SiNANO-NEREID Workshop:

Equipment and Manufacturing Science

Leuven, September 11th, 2017

WP6

Technologies/concepts covered by the Roadmap

- Difficult to select materials and equipment
  Rely on the output of other WPs

- Emerging technologies beyond CMOS

  This Workshop: Strengthen efforts in 2D materials (TFETs, optoeletronics, topological structures,)
  Requires manufacturing and tooling

Large area growth of 2D Materials for Nanoelectronics

A. Dimoulas

Institute of Nanoscience and Nanotechnology,
National Center for Scientific Research DEMOKRITOS,
Athens, Greece
and
Chair of Excellence, CEA & U. Grenoble Alpes

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Collaborators

NCSR DEMOKRITOS P. Tsipas, D. Tsoutsou, E. Xenogiannopoulou
CEA-INAC G. Renaud, H. Okuno, C. Alvarez, R. Sant
CNRS-LTM T. Baron
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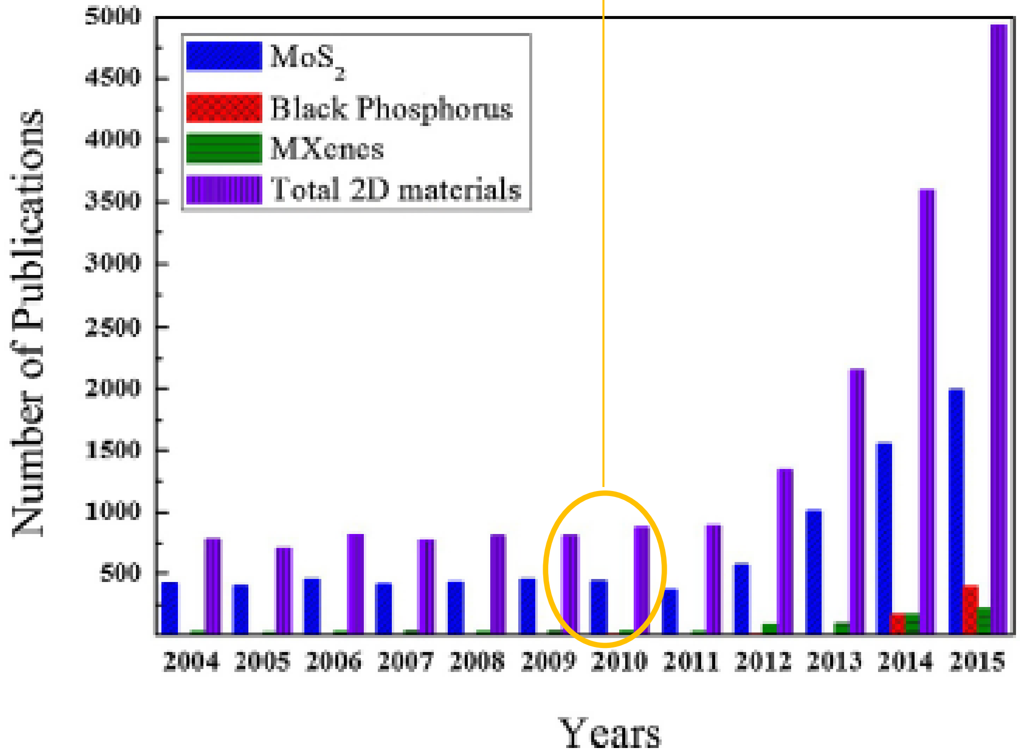
Outline

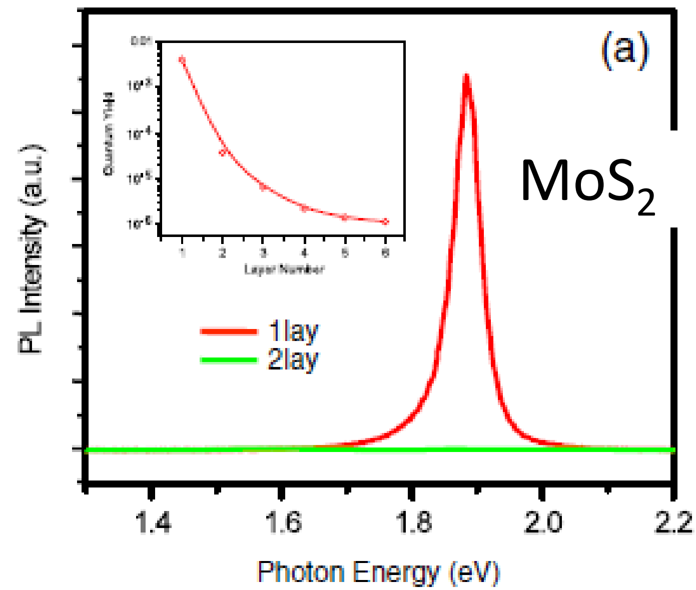
- **2D materials basics & applications**
- **Scalable growth of 2D materials**
  VPD, CVD, MOCVD
- **MBE-grown 2D materials**
  -Structural
  -Electronic band structure,
  -W. d. Waals heterostructures

2D Materials research history

2D Metal Dichalcogenides

Mak et al, *Phys. Rev. Lett.* **105** 136805 (2010)





Source: American Chemical Society database
https://www.acs.org/content/acs/en.html (2016)

Intense PL only for 1L MoS_2
1L→2L : Direct → Indirect

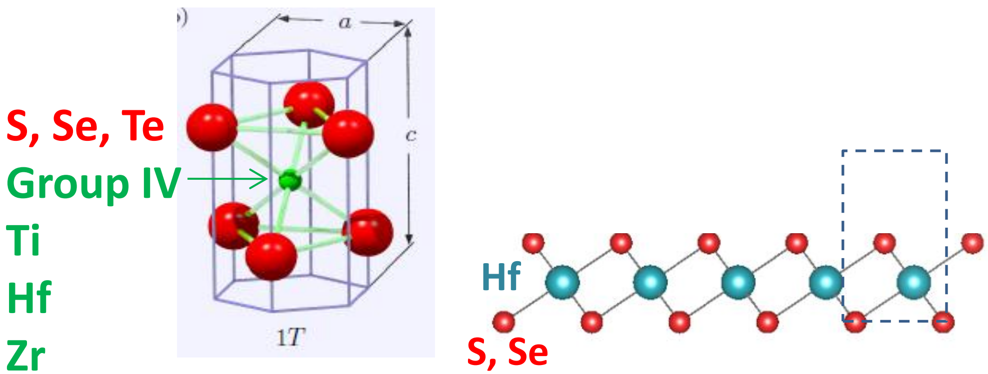
2D dichalcogenide materials

Large variety of physical properties and crystal structures

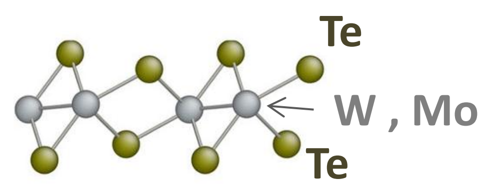
semiconductors	(Mo, W)S_2, (Mo, W)Se_2, (Hf, Zr)Se_2, $SnSe_2$
metals	$TaSe_2$, $TiSe_2$
semimetals	$HfTe_2$, $ZrTe_2$
superconductors	$NbSe_2$
Weyl semimetals	WTe_2, $MoTe_2$
topological insulators	Bi_2Se_3, Bi_2Te_3 monolayer WTe_2, $MoTe_2$

Crystal Structure

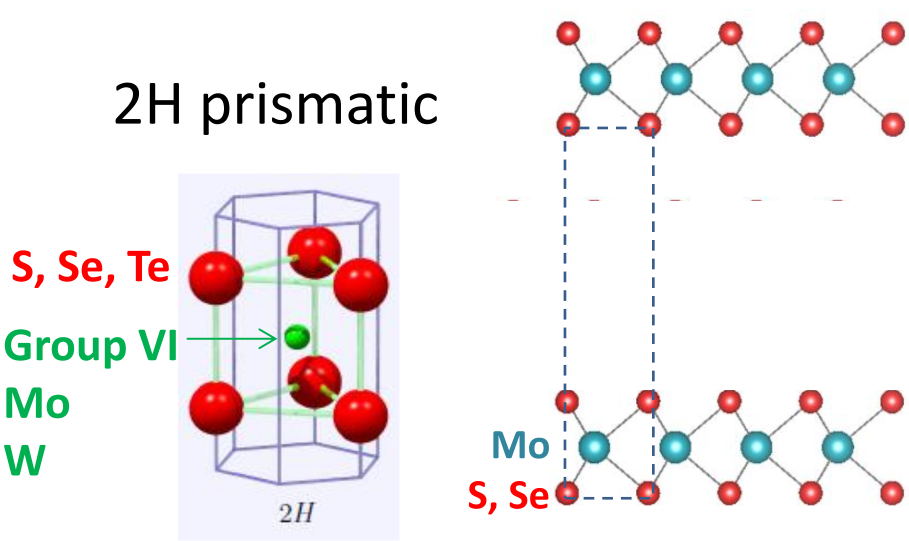
1T octahedral



Distorted 1T’



2H prismatic



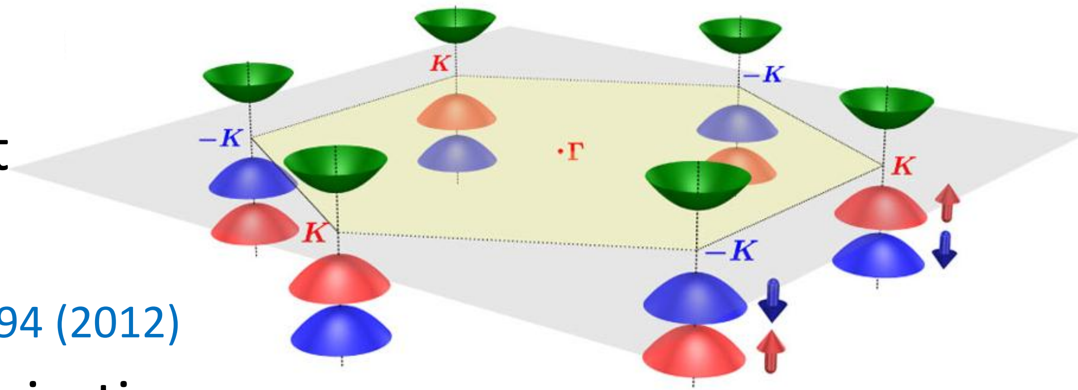
$MoTe_2$ @ RT
-2H semiconductor stable
-1T’ metalic metastable

Possibility for
Semiconductor to metal
transition

1 ML MoS_2: Broken Inversion Symmetry

D. Xiao et al., *Phys. Rev. Lett*. **108**, 196802 (2012)

- Spin-Valley coupling
  Spin polarized transport
  "*Valleytronics*"

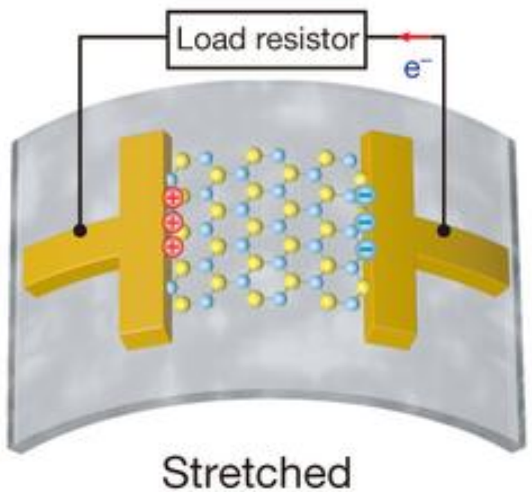


K.F. Mak et al., *Nat. Nanotech*. **7**, 494 (2012)

- Control valley spin polarization by circularly polarized light

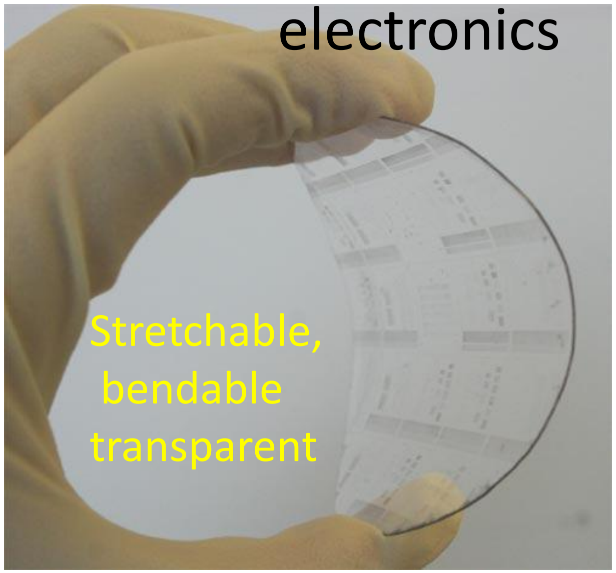
W. Wu et al., *Nature* **514**, 470 (2014)

- Piezoelectricity in MoS_2 for energy conversion



Benefits of Atomically Thin Layers

Flexible, transparent electronics

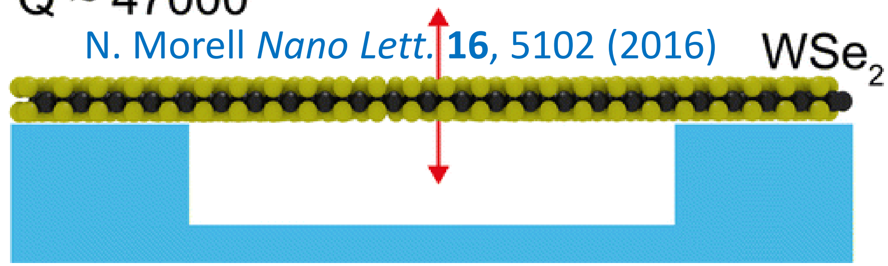


High mechanical strength

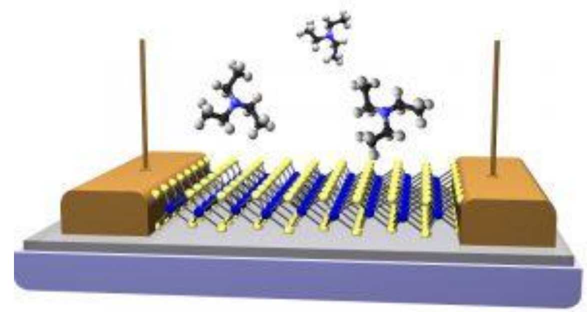
Electromechanical resonators

Q ~ 47000

N. Morell *Nano Lett.* **16**, 5102 (2016)



Sensitive chemical sensors

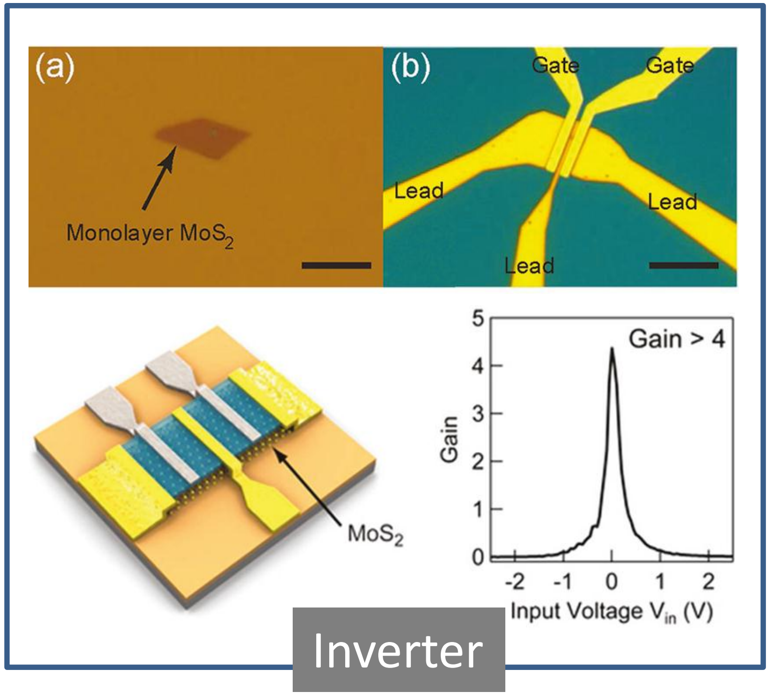


High surface to volume ratio

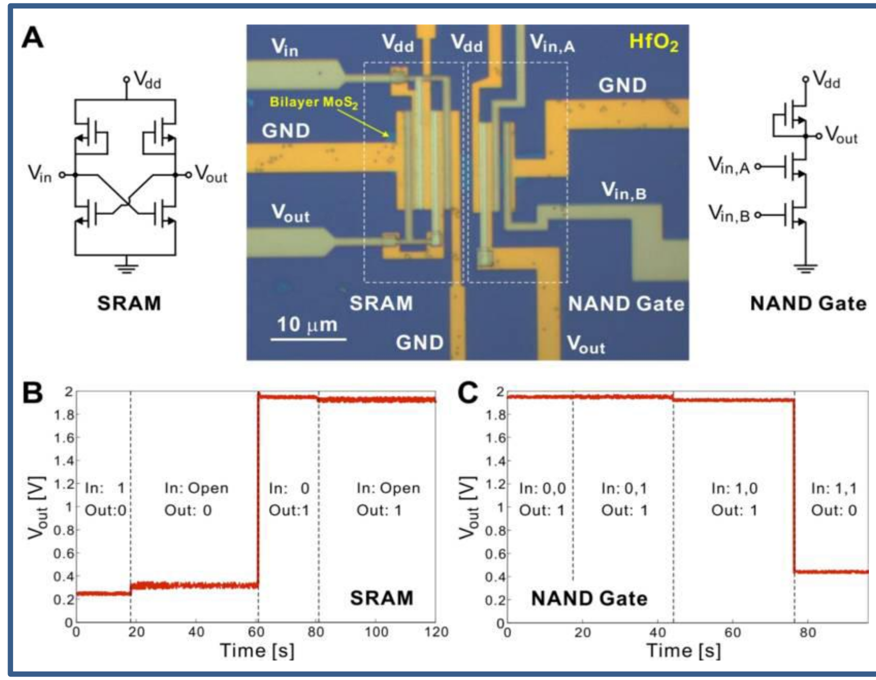
F.K. Perkins *Nano Lett.*, **13** 668 (2013)

