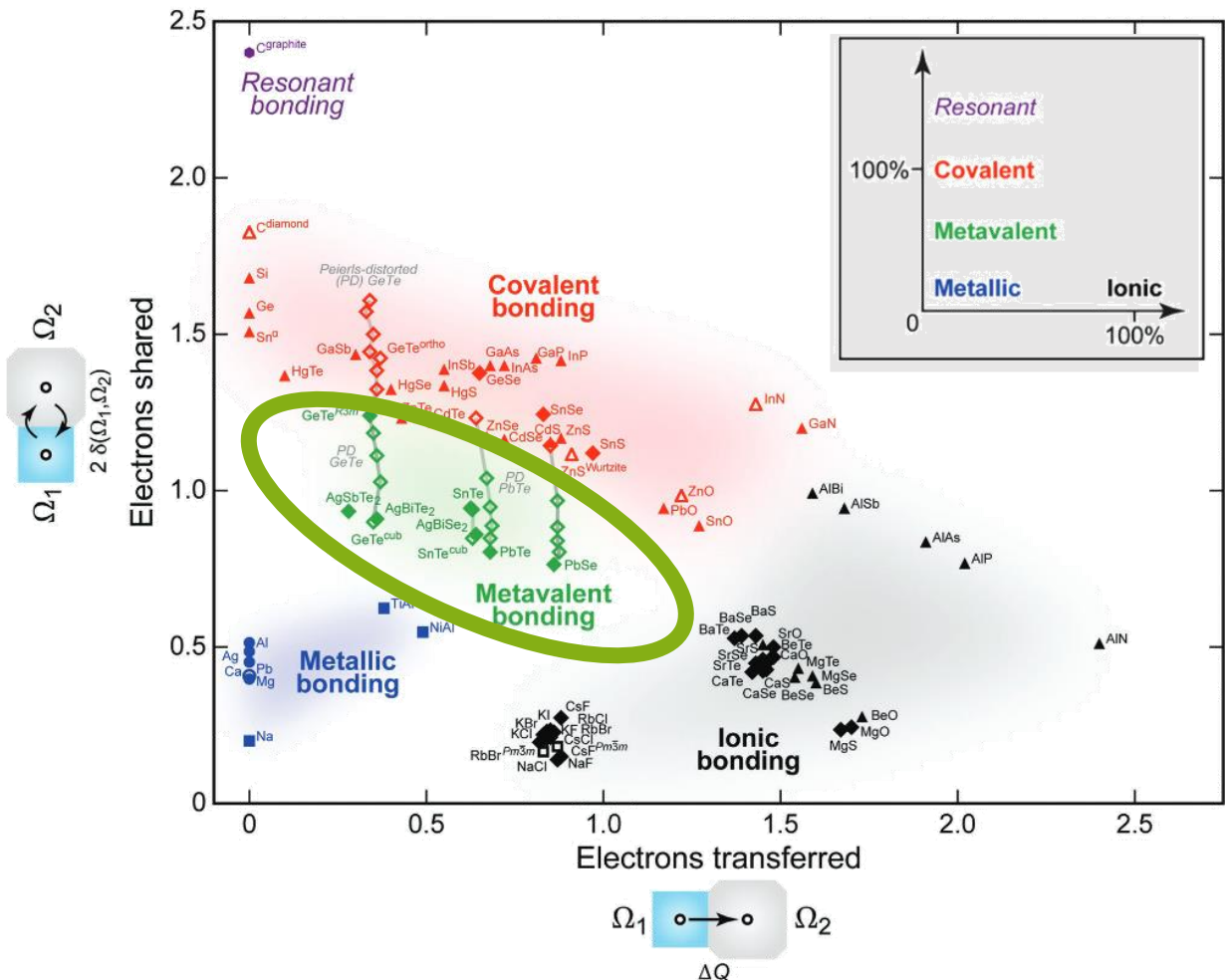
METAVALENT BONDING

Unique bonding mechanism present in the CRYSTALLINE PHASE OF PCM (« INCIPIENT METALS »).

- IV-VI chalcogenides
- *p*-bonded materials
- Octahedral atomic arrangement



Difference in the bonding mechanism Between amorphous and crystalline phases

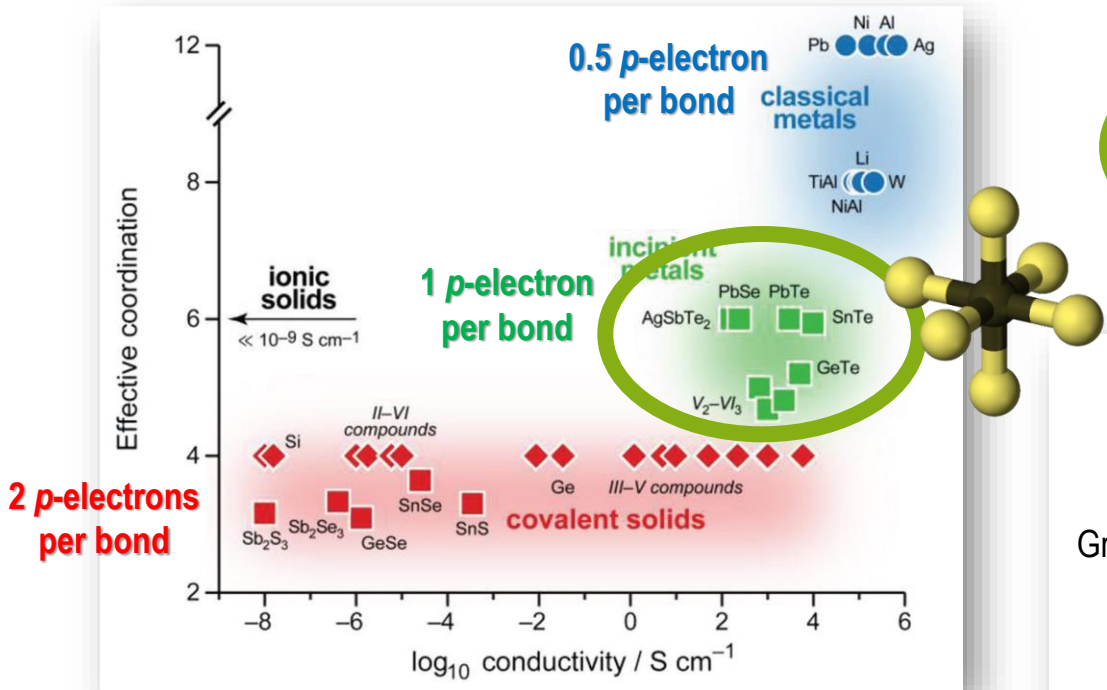


PHASE CHANGE CHALCOGENIDES (PCM)

Physics of PCM : Metavalent Bonding (MVB) mechanism

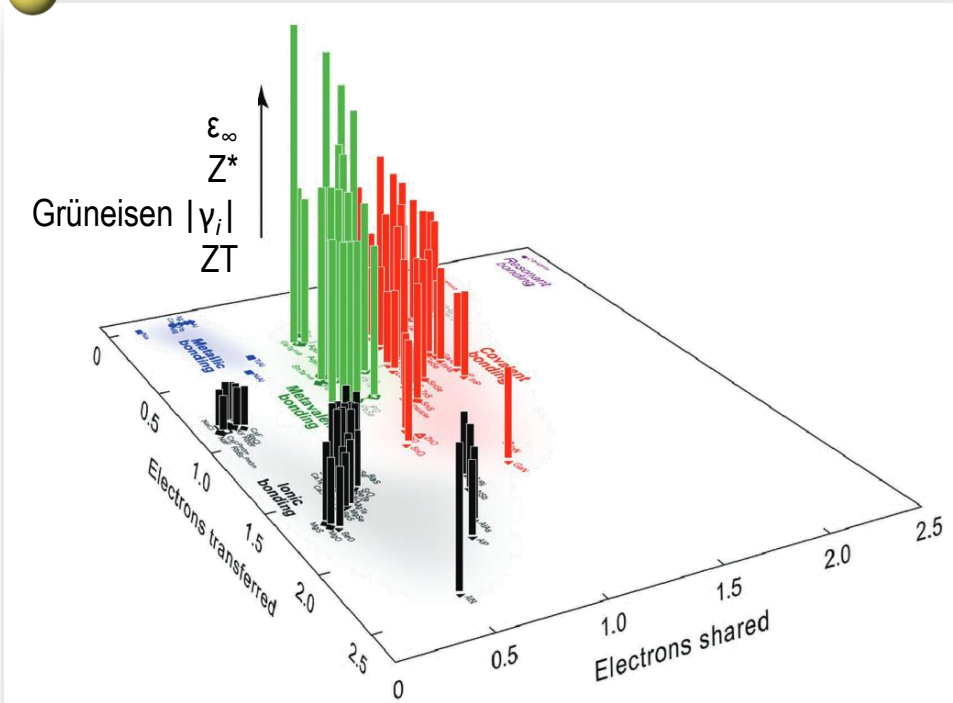
Signatures and properties of MVB :

- Coordination excess:**
Half filled orbitals (or non-saturated covalent bond)



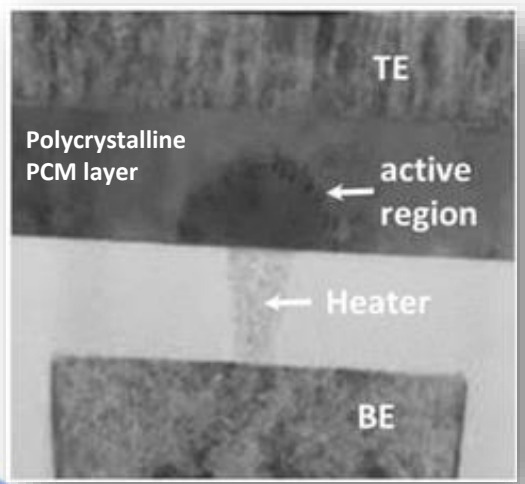
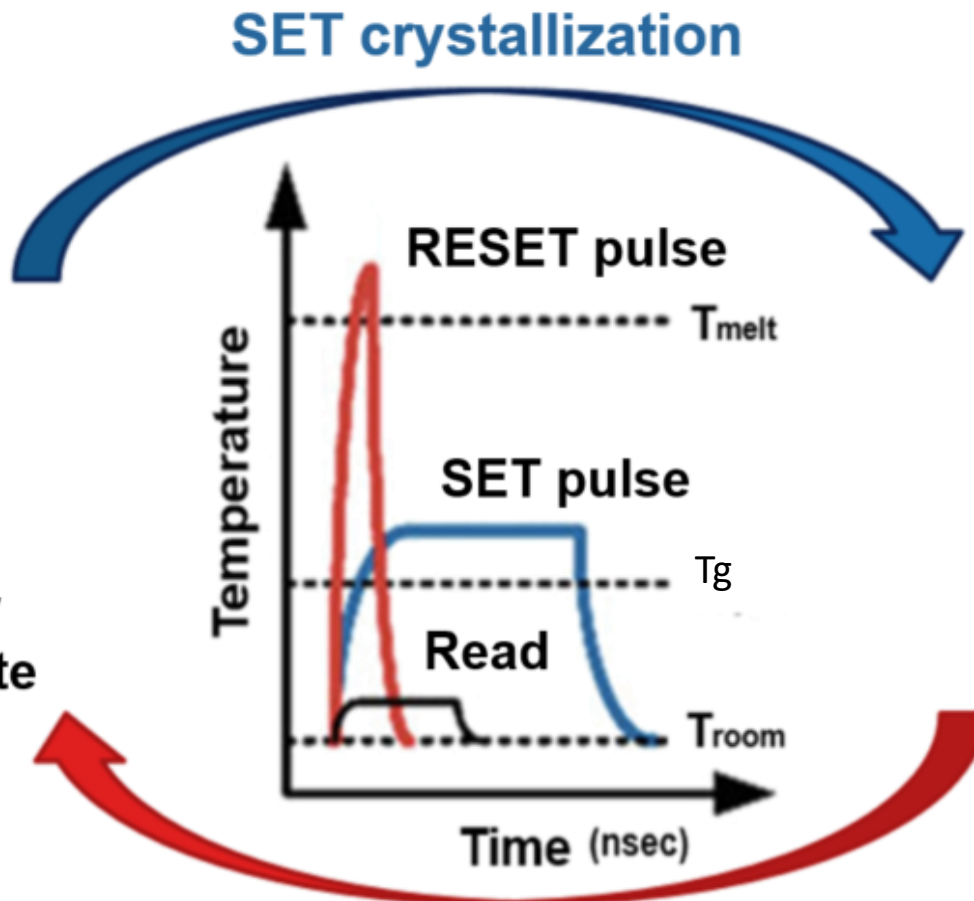
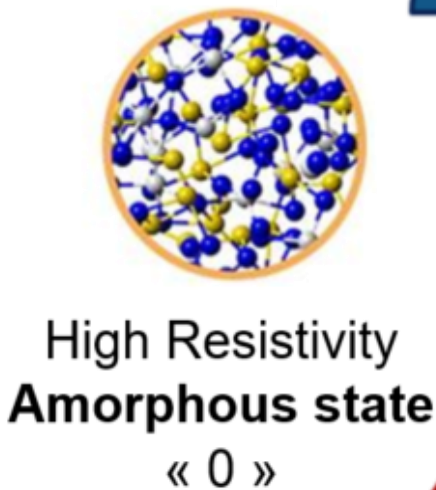
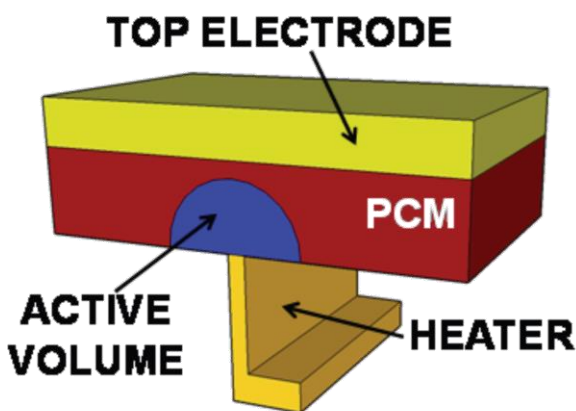
In MVB solids
→ Electrons are « locally » delocalized along certain bonds

- Moderate degree of distorsion of the lattice :**
To favor the alignment and overlap of *p* orbitals
- Large electronic polarizability and anharmonicity of the lattice :**
Very large dielectric constant, Grüneisen parameters very large + high effective Born charge Z^* .



PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES

PC memories



PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES

Still several scientific and technological challenges !

Resistive Memory and PCM requirements

Power
consumption

**Reducing the
power
consumption
for high density
matrices !**

High endurance
Thermal Stability

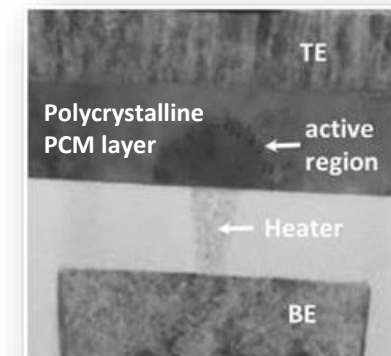
**Amorphous
phase stability
at high T for
embedded
applications**

Fast
programming

**Fast
crystallization !**

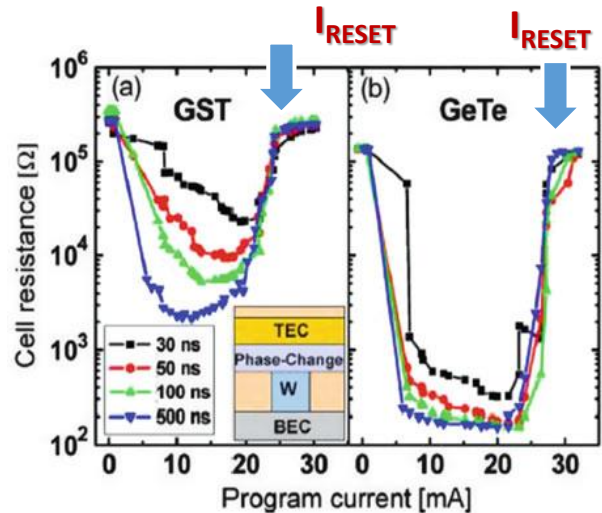
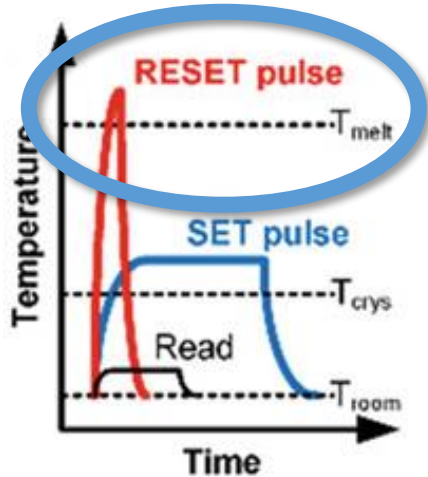
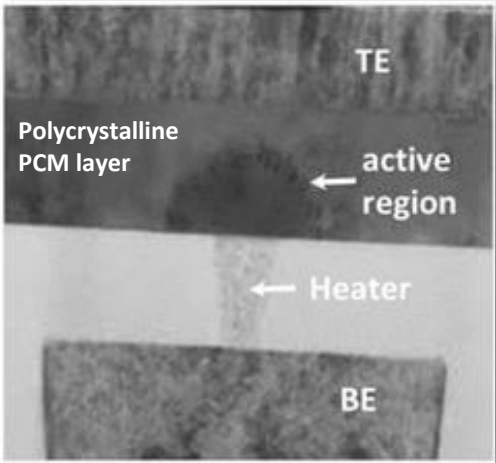
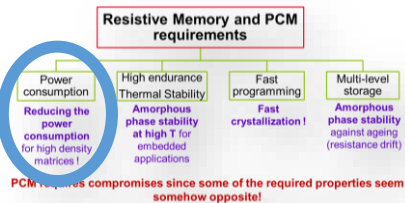
Multi-level
storage

**Amorphous
phase stability
against ageing
(resistance drift)**

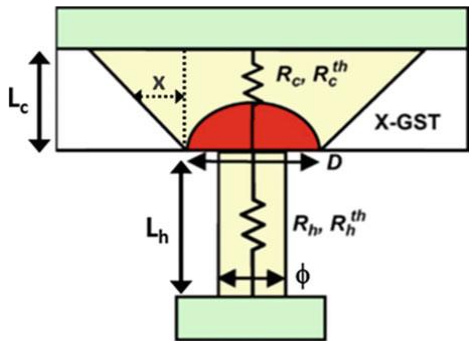


PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES

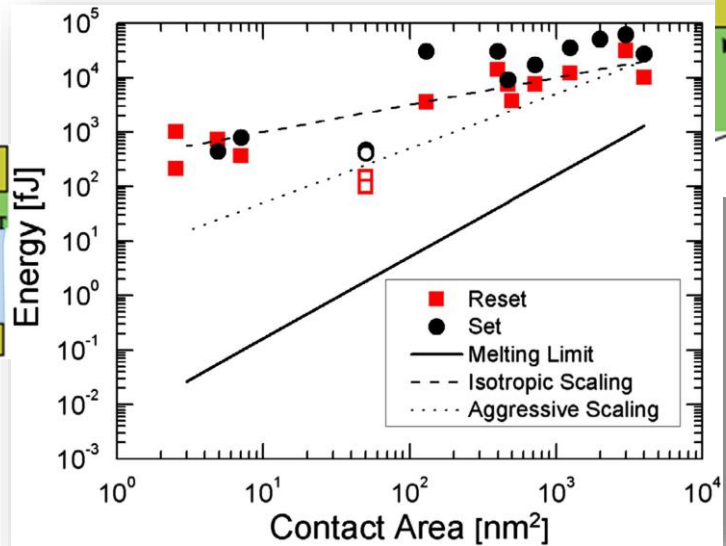
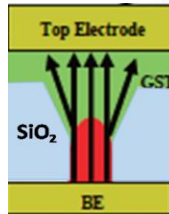
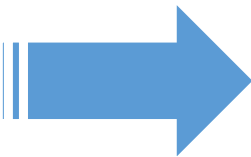
Reduce the energy consumption of PC memories: confinement !



Thermal optimization of the PC memory cell
to limit energy and heat losses
during RESET operation
(Melting of the PC material at high T followed by quenching).

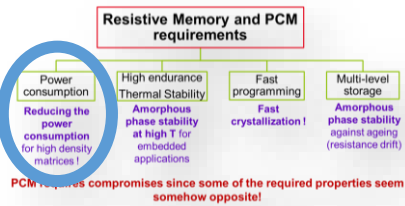


Confining heat in the PC
memory cell by using a
confinement structure as
small as possible !



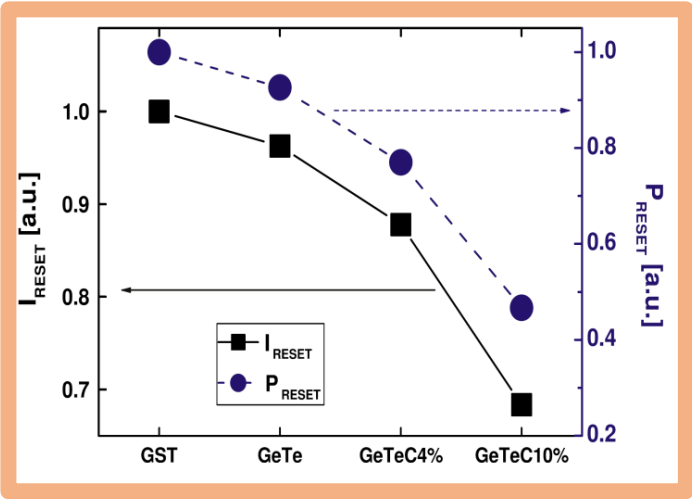
PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES

Reduce the energy consumption of PC memories: confinement !



Extra gain thanks to the reduction of the thermal conductivity of the polycrystalline phase of the PCM !

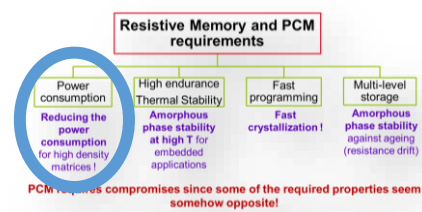
	Thermal conductivity of thin PCM films @ 300K K_{th} (W/(m.K))	
	Amorphous phase	Crystalline phase
GeTe	~0.2-0.25	~3 to 5.5 [1]
GST compounds	~0.2-0.25	~0.4 to 5 (cubic to hex)
C-doped GeTe	~0.2-0.25	0.95-1.44 [1]



[1] J. Paterson, PhD thesis, Grenoble Alpes University (2020).
K. Ghosh et al., PRB **101**, 214305 (2020).
R.J. Warzoha et al APL **115**, 023104 (2019).
D. Campi et al PRB **95**, 024311 (2017).
K S Siegert et al Rep. Prog. Phys. **78** 013001 (2015).
R. Fallica et al Phys. Status Solidi RRL **7**, No. 12, 1107–1111 (2013).
J. M. Yanez-Limon, PRB **52** 16321 (1995),

G. Betti Beneventi et al., Solid-state electronics 65-66, 197–204 (2011).

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



Reduce the energy consumption of PC memories: confinement !

How can we still decrease the thermal conductivity K_{th} of the polycrystalline phase of the PCM ?

$$k_{Th} = k_{el} + k_{ph}$$



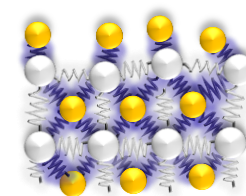
Heat transport by electrons - Wiedemann-Franz law for metals

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = 2,4428... \times 10^{-8} W \cdot \Omega \cdot K^{-2}$$

- ❑ Electronic conductivity σ (carrier type/concentration/mobility)
- ❑ Lorentz factor $L \propto |S|$ (Seebeck coefficient)

$$L = 1.5 + \exp \left[-\frac{|S|}{116} \right]$$

Ex. GeTe: $L \approx 2.4 \cdot 10^{-8} V^2 K^{-2}$

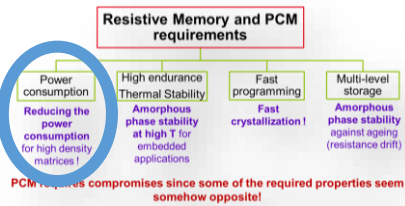


Heat transport by phonons

- ❑ Umklapp anharmonic diffusion (3 phonons process)
- ❑ Diffusion on point defects (vacancies, defects ...)
- ❑ Diffusion at grain boundaries or at chemical heterogeneities
- ❑ Electron or magnon diffusion

Reduction of K_{th} by introducing diffusion centers for phonons and/or electrons !

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



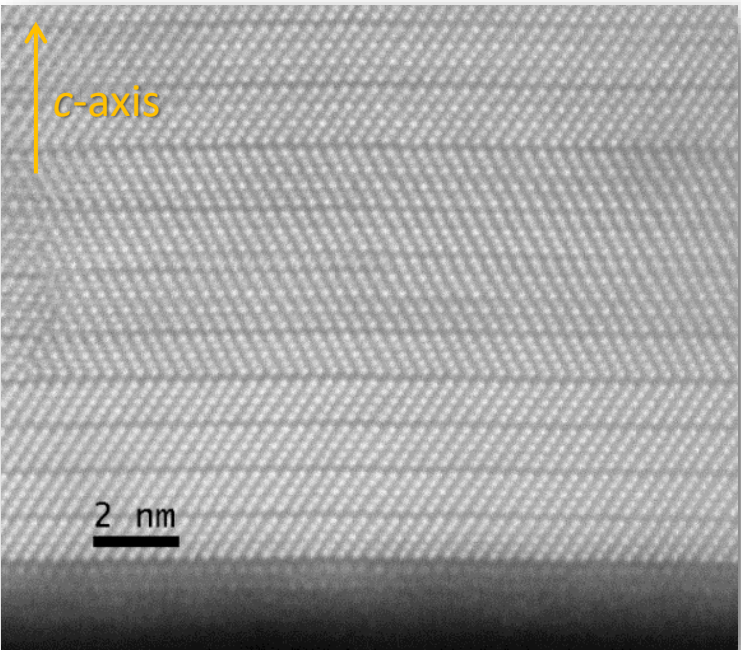
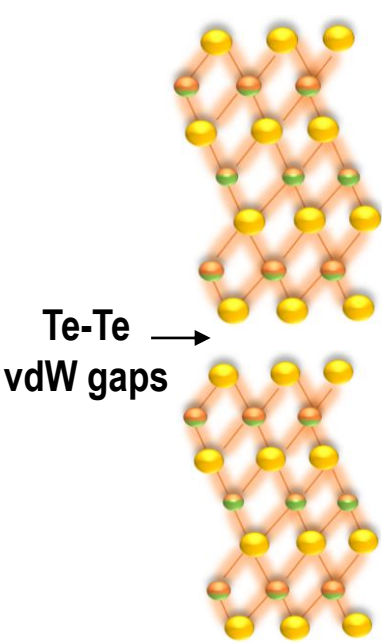
Reduce the energy consumption of PC memories: confinement !

