MSE-649 Seminar

Assembly Techniques to Fabricate 2D Heterostructures

Presenters:

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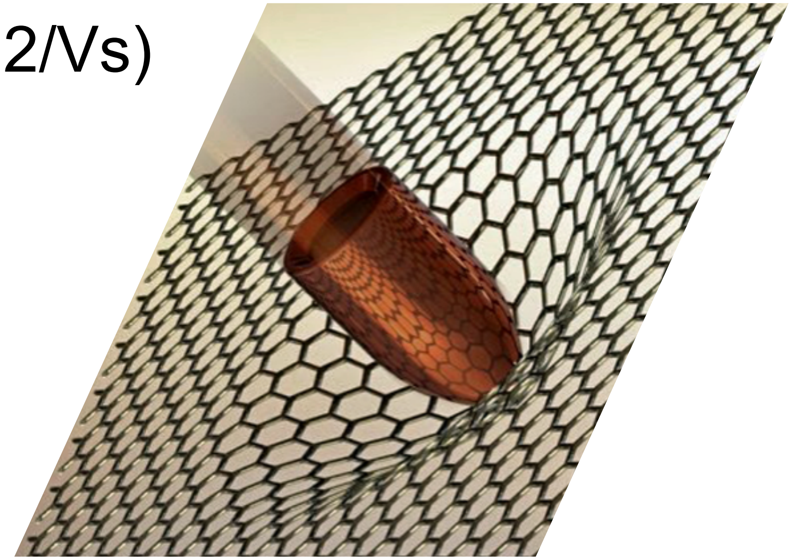
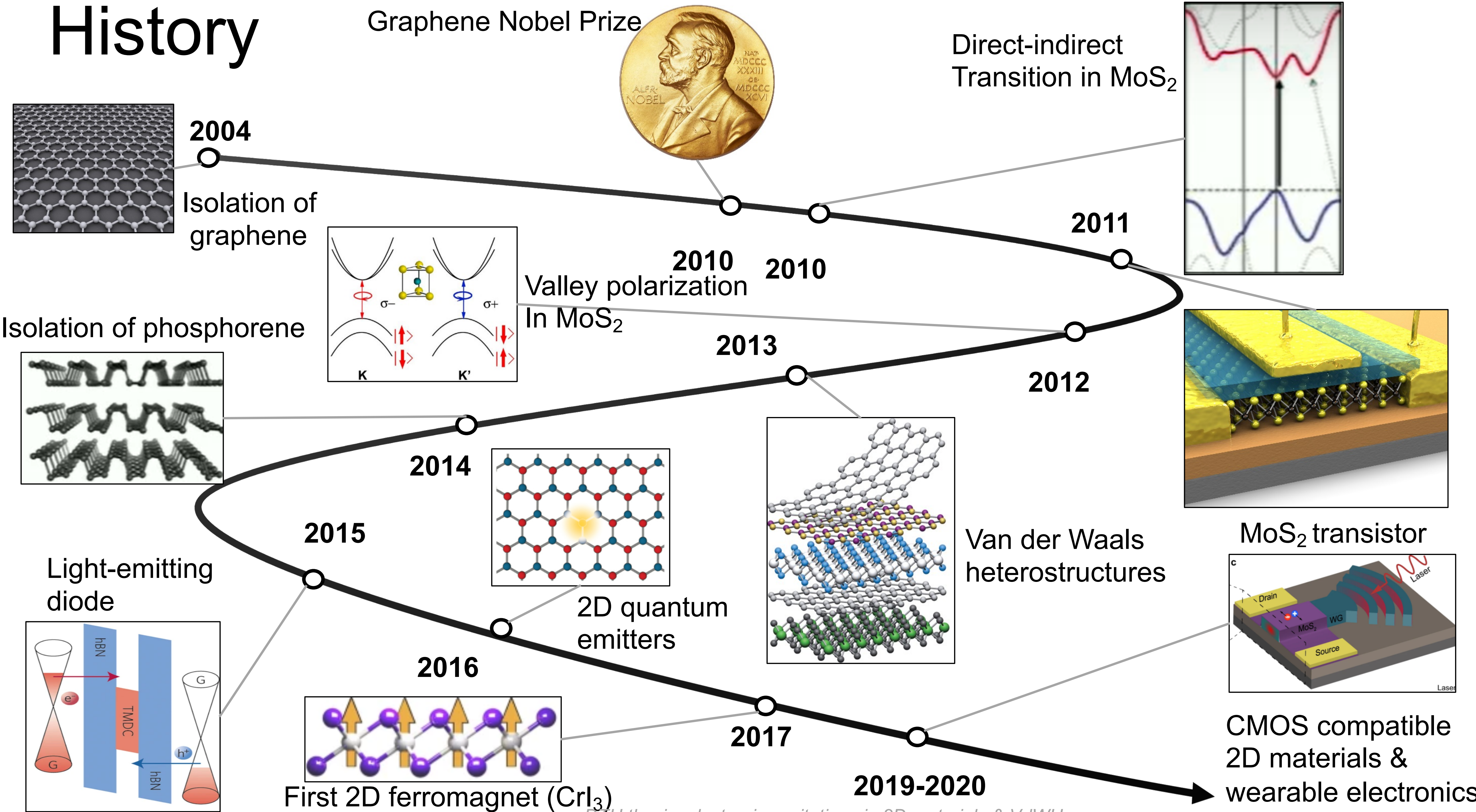
What is a 2D material?