MoS_2 Devices and Circuits

EPFL: Radisavlejvic, Kis, et al.,
ACS Nano **12**, 9934 (11)



MIT: H. Wang, T. Palacios, et al.,
Nano Lett. **12**, 4674 (12)



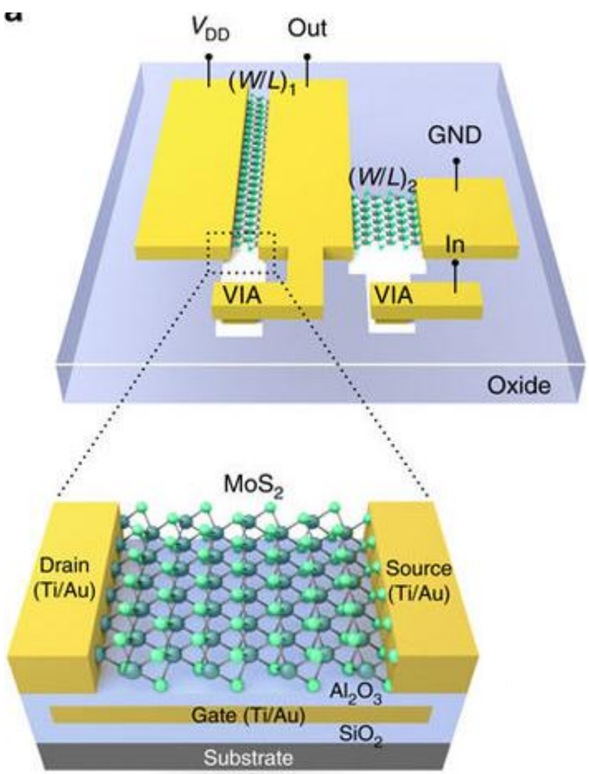
- Large potential to impact nanoelectronics

Microprocessor based on a 2D semiconductor

S. Wachter et al., *Nature Communications* **8**, 14948 (2017)

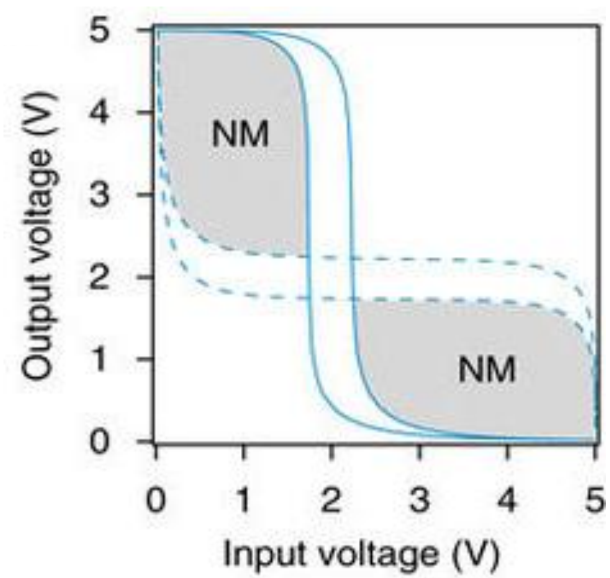
Scalable 1-bit microprocessor with 115 transistors made of CVD MoS_2 (2ML)

Inverter



Voltage gain ~ 60

SNM ~ 0.59 x (V_{dd}/2)

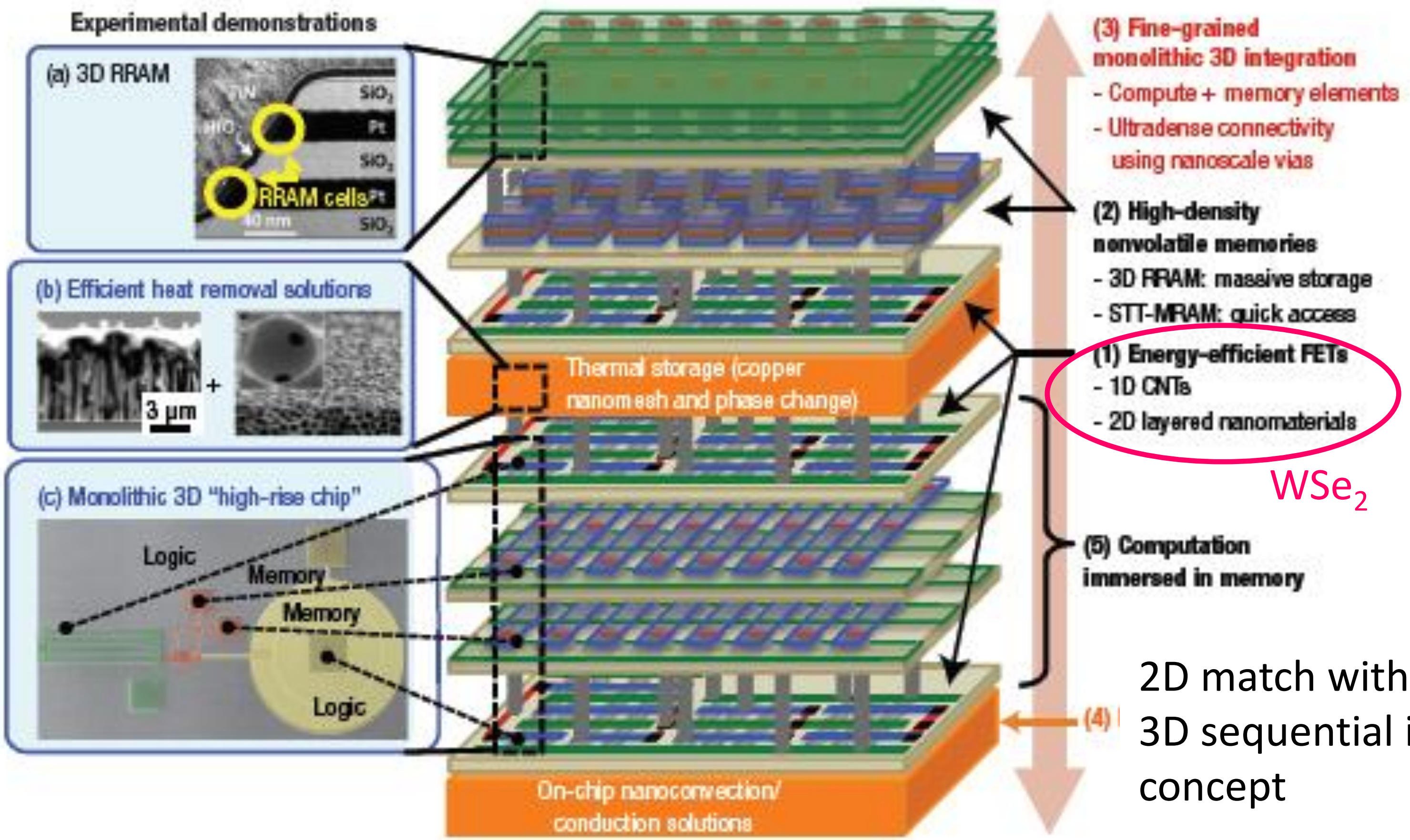


NEREID

Re-Booting Computer

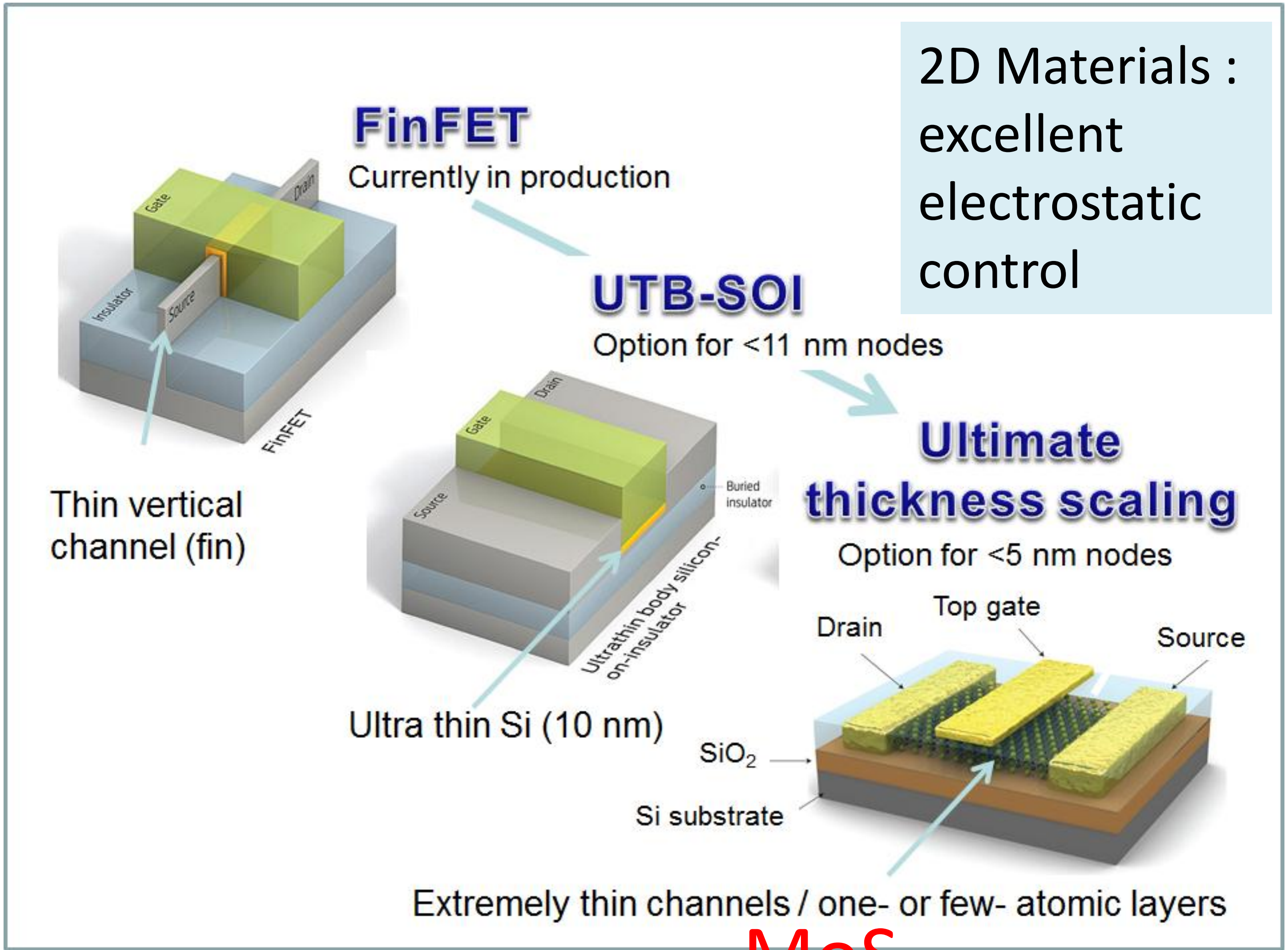
Energy-Efficient Abundant-Data Computing: The N3XT 1,000X

M.M.S Aly et al., *IEEE Computer* **48**, 24 (2015)



2D match with
3D sequential integration
concept

Device Scaling



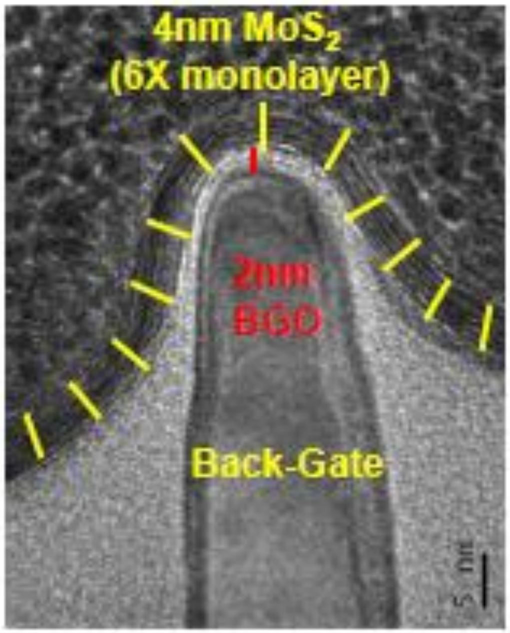
2D Materials : excellent electrostatic control

MoS_2

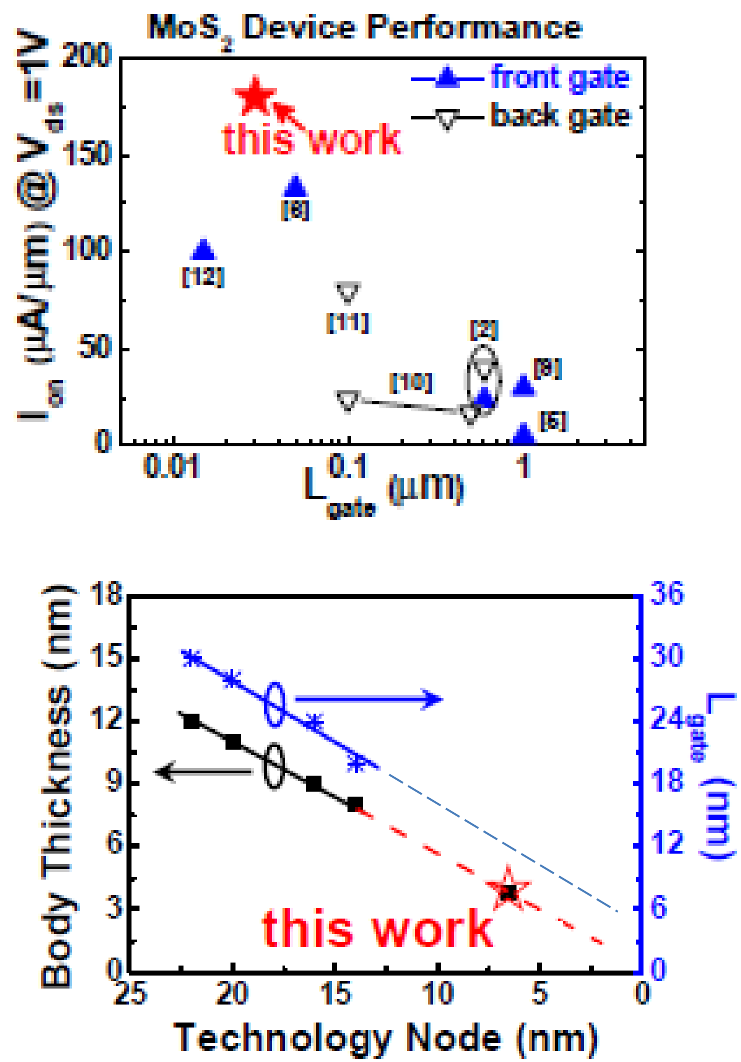
First CVD MoS_2 FinFET

Back gated → reconfigurable between low power/high performance

M.-C Chen et al., *IEDM* 2015

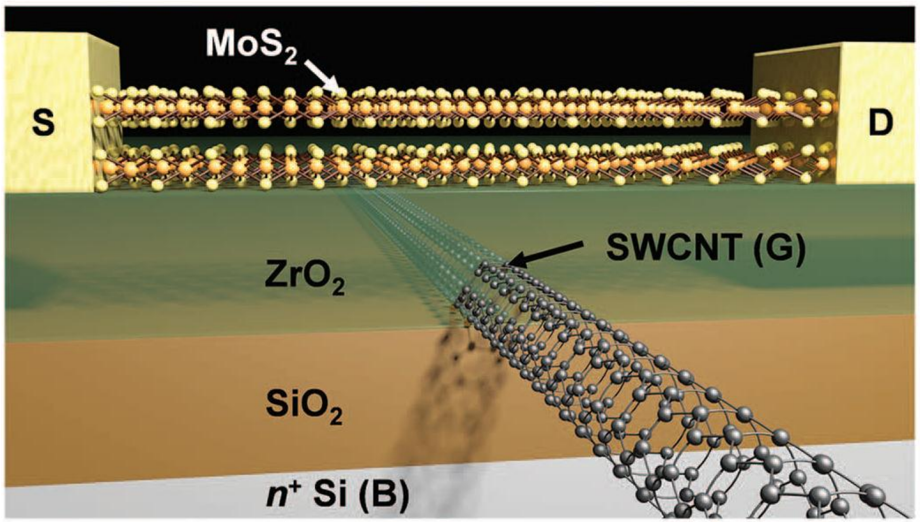


MoS_2 by CVD

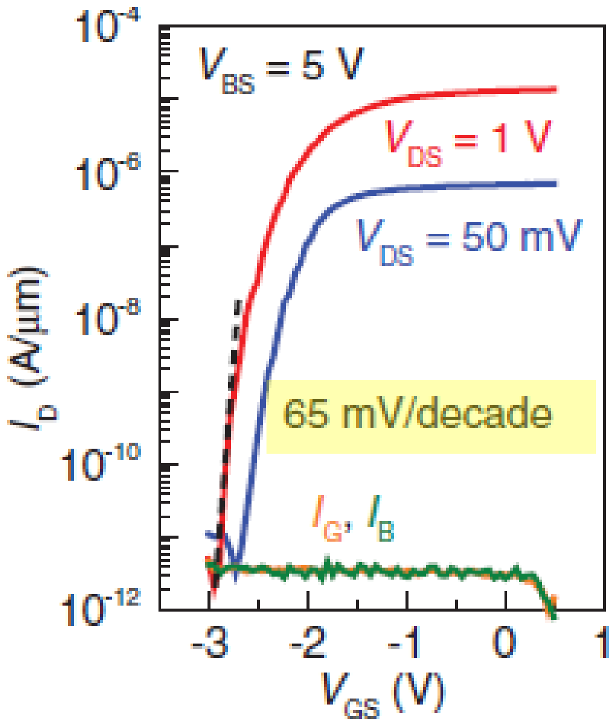


MoS_2 FET with 1 nm Gate Length

S. B. Desai *Science* **354**, 6308 (2016)



Ideal switching characteristics



Simulations :