How can we still decrease the thermal conductivity K_{th} of the polycrystalline phase of the PCM ?

Introduction of diffusion centers for phonons and/or electrons !

GST 2D & super-lattices (SL) van der Waals $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_m]_n$

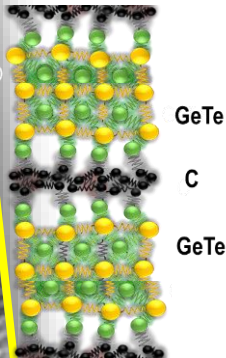
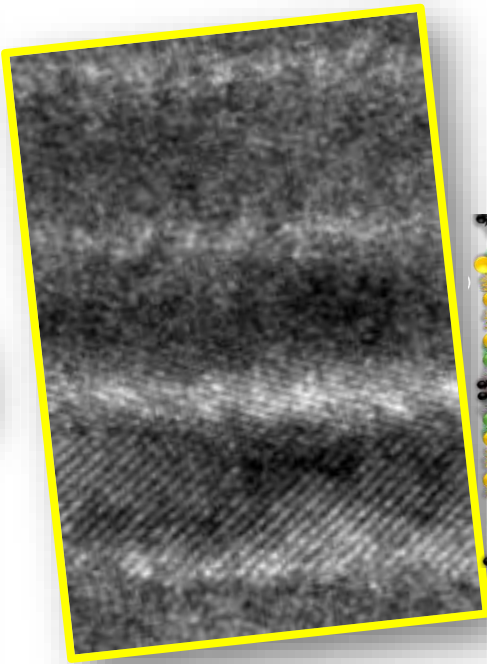
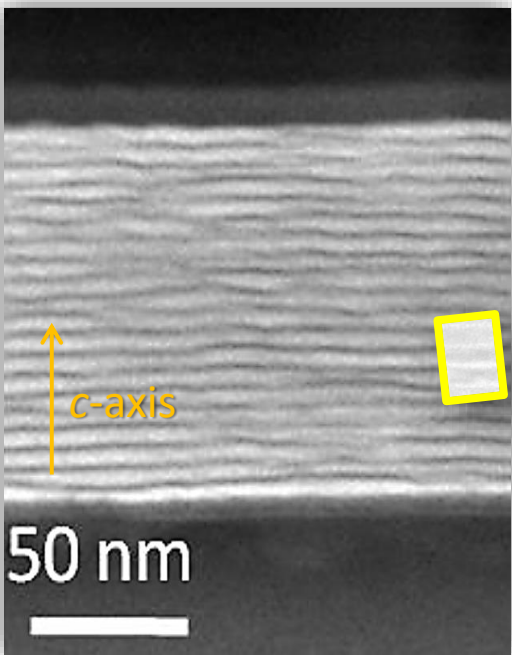
Modify electronic transport along the *c*-axis with vdW Te-Te gaps



D. Térébénec, et al., Physica Status Solidi (RRL) – Rapid Research Letters 15, 2000538 (2021).

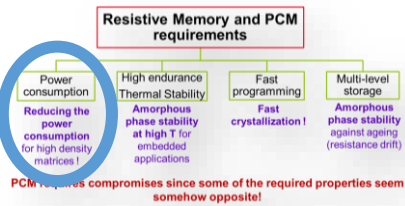
Nanocomposites PCM → GeTe/C multilayers

Modify phonon propagation along the *c*-axis by introducing heterogeneities of elastic constants



D. Térébénec, et al., Physica Status Solidi (RRL) – Rapid Research Letters 2200054 (2022).

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



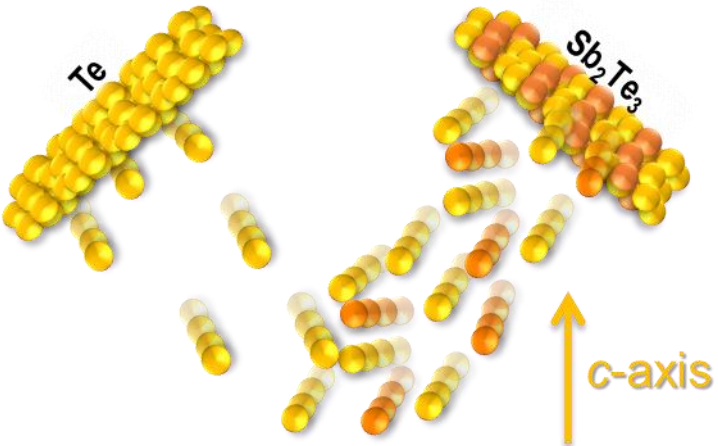
Reduce the energy consumption of PC memories: confinement !

How can we still decrease the thermal conductivity K_{th} of the polycrystalline phase of the PCM ?

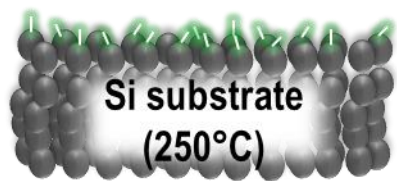
Introduction of diffusion centers for phonons and/or electrons !

GST 2D & super-lattices (SL) van der Waals $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_m]_n$

Modify electronic transport along the c-axis with vdW Te-Te gaps



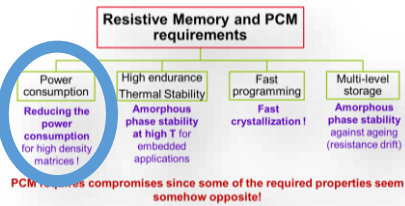
- Te
- Sb
- Ge



P. Kowalczyk et al., *Small* **2018**, 14, 1704514.

F. Hippert, et al., *J. Phys. D: Appl. Phys.* **2020**, 53, 154003.

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



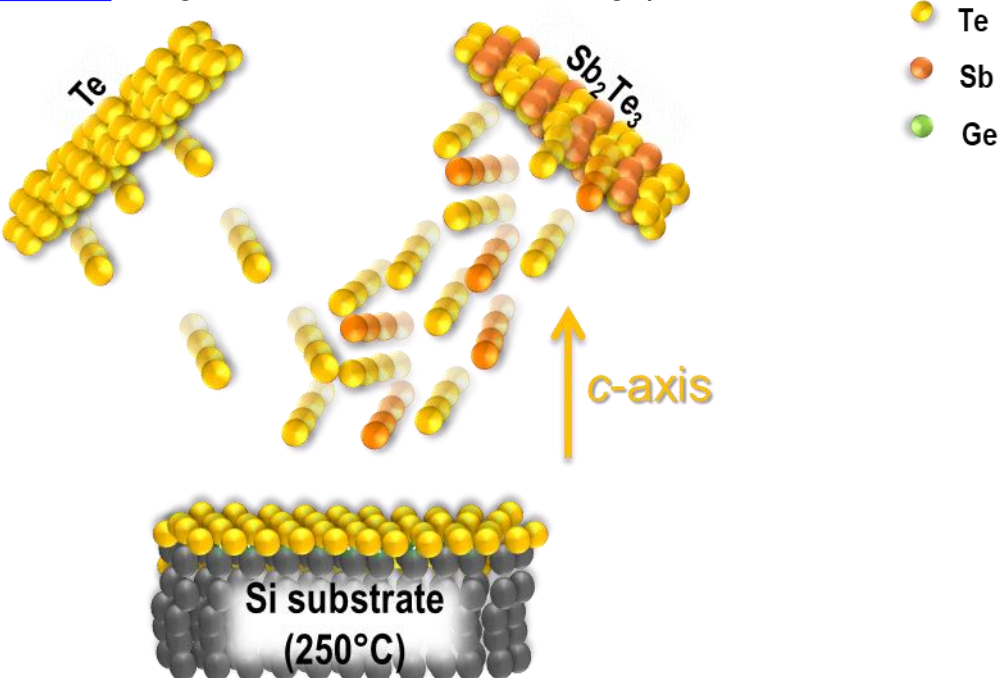
Reduce the energy consumption of PC memories: confinement !

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Introduction of diffusion centers for phonons and/or electrons !

GST 2D & super-lattices (SL) van der Waals $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_m]_n$

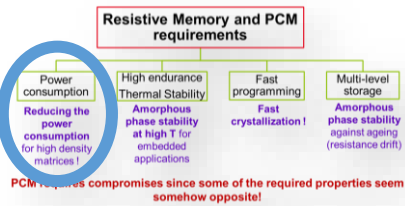
Modify electronic transport along the *c*-axis with vdW Te-Te gaps



P. Kowalczyk et al., *Small* **2018**, 14, 1704514.

F. Hippert, et al., *J. Phys. D: Appl. Phys.* **2020**, 53, 154003.

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



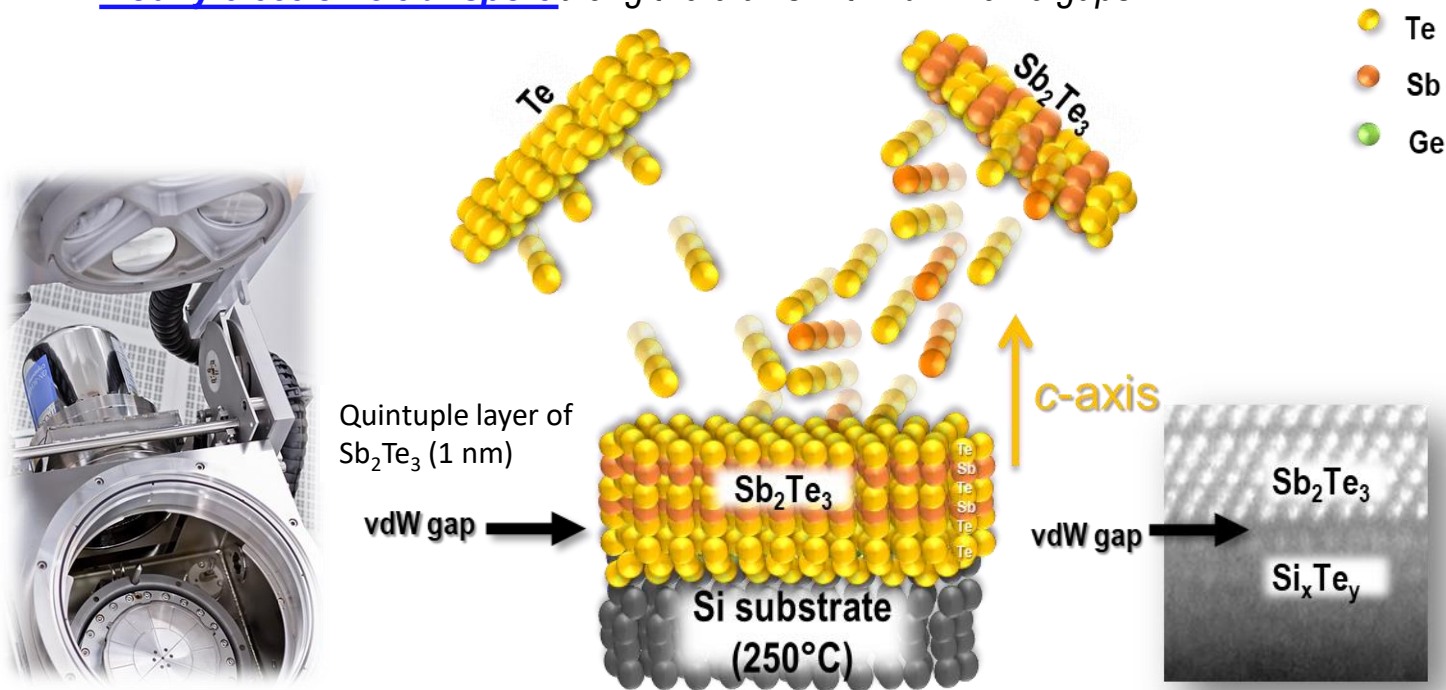
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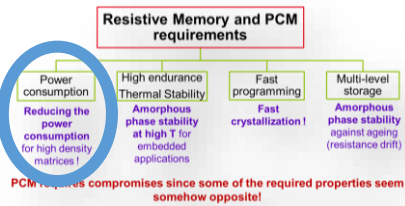
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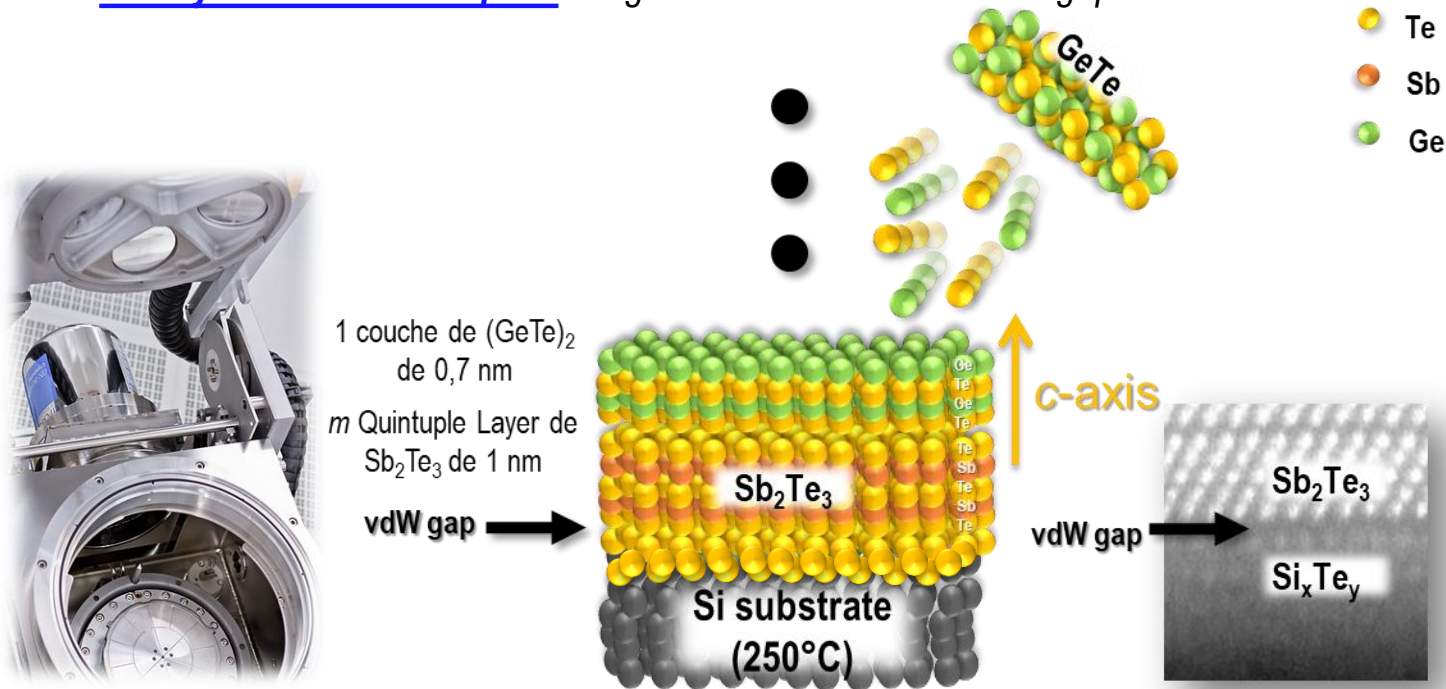
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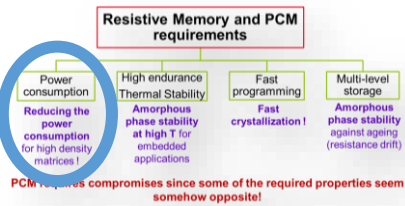
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PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



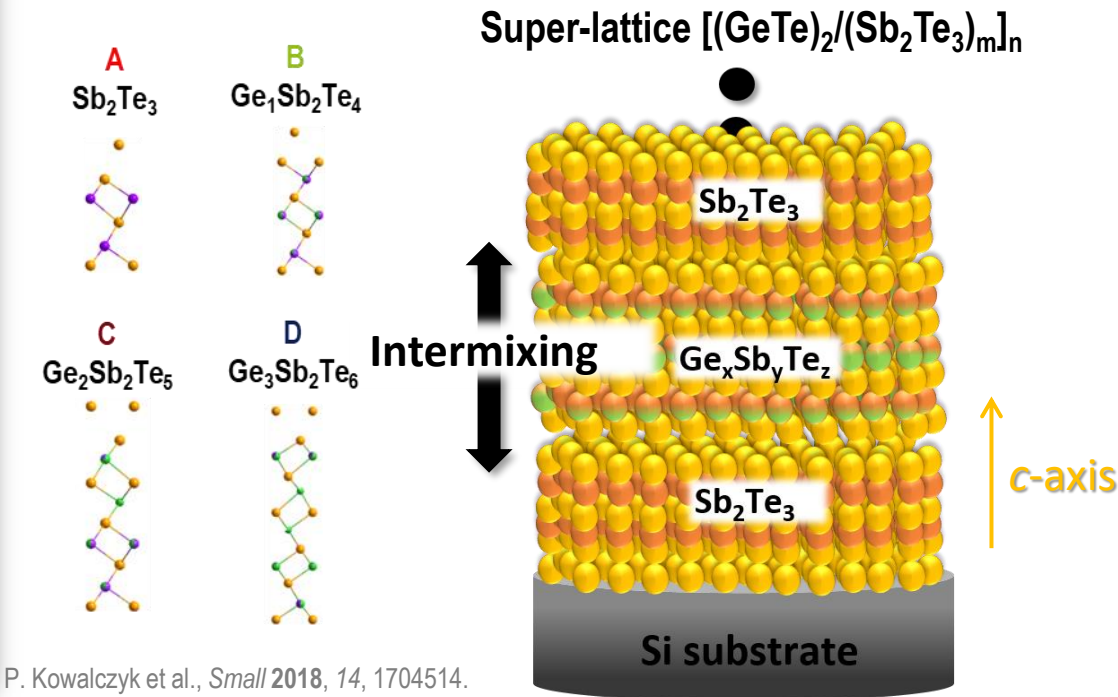
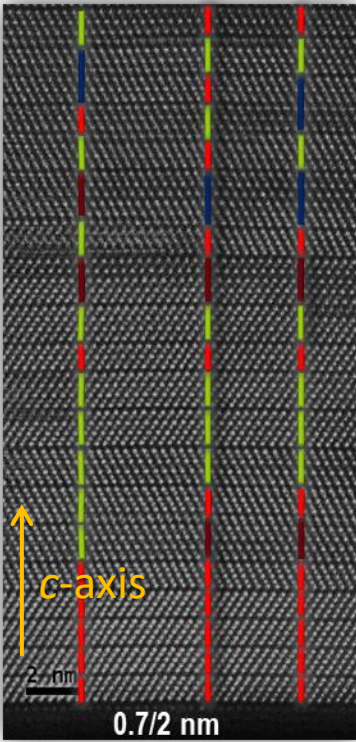
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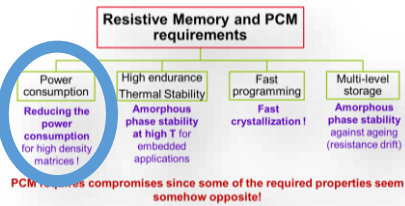
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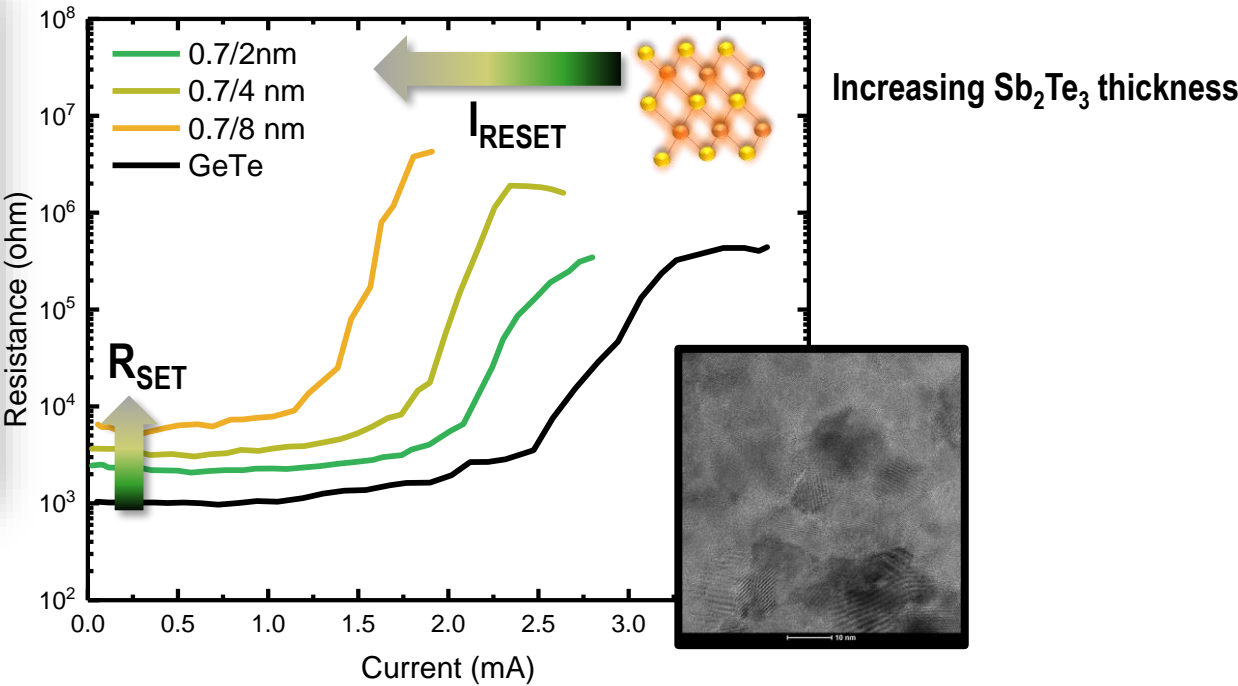
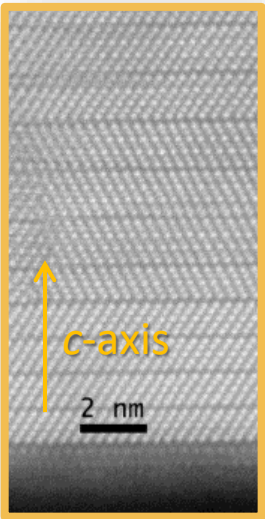
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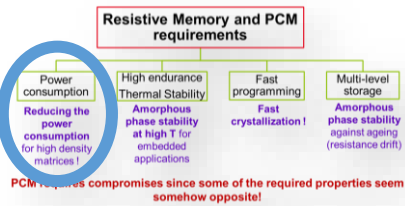
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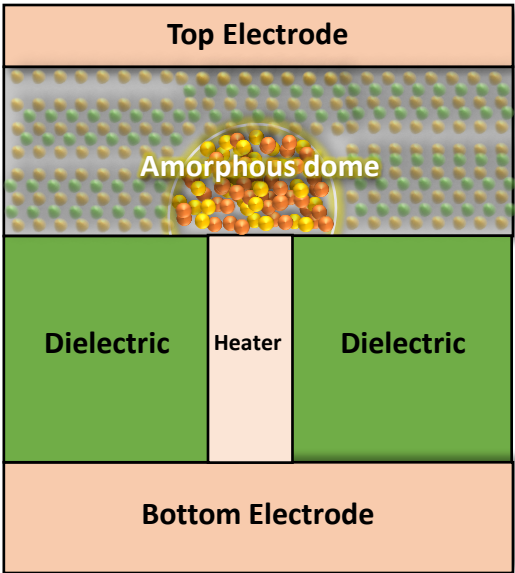
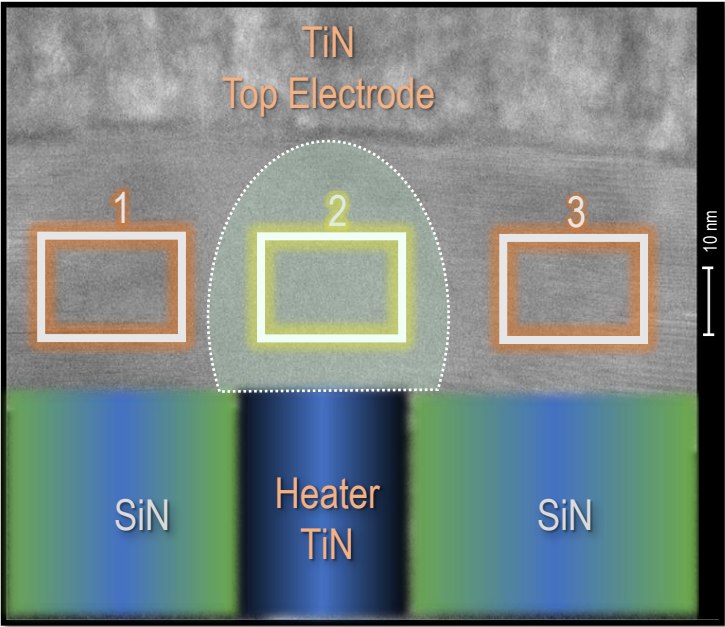
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Modify electronic transport along the c-axis with vdW Te-Te gaps

0.7/8 SL in the RESET state

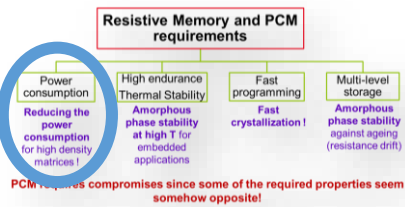


PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES

Reduce the energy consumption of PC memories: confinement !