- Graphene as an example:
  - Best electrical conductor (RT mobility 100.000 cm2/Vs)
  - Strongest material (Stength 130 GPa)
  - Exceptional heat conductor (2000 W/mK)
  - Almost transparent (absorbance 2%)
  - Light weight and flexible (Stretchability (20%))
  - Unique physics
    - Electrons behave as massless particles
    - Klein tunneling
    - Half-integer quantum Hall effect



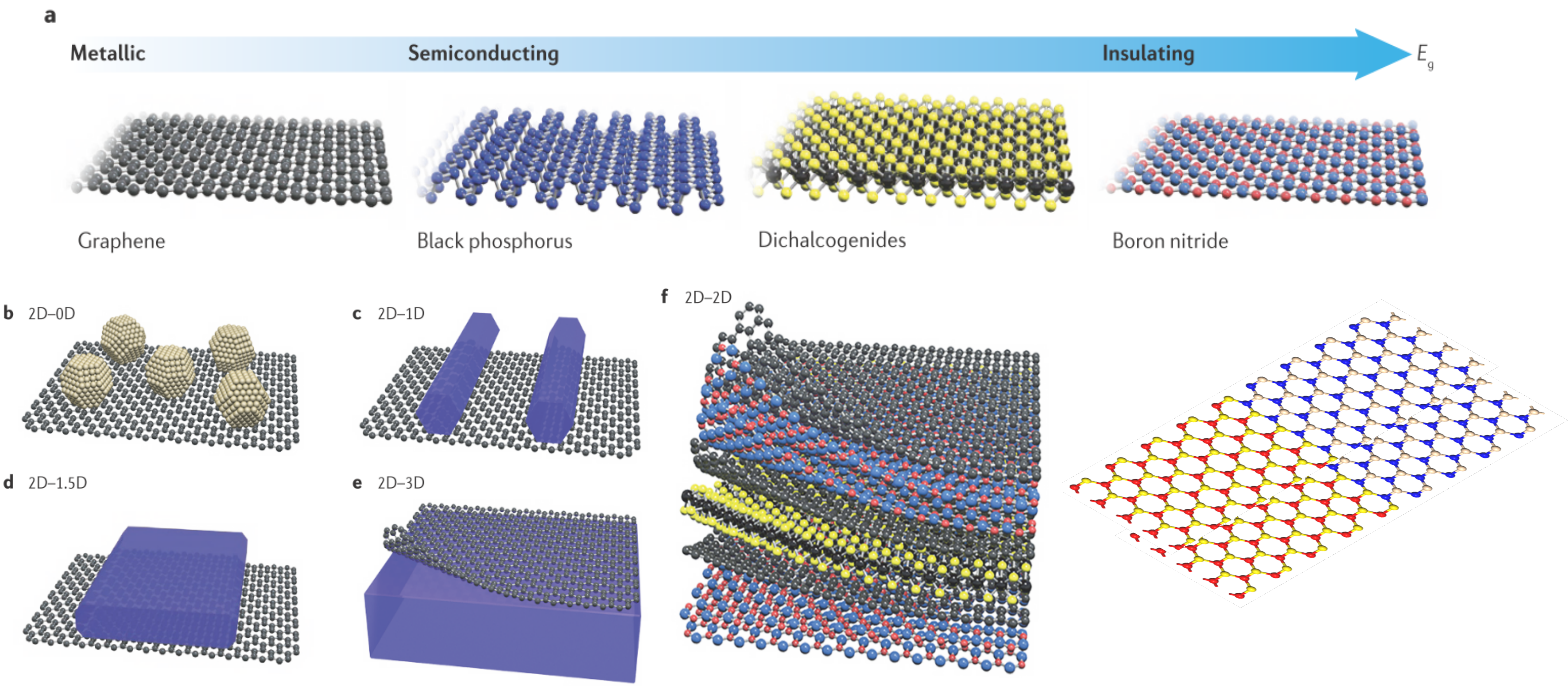
History



Graphene Nobel Prize
2004
Isolation of graphene
2010
2010
Direct-indirect Transition in MoS$_2$
2011
Valley polarization In MoS$_2$