Could impact low power technology

2 orders of magnitude better than Si

in OFF state leakage

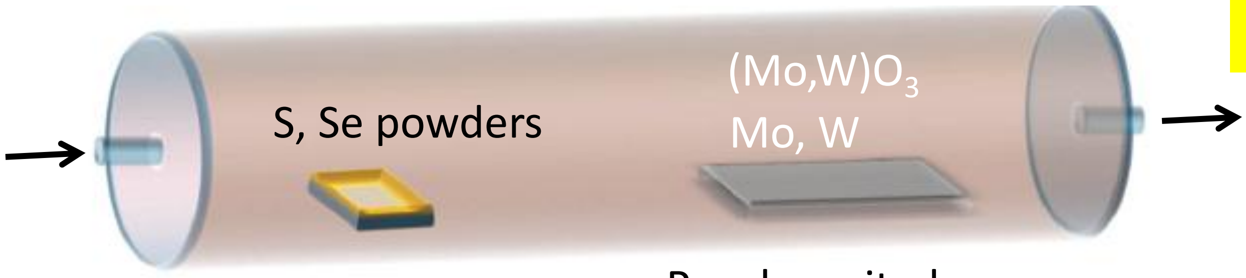
Realized on flakes

Scalable synthesis of 2D materials

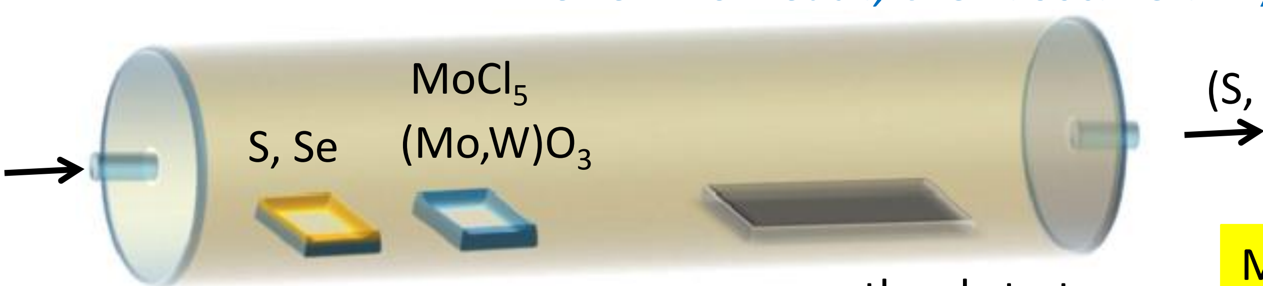
- Vapor Phase Deposition-sulphurization
- Chemical Vapor Deposition
- Metalorganic Vapor Phase deposition
- Atomic Layer Deposition
- Sputtering
- Thermal Decomposition
- Molecular Beam Epitaxy

Chemical Vapor Deposition

- VPD from solid sources –sulphurization



- CVD from all-solid sources Y.-H. Lee et al, *Adv. Mater.* **24**, 2320 (2012)
Review Y Shi et al., *Chem. Soc. Rev.* **44**, 2744 (2015)

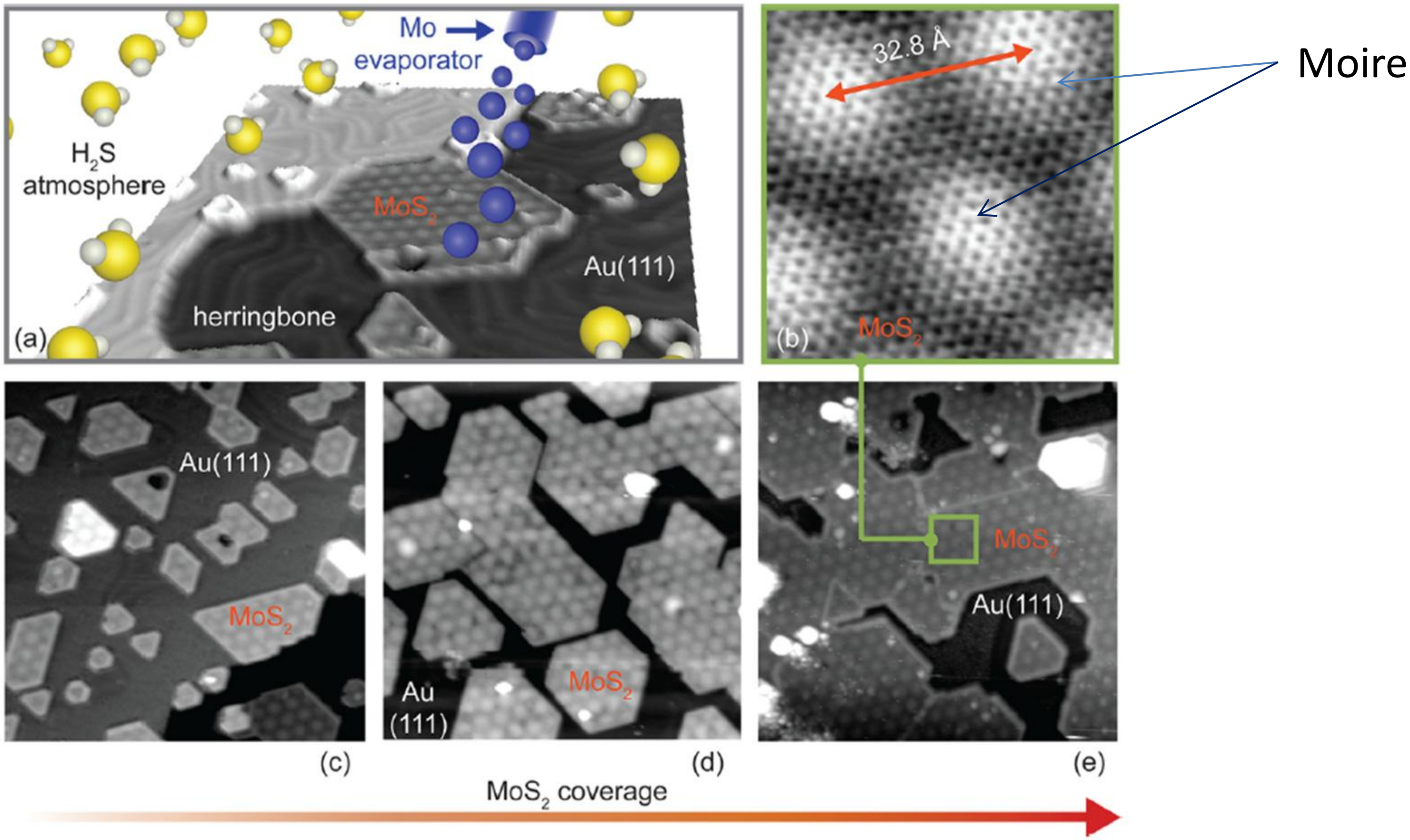


VPD using gas precursors

Mo + H_2S UHV-compatible

S.S. Grønborg, et al., *Langmuir*, **31**, 9700 (**2015**)

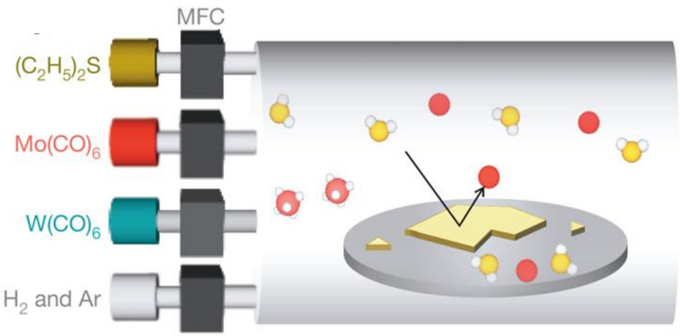
Typically submonolayer coverage → Cycle-based epitaxial growth



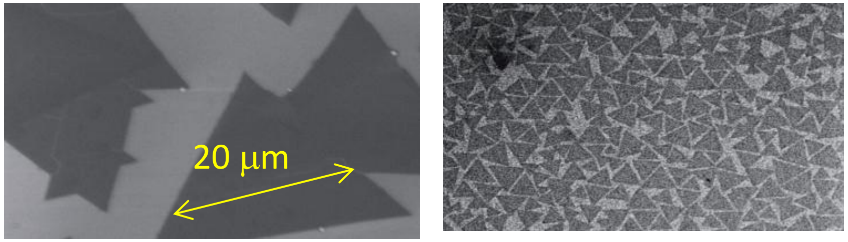
Wafer scale synthetic 2D Semis- MOCVD

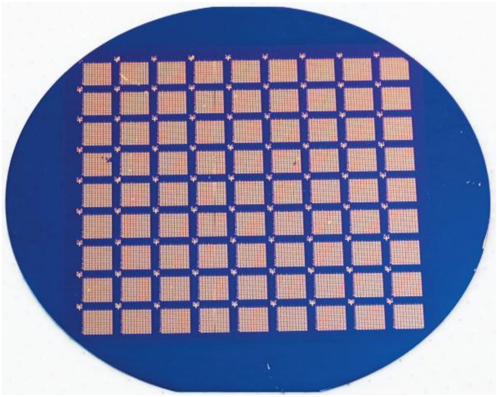
K. Kang et al., *Nature* **520**, 657 (2015)

All-gas precursors

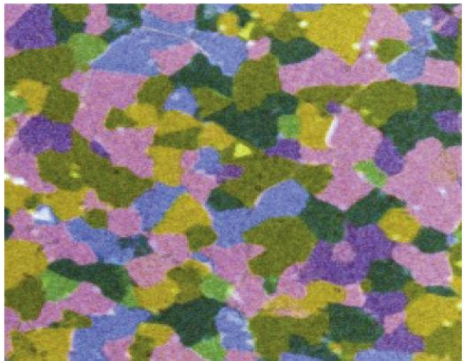


Full coverage, good thickness control,
High spatial homogeneity





MoS_2 (and WS_2) on 4-inch Si/SiO_2



The material is polycrystalline

FETs : 99% yield

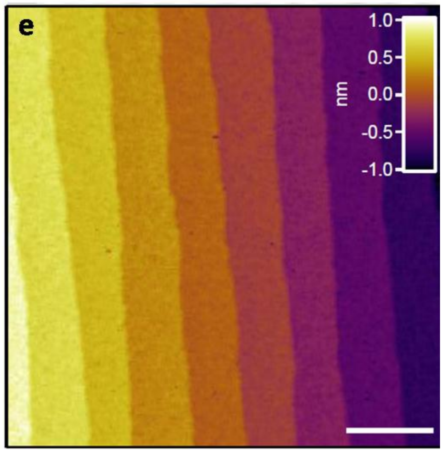
Record field effect mobility (at that time) for synthetic material ~ 30 cm^2/Vs @RT

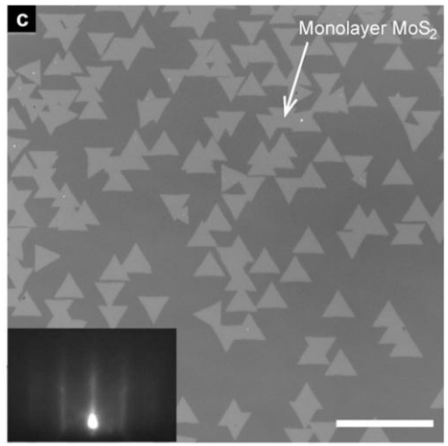
> Need for epitaxial growth of single crystalline 2D layers

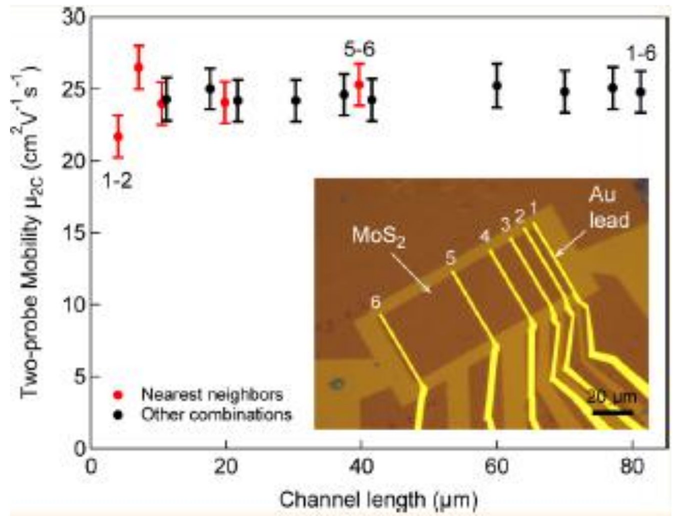
Large area epitaxial MoS_2 on c-sapphire

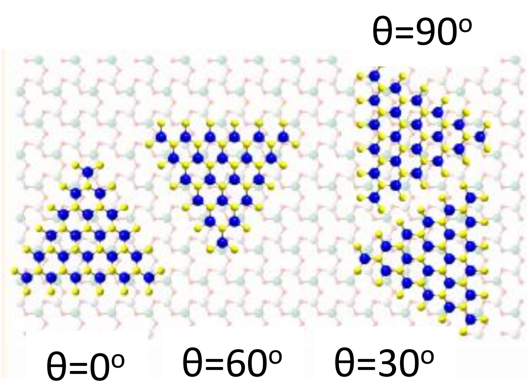
D. Dumcenco et al., *ACS Nano* **9**, 4611 (2015)

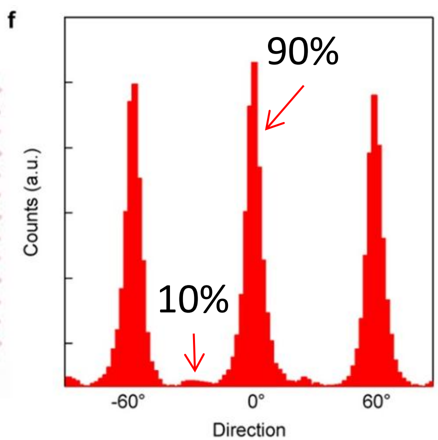
C-sapphire preparation
1000 C /1 h in air