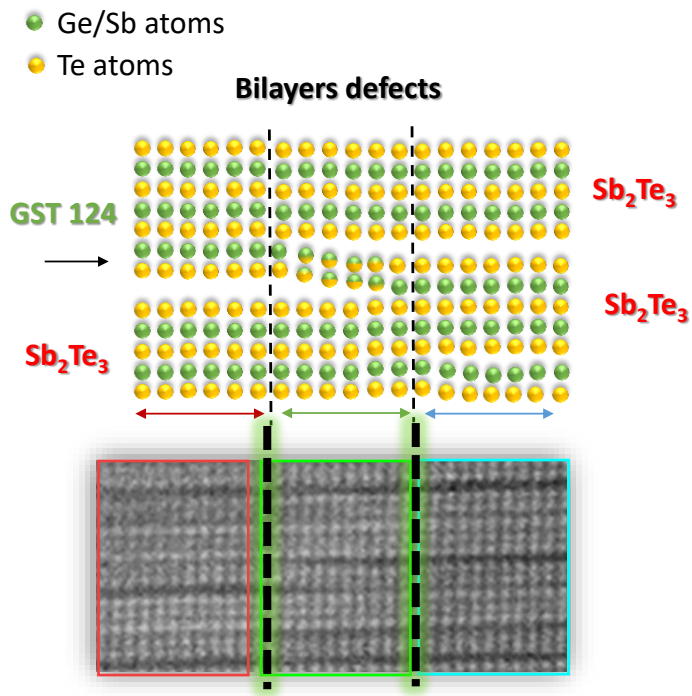
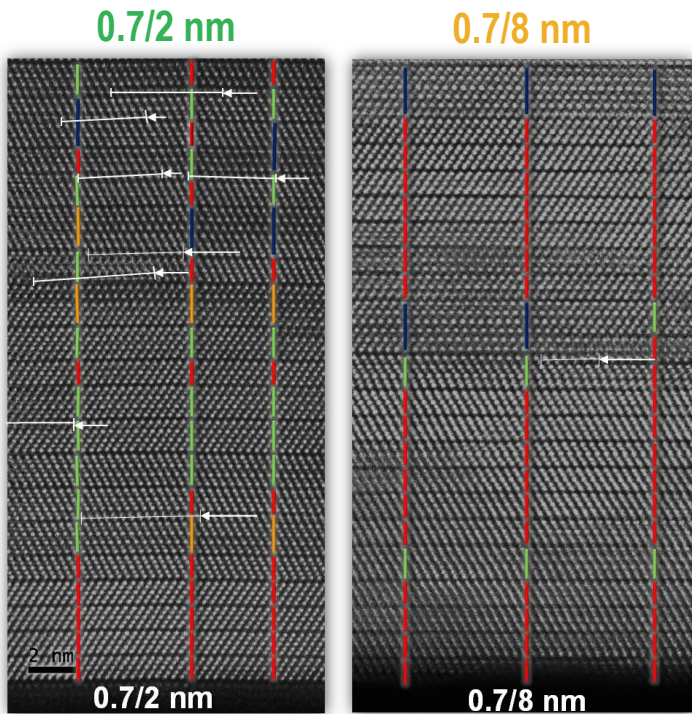
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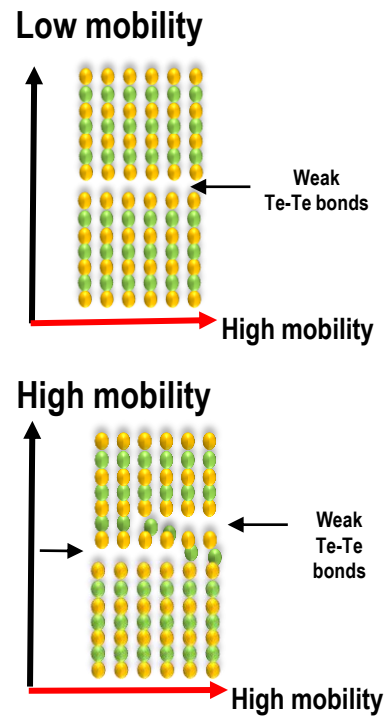
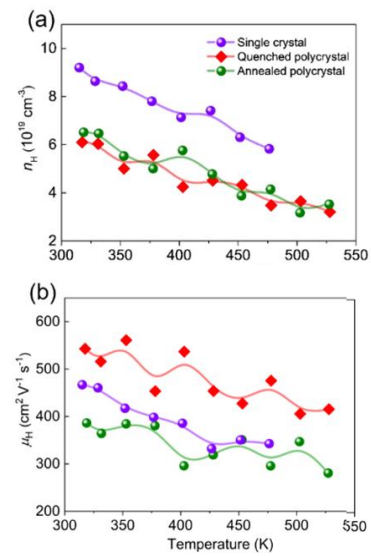


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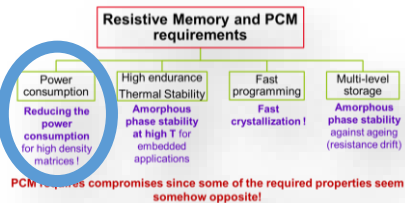
Modify electronic transport along the c-axis with vdW Te-Te gaps



Impact of Swapped Bilayers on the mobility of charge carriers in polycrystalline Sb_2Te_3



PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



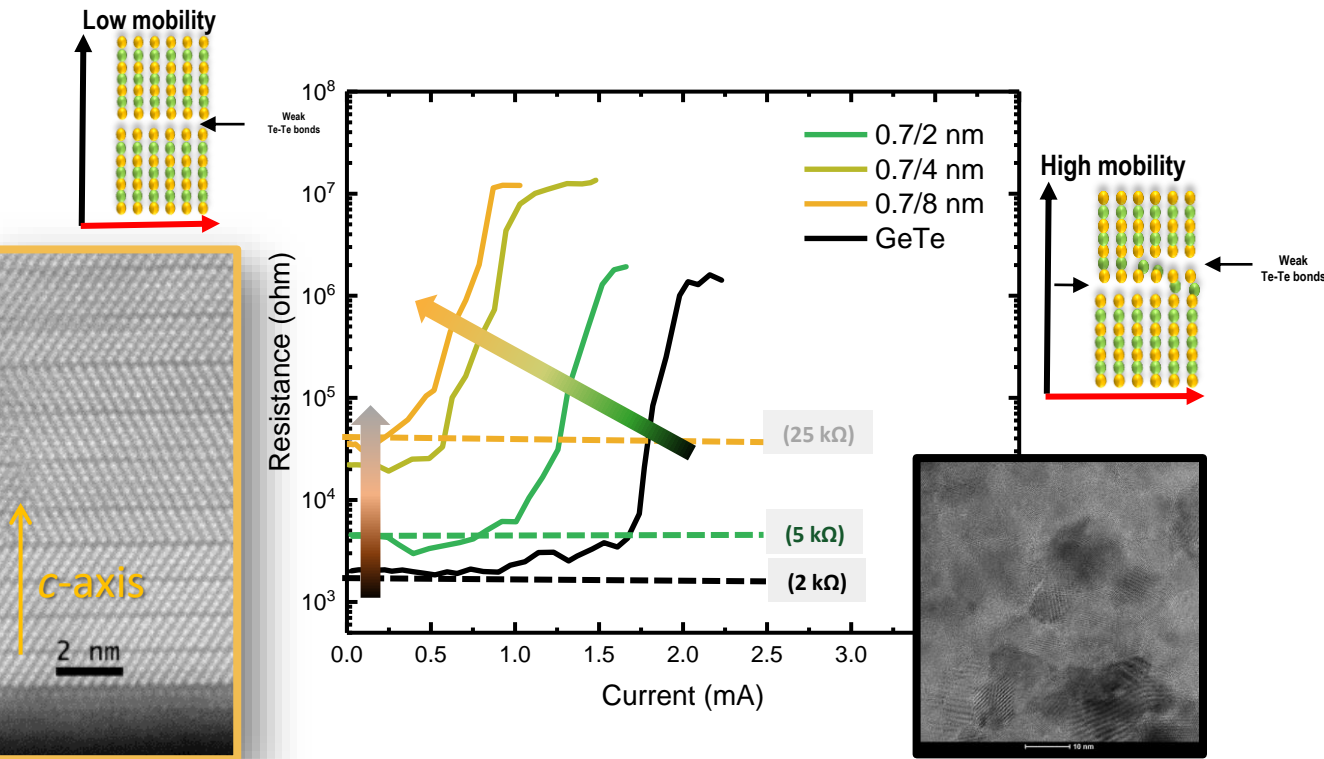
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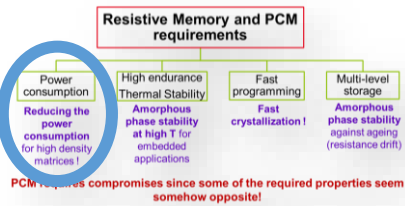
Modify electronic transport along the *c*-axis with vdW Te-Te gaps



The main difference between SLs is the degree/density of disorder/defects in the crystalline structure at the vdW gaps

The difference of R_{SET} between SLs can be attributed to the number of swapped bilayers in the crystalline structure.

PHASE CHANGE CHALCOGENIDES (PCM) AND PHASE CHANGE MEMORIES



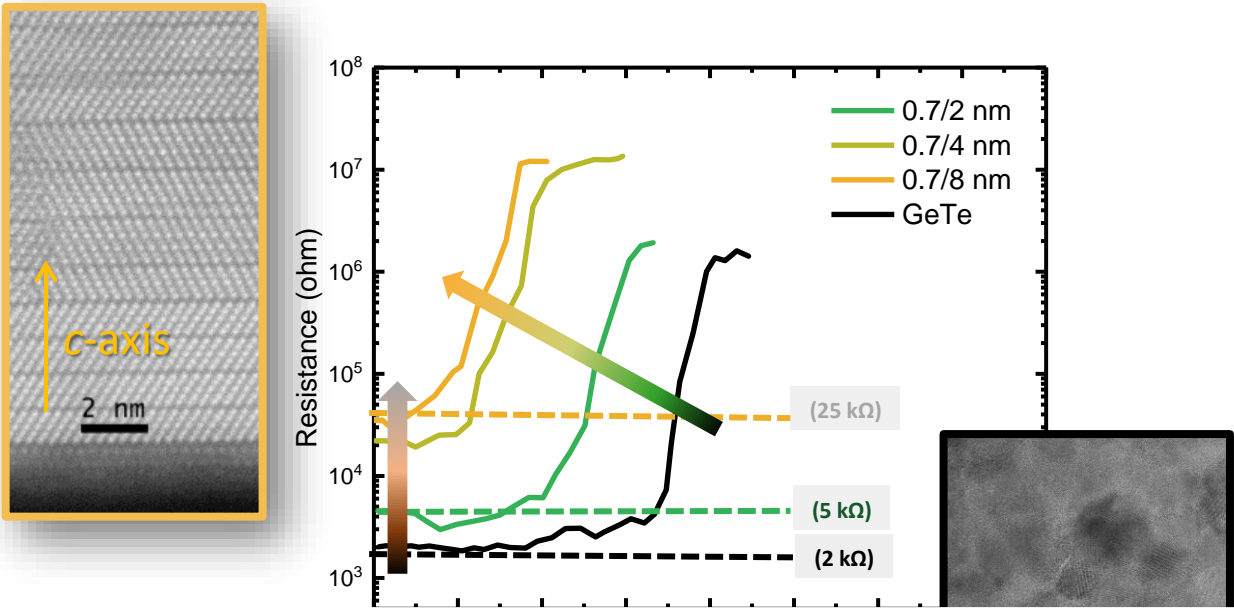
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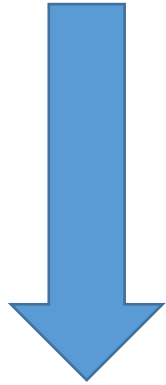


Challenge: understand experimentally and theoretically the anisotropy of thermal and electronic properties in these systems !

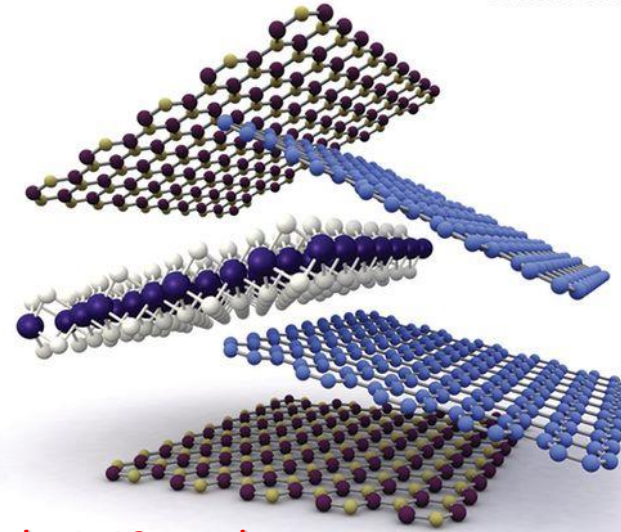
The different growth methods: MBE

Mechanically-assembled stacks

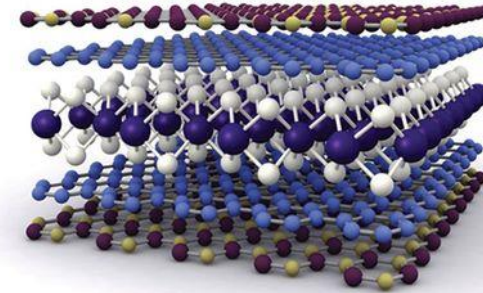
TODAY



FUTURE

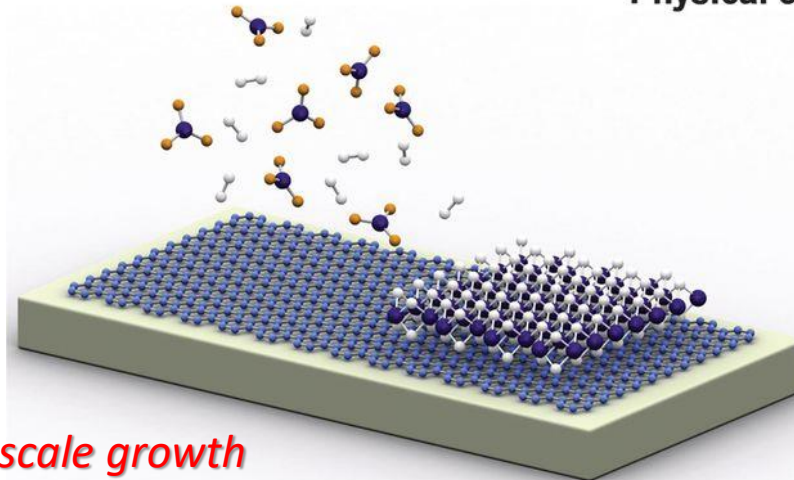


Flakes are only 1-10 μm large

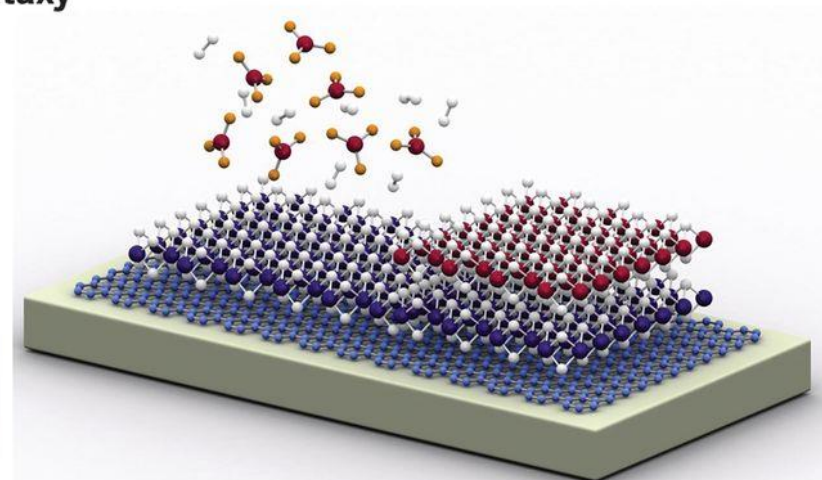


transistor, photodetectors...with flakes

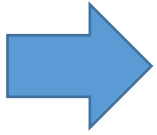
Physical epitaxy



Wafer scale growth

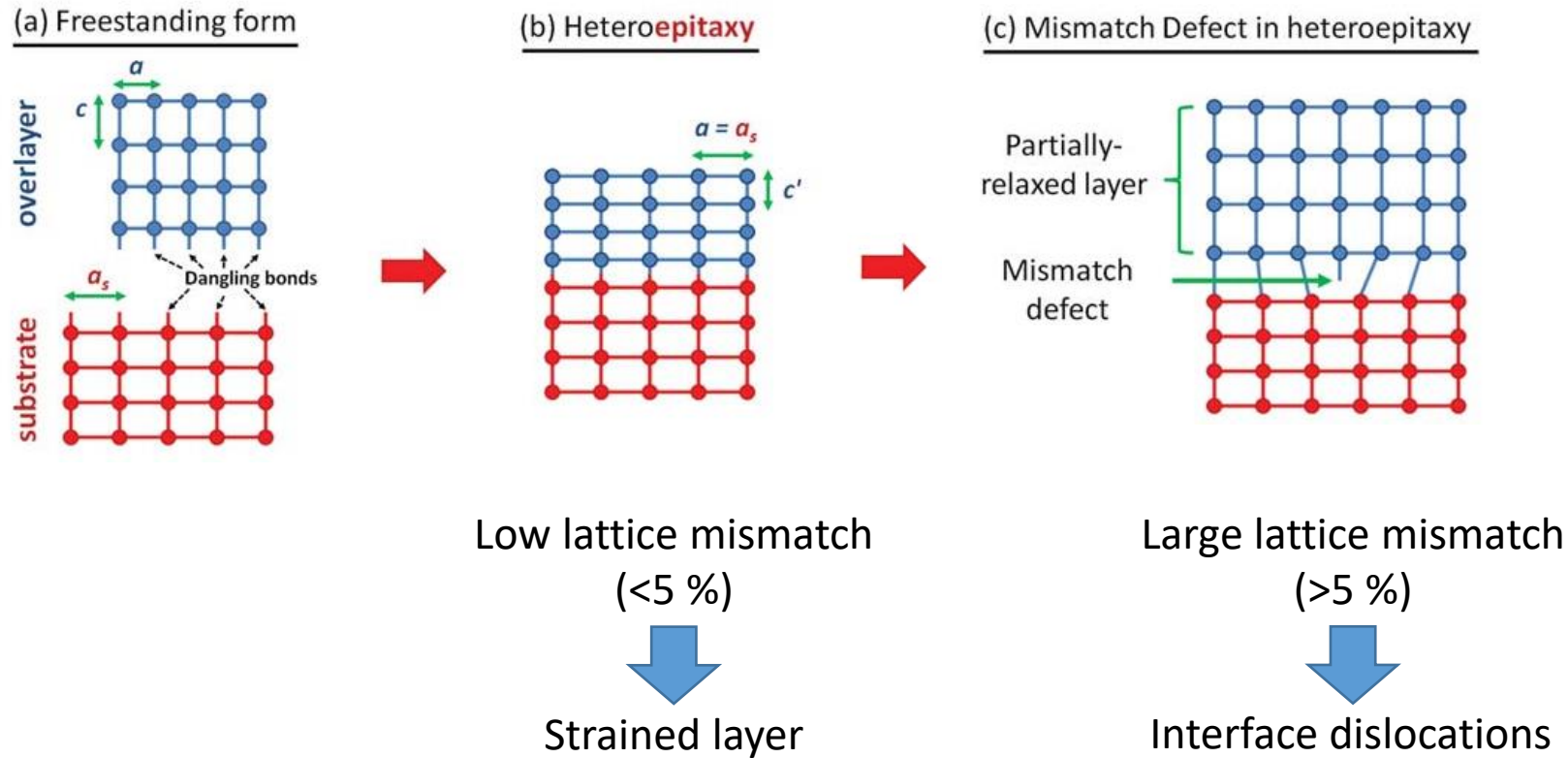


FUTURE



Develop the growth on large scales of single crystalline 2D materials by using epitaxial growth like for Si, Ge, GaAs or GaN technologies after almost 60 years of effort

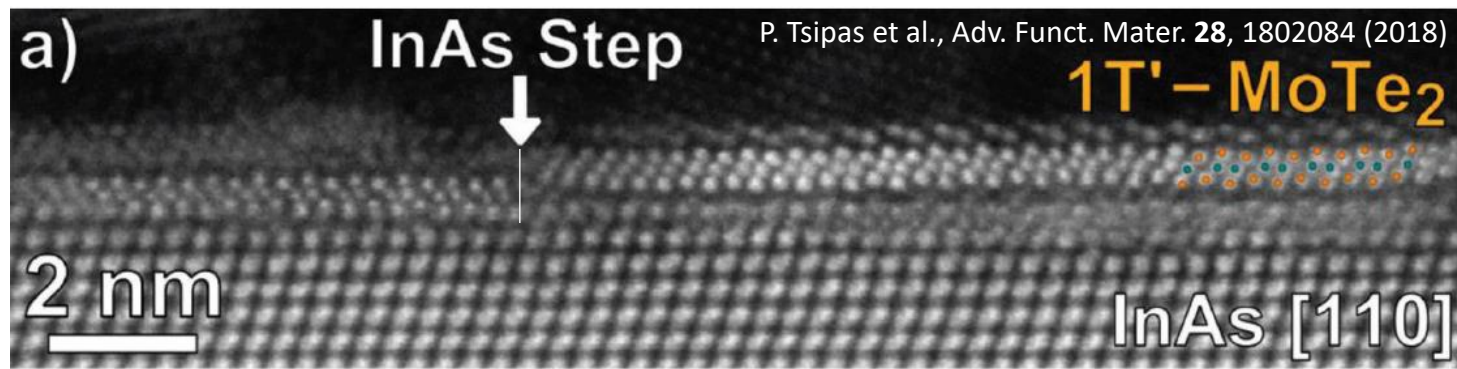
Principle of epitaxial growth:



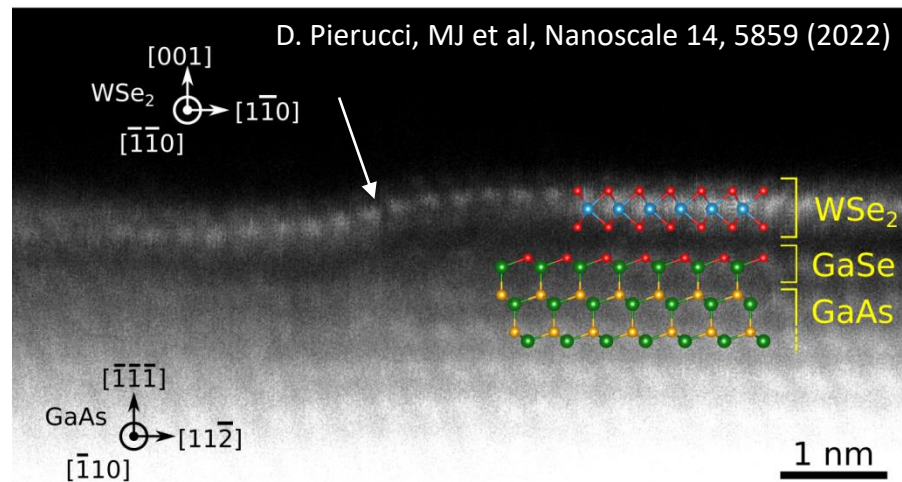
NO substrate with hexagonal symmetry and low lattice mismatch for the epitaxial growth of 2D Materials!