2012
MoS$_2$ transistor
2013
Van der Waals heterostructures
Isolation of phosphorene
2014
2D quantum emitters
2015
Light-emitting diode
hBN
TMDC
hBN
G
G
2016
2017
First 2D ferromagnet (CrI$_3$)
2019-2020
CMOS compatible 2D materials & wearable electronics
Drain
Source
MoS$_2$
WG
Laser

2DLM and van der Waals heterostructures

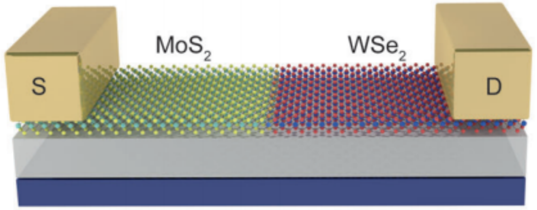
- 2d material types >1000

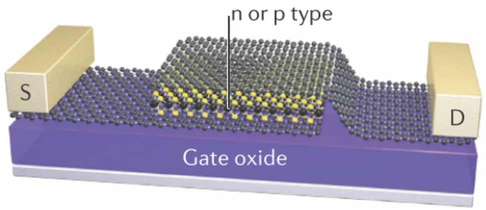


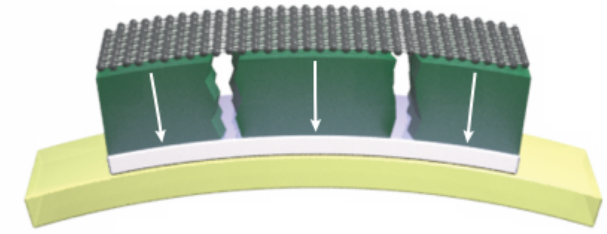
Van der Waals heterostructures and devices. Nature Reviews Materials, 2016.