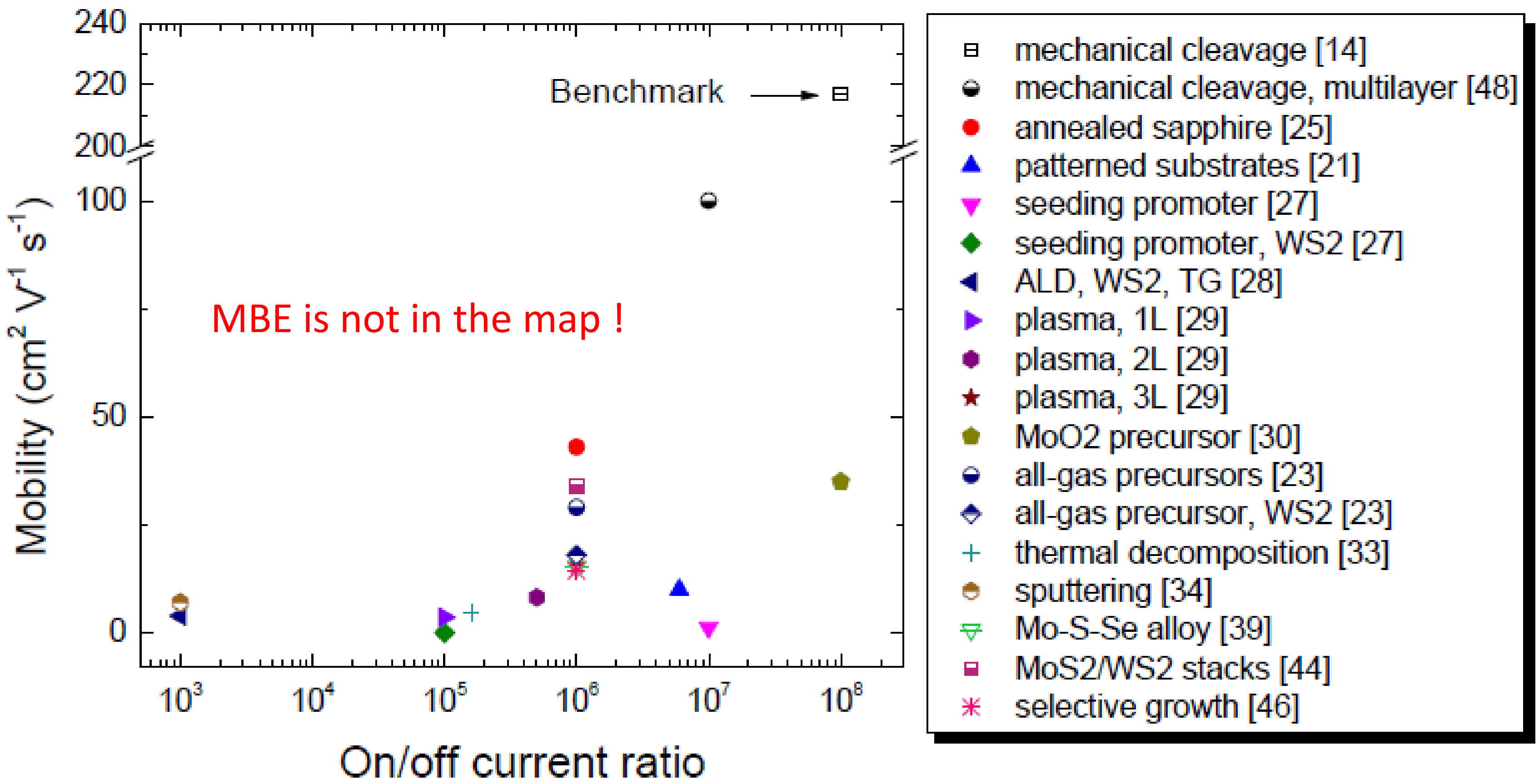




Mobility not affected much by grain boundaries

Summary of Results

Review: J. Li and M. Oestling, *Electronics* **4**, 1033 (2015)

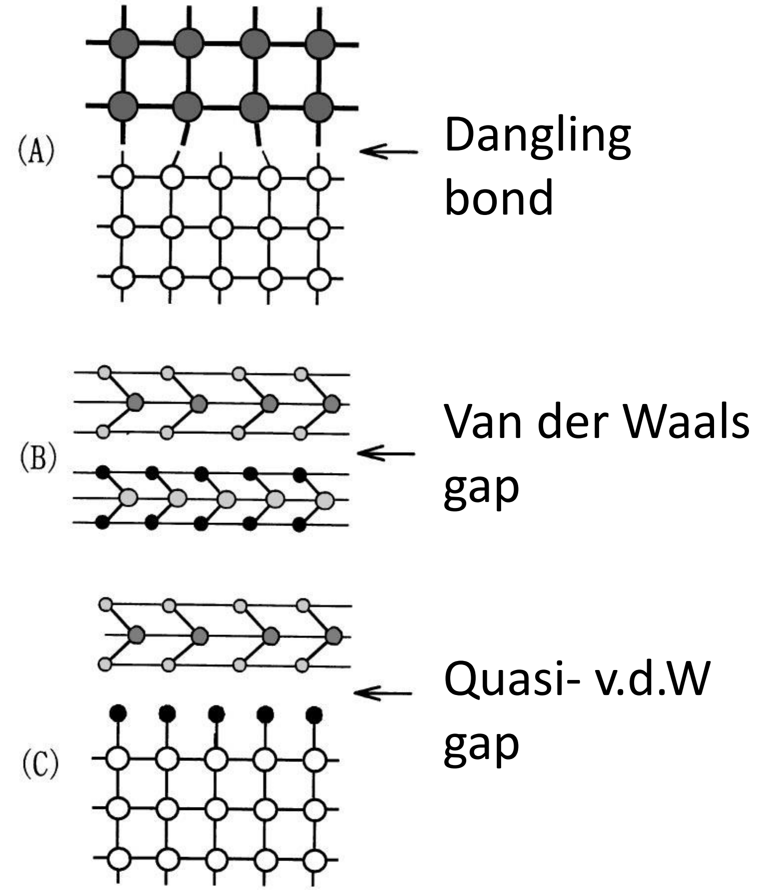


Van der Waals Epitaxy by MBE

Early pioneering work (80's and 90's)
A. Koma and co-workers, Japan

First to introduce the concept of
v. d. Waals epitaxy by MBE

- No heteroepitaxial defects
  (e.g. misfit dislocations)
- No strain-own lattice constant
- In-plane alignment
  (rotationally commensurate)



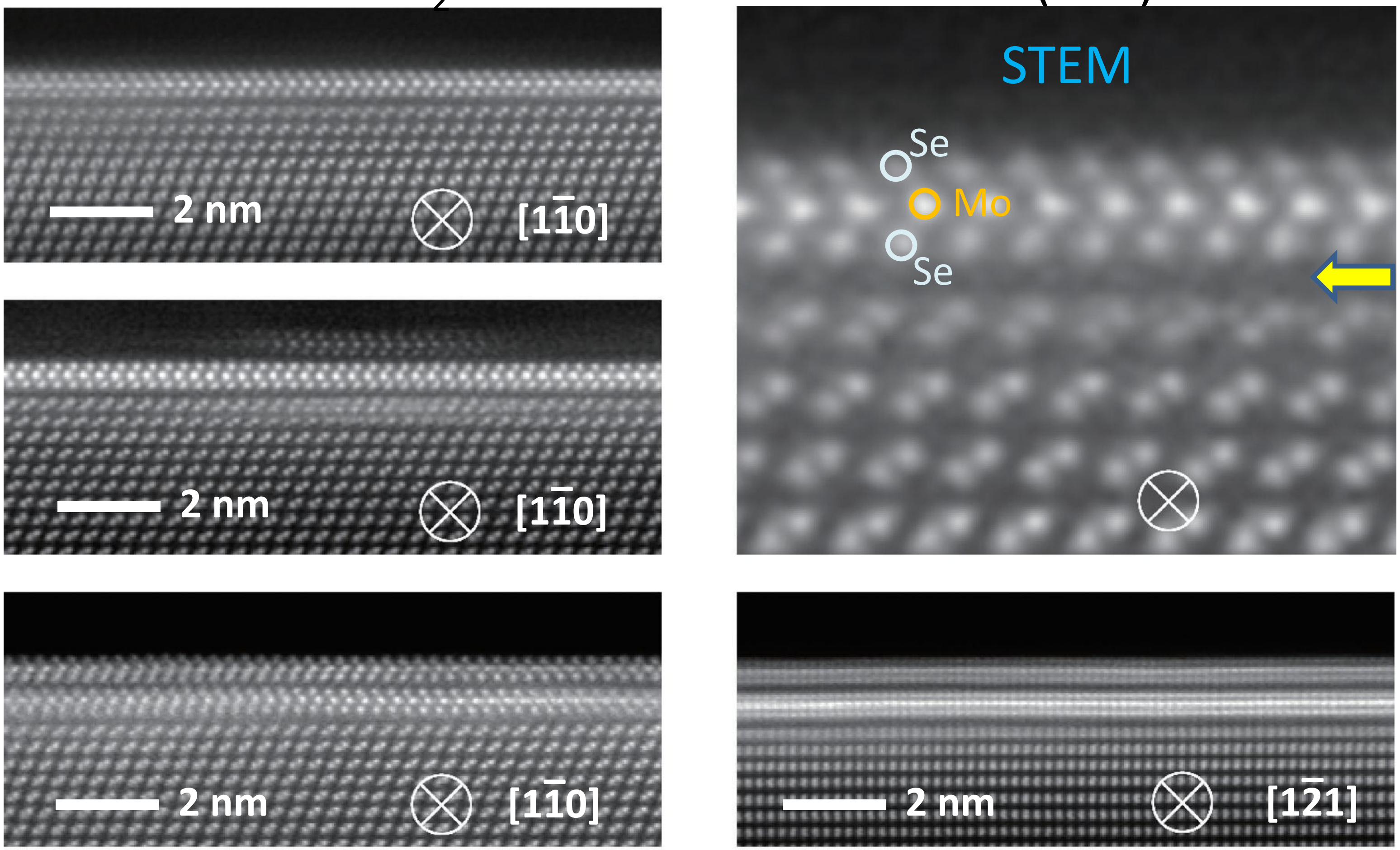
A. Koma, *J. Crys. Growth* 201/202 236 (99)

R. Schlaf, W. Jaegerman and co-workers, *J. Appl. Phys*. **85**, 2732 (1999)

Recent example of v. d. Waals epitaxy

K. Onomitsu et al., *Applied Physics Express* **9**, 115501 (2016)

$MoSe_2$ on Se-terminated GaAs (111) B

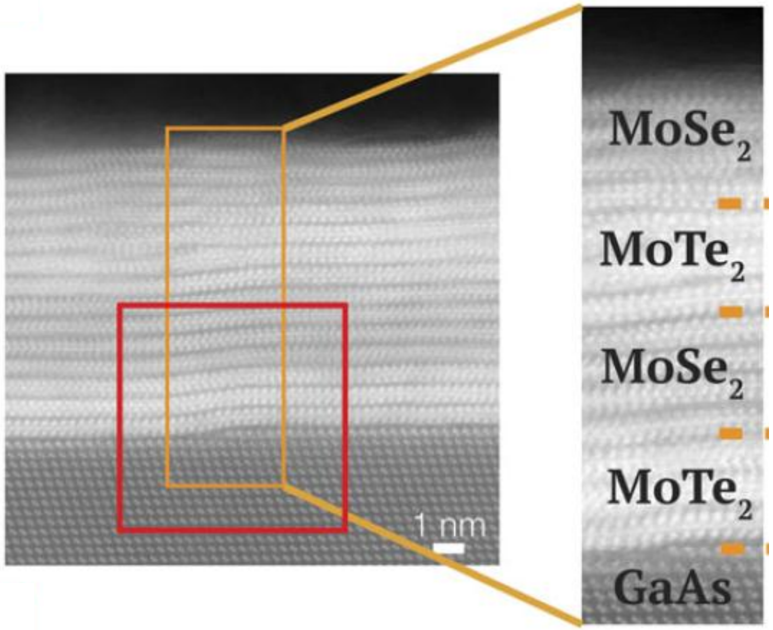


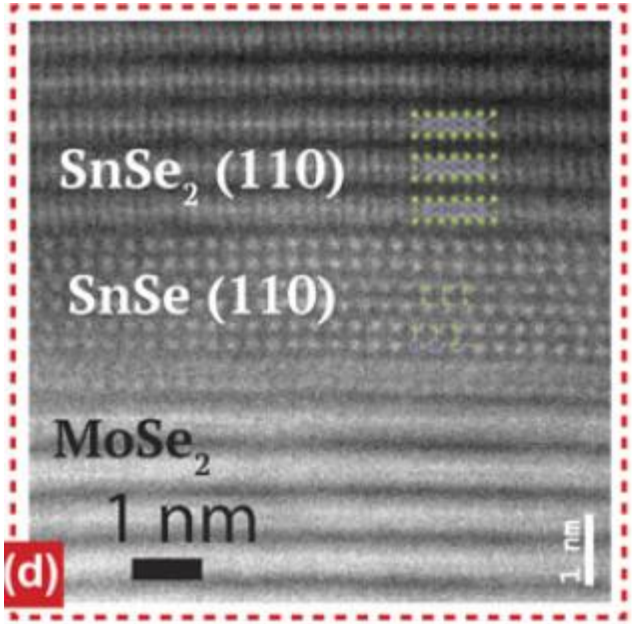
Quasi vd Waals gap

Key point: Extremely slow Mo evaporation rate: 1 L/3300 sec !

Controlled MBE growth of superlattices

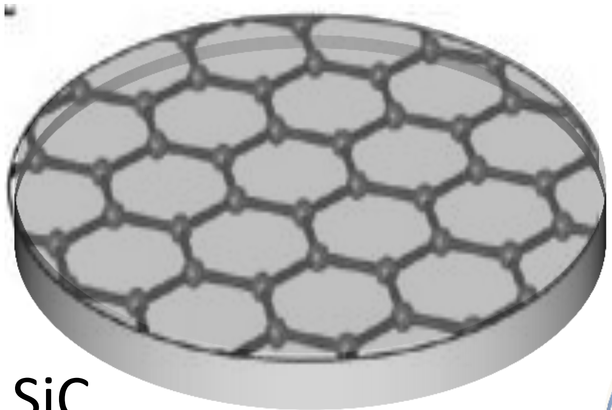
S. Vishwanath, et al., *J. Mater. Res.* 31, 900 (2016)





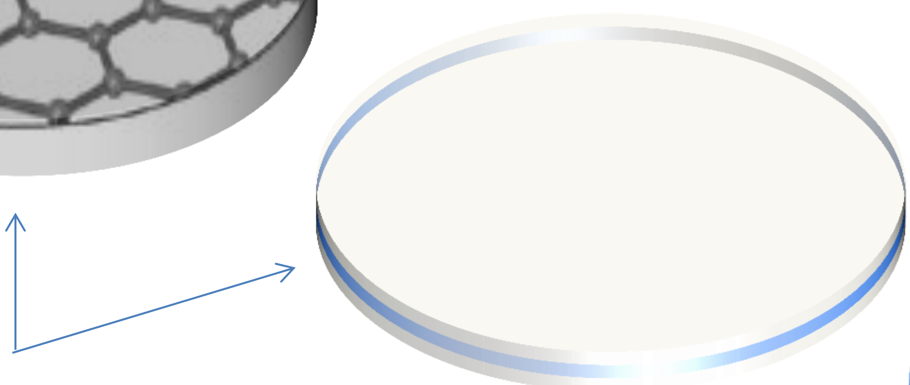
Crystalline substrate options

Epitaxial graphene on SiC



SiC

Sapphire(0001) C-plane



AlN(0001)/Si(111)
InAs(111)/Si(111)

Si

- Expensive
- Small size (6 inch)
- Incompatible with advanced semiconductor processing in pilot lines