Extra constraints for 2D materials:

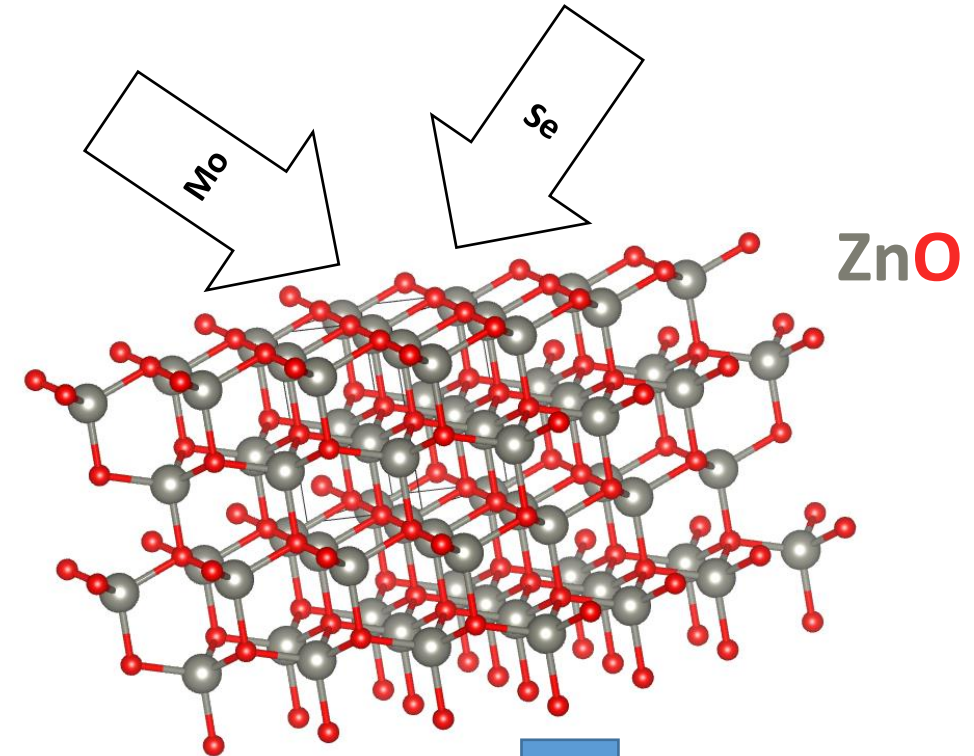
- Substrate topography important: should be perfectly flat
- Chemical reaction with chalcogen atoms (depends on the formation enthalpy of the different compounds and T)



Layer breaking at atomic steps

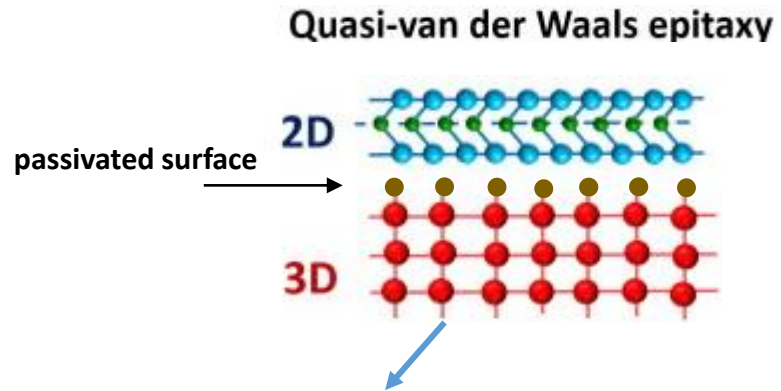


Local strain



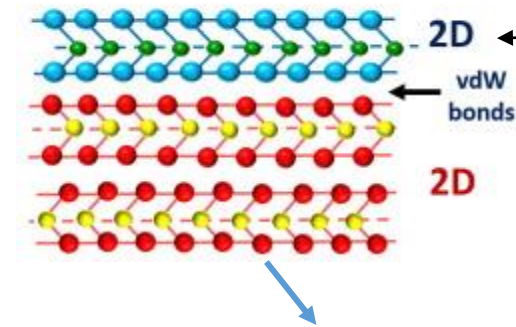
Formation of MoO₃ and ZnSe

Solution: reduce substrate-2D material interaction from dangling bonds (0.1-1 eV/at) to vdW bonds (~ 10 meV/at)



MoSe₂, NbSe₂ / passivated GaAs(111) surface
K. Ueno, A. Koma, Appl. Phys. Lett. **55**, 327 (1990)

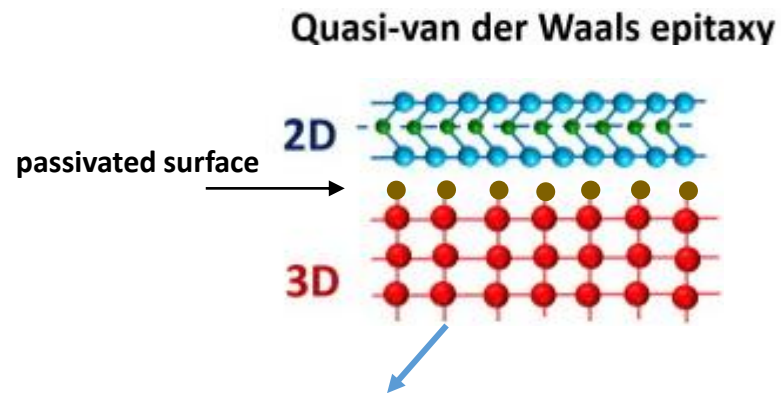
van der Waals epitaxy



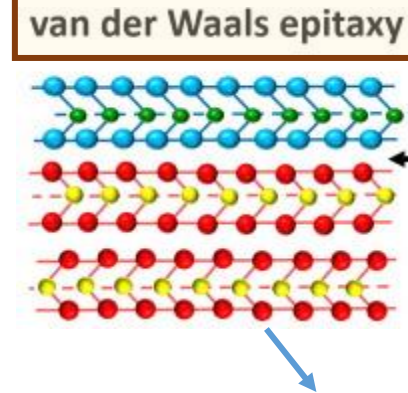
fully relaxed monolayer

MoSe₂, NbSe₂ / mica
K. Ueno, A. Koma, J. Vac. Sci. Technol. A **8**, 68 (1990)

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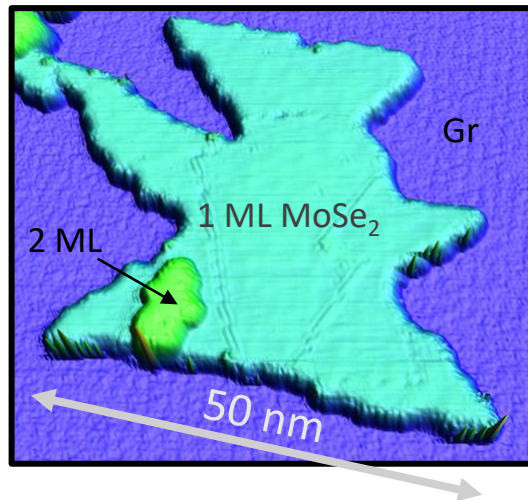
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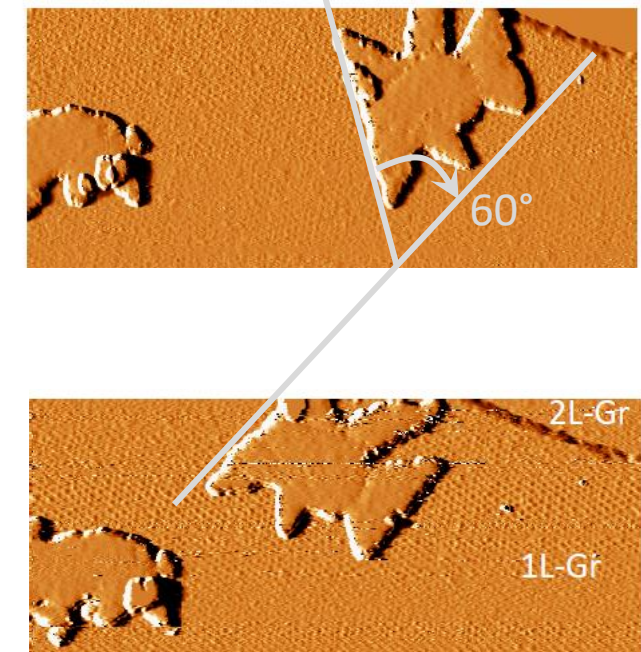
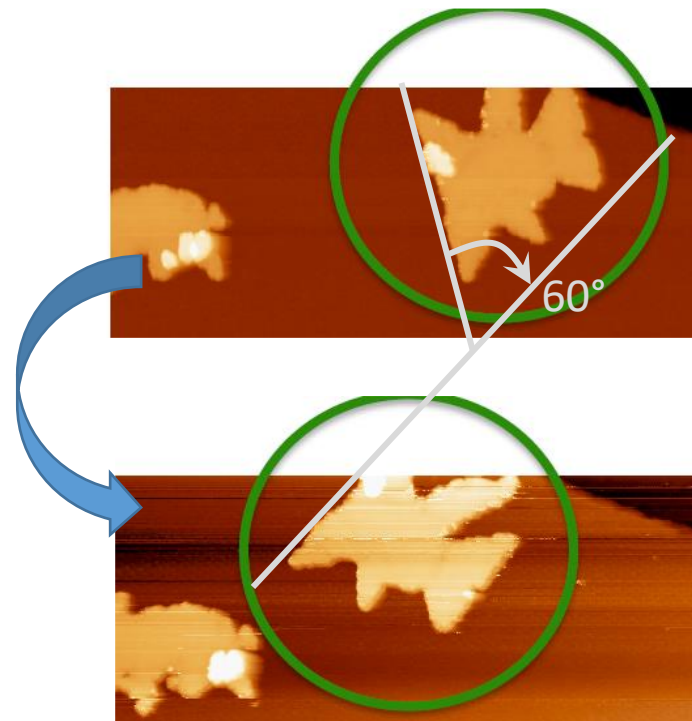
fully relaxed monolayer

MoSe₂, NbSe₂ / mica
K. Ueno, A. Koma, J. Vac. Sci. Technol. A **8**, 68 (1990)

vdW epitaxy of MoSe₂ on graphene/SiC



Dau et al., ACS Nano **12**, 2319 (2018)

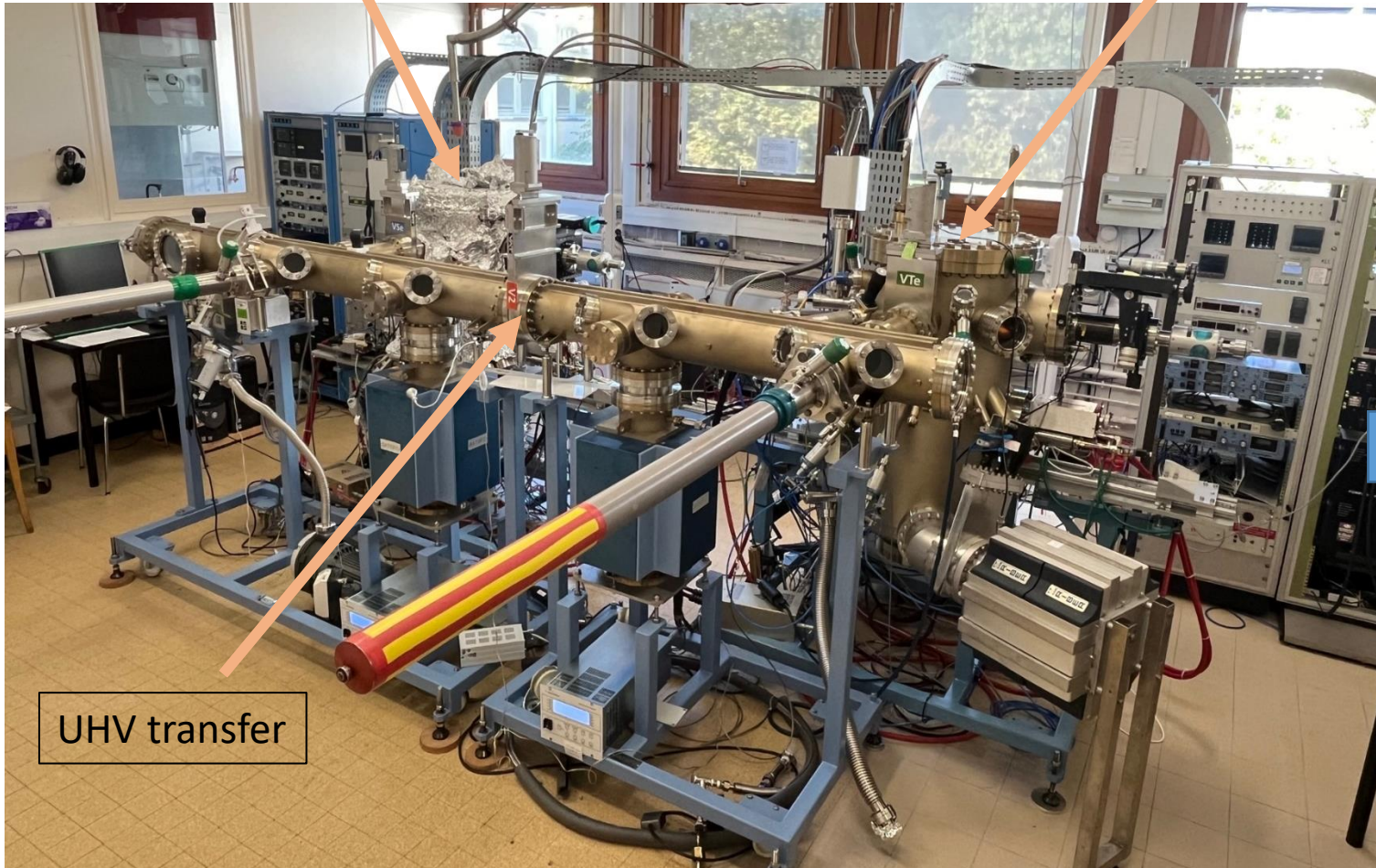


Molecular beam epitaxy (MBE)

@ Spintec

selenides

tellurides

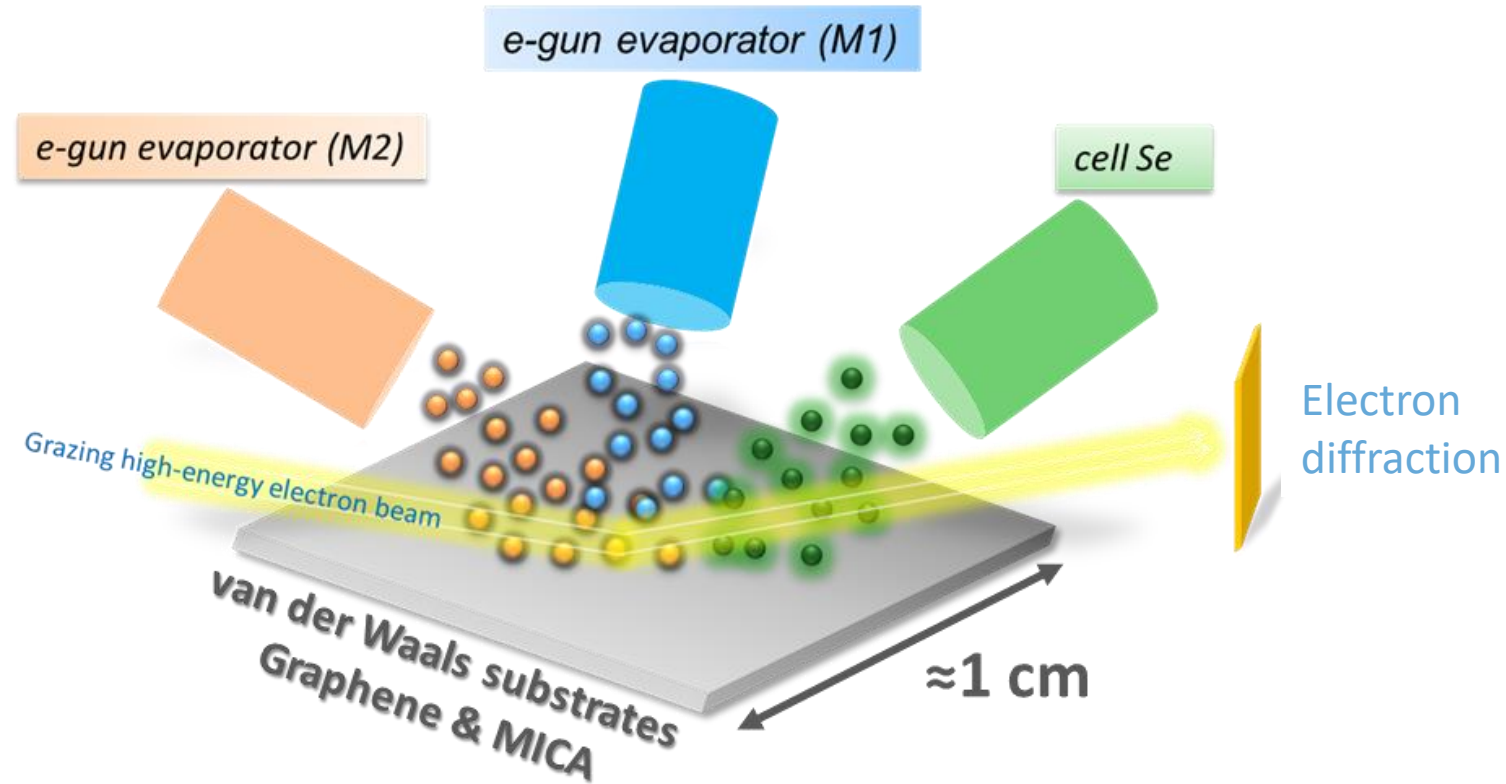


UHV transfer

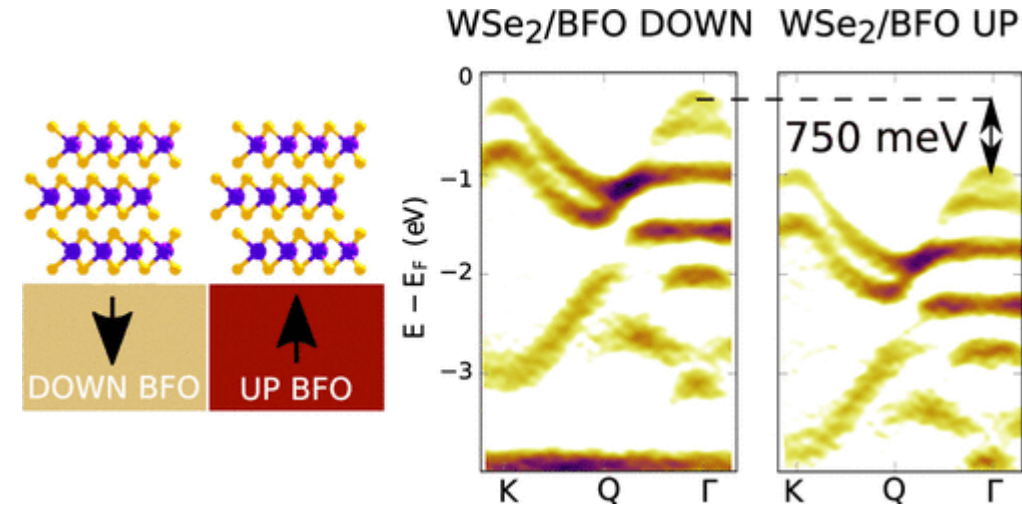
Ultrahigh vacuum (UHV)
 10^{-10} mbar

15 metals available in each reactor

Molecular beam epitaxy (MBE)



vdW: easy to detach the film



R. Salazar et al., Nano Lett. 22, 9260 (2022)

- High crystalline quality, UHV conditions: low density of impurities
- Accurate control of number of layers by using quartz microbalance
- Stacking of different MSe₂ or MTe₂ monolayers for complex vertical heterostructures
- Flexible choice of metals : Mo, W, Nb, Pt, Pd, V, Fe, Mn + doping and alloys

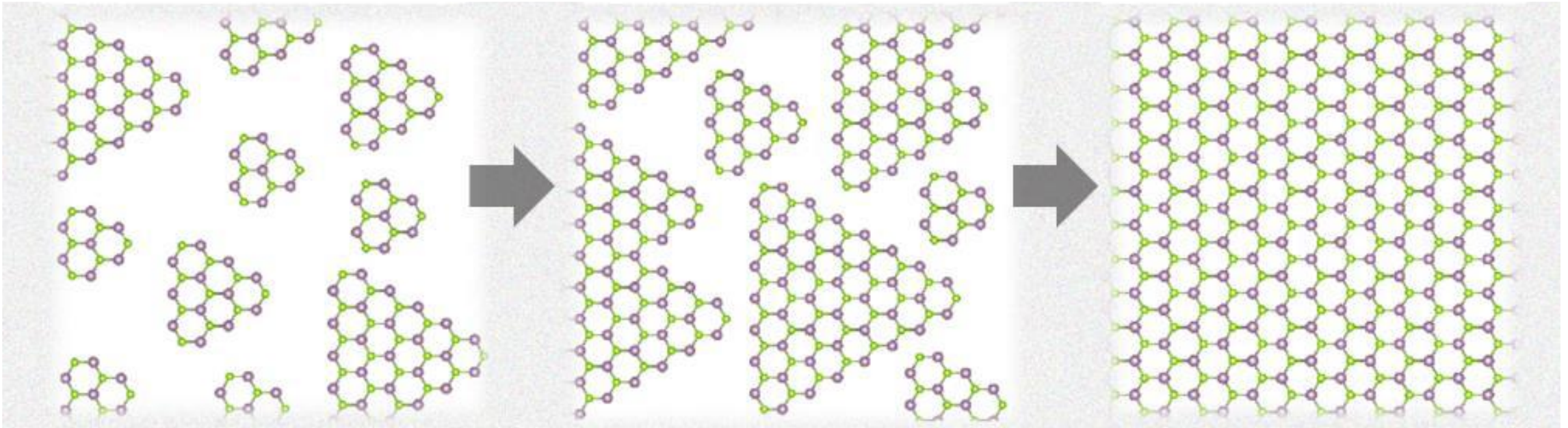
By MBE...

low growth T, high nucleation rate

ORIENTED NUCLEI

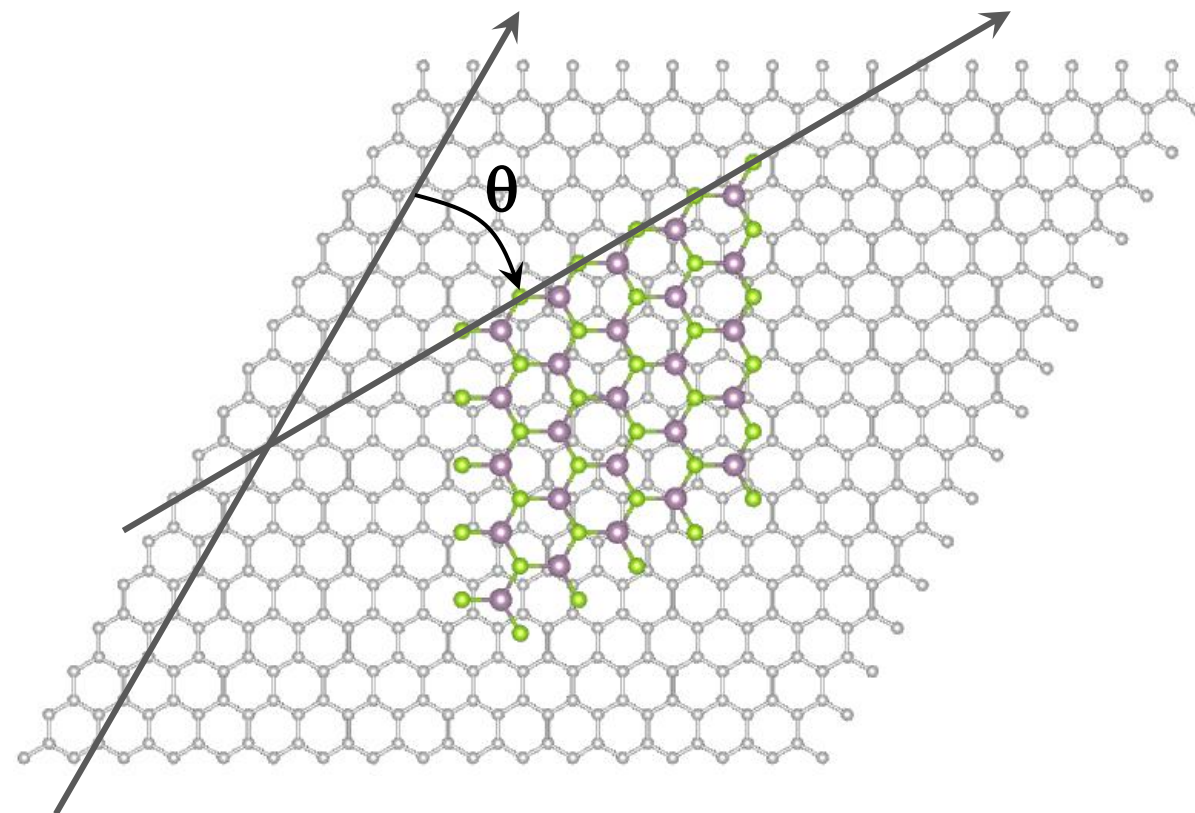
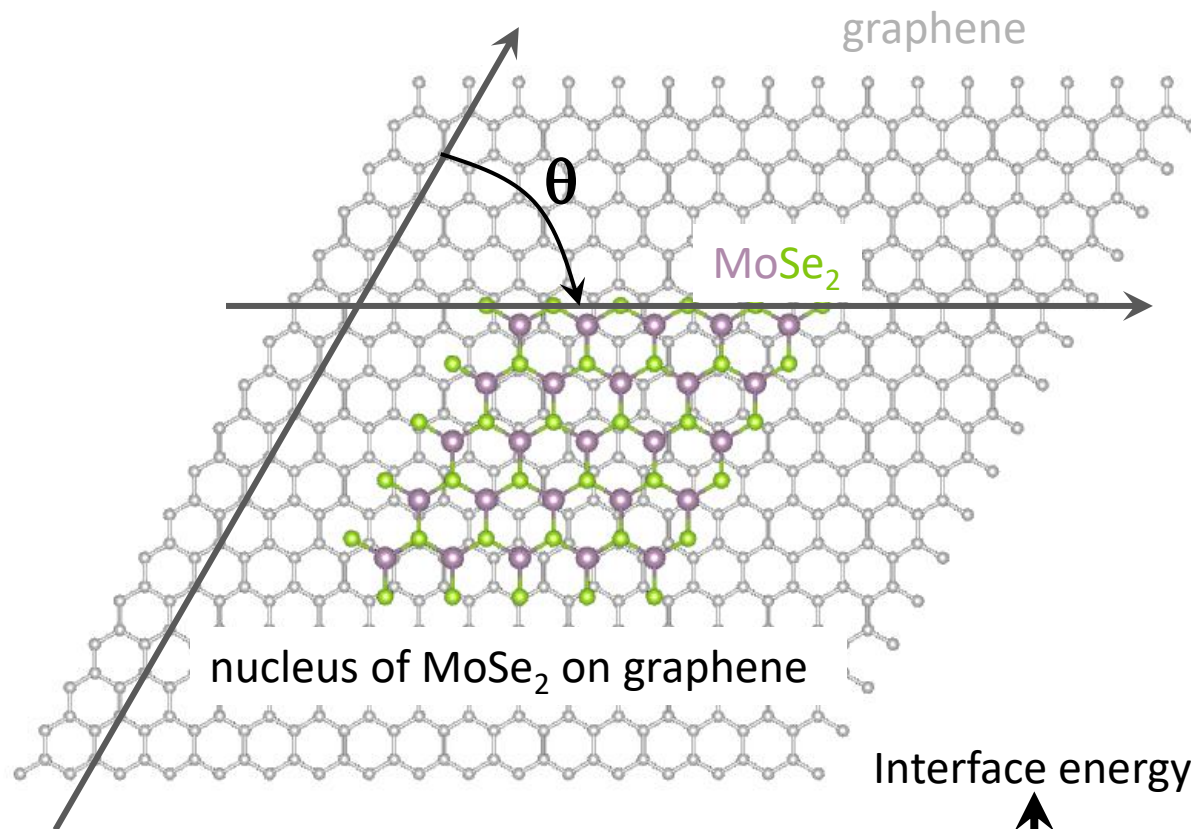
GROWTH