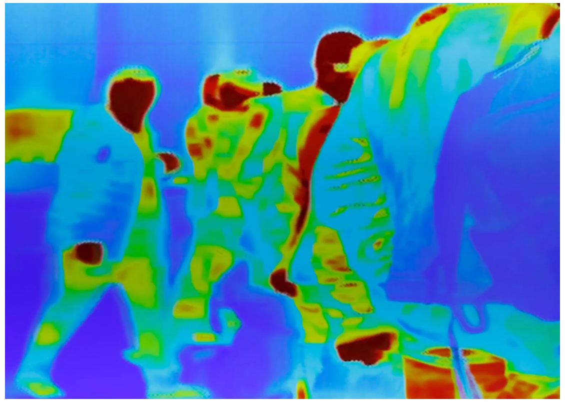
Motivation and challenges

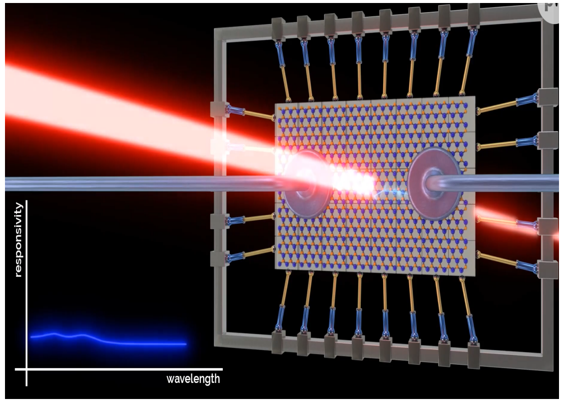
- Control
  - Generation
  - Transportation
  - Recombination
- Unique electronic and photo-electronic devices
  - Ultrathin
  - High power
  - Flexible devices
  - Straintronics
- Challenge
  - Scalable synthesis







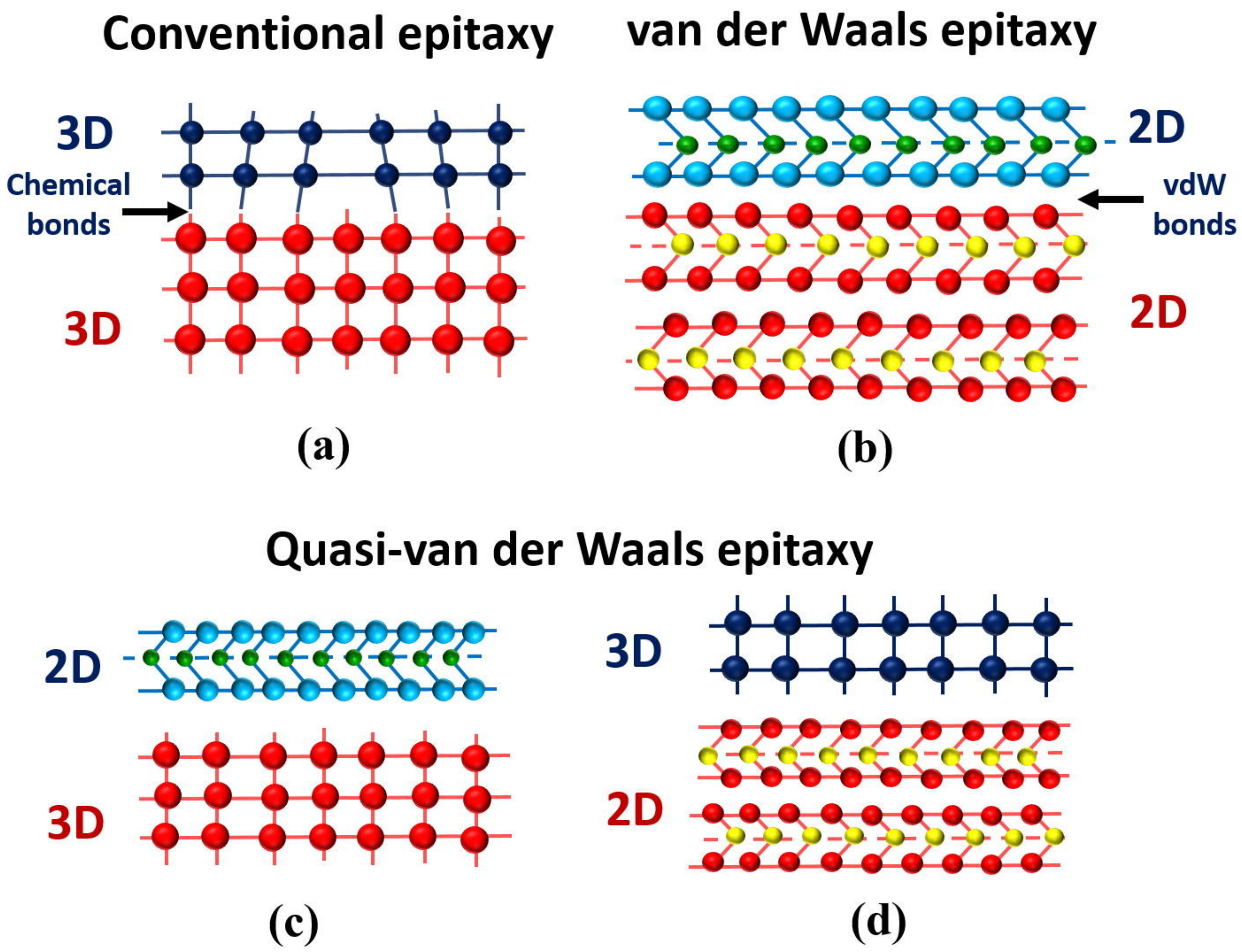




"Atomically thin p–n junctions based on two-dimensional materials." Chemical Society Reviews, 2018