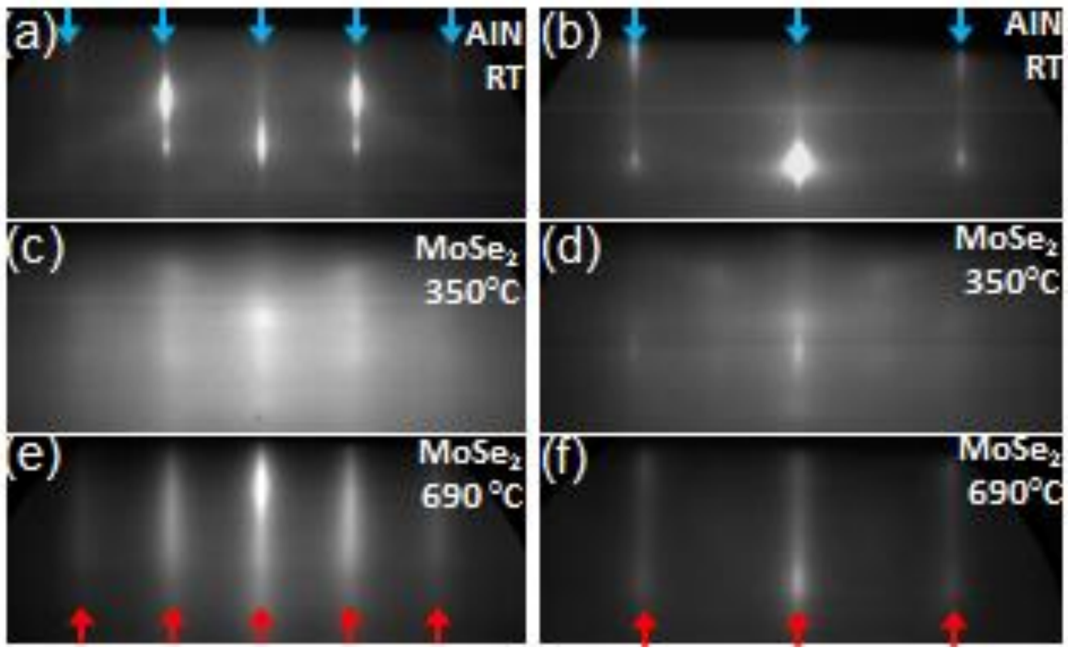
$MoSe_2$ on AlN-MBE growth details

E. Xenogiannopoulou et al., *Nanoscale* **7**, 7896(15)

MOCVD AlN(0001)/Si(111) provided by IMEC

Preparation: HF-based solution + UHV annealing @ 700 C, 10 min

[11-20] azimuth [1-100] azimuth



Two-step growth

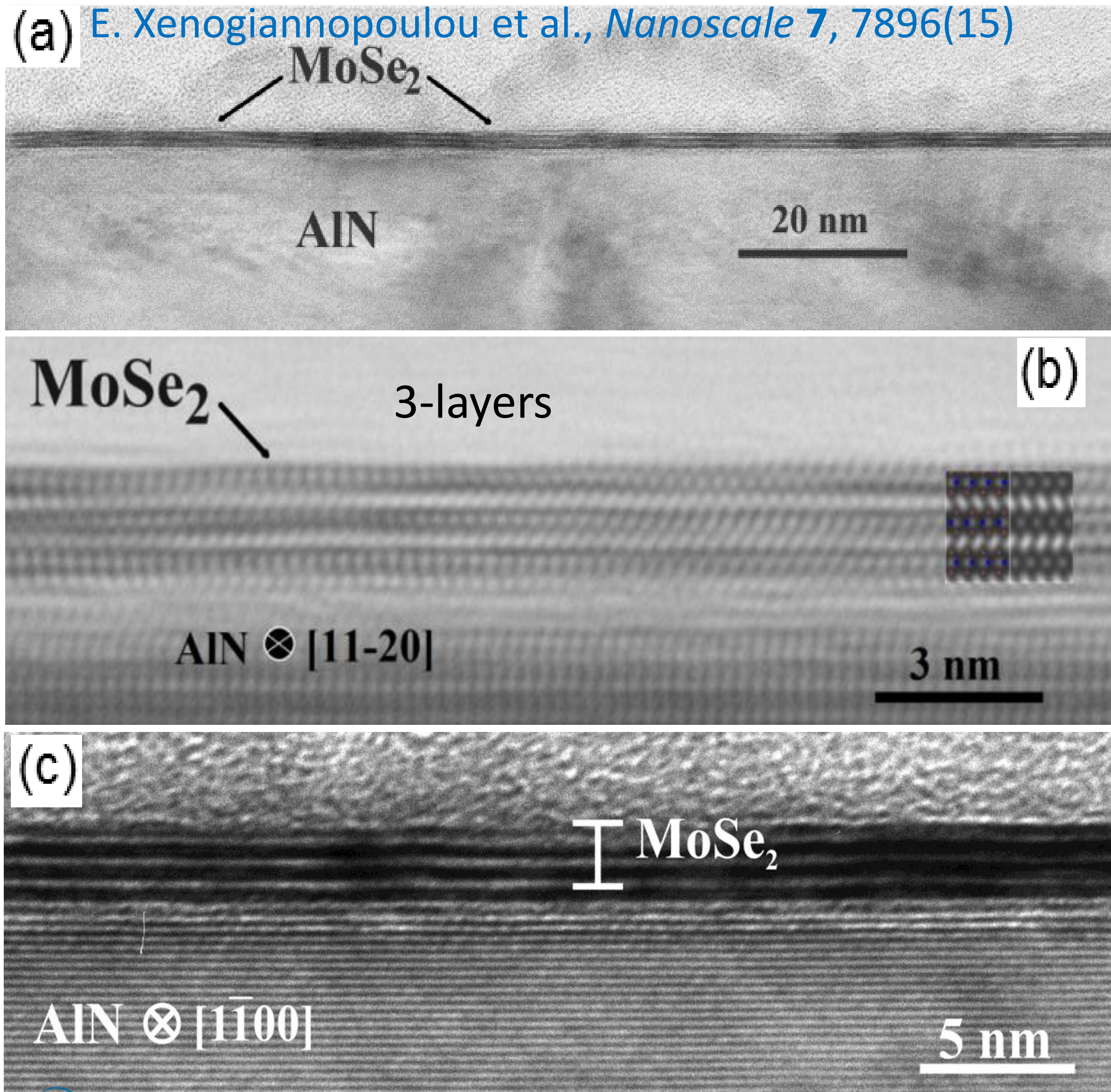
Mo : e-gun
Se : effusion cell
Se/Mo : 15/1
Rate : 1 ML /30 sec

UHV PDA, 10 min
To improve crystallinity

- Good in-plane alignment no 30° or 90° rotation domains
- Epitaxial despite +6% lattice mismatch

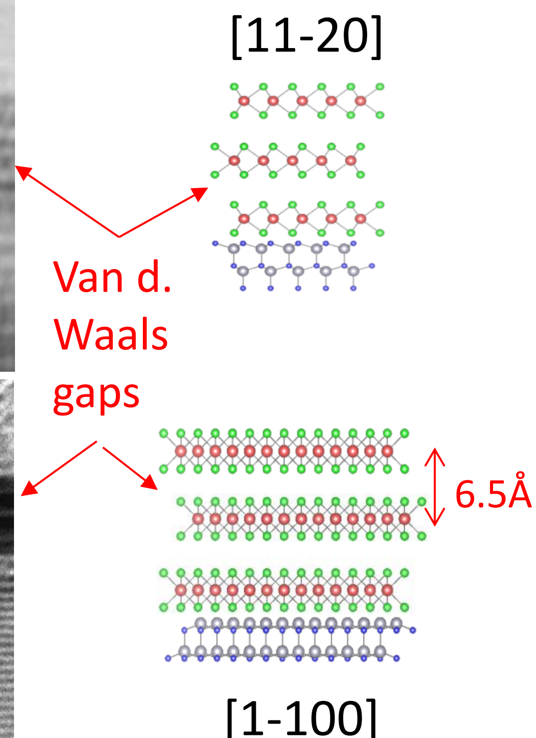
MoSe$_2$ on AlN -HRTEM

E. Xenogiannopoulou et al., *Nanoscale* **7**, 7896(15)



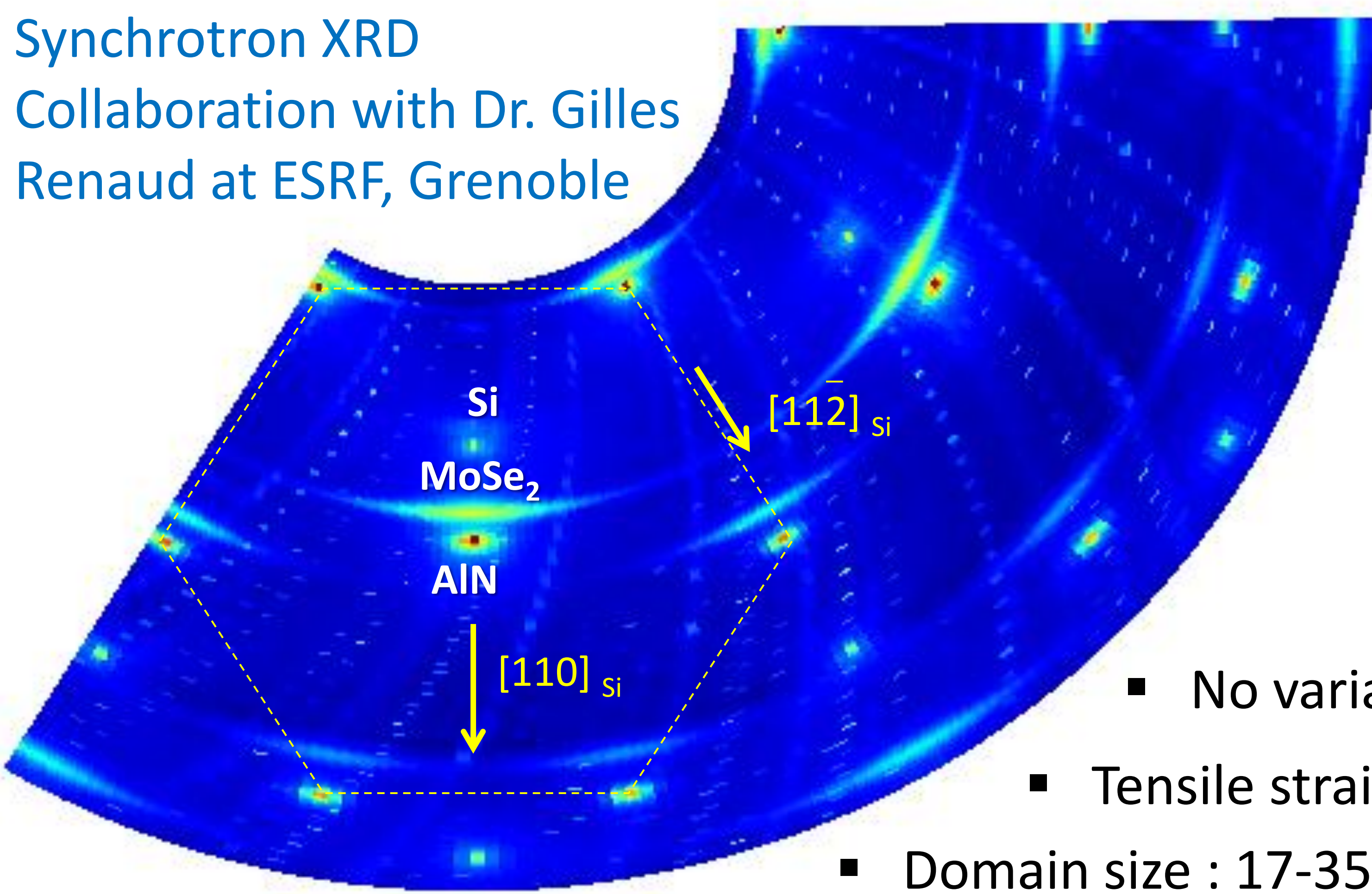
Continuous, uniform, smooth surface and interfaces

No dislocations or defects



$MoSe_2$ Reciprocal Space Mapping

Synchrotron XRD
Collaboration with Dr. Gilles Renaud at ESRF, Grenoble



- No variation with T_{ann}
- Tensile strain ~ 0.3 %
- Domain size : 17-35 nm
- Preferential orientation but large in-plane mosaic spread of $MoSe_2$ (7° FWHM) compared to AlN.

$SnSe_2$ / WSe_2 vdW on Bi_2Se_3 /AlN

Bi_2Se_3 is grown with good quality on AlN P. Tsipas et al., *ACS Nano* **8**, 6614 (2014)

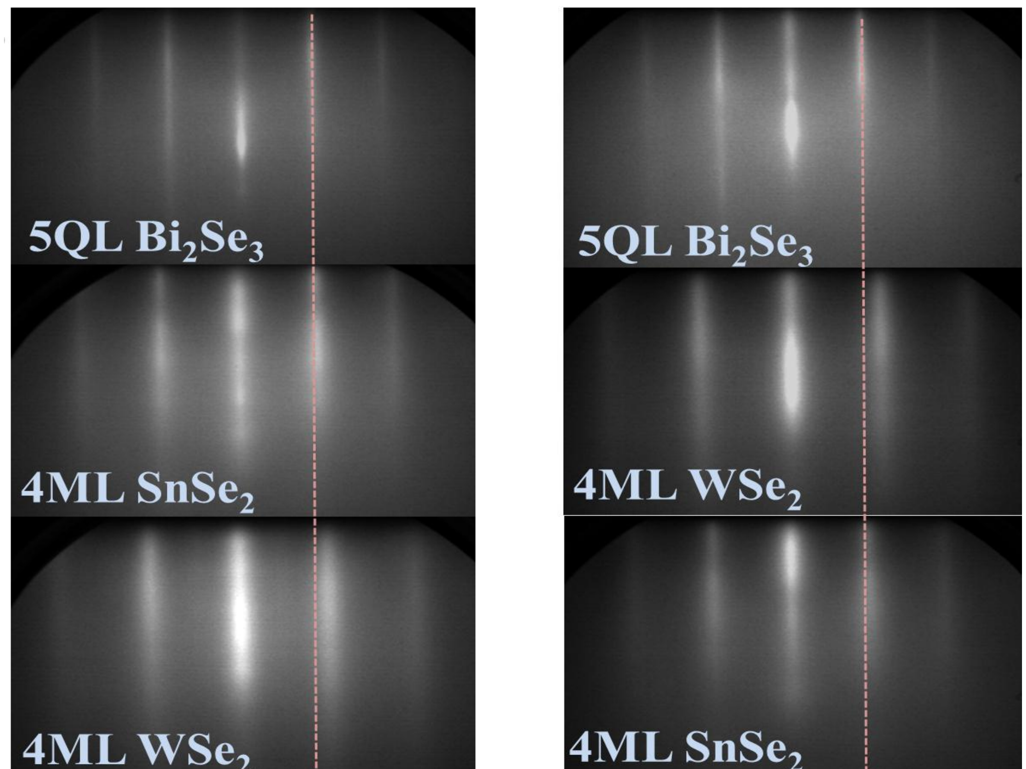
Improves the quality of $SnSe_2$ and WSe_2 epilayers

Growth is limited to < 300 C, since Bi_2Se_3 is unstable above this T

RHEED [11-20] azimuth

-7.5 %c

-14.5 %

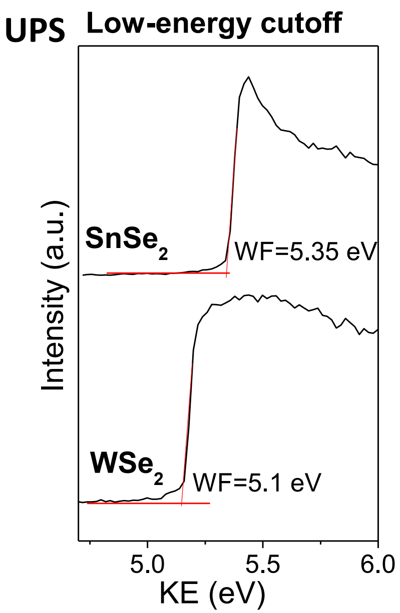


-21 %

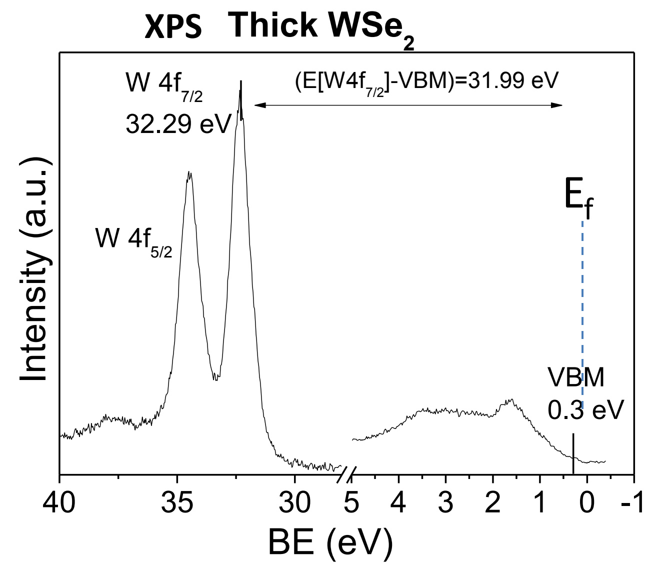
+14.5 %

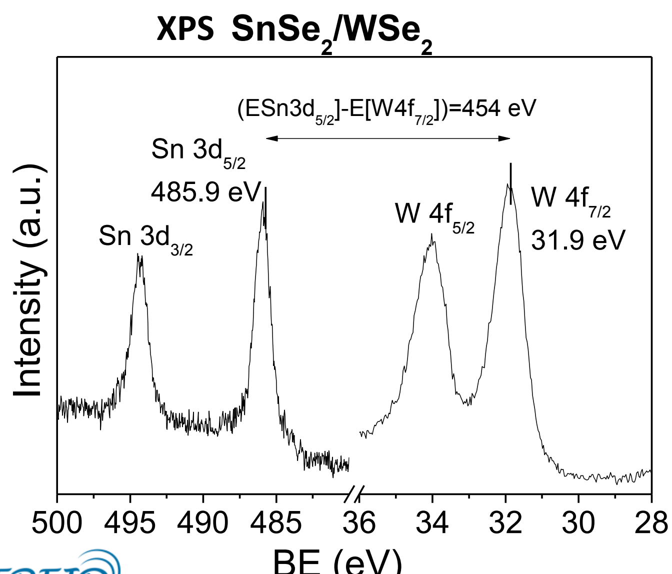
Azimuthal alignment despite large lattice mismatch → vdW epitaxy

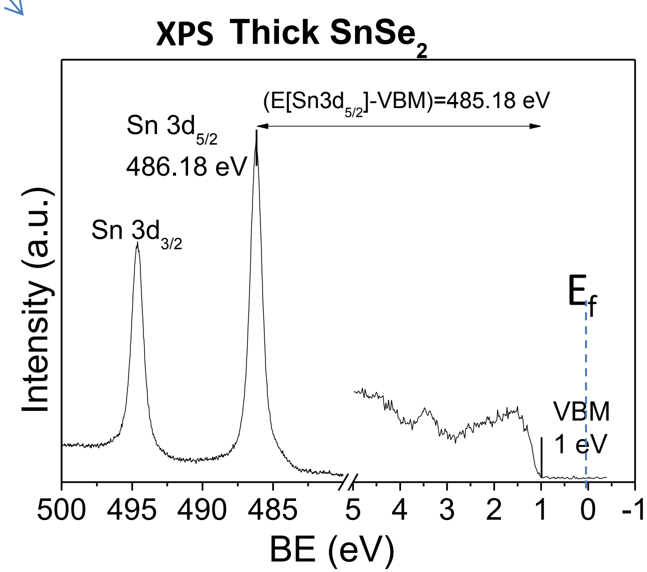
$WSe_2/SnSe_2$ v.d. Waals Heterostructures