COALESCENCE

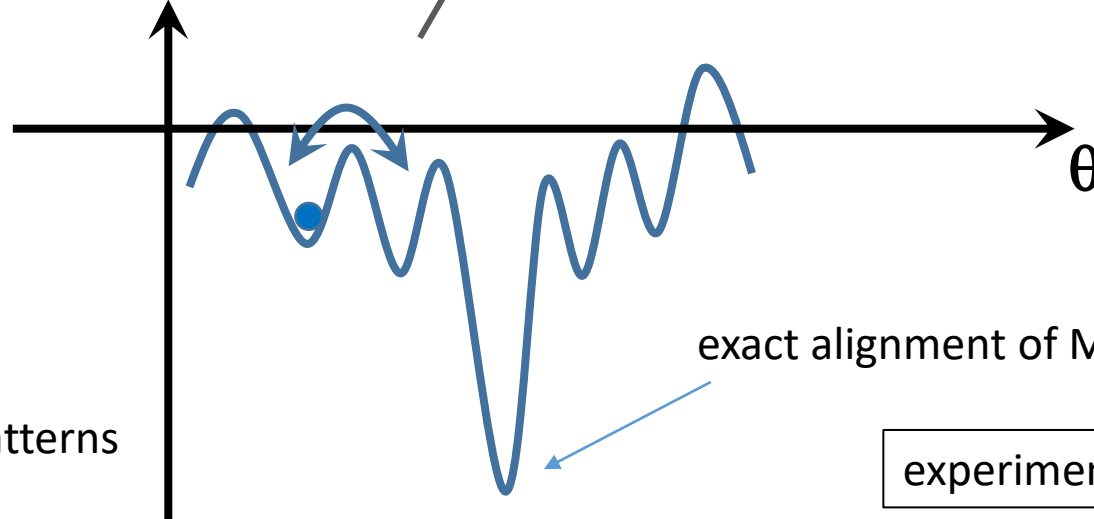


1st issue: mosaic spread

a consequence of low interaction between substrate and 2D layer



Interface energy

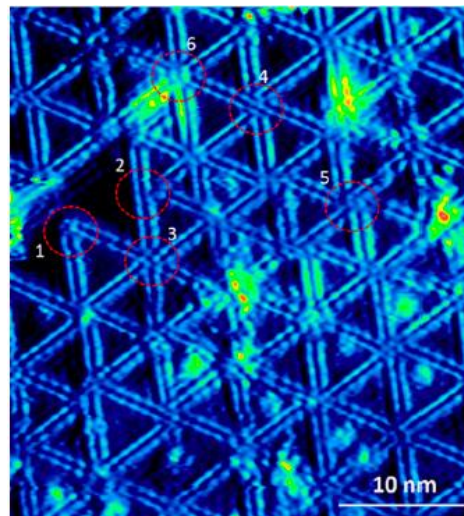
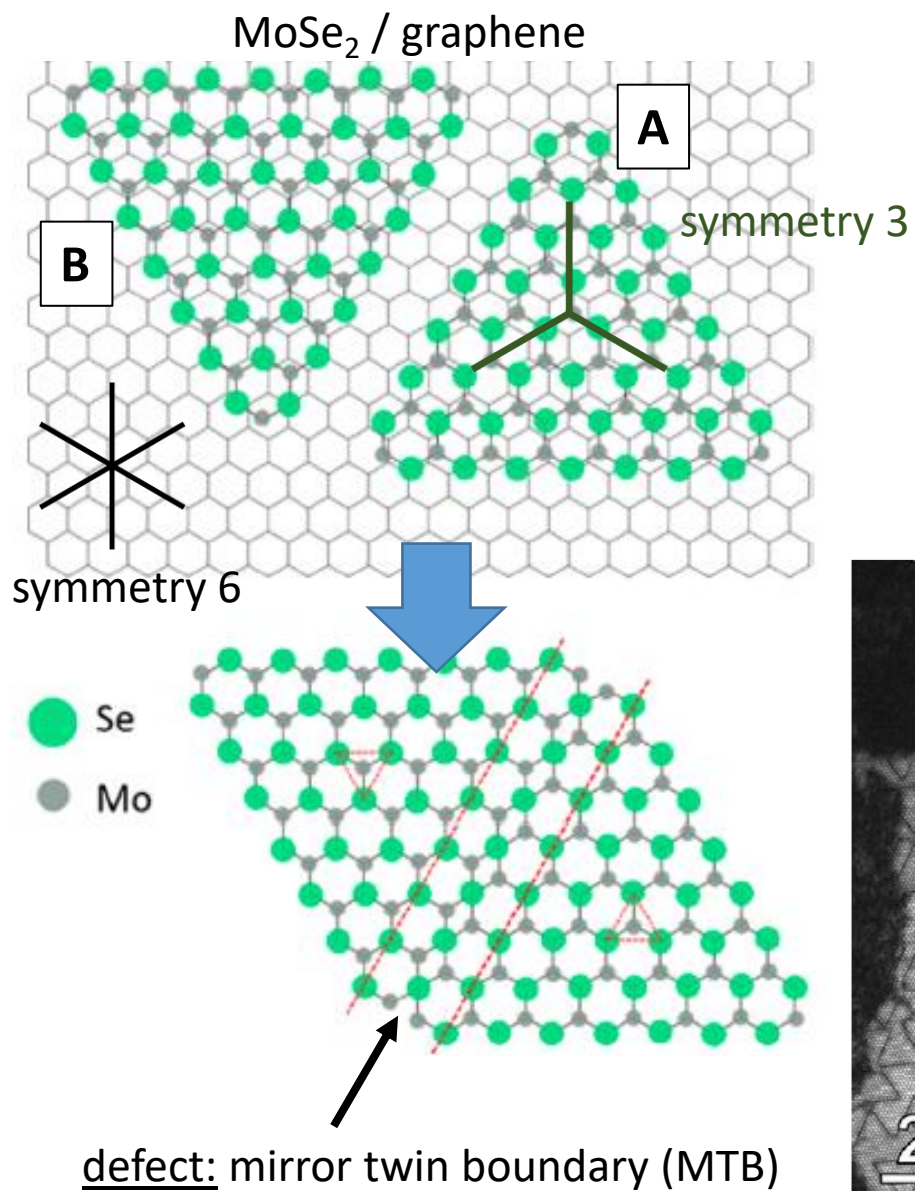


exact alignment of MoSe_2 & graphene lattices

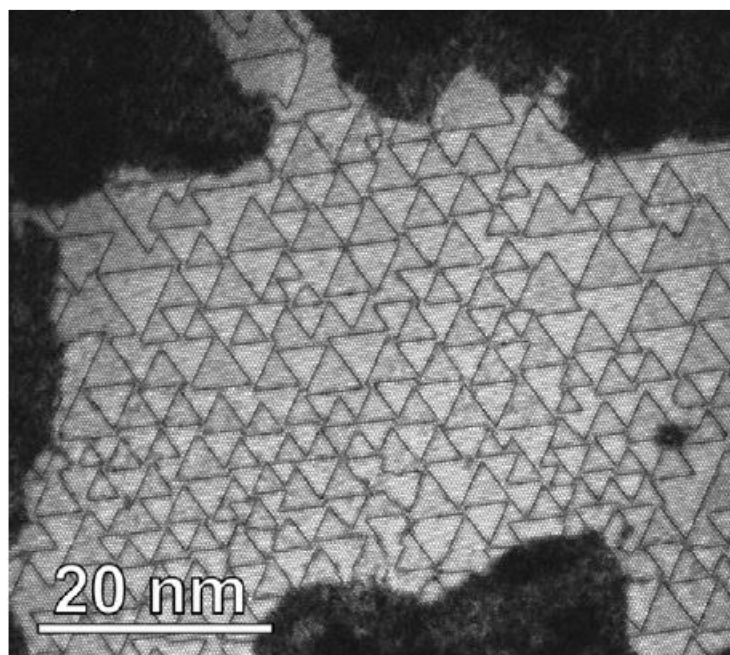
experimentally MoSe_2/Gr : $\pm 3^\circ$

Atomic coincidences lead to Moiré patterns

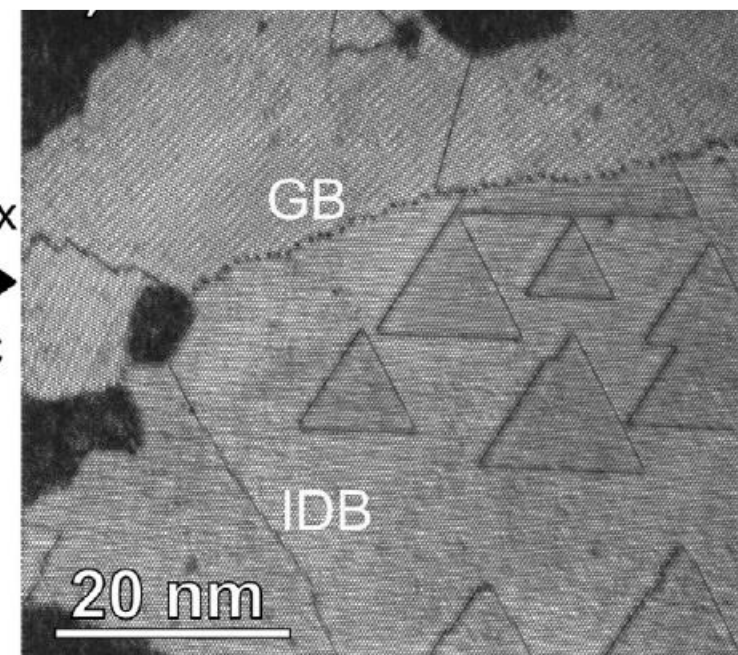
2nd issue: symmetry 3 versus symmetry 6



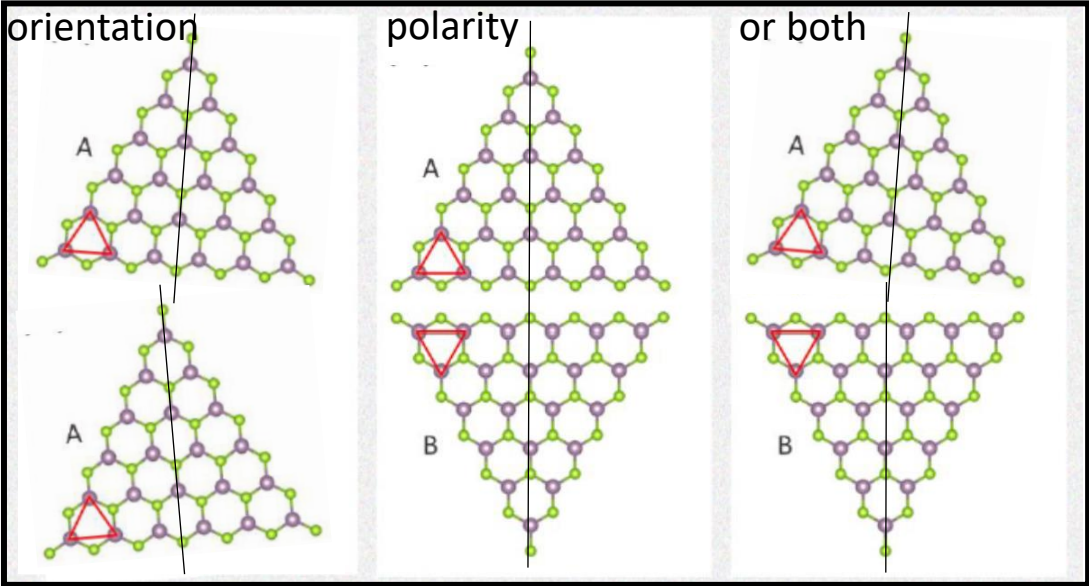
MTBs can form a wagon-wheel regular pattern



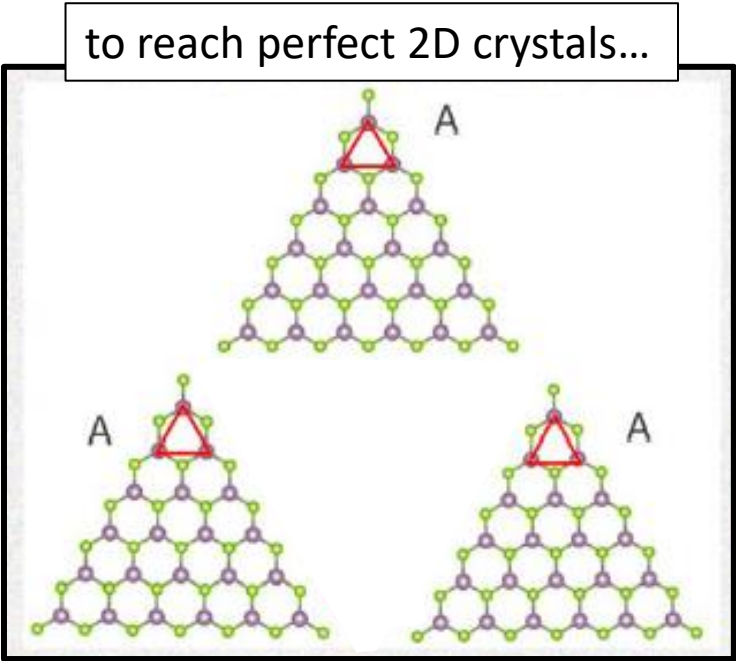
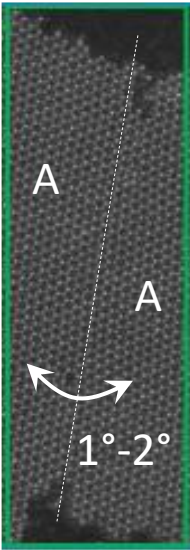
Se Flux
700°C



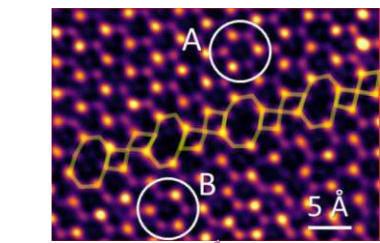
Controlling grain orientation AND polarity



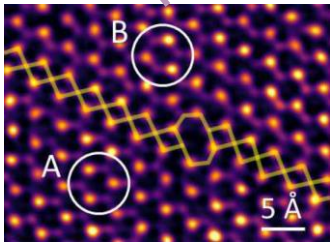
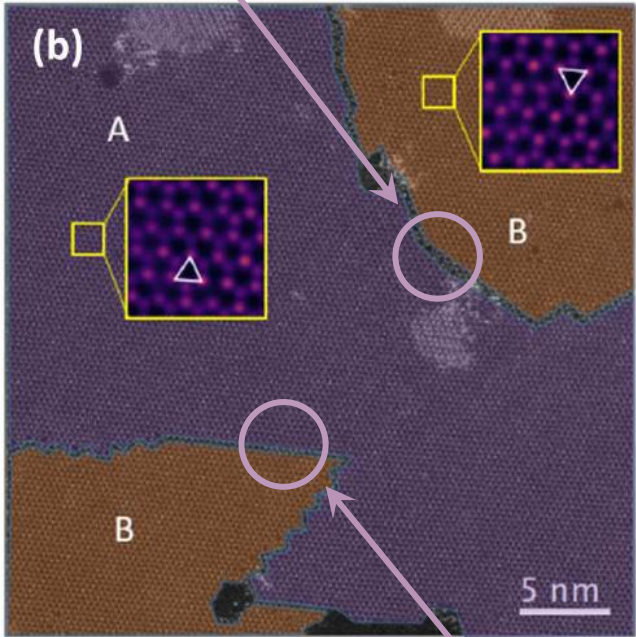
low defective boundary



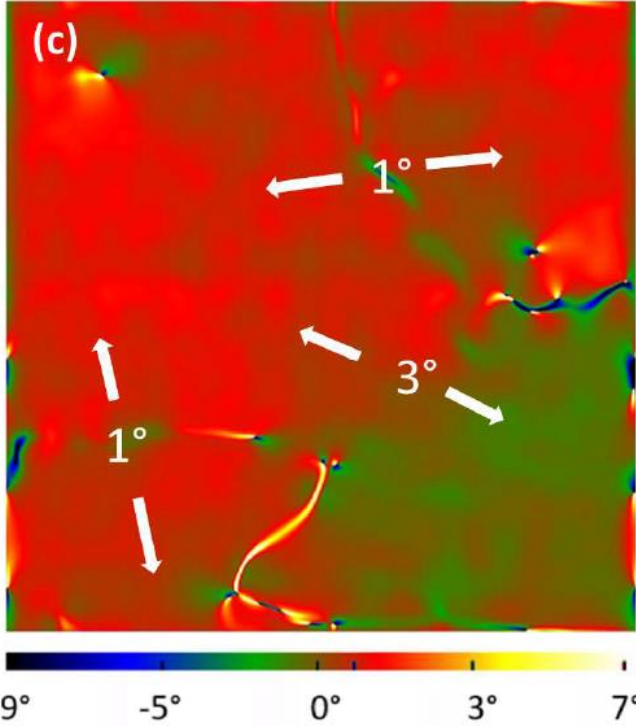
4/4/8 defect between misaligned A & B grains



C. Vergnaud, PhD 2020
D. Dosenovic et al., arXiv:2306.05505



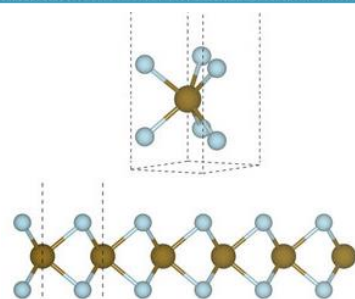
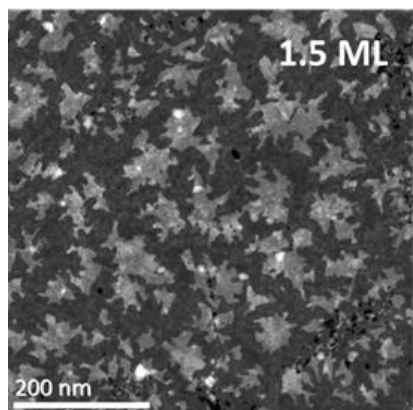
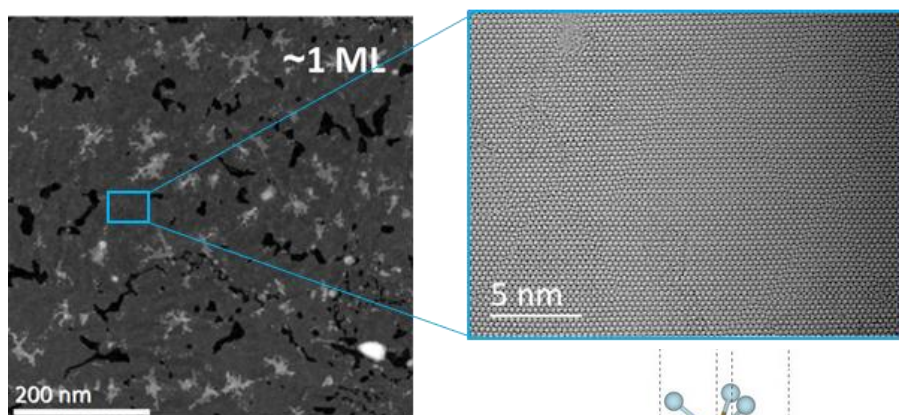
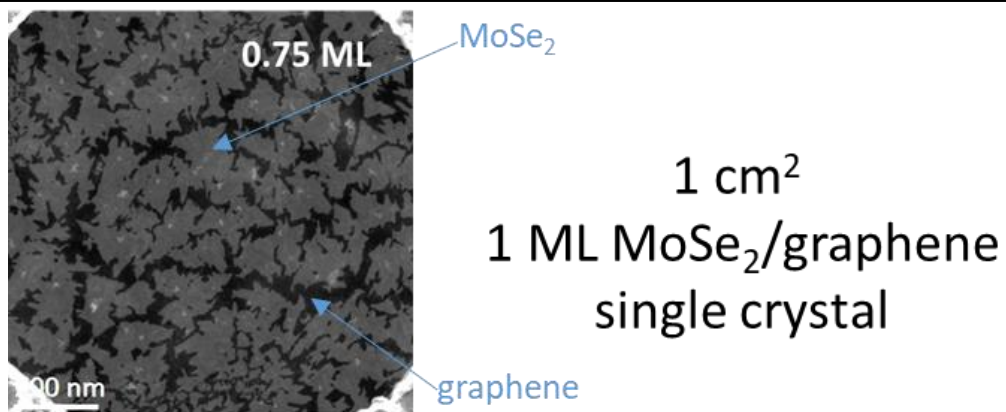
4/4P defect between aligned A & B grains= MTB



OUTLINE

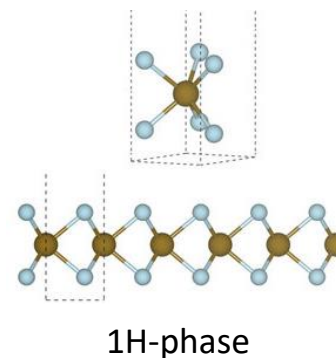
1. Introduction to 2D and van der Waals materials
2. Growth of 2D materials and chalcogenides: from exfoliation to molecular beam epitaxy
- 3. Recent achievements in MBE-grown 2D materials: narrow excitonic lines, doping, alloys, superconductivity, ferroelectricity, ferromagnetism**
4. 2D magnets for spintronics: $\text{Cr}_{1+\delta}\text{Te}_2$, $\text{Fe}_{3-5}\text{GeTe}_2$
5. Conclusion and perspectives

Recent achievements on epitaxial growth of 2D materials

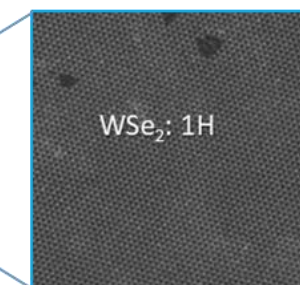
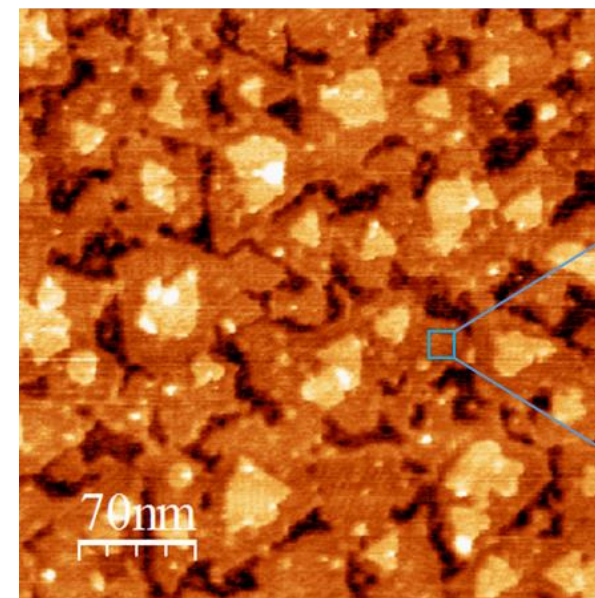


1H-phase
inversion symmetry breaking
spins out-of-plane

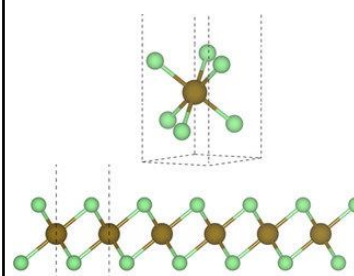
Dau et al., ACS Nano **12**, 2319 (2018)



1 cm²
1 ML WSe_2 /mica
single crystal

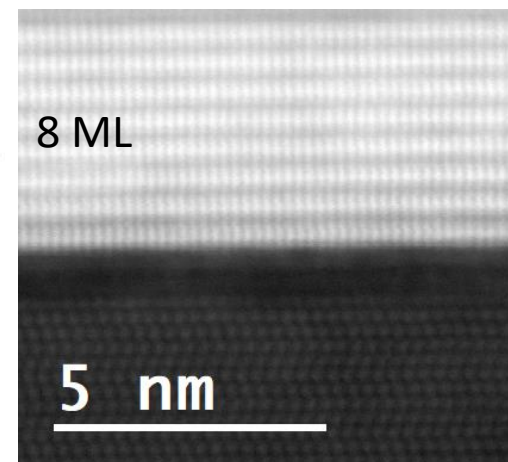


C. Vergnaud, PhD 2020

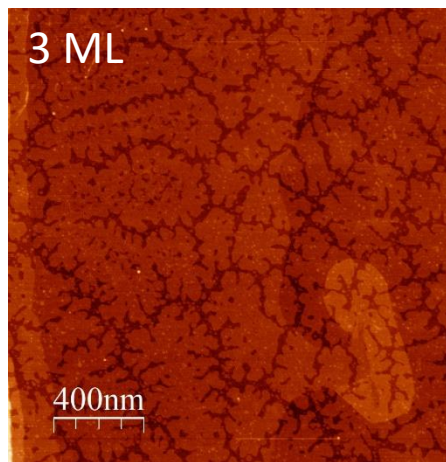


1T-phase
inversion symmetry breaking
Rashba SOC

1 cm², PtSe_2 /graphene



K. Abdukayumov, PhD 2022

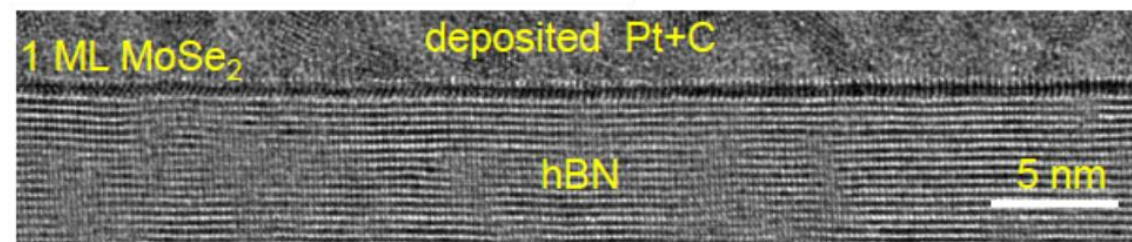
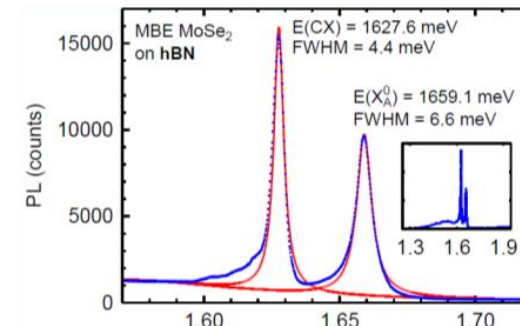


Recent achievements on epitaxial growth of 2D materials

MBE growth of MoSe₂ on exfoliated hBN flakes

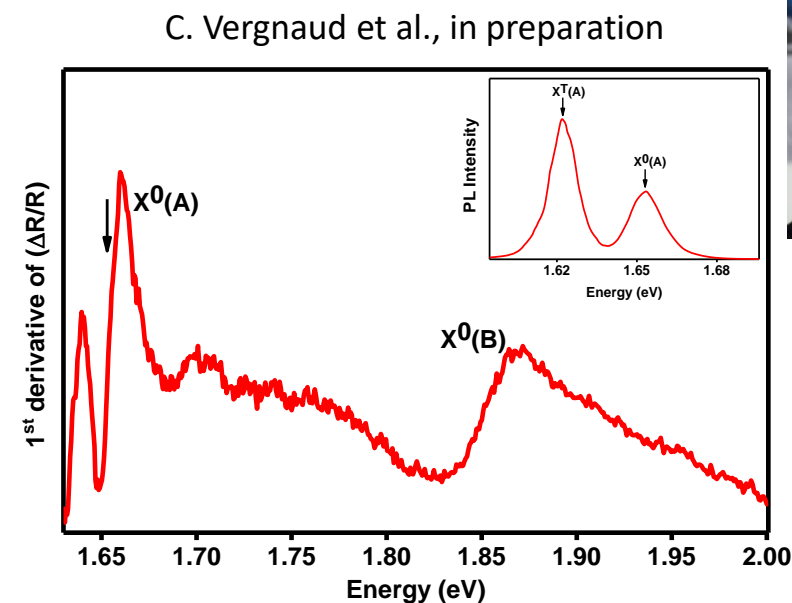
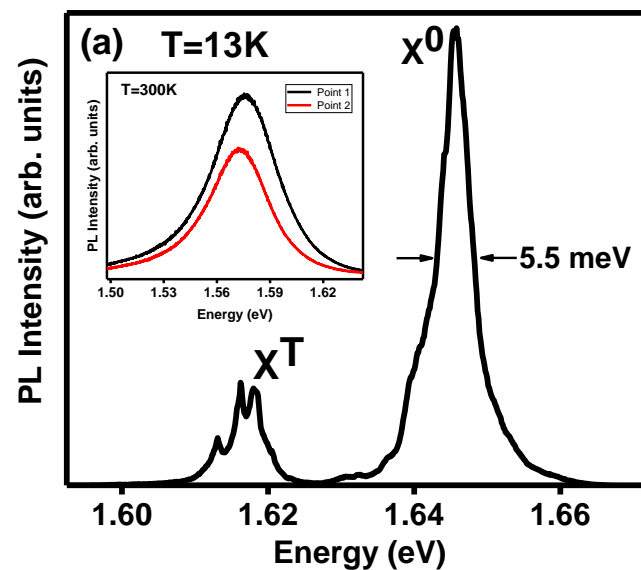
Epitaxial MoSe₂ on hBN