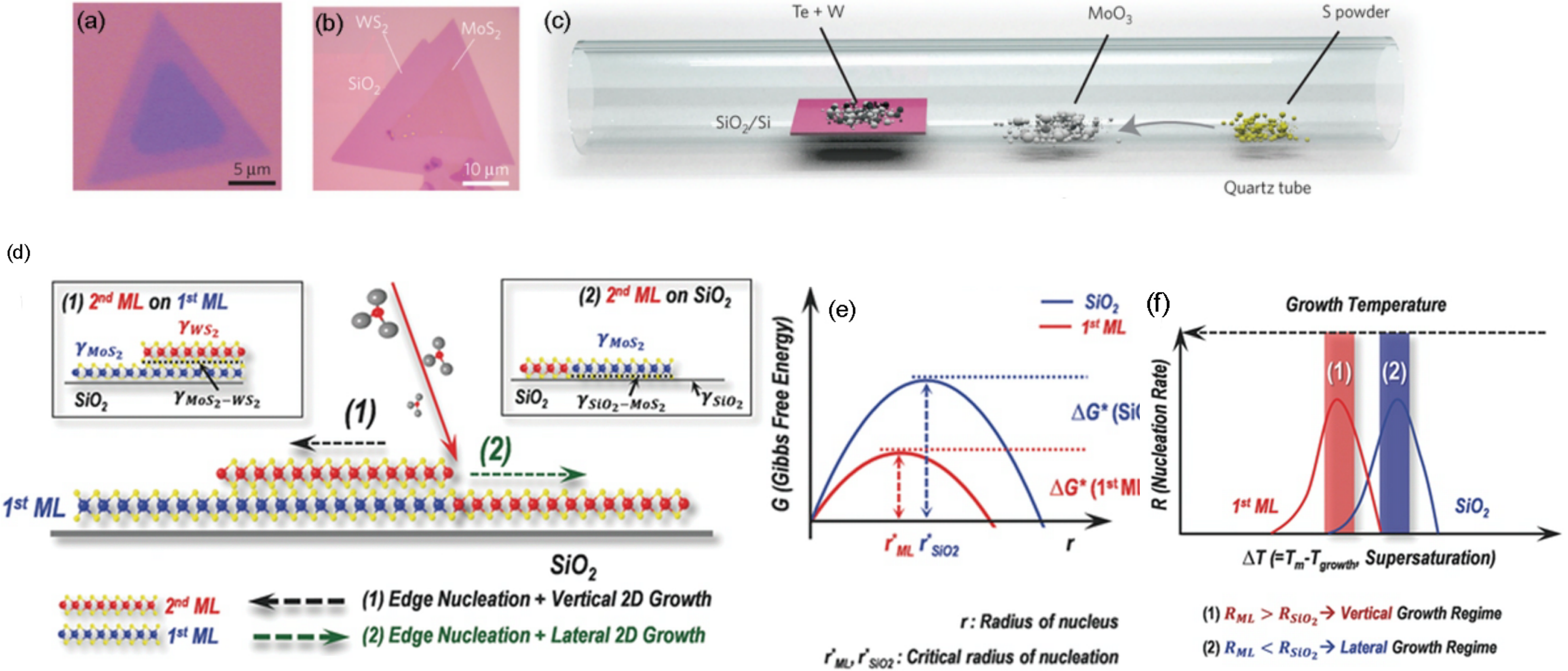
Conventional vs van der Waals epitaxy

- Conventional
  - chemical bonds determine
    - lattice matching
    - Orientation
- vdW
  - Weak intermolecular/interionic coulombic interactions
- QvdW
  - 2d onto 3D



MICAtronics: A new platform for flexible X-tronics. FlatChem, 2017.

Lateral and Vertical heterostructures