Kraut's method
for band offsets

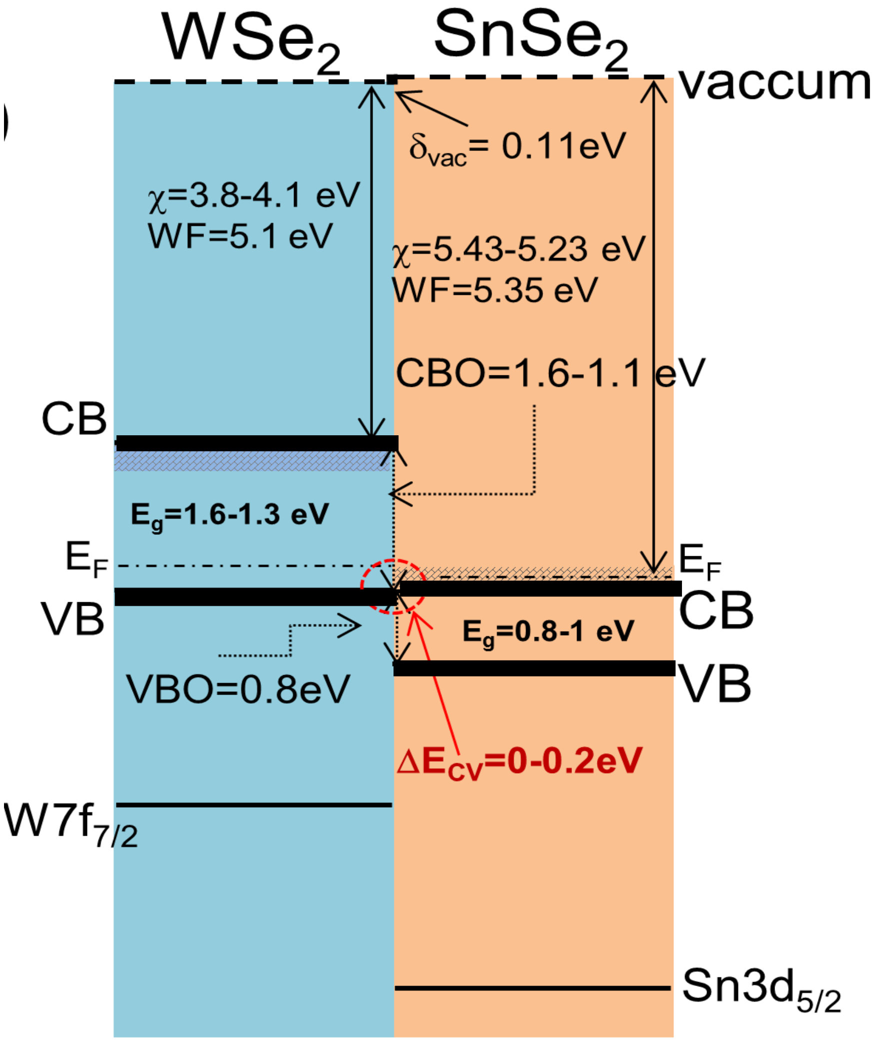


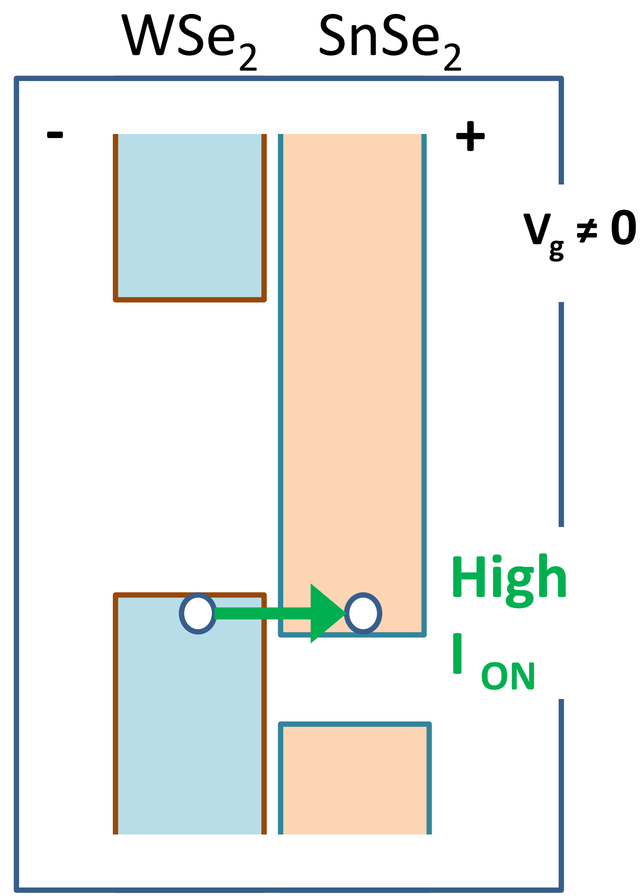




Ideal band line-up for 2D TFETs

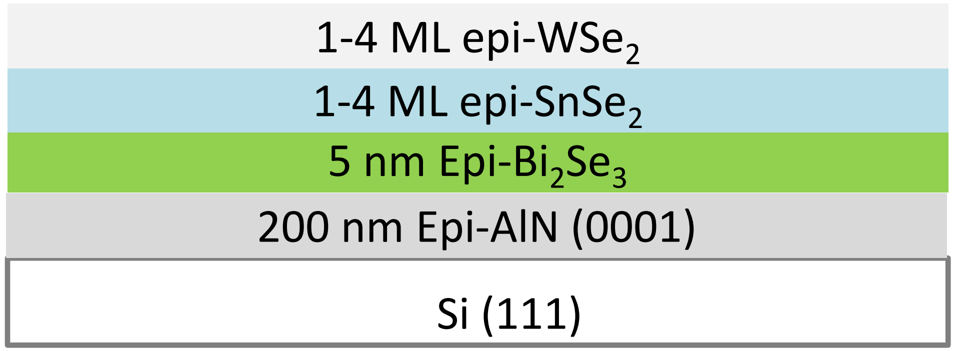
K.E. Aretouli et al., *ACS Appl. Mater* Interfaces **8**, 23222 (2016)

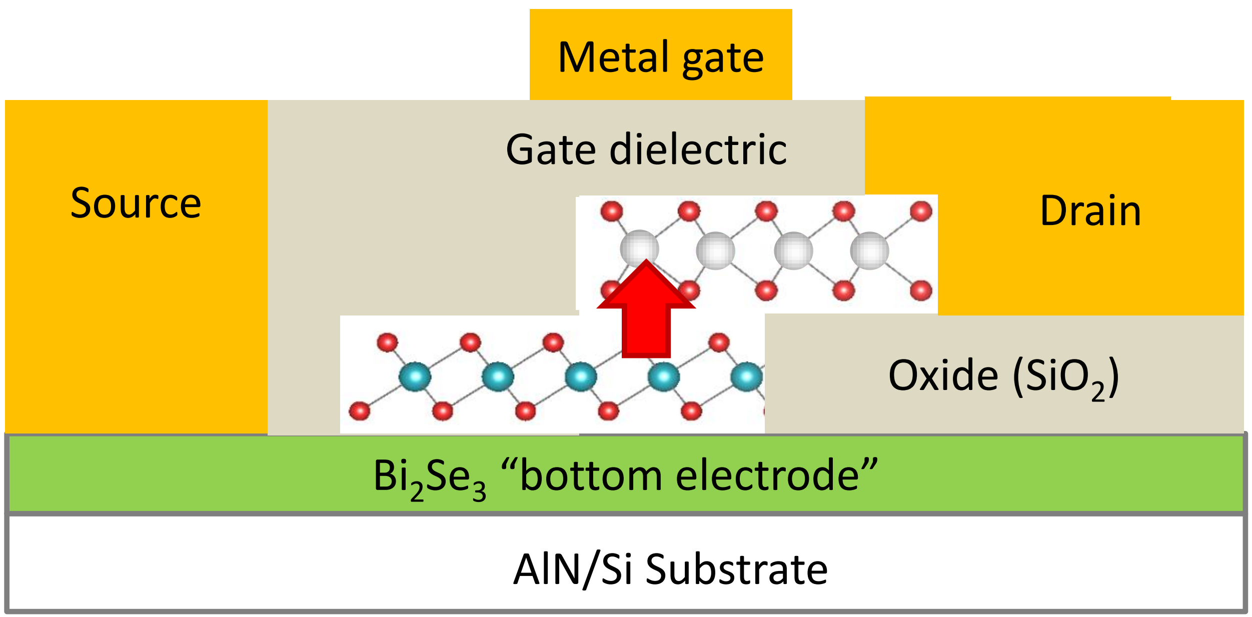




Nearly broken gap
high performance 2D TFETs

2D Vertical TFET Device layout





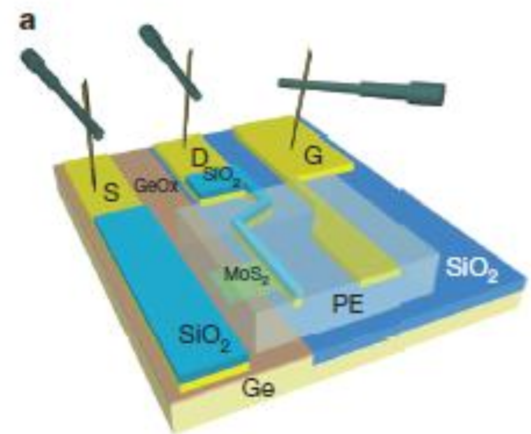
Recently implemented using WSe_2/$SnSe_2$ <u>flakes</u> and back-gating, but SS > 100 mV/dec T. Roy et al., *Appl. Phys. Lett*. **108**, 083111 (2016)

Hybrid 3D -2D vertical TFETs

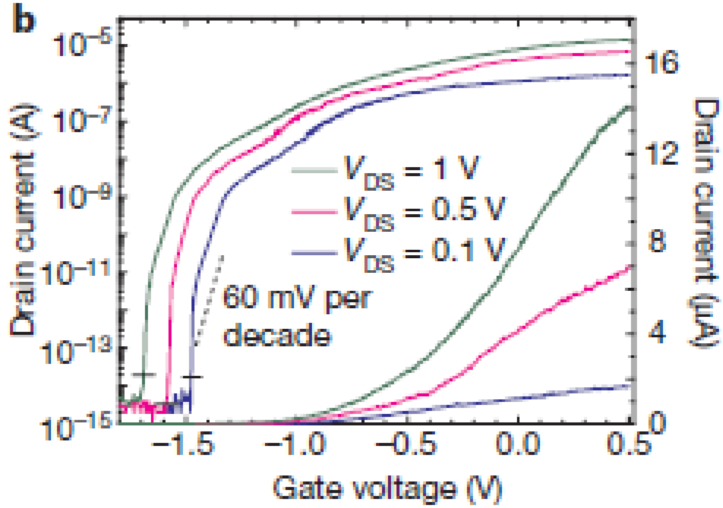
D. Sarkar, G. Banerjee and co-workers, *Nature* **526**, 91 (2015)

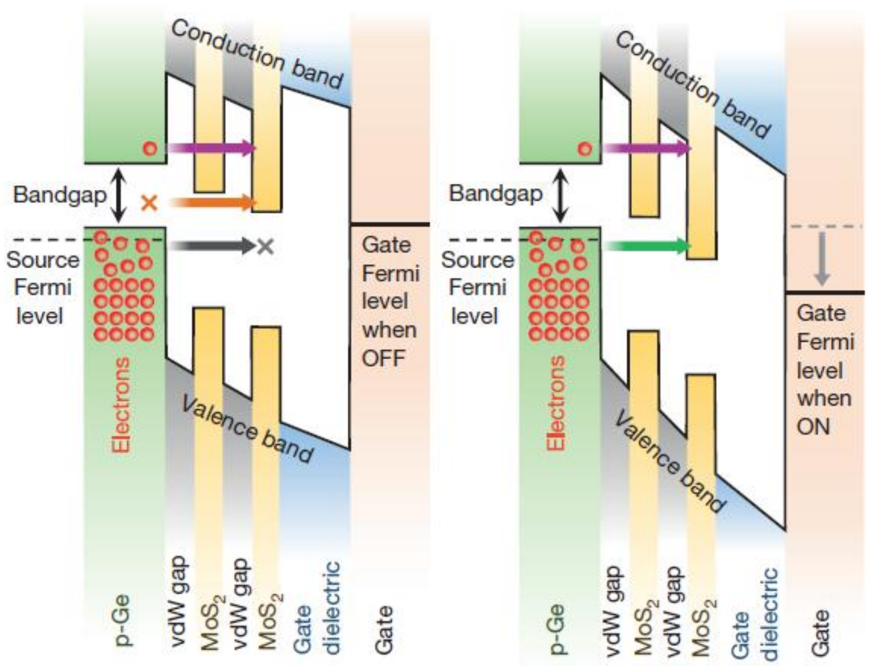
Important new development

3D (Ge) / **2D** (MoS_2) TFET
on exfoliated flakes



SS < 60 mV/dec , V_{ds} =0.1 V





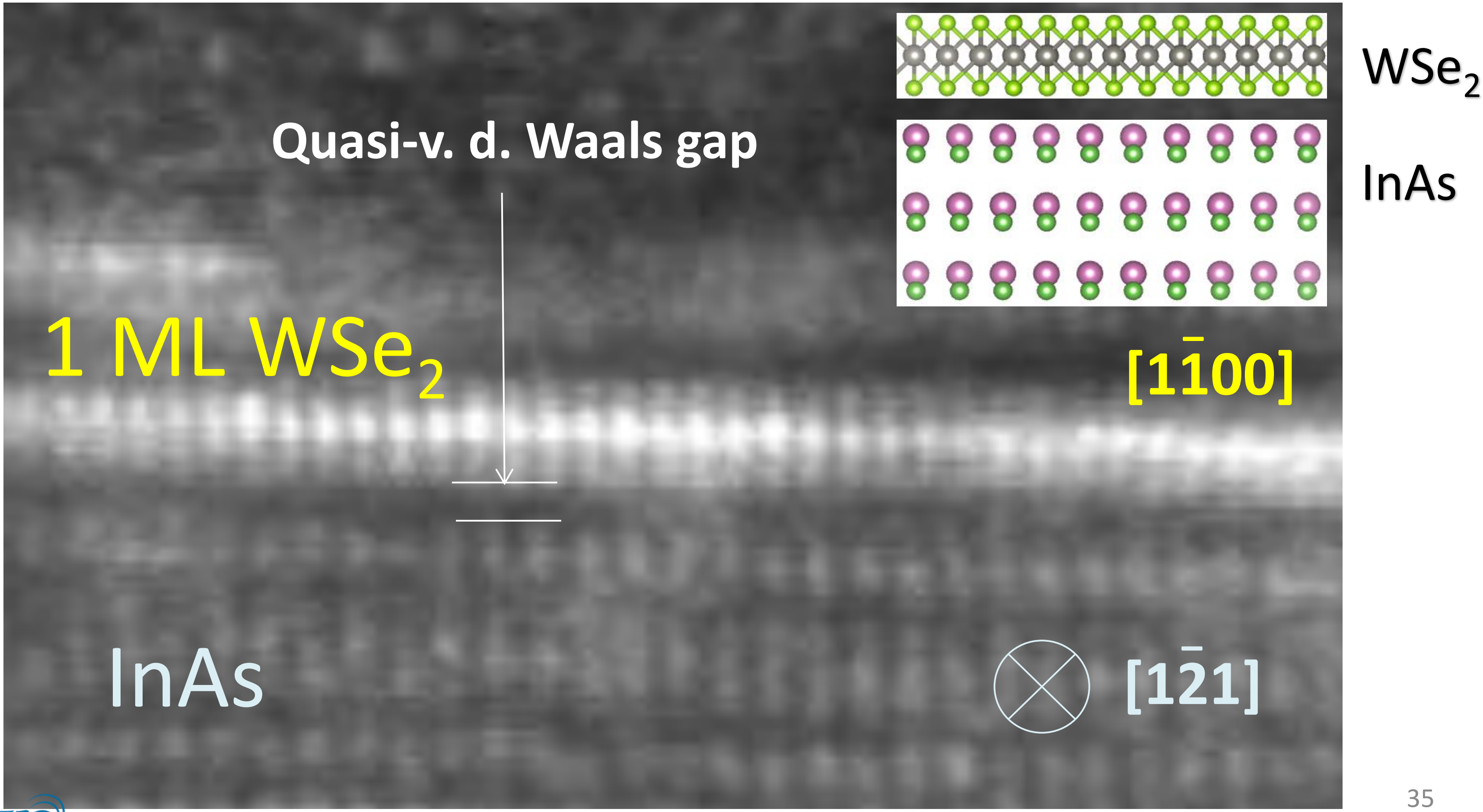
OFF state

ON state

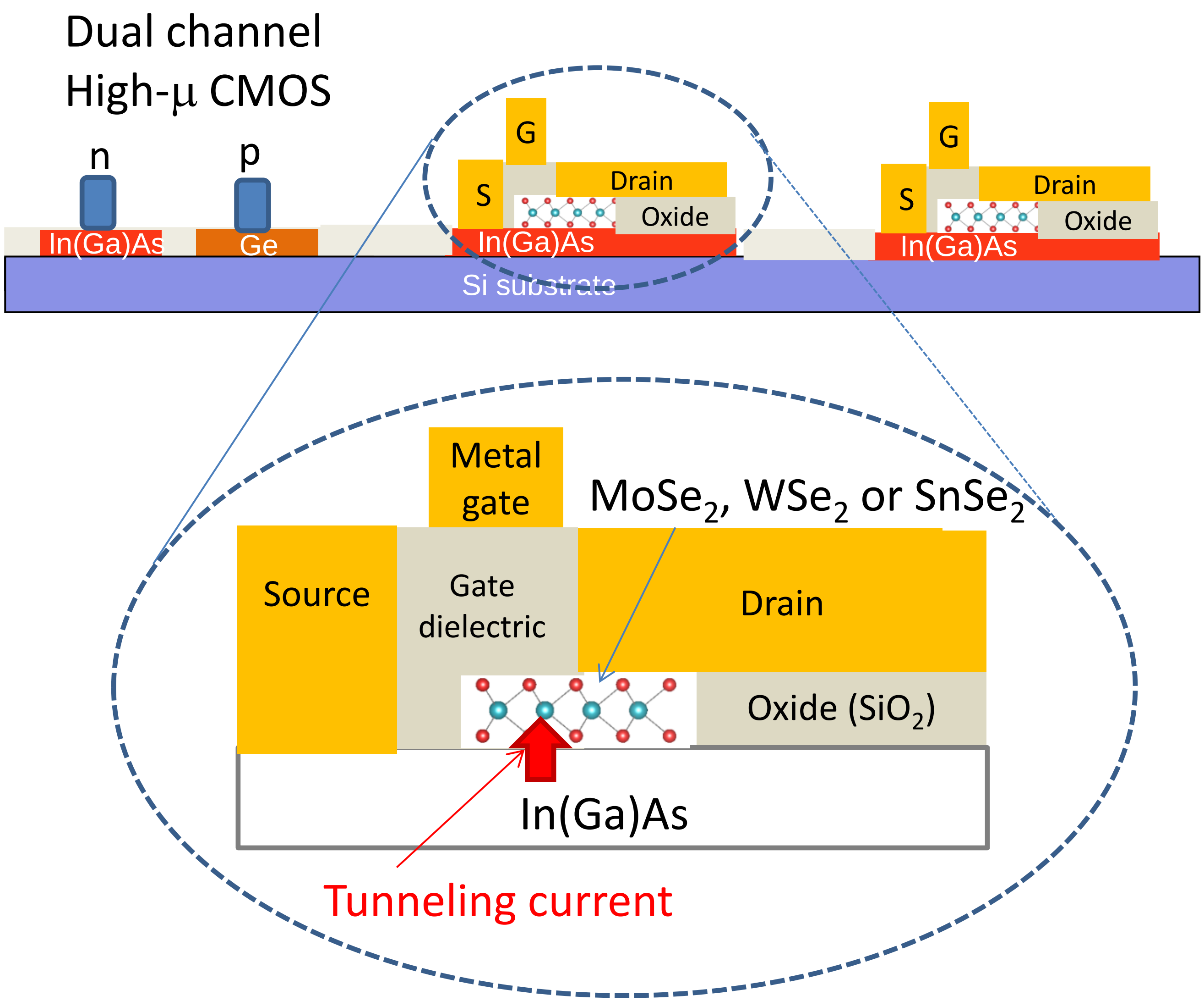
Epitaxy of WSe_2 on InAs/Si(111)

Cross section STEM

NCSRD-CEA-CNRS/LTM collaboration (unpublished)
(C. Alvarez, H. Okuno, T. Baron, A. Dimoulas)



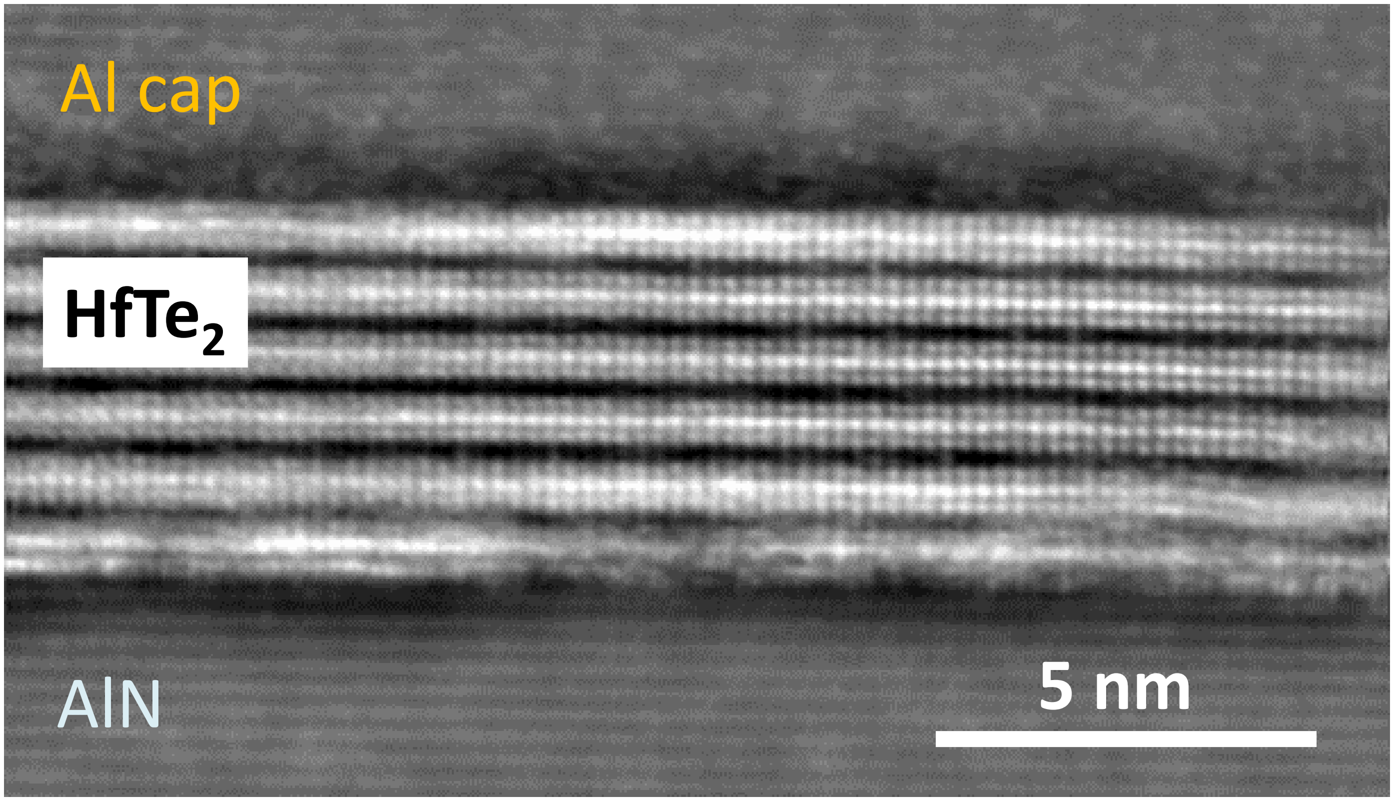
Co-integration of 3D-2D vertical TFET with advanced dual channel CMOS platform



$HfTe_2$ on AlN – HAADF STEM

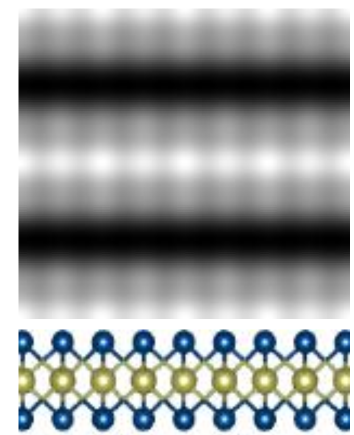
NCSRD-CEA collaboration

C Alvarez, H. Okuno, A.Dimoulas



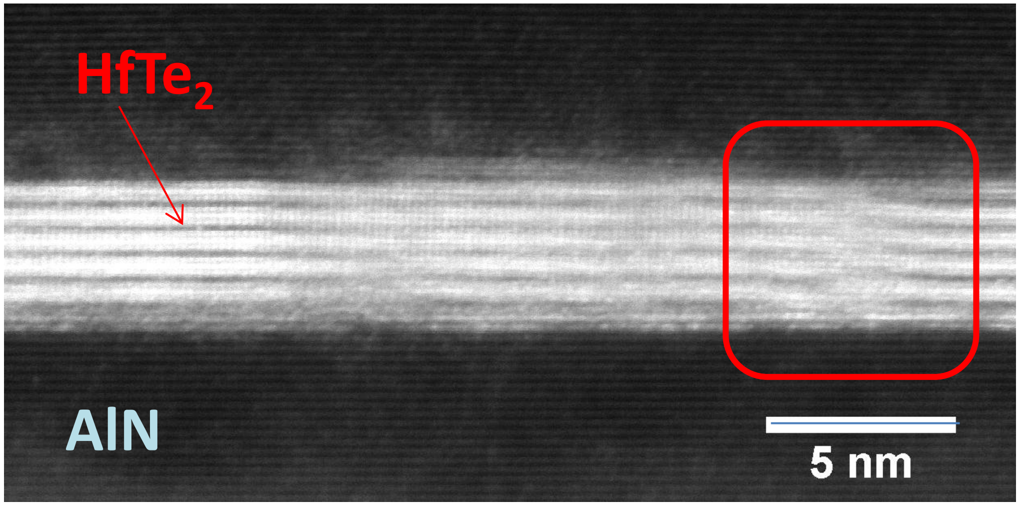
simulation

(1-100) zone



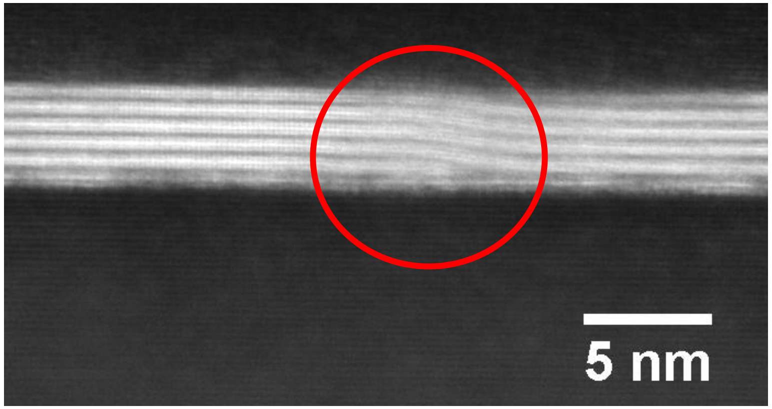
Consistent with 1T-$HfTe_2$

$HfTe_2$ Film Defects and Faults



- Grain boundary causing misalignment of the layers
- No clear correlation of defects with the substrate

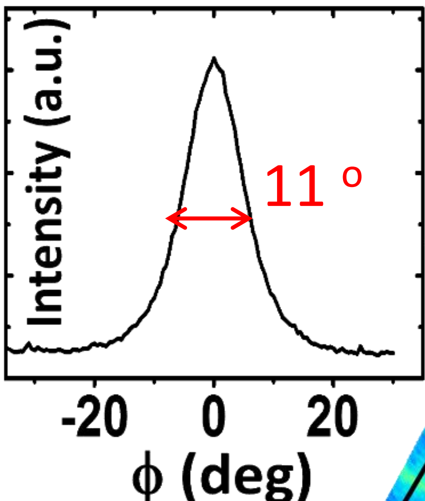
- Layer overlapping
- Shows competing grains during growth

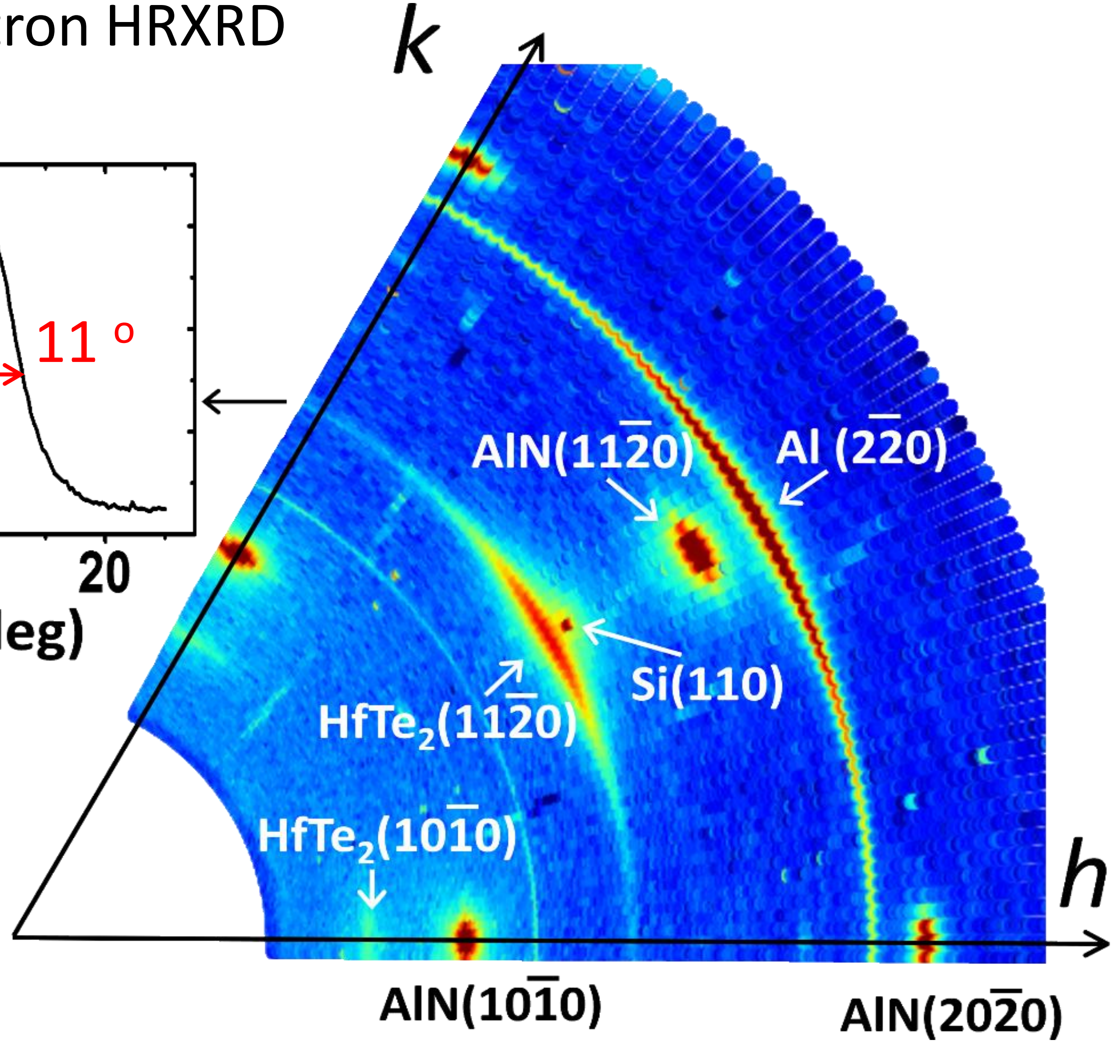


$HfTe_2$ Reciprocal Space Mapping

S. A. Giamini et al., *2D Mater.* **4**, 015001 (2017)

Synchrotron HRXRD
at ESRF



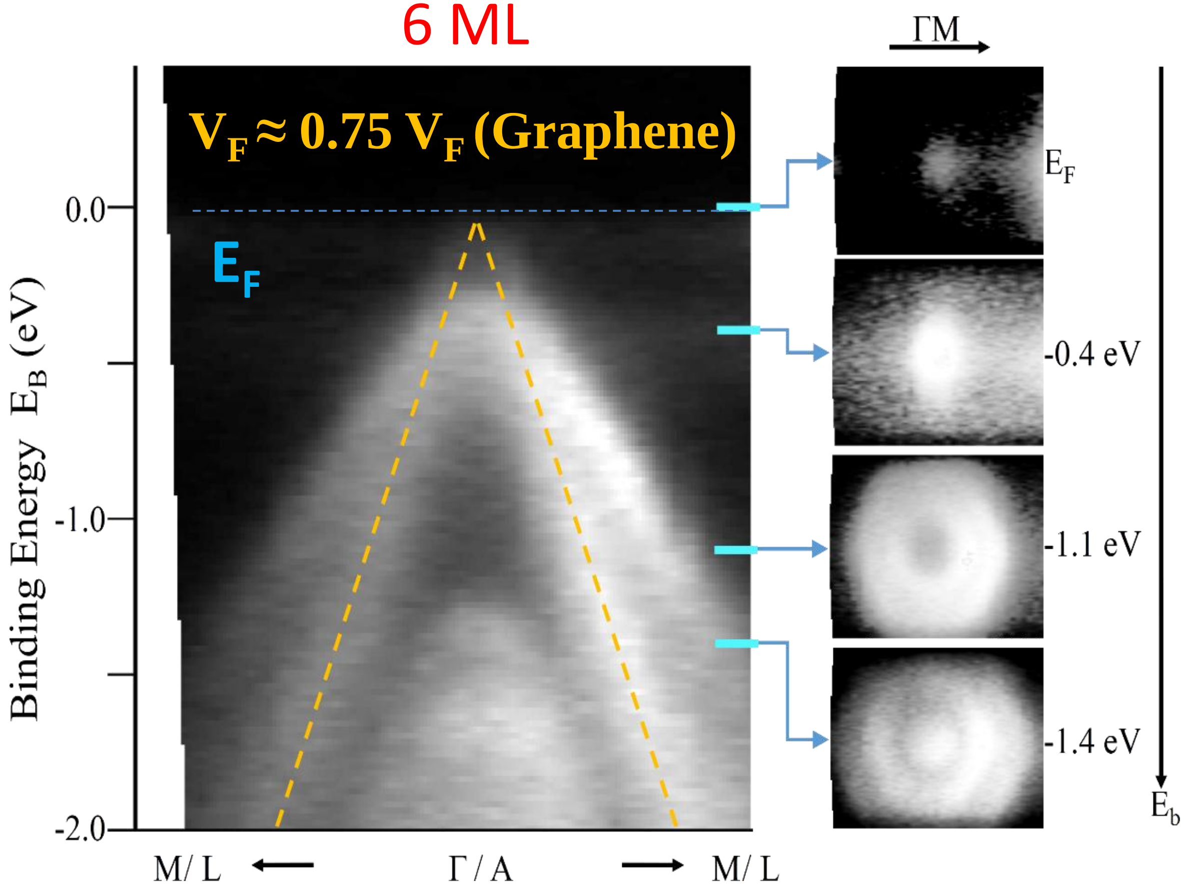


MBE $HfTe_2$ in-situ ARPES “Dirac-like” cone

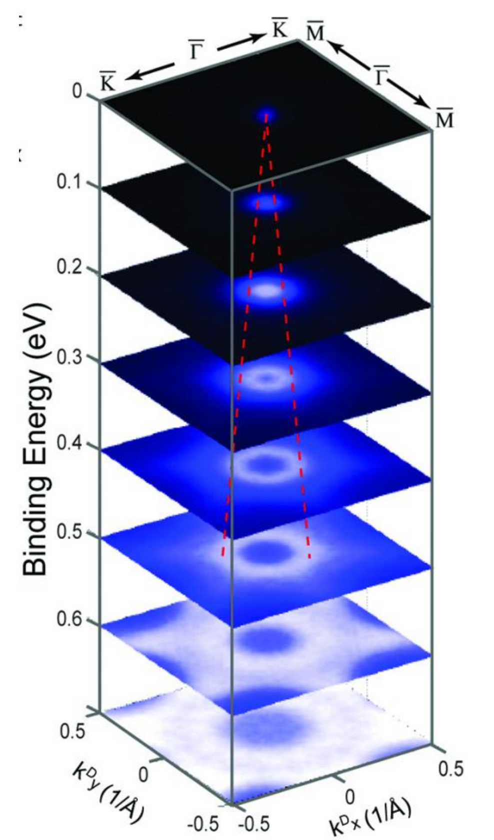
S. A. Giamini et al., *2D Mater.* **4**, 015001 (2017)

Z. K. Liu et al., Science, 343, 864 (14)

6 ML



Na_3Bi topological
3D Dirac semimetal

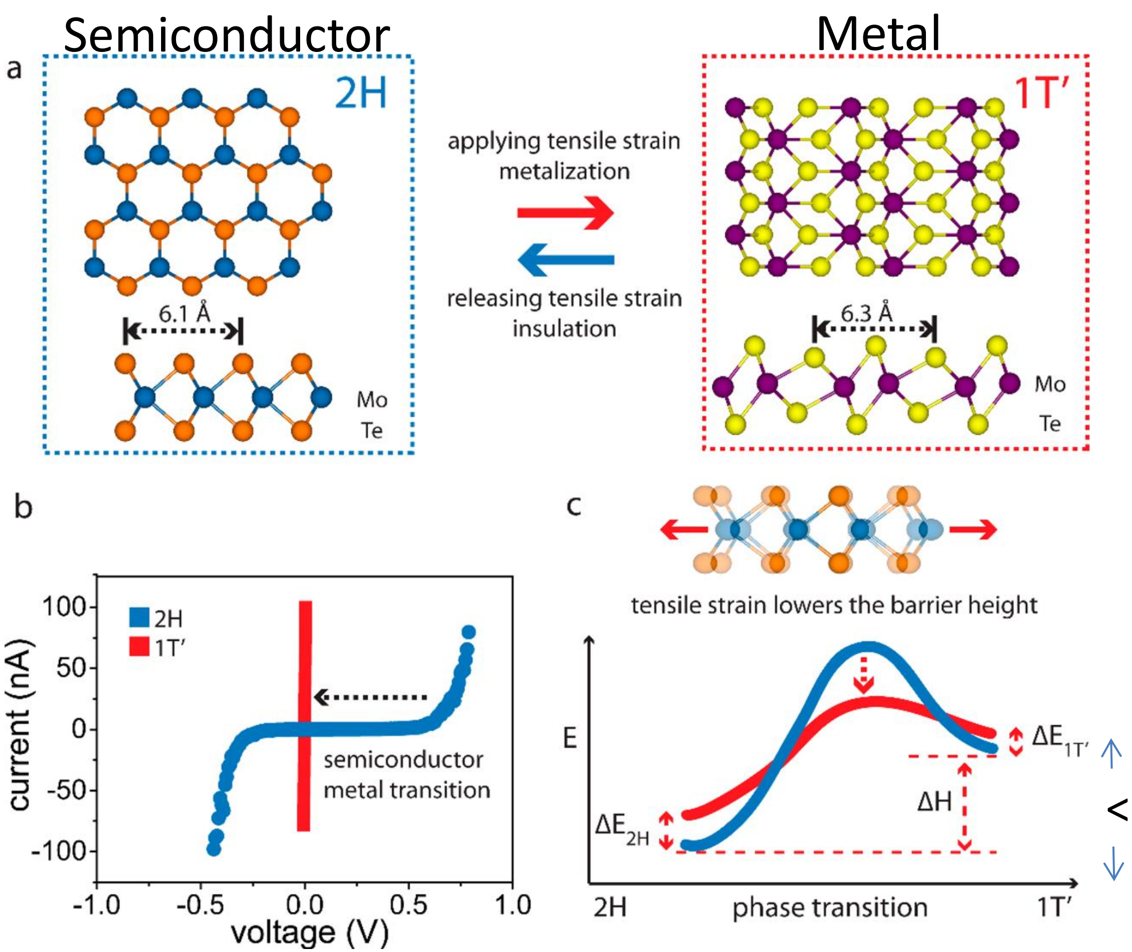


$HfTe_2$ an <u>epitaxial</u> topological Dirac semimetal?

Distorted 1T’ $MoTe_2$

S. Song et al., *Nano Lett*. **16**, 188 (2016)

Strain-induced reversible semiconductor to metal transition (SMT)

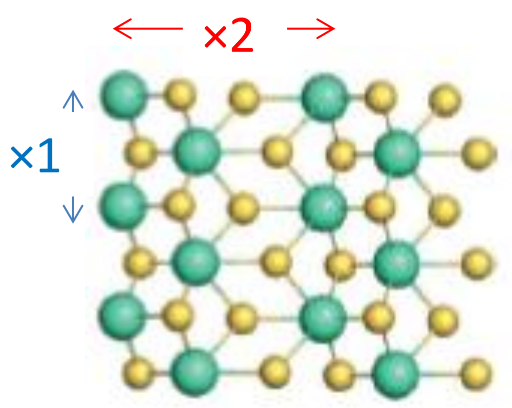


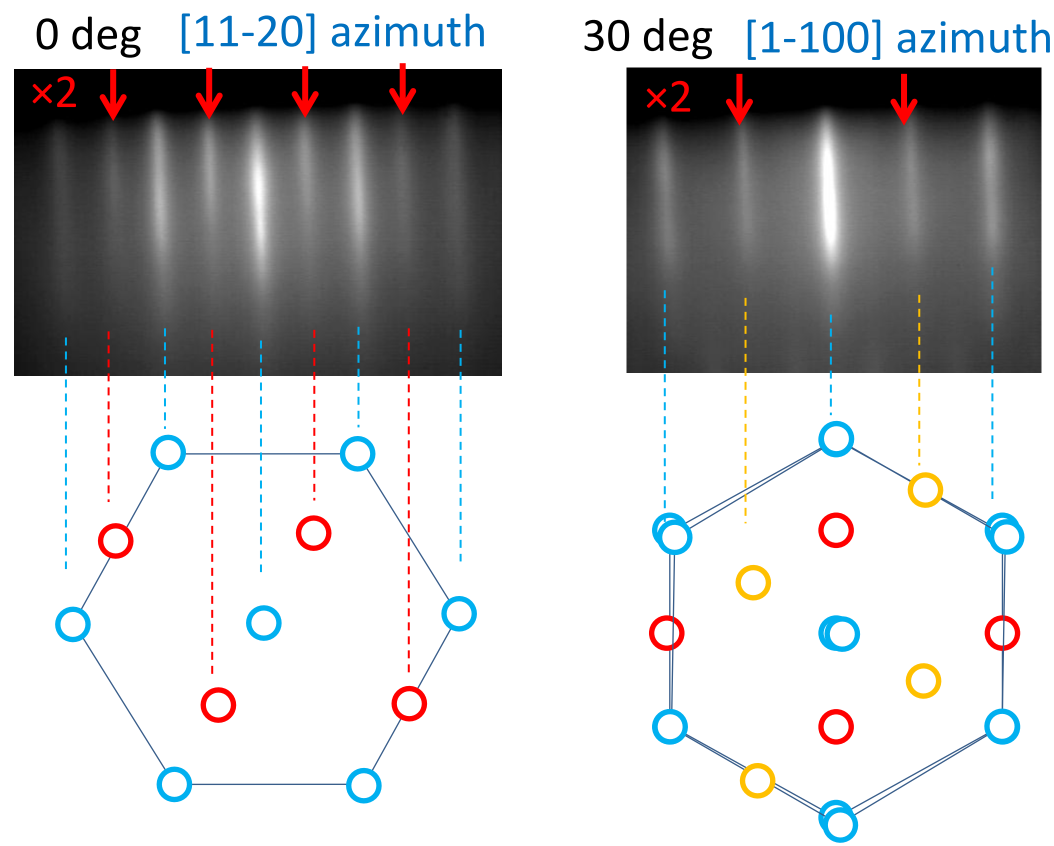
< 0.1 eV

- Non volatile
  phase change memories
- (Steep slope ?) switching
- Can SMT be induced
  by field effect ?
- Can you make
  1T’ $MoTe_2$ epitaxial ?

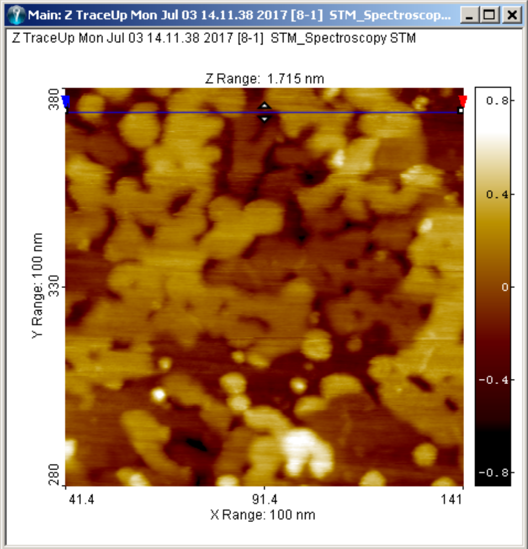
MBE growth of $MoTe_2$ on InAs(111)/Si(111)

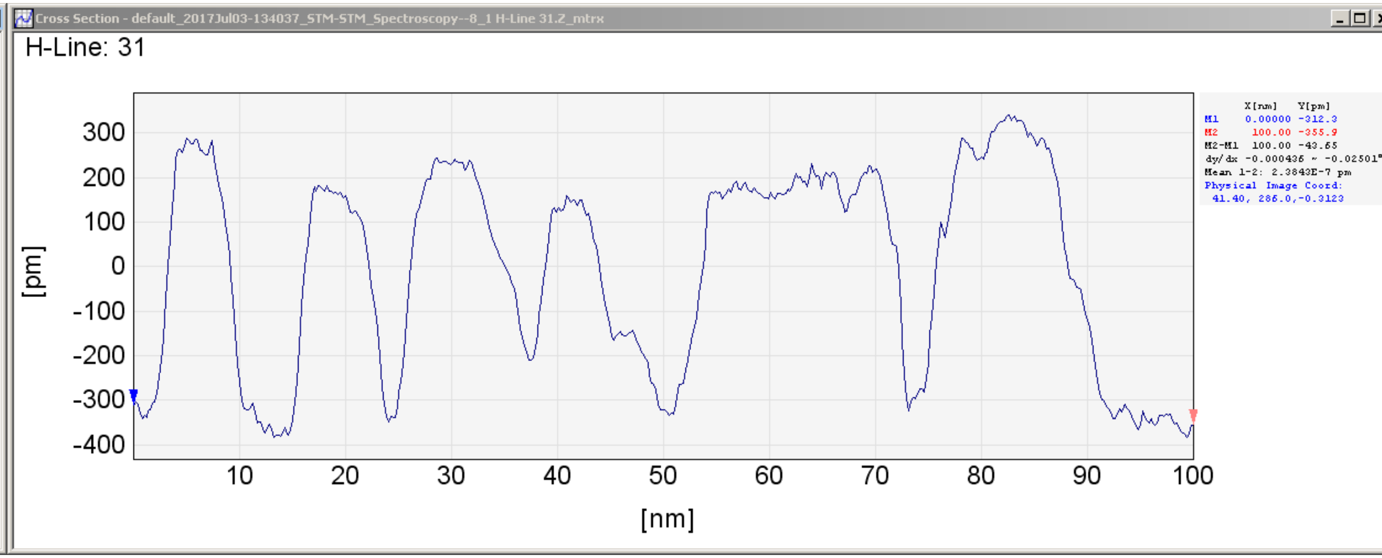
- Interrupted growth at 290 C + Annealing at 400 C , 1h
- 2x2 reconstruction: signature of a distorted T’ phase

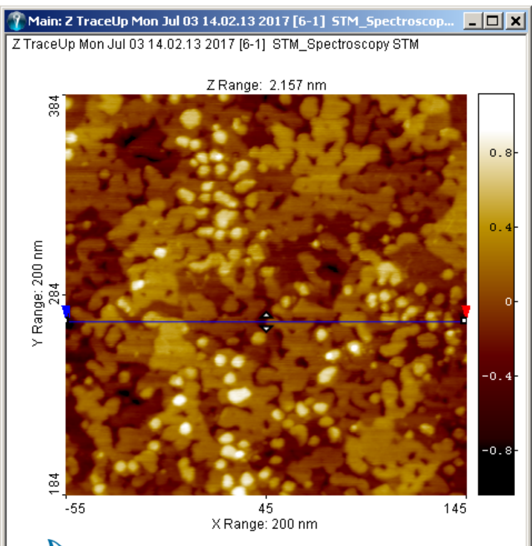


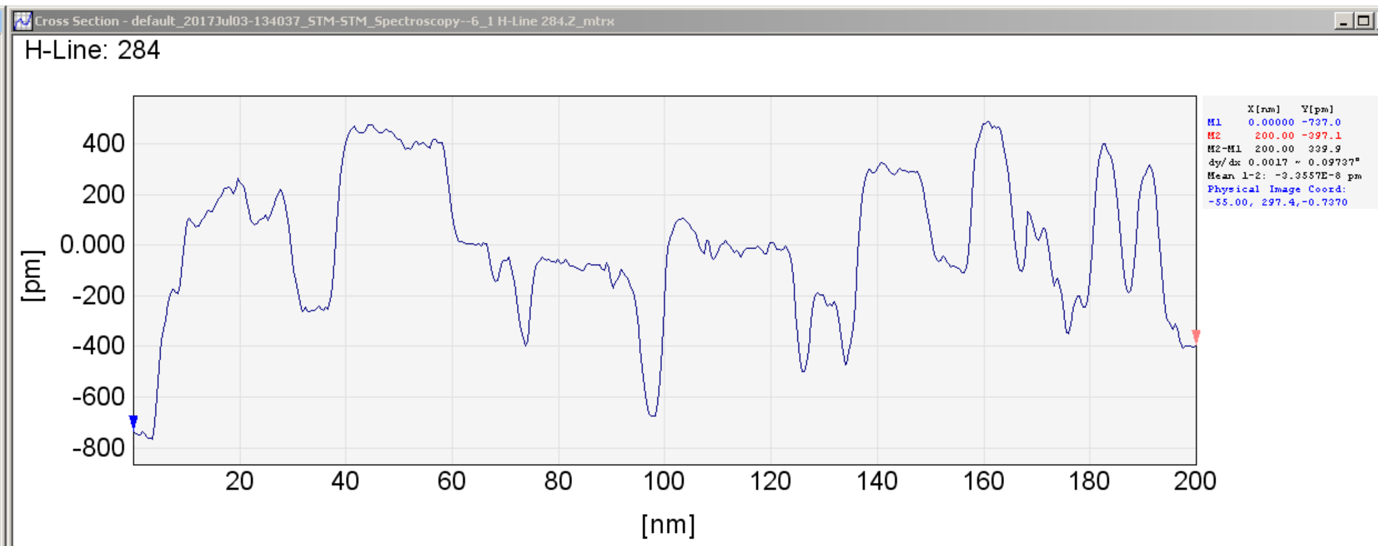


1-2 ML epitaxial $MoTe_2$ –*in situ* STM









Summary

- 2D materials can impact nanoelectronics (scaling, TFET)
- MBE 2D TMDs on AlN (0001) substrates:
  Uniform growth /no heteroepitaxy defects/Large mosaicity
- MBE $SnSe_2/WSe_2$ vdW heterostructures
  Ideal nearly broken gap band alignments for 2D TFETs
- MBE TMDs on InAs (111): Much improved epitaxy
- MBE HfTe2 and ZrTe2 : Dirac like cones at the zone center.
  Candidates for epitaxial Dirac semimetals
- MBE Distorted 1T' $MoTe_2$ can be grown on InAs; stable at RT