PL linewidth: better than flakes

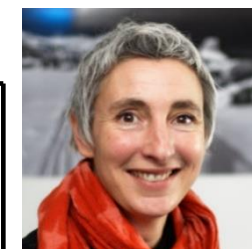


W. Pacuski et al., Nano Lett. 20, 3058 (2020)

@ Spintec in collaboration with LPCNO (Toulouse, X. Marie, C. Robert)



C. Vergnaud et al., in preparation

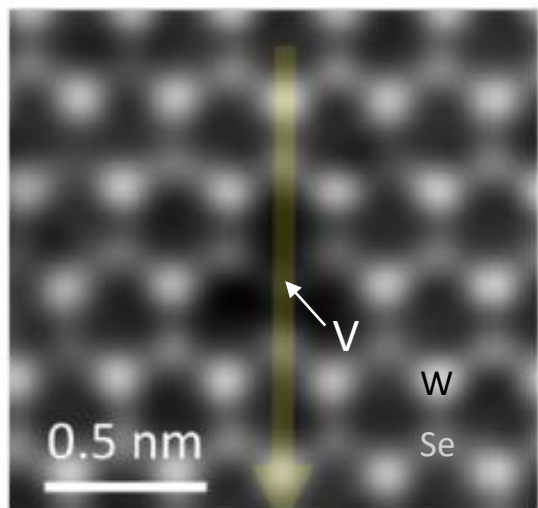


C. Vergnaud

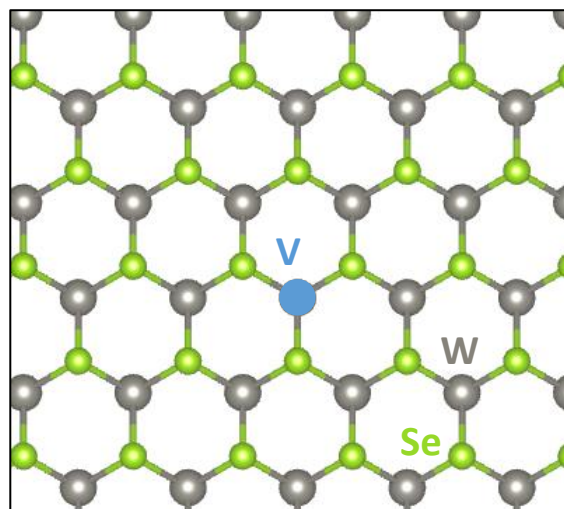
CVD MoS₂: 5 meV at 4 K (S. Shree et al., 2D Mater. 7, 015011 (2020))

Recent achievements on epitaxial growth of 2D materials

p-type doping of WSe_2 with vanadium atoms

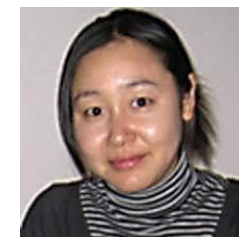
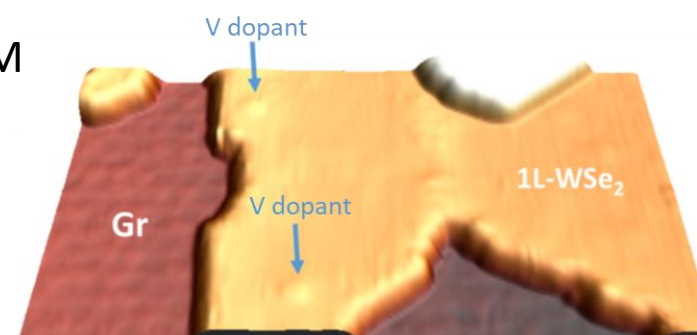


V atoms substitute W atoms

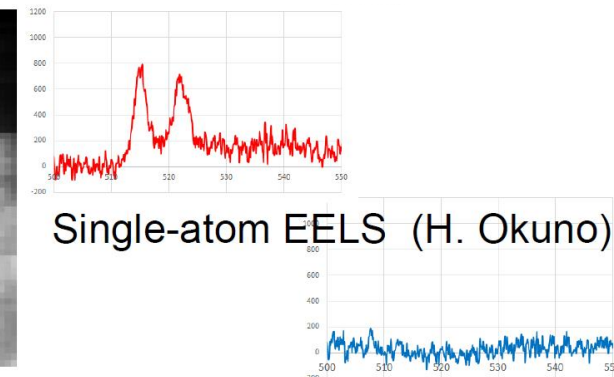
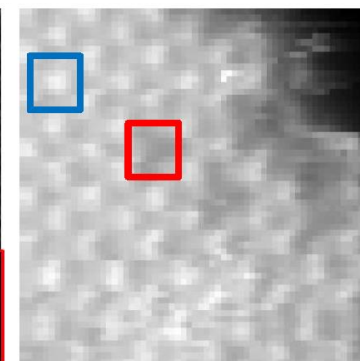
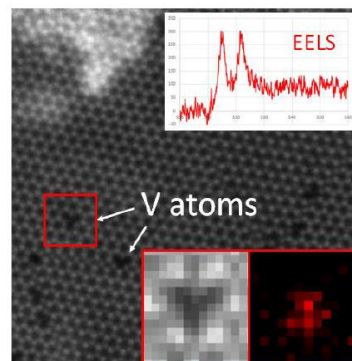


Atomic model

STM



H. Okuno



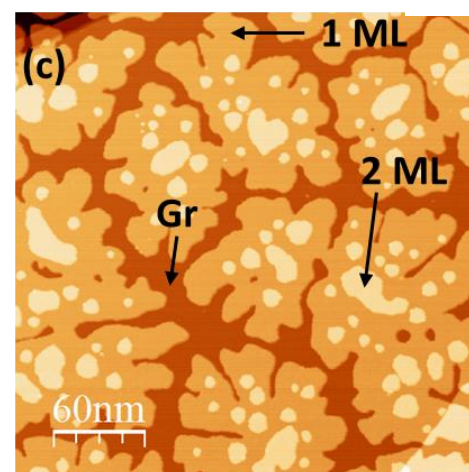
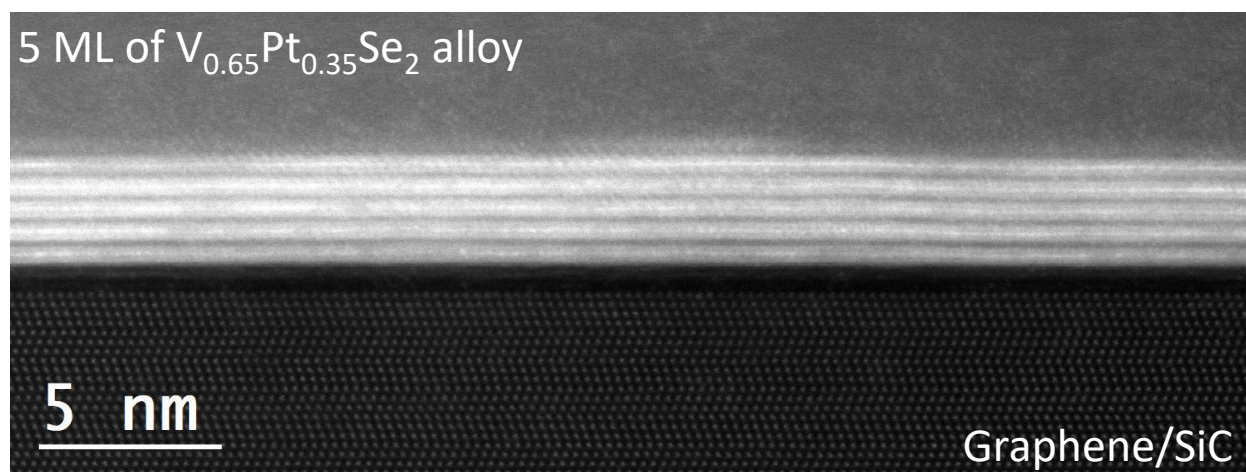
Single-atom EELS (H. Okuno)

P. Mallet et al., Phys. Rev. Lett. **125**, 036802 (2020)

E. Velez et al., ACS Appl. Electron. Mater. **4**, 259 (2022)

E. Velez et al., Phys. Rev. B **106**, 075432 (2022)

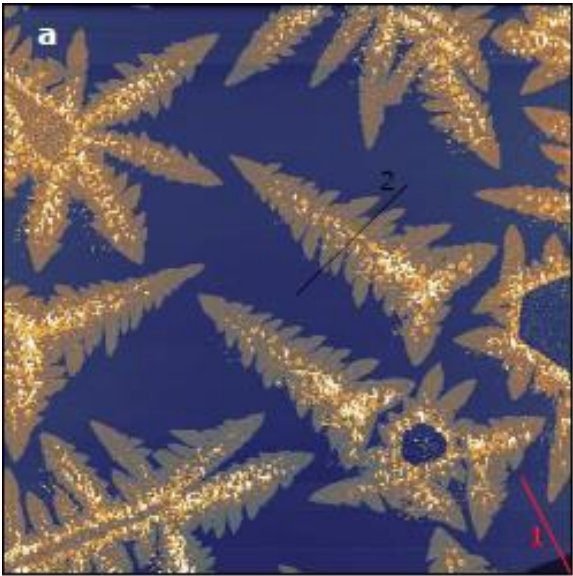
Alloying VSe_2 and PtSe_2



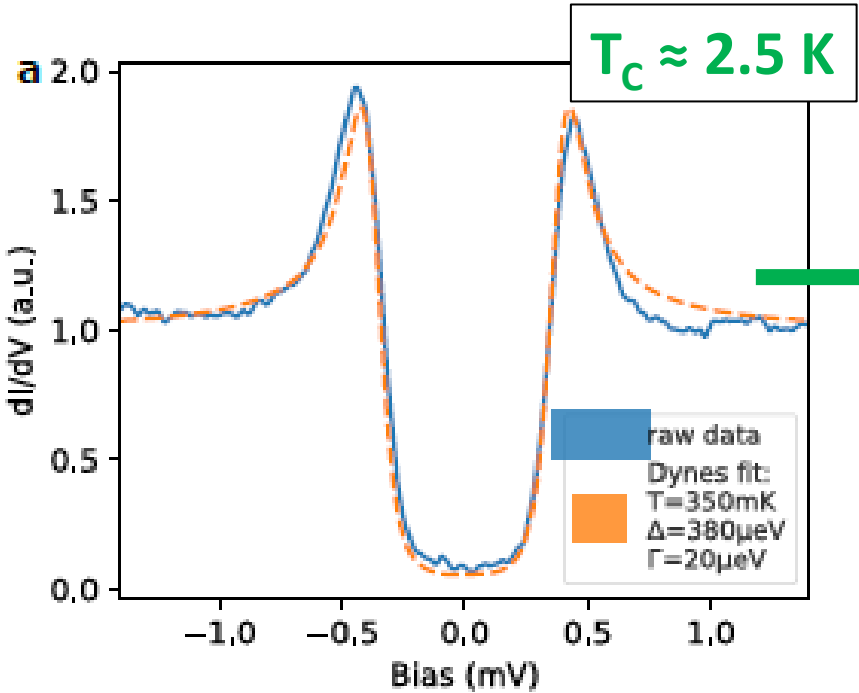
large scale homogeneous alloy

2D superconductivity

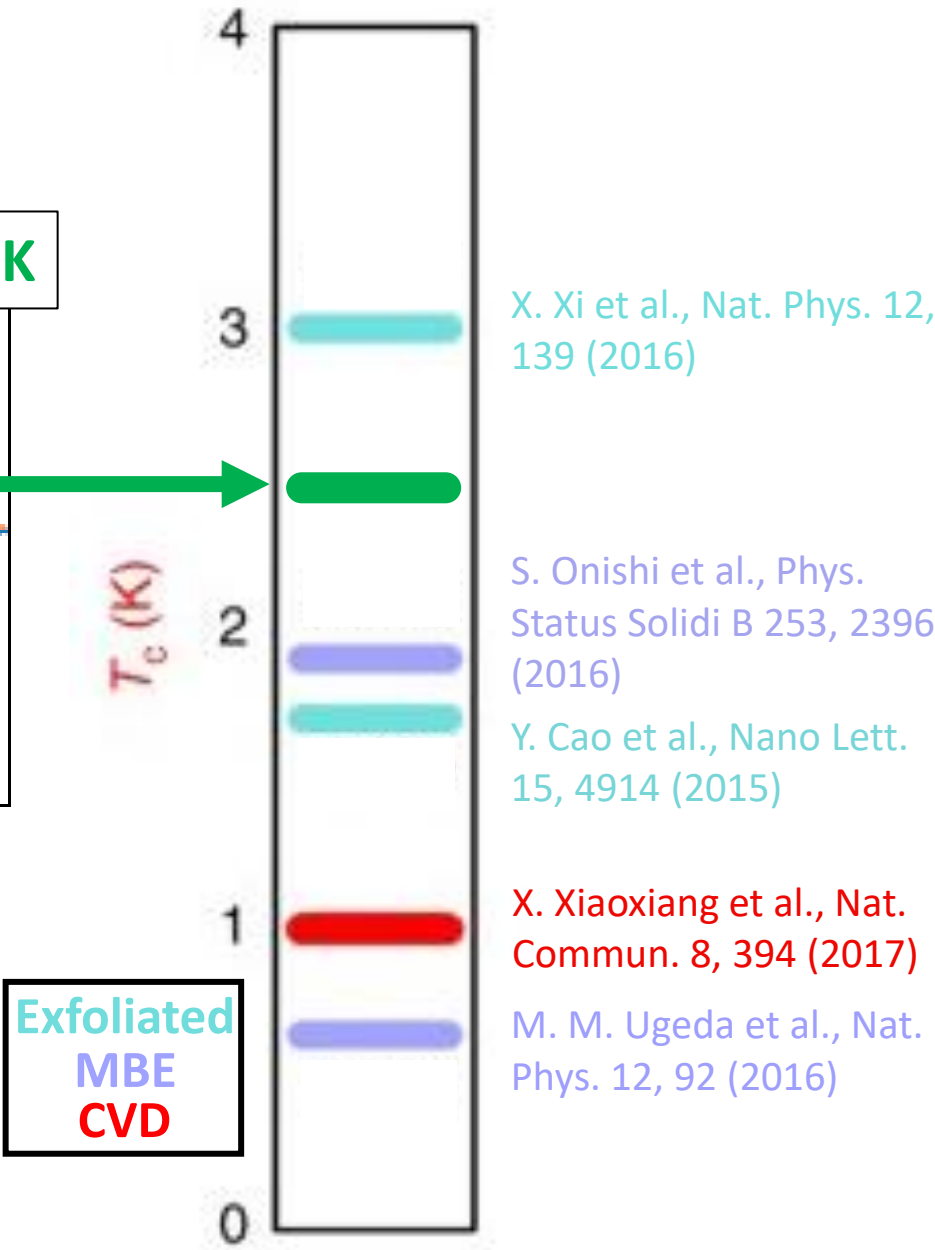
1 ML NbSe₂ / graphene / SiC



STM image, first growth stage



STS on ML flake

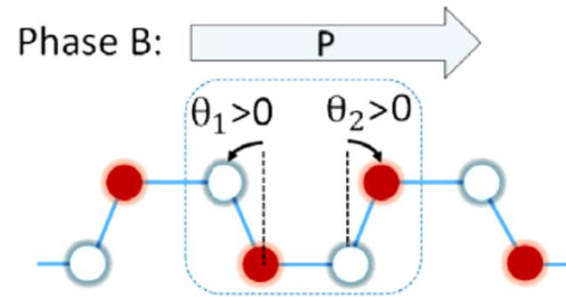


2D ferroelectricity

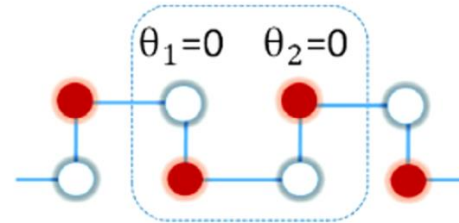
C. Wang et al., Nat. Mater. 22, 542 (2023)

1 monolayer MX

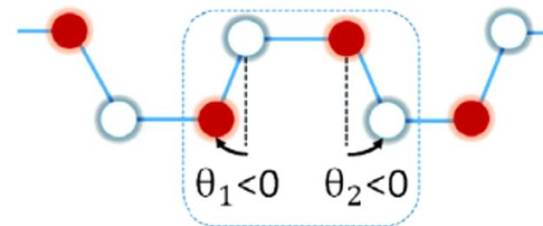
● M: Sn, Ge ○ X: Se, S



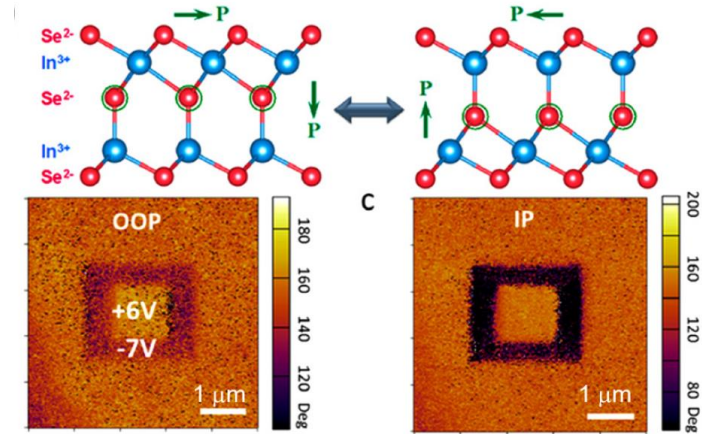
Phase A: $P=0$



Phase B': $\xleftarrow{-P}$

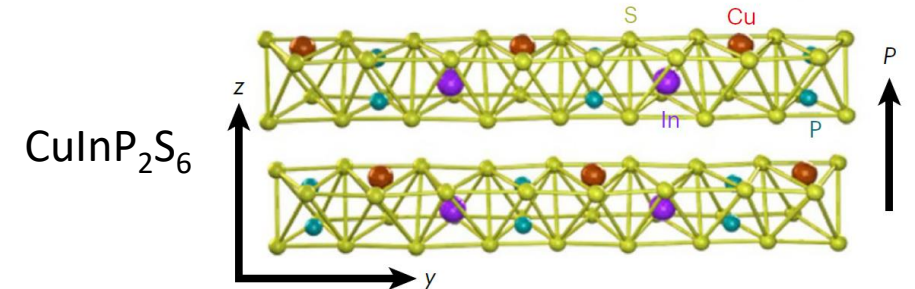


1 monolayer In_2Se_3

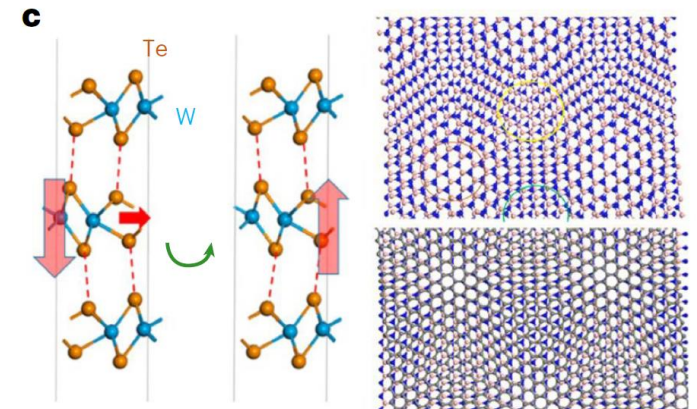


PFM @ RT

multilayers

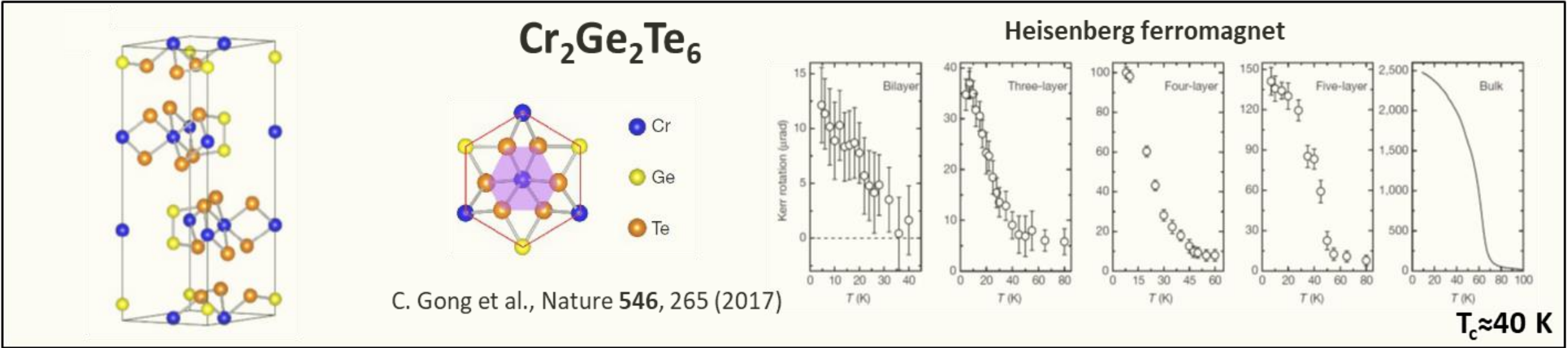
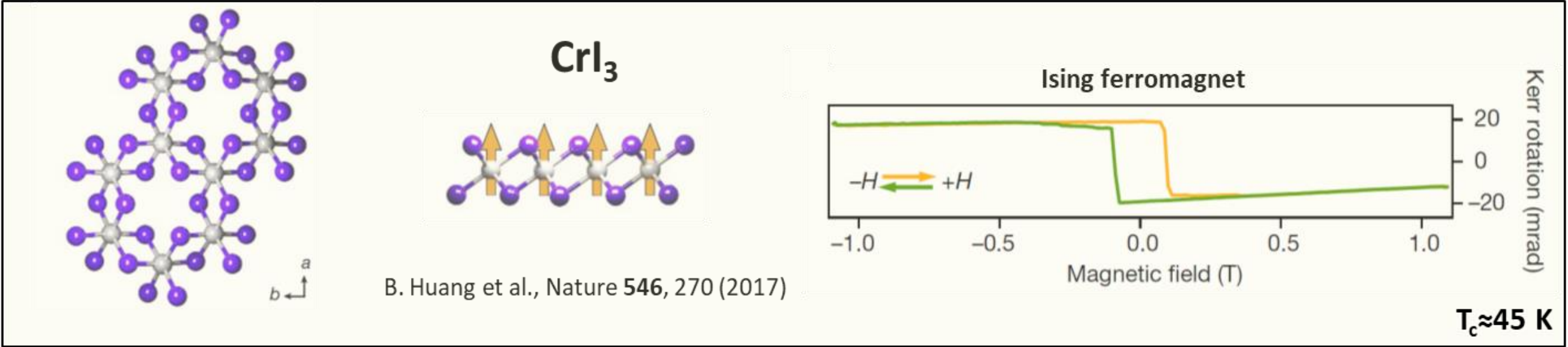


WTe_2



Material (ref.)	Space/ point group	P (μCcm^{-2})	E_c (kVcm^{-1})	T_c (K)	Bandgap (eV)
Experimentally confirmed materials					
CuInP_2S_6 (refs. ^{2,27})	Cc	2.55	77	5ML, >320	Bulk, 2.7
CuCrP_2S_6 (ref. ²²)	Pc	10^{-5}	—	Bulk, 32	—
SnTe (refs. ^{8,15})	$Pnm2_1$	1ML, 22^T	—	1ML, 270; bulk, 100	1ML, 1.6; bulk: 0.3
SnSe (ref. ¹⁵)	$Pnm2_1$	—	1ML, 140	1ML, >380	1ML, 2.1; bulk: 0.9
SnS (ref. ¹⁵)	$Pnm2_1$	—	9ML, 25; bulk, 10.7	1ML, >300	1ML, 1.6; bulk: 1.2
GeTe (ref. ¹⁹)	$R3m$	1ML, 32.8	-0.2Vnm^{-1}	1ML, 570 ^T	Bulk, 0.6
$\alpha\text{-In}_2\text{Se}_3$ (refs. ^{9,10})	$R3m$	Bulk, 11.34 ^T ; 1ML, 2.14 ^T	5nm: 200	4ML, 700	1ML, 2.8; bulk, 1.45
$d1\text{T-MoTe}_2$ (refs. ^{14,28})	$d\text{-}P\bar{3}m$	—	—	1ML, 330	2–3ML, 0; bulk, 0
$\text{T}_d\text{-WTe}_2$ (refs. ^{12,13})	$Pnm2_1$	0.2pCm^{-1}	0.05Vnm^{-1}	2–3ML, 350	2–3ML, 0; bulk, 0
WSe_2 , MoSe_2 , WS_2 , MoS_2 (refs. ^{20,21})	—	-2.0pCm^{-1}	-0.2Vnm^{-1}	2ML, >300	—
Heterobilayer MoS_2/WS_2 (ref. ³²)	$3m$	1.45pCm^{-1}	2.4Vnm^{-1}	2ML, >300	2ML, 0
Twisted bilayer h-BN (refs. ^{17,18})	—	-1.88pCm^{-1}	-0.1Vnm^{-1}	2ML, >300	Bulk, >5
Twisted bilayer graphene/h-BN (ref. ¹⁶)	—	-0.09	-0.2Vnm^{-1}	2ML, >300	—
BA_2PbCl_4 (ref. ¹¹)	$Cmc2_1$	13	50nm, 350	2ML, >300	Bulk, 3.65
NiI_2 (refs. ^{23,24})	$d\text{-}R\bar{3}m$	0.0125	—	Bulk, 59.5; 1ML, 21	Bulk, 1.2

2D ferromagnetism



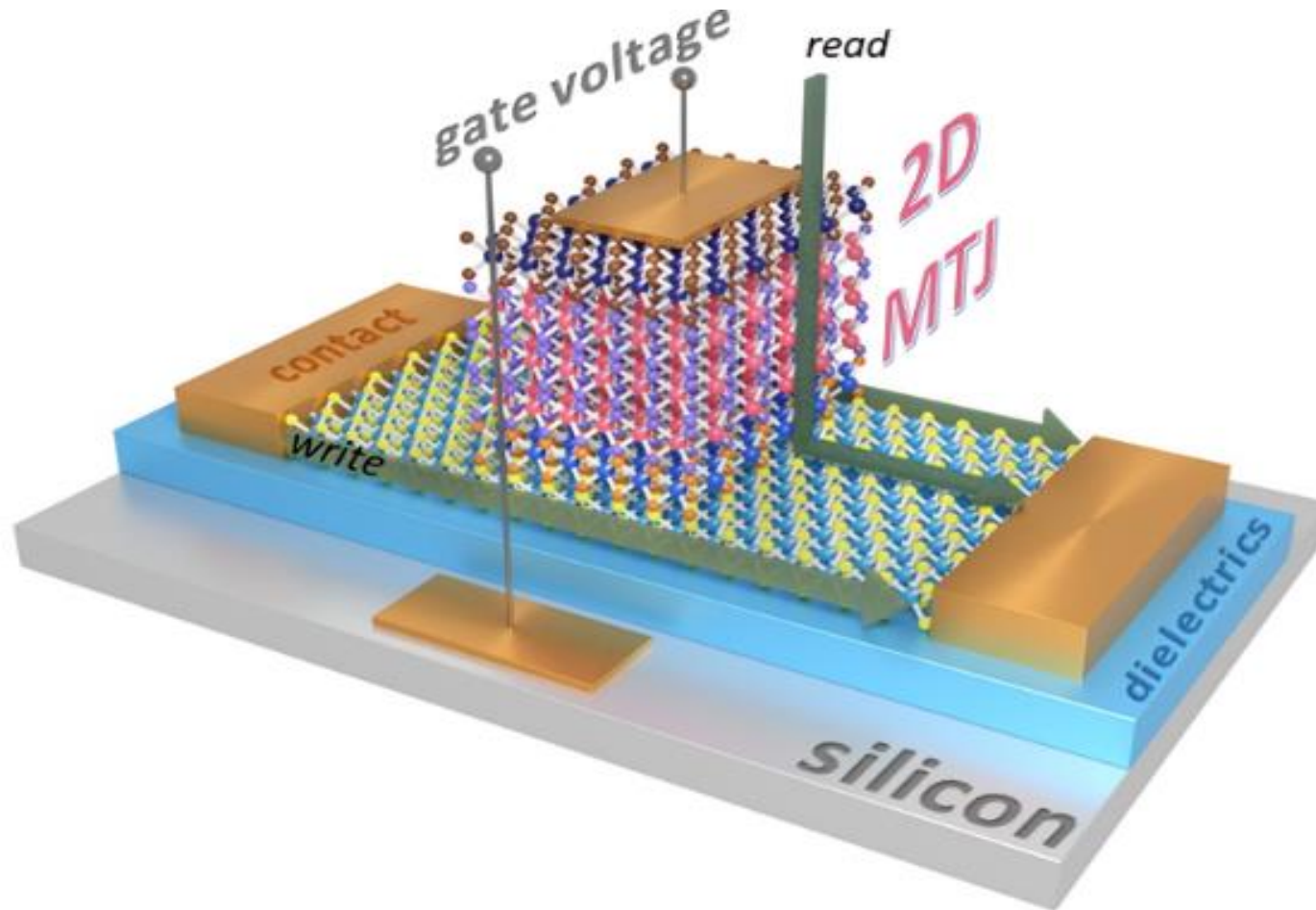
and more recently: Fe₃₋₅GeTe₂, Cr_{1+δ}Te₂ with T_c close to RT

May et al., *ACS Nano*. **13**,4436 (2019)
X. Zhang et al. *Nature Comm.***12**, 2492 (2021)

OUTLINE

1. Introduction to 2D and van der Waals materials
2. Growth of 2D materials and chalcogenides: from exfoliation to molecular beam epitaxy
3. Recent achievements in MBE-grown 2D materials: narrow excitonic lines, doping, alloys, superconductivity, ferroelectricity, ferromagnetism
- 4. 2D magnets for spintronics: $\text{Cr}_{1+\delta}\text{Te}_2$, $\text{Fe}_{3-5}\text{GeTe}_2$**
5. Conclusion and perspectives

Building « all 2D » magnetic memory (SOT-MRAM)



- Clean and sharp vdW interfaces
- Electric field manipulation of magnetization
- Perpendicular magnetic anisotropy
- Low symmetries for spin-orbit torques
- Large magnetoresistances

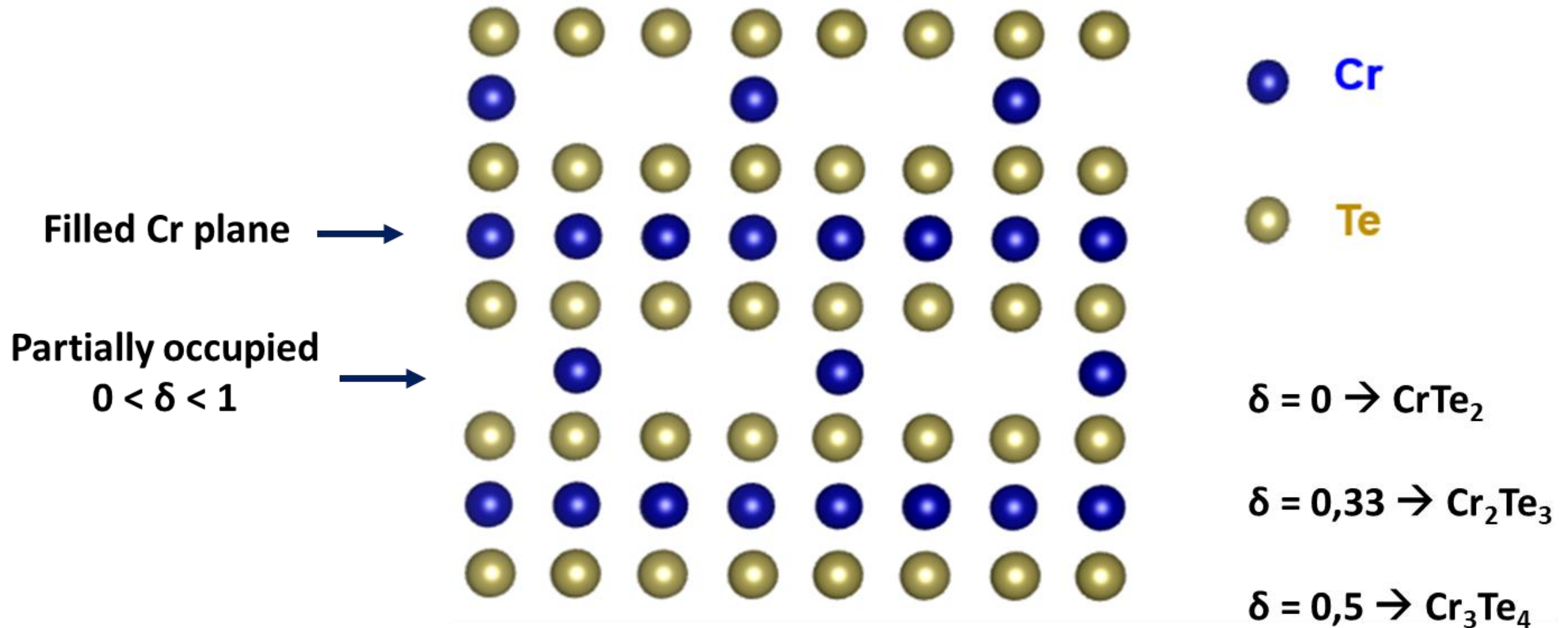
Crystal structure of $\text{Cr}_{1+\delta}\text{Te}_2$



PhD Quentin Guillet

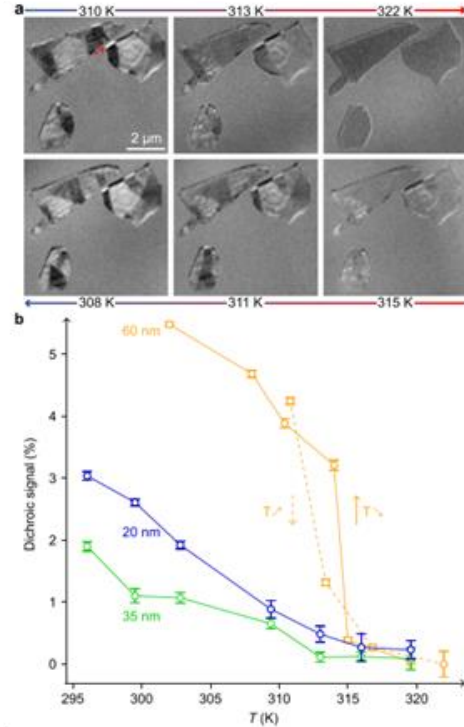


Hervé Boukari



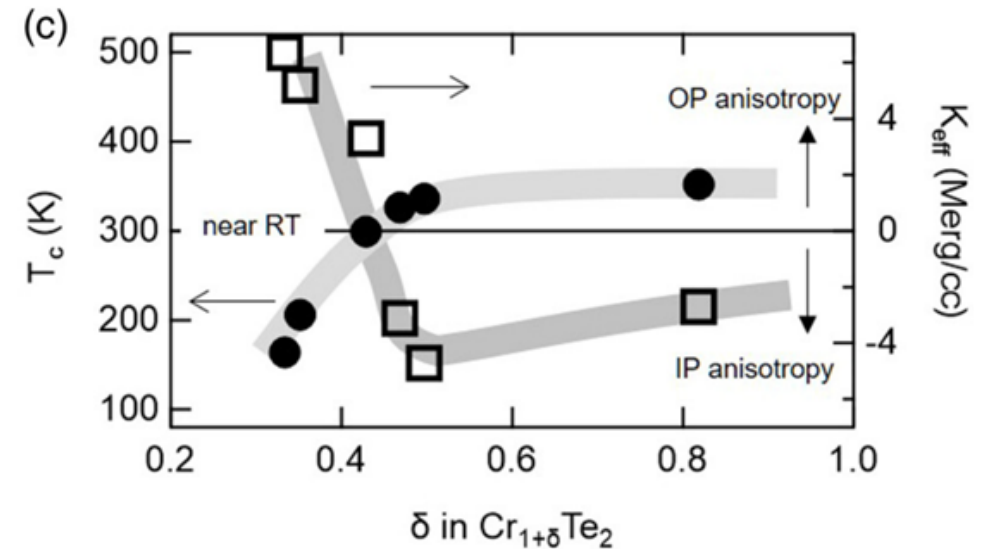
Motivations for the study of $\text{Cr}_{1+\delta}\text{Te}_2$

In-Plane Magnetic Domains and Néel-like Domain Walls in Thin Flakes of the Room Temperature CrTe_2 Van der Waals Ferromagnet



A. Purbawati et al. *ACS Appl. Mater. Interfaces* **12** (2020)

Tailoring magnetism by self-intercalation in $\text{Cr}_{1+\delta}\text{Te}_2$

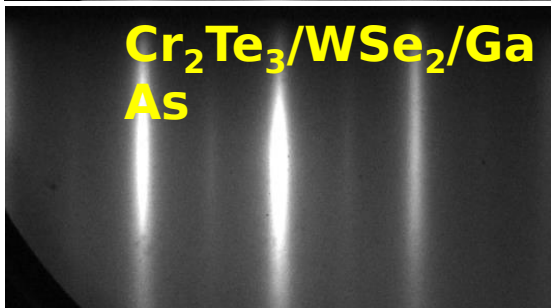
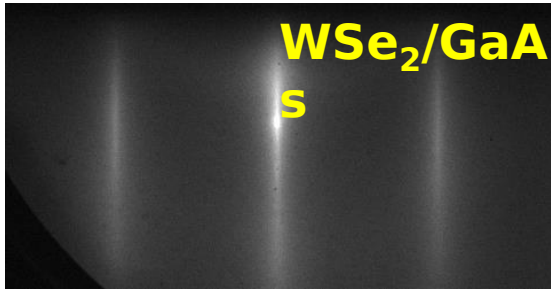


Y. Fujisawa et al. *Physical Review Materials* **4** (2020)

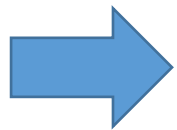
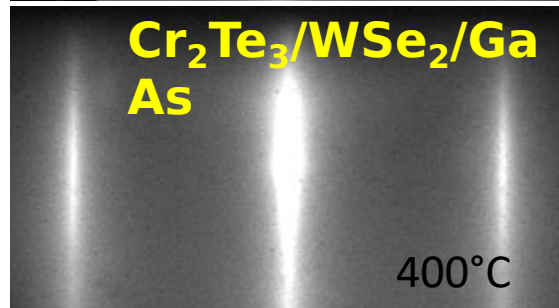
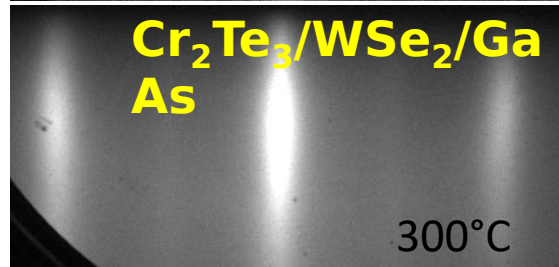
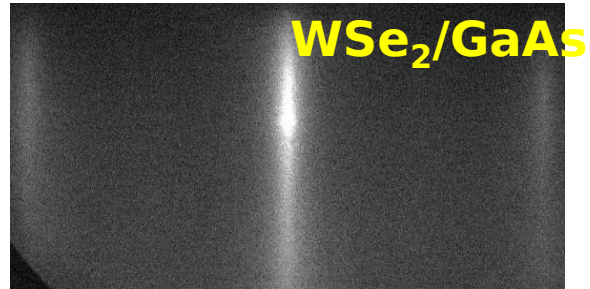
$\text{Cr}_{1+\delta}\text{Te}_2$ van der Waals ferromagnet

RHEED patterns

[100]



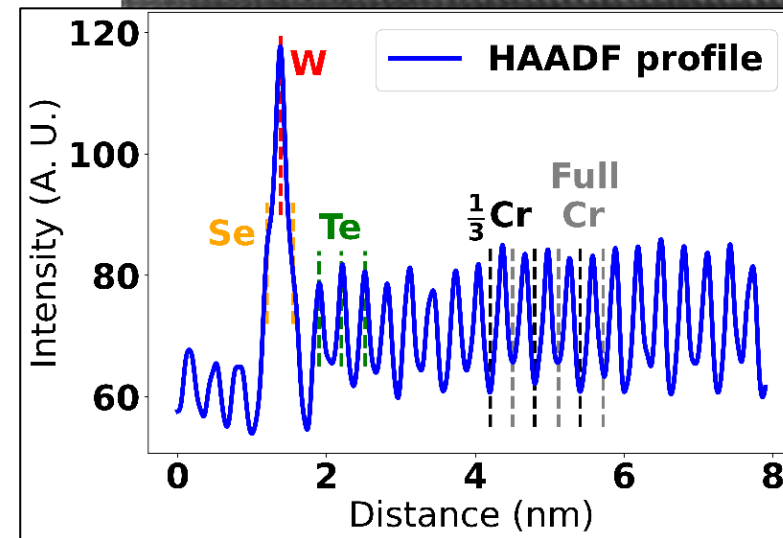
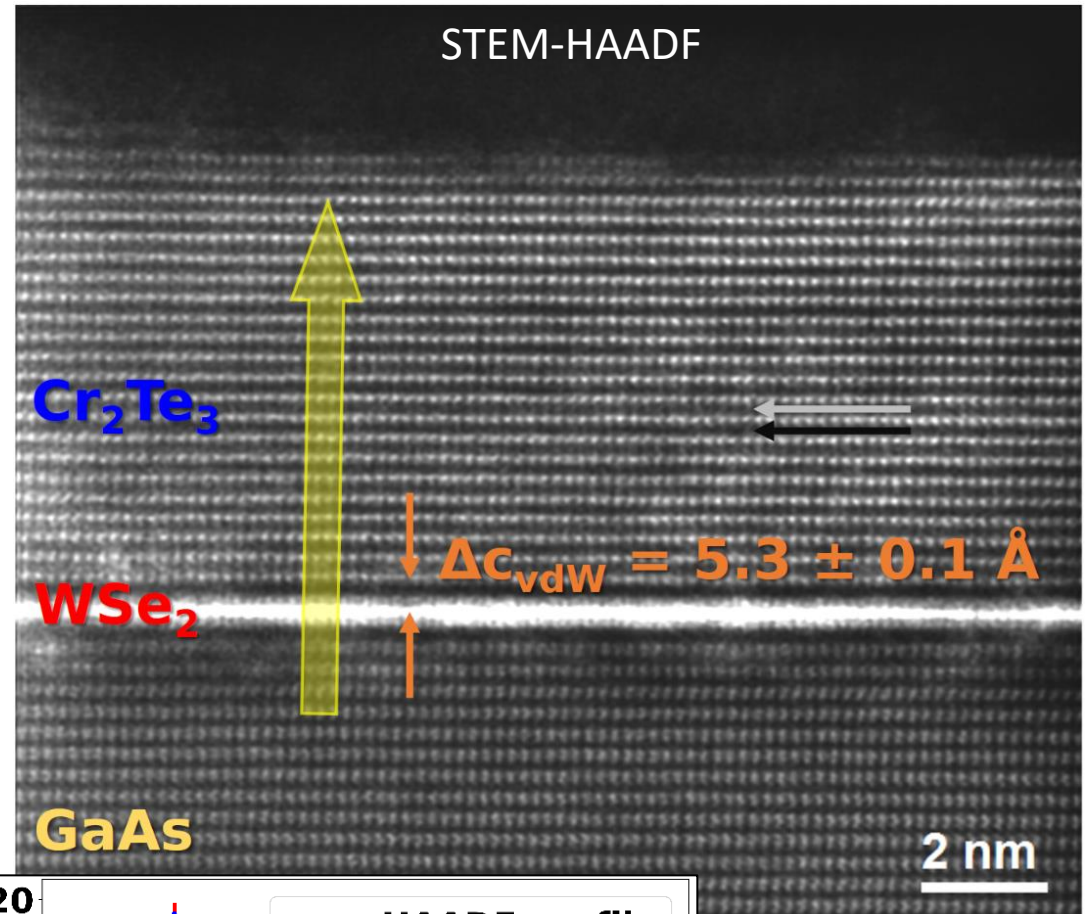
[110]



Same growth on **graphene** and **Bi₂Te₃**

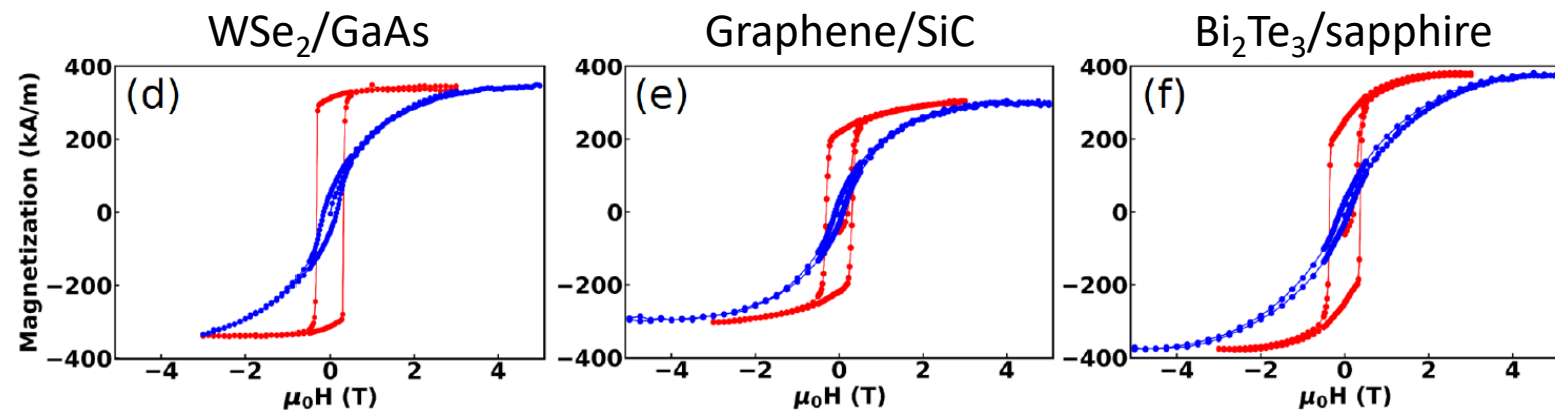
Q. Guillet et al., Phys. Rev. Mater. 7, 054005 (2023)

STEM-HAADF

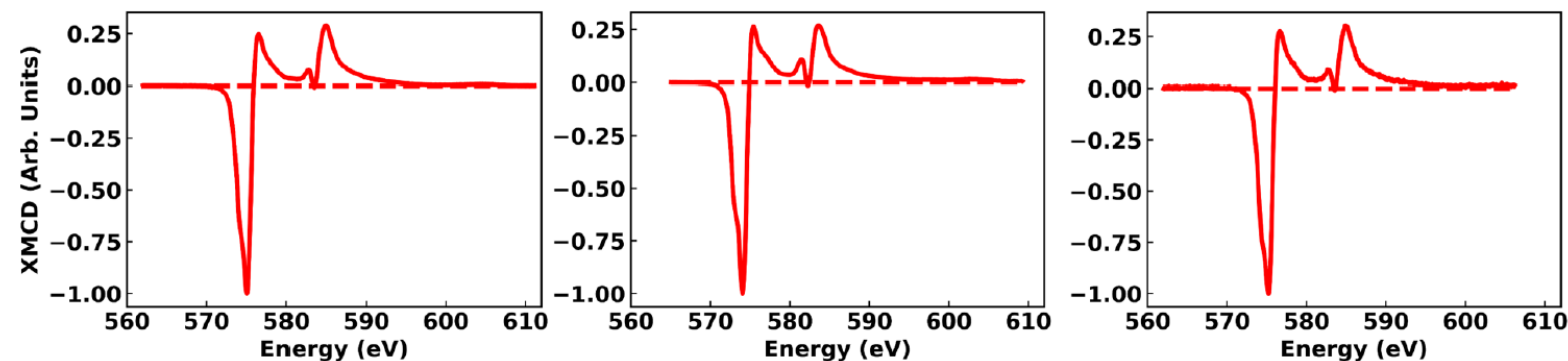


Cr_{1+δ}Te₂ van der Waals ferromagnet

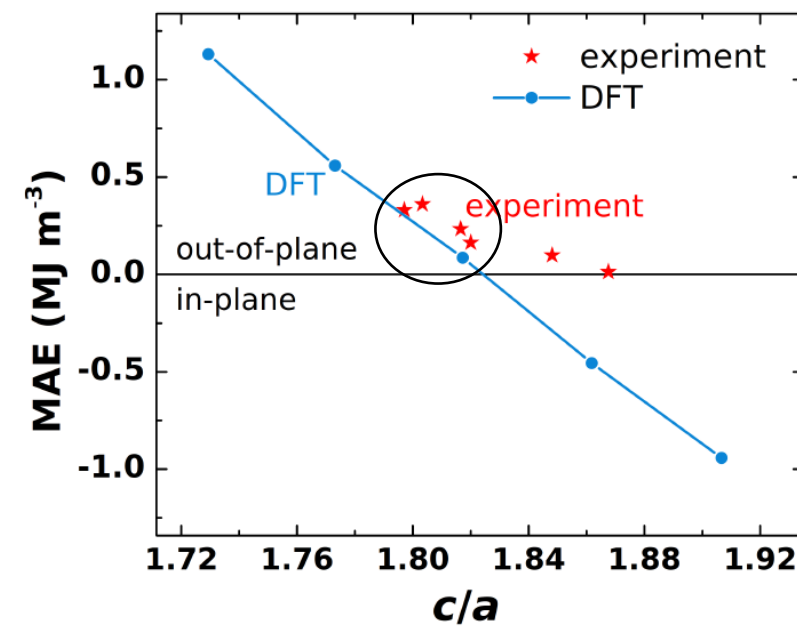
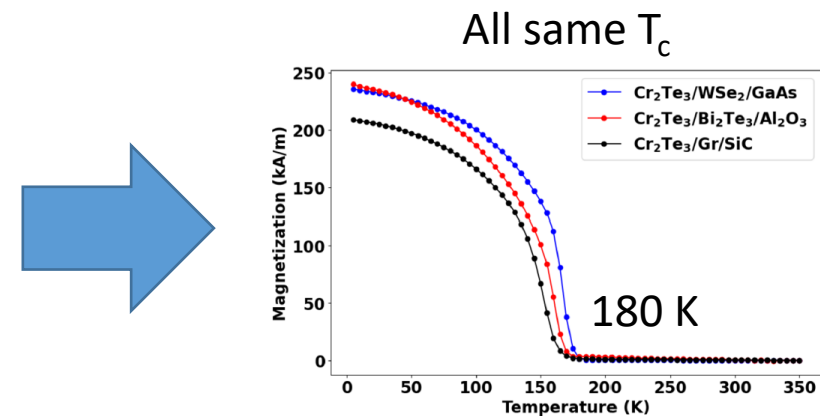
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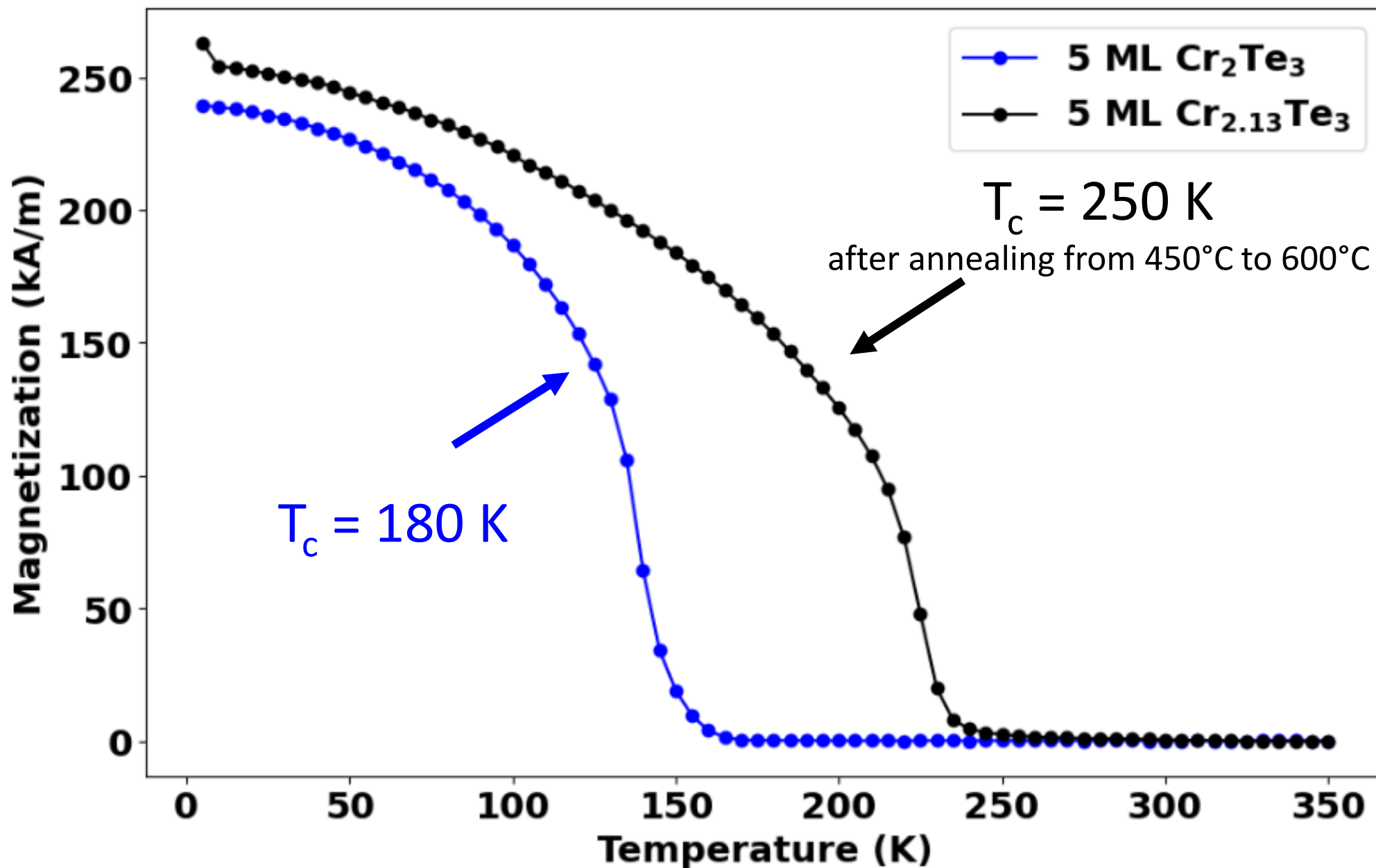


XMCD



(coll. SOLEIL/DEIMOS, P. Ohresser, F. Choueikani)





Fe₃₋₅GeTe₂ van der Waals ferromagnet

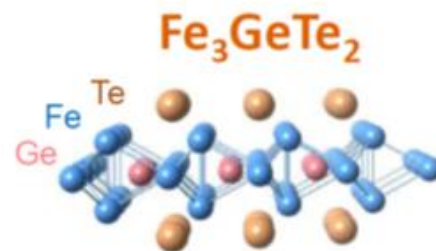
LETTERS

<https://doi.org/10.1038/s41563-018-0149-7>

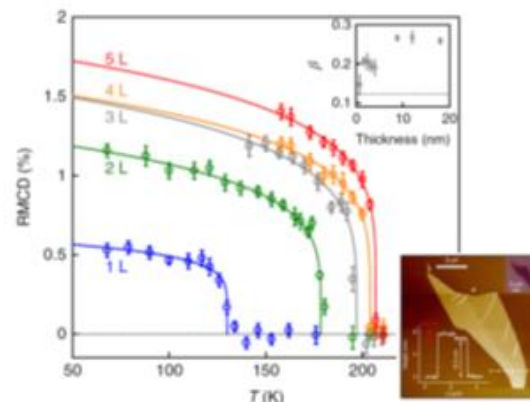
nature
materials

Two-dimensional itinerant ferromagnetism in atomically thin Fe₃GeTe₂

Zaiyao Fei^{1,8}, Bevin Huang^{1,8}, Paul Malinowski¹, Wenbo Wang², Tiancheng Song¹, Joshua Sanchez¹, Wang Yao², Di Xiao⁴, Xiaoyang Zhu⁵, Andrew F. May⁶, Weida Wu², David H. Cobden¹, Jiun-Haw Chu^{1*} and Xiaodong Xu^{1,7*}



Fei et al.
Nature Mater. 17, 778 (2018)

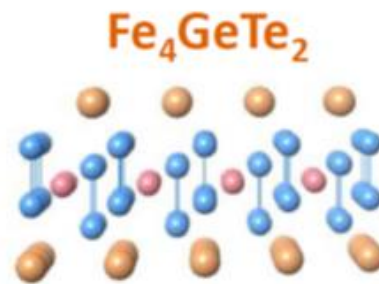


T_c ~ 230K
Strong PMA
Bulk/flakes/MBE

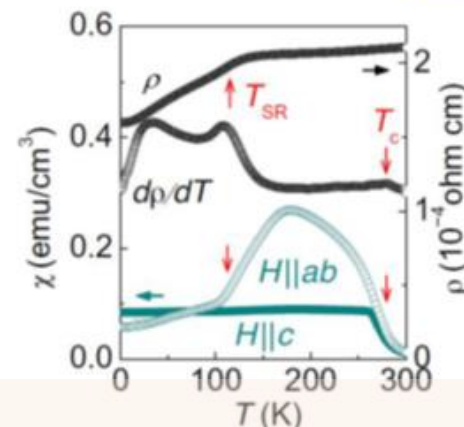
SCIENCE ADVANCES | RESEARCH ARTICLE

Nearly room temperature ferromagnetism in a magnetic metal-rich van der Waals metal

Junho Seo^{1,2*}, Duck Young Kim^{3*}, Eun Su An^{1,2*}, Kyoo Kim⁴, Gi-Yeop Kim⁵, Soo-Yoon Hwang⁵, Dong Wook Kim⁶, Bo Gyu Jang⁶, Heejung Kim⁴, Gyeongsik Eom⁷, Seung Young Seo^{1,5}, Roland Stania¹, Matthias Muntwiler⁸, Jinwon Lee^{1,2}, Kenji Watanabe⁹, Takashi Taniguchi⁹, Youn Jung Jo¹⁰, Jieun Lee⁷, Byung Il Min², Moon Ho Jo^{1,5}, Han Woong Yeom^{1,2}, Si-Young Choi^{5†}, Ji Hoon Shim^{6†}, Jun Sung Kim^{1,2†}



Seo et al.
Sci. Adv. 6, eaay8912 (2020)



T_c ~ 270K
Weak PMA
Bulk/flakes only

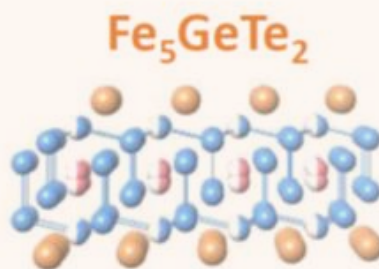
ACS NANO

Cite This: ACS Nano 2019, 13, 4436–4442

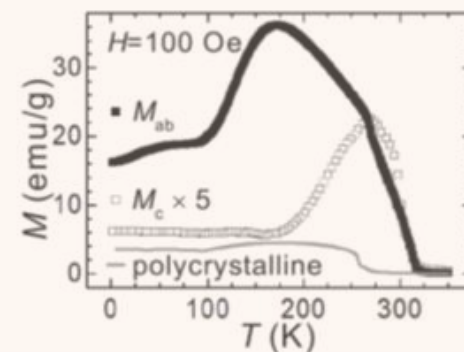
www.acsnano.org

Ferromagnetism Near Room Temperature in the Cleavable van der Waals Crystal Fe₅GeTe₂

Andrew F. May^{1,2}, Dmitry Ovchinnikov¹, Qiang Zheng¹, Raphael Hermann¹, Stuart Calder¹, Bevin Huang¹, Zaiyao Fei¹, Yaohua Liu¹, Xiaodong Xu^{1,3} and Michael A. McGuire¹



May et al.
ACS Nano. 13, 4436 (2019)



T_c ~ 300K
Small/no PMA
Bulk/flakes only

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

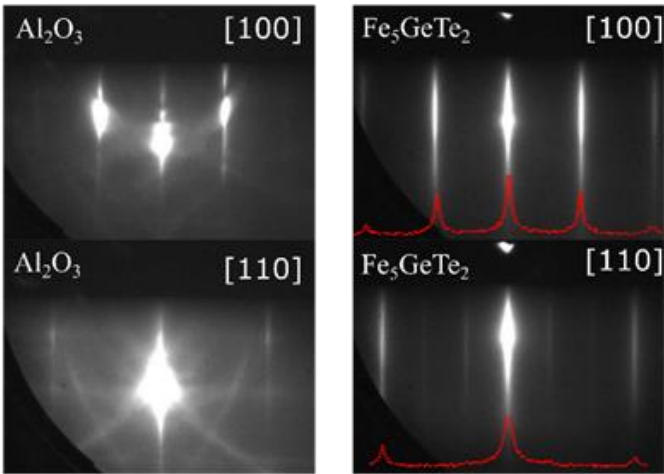
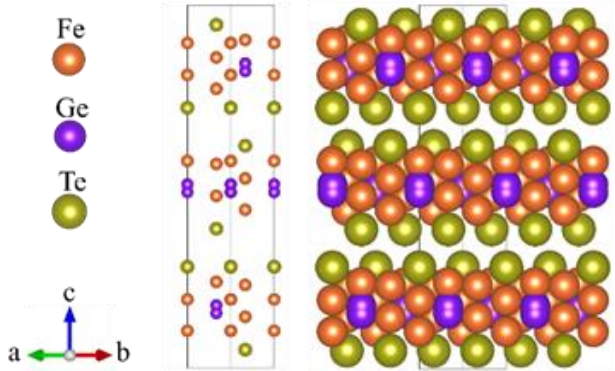
²Department of Physics, University of Washington, Seattle, Washington 98195, United States

³Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

⁴Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195, United States

$\text{Fe}_{3.5}\text{GeTe}_2$ van der Waals ferromagnet

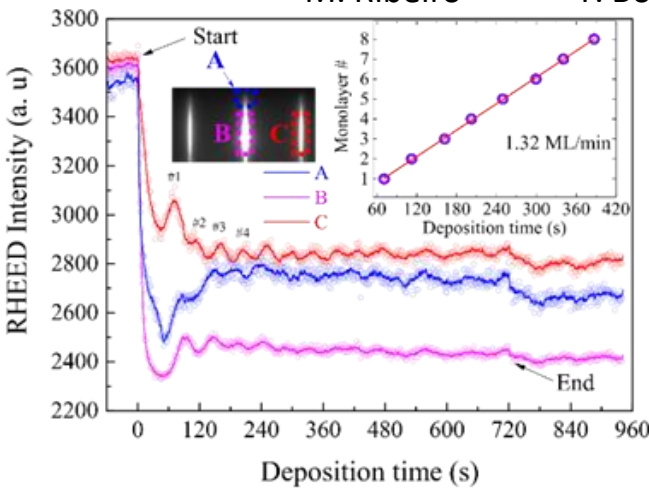
Uniform, high crystallinity (mosaicity $\sim 3^\circ$)



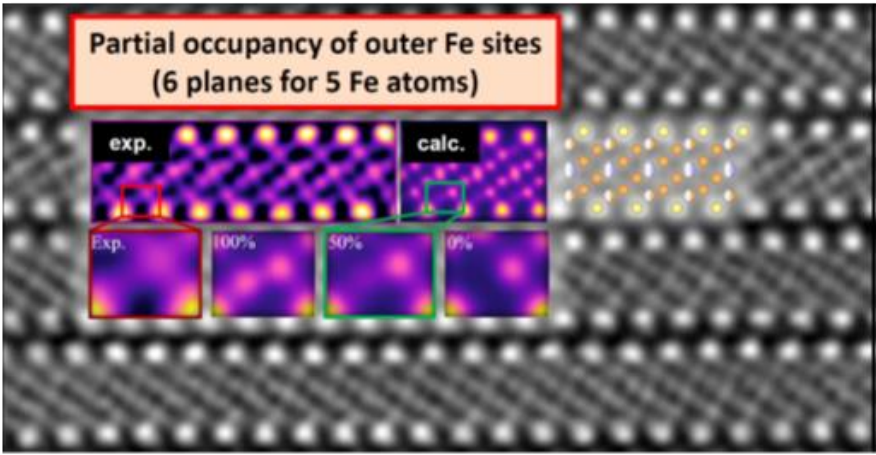
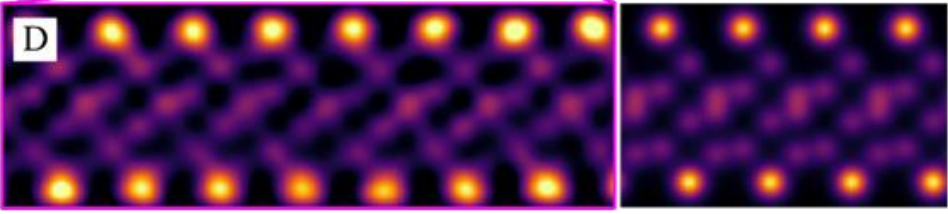
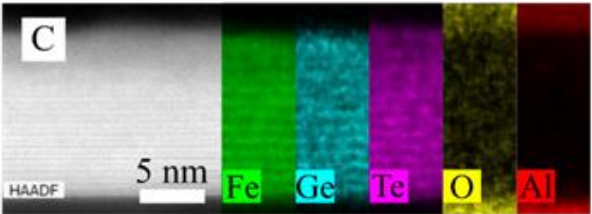
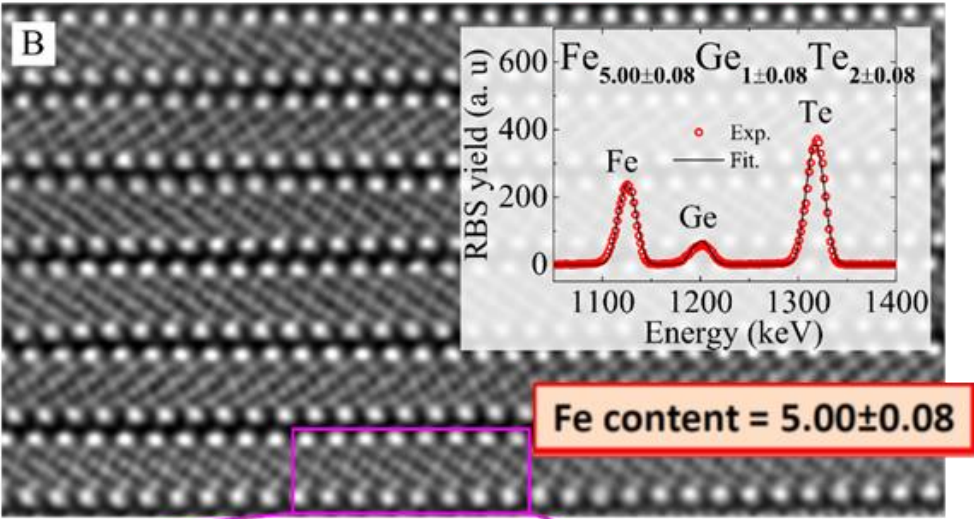
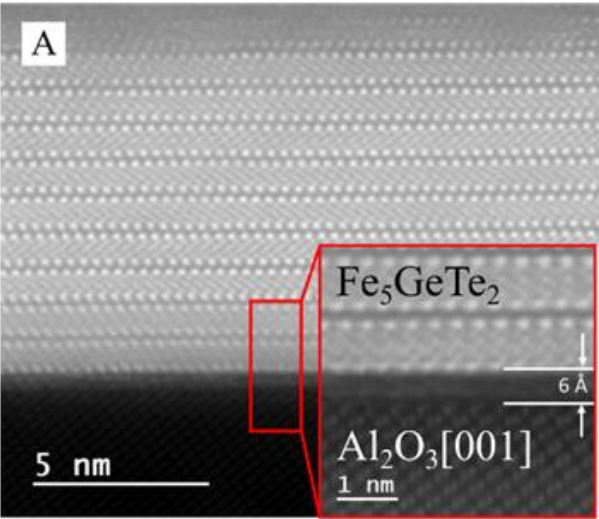
Layer-by-layer growth

M. Ribeiro

F. Bonell



Ribeiro, MJ et al, npj 2D Mater. & Appl. 6, 1 (2022)

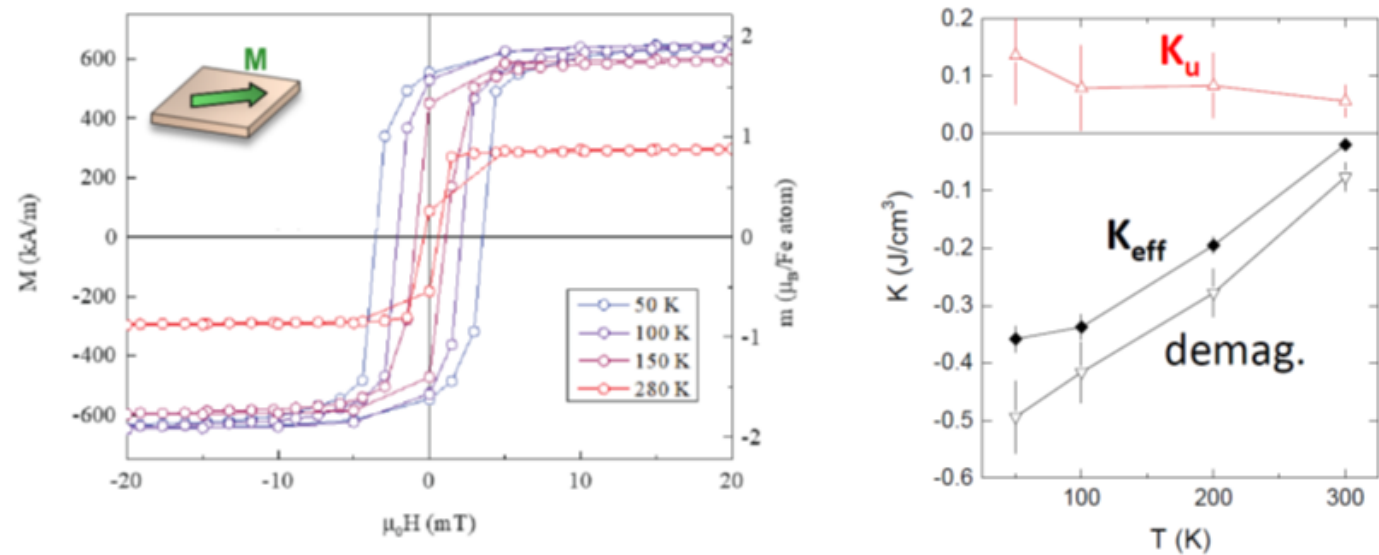


Fe_{3.5}GeTe₂ van der Waals ferromagnet

SQUID

in-plane anisotropy, weak out-of-plane one

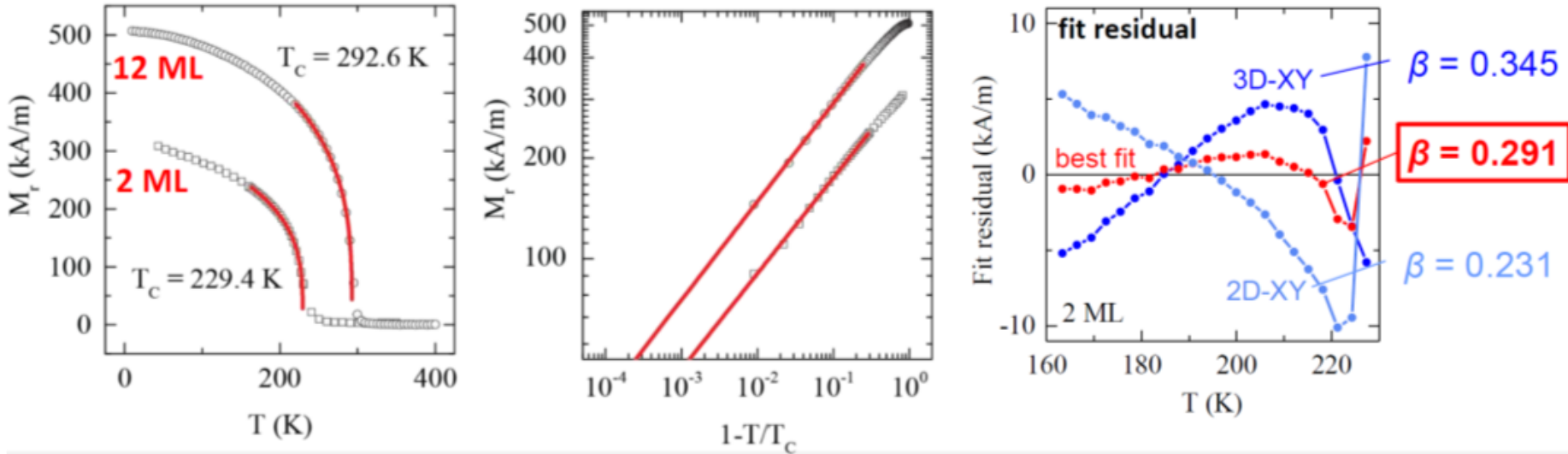
Ribeiro, MJ et al, npj 2D Mater. & Appl. 6, 1 (2022)



Easy-plane FM
Monotonous M(T)
Quasi-3D critical behavior
β thickness-independent
High T_c = 230 K in bilayer

Plot of remanent magnetization

$$M_r \propto \left(\frac{T_c - T}{T_c}\right)^\beta$$



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- 5. Conclusion and perspectives**

Conclusion

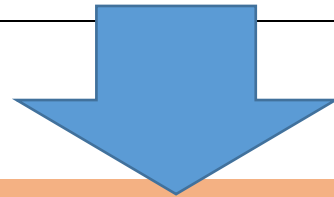
Van der Waals epitaxy by MBE opens new perspectives as compared to flakes:

- Growth of 2D materials on large areas with superior properties
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Conclusion

Van der Waals epitaxy by MBE opens new perspectives as compared to flakes:

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- Growth of 2D ferromagnets in the limit of one monolayer
- Growth of vdW heterostructures with ultraclean interfaces



- Great effort should be dedicated to the development of large scale epitaxial 2D materials
- Selection of the best substrate : hBN (ultraflat, inert, 3-fold symmetry)
- Growth models for vdW epitaxy are missing

Acknowledgements

@ CEA Grenoble



Frédéric Bonell



Isabelle de Moraes



Matthieu Jamet



Alain Marty



Céline Vergnaud



Hasan Abdukayumov
PhD



Quentin Guillet
PhD



Mario Ribeiro
Postdoc



Jules Courtin
Postdoc



Hervé Boukari



Hanako Okuno



Denis Jalabert



Dorde Dosenovic



La Région
Auvergne-Rhône-Alpes

Minatec Labs project



agence nationale
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AU SERVICE DE LA SCIENCE

MAGICVALLEY, ANR-18-CE24-0007
ELMAX, ANR-20-CE24-0015



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IDEX Université Grenoble Alpes

EPI2D project



nanoPOLY



ESR/EquipEx+
2DMAG



2DMAT project

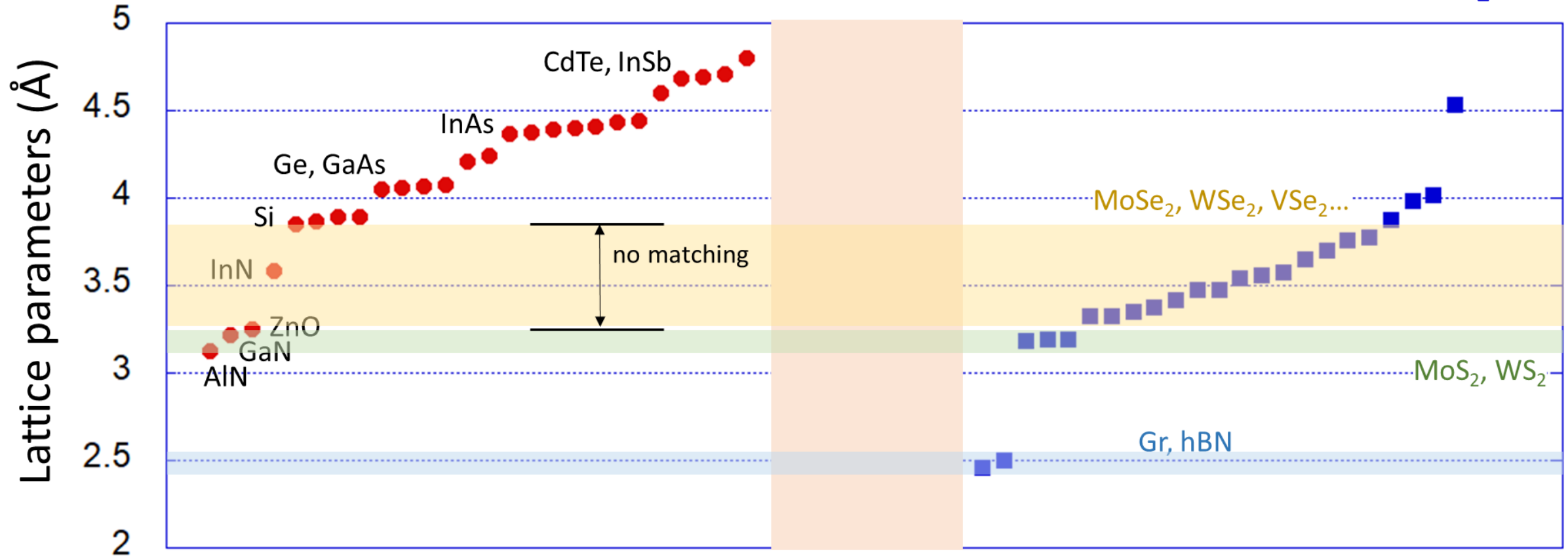
2D materials: hexagonal symmetry & atomically thin



need for hexagonal bulk crystals or (111) facets of cubic bulk crystals with very good lattice matching

Substrates (Si, Ge, GaAs...)

2D Materials (Gr, hBN, MoS₂...)



without considering commensurability, crystal rotations or metallic surfaces:

NO substrate with low lattice mismatch for the epitaxial growth of 2D Materials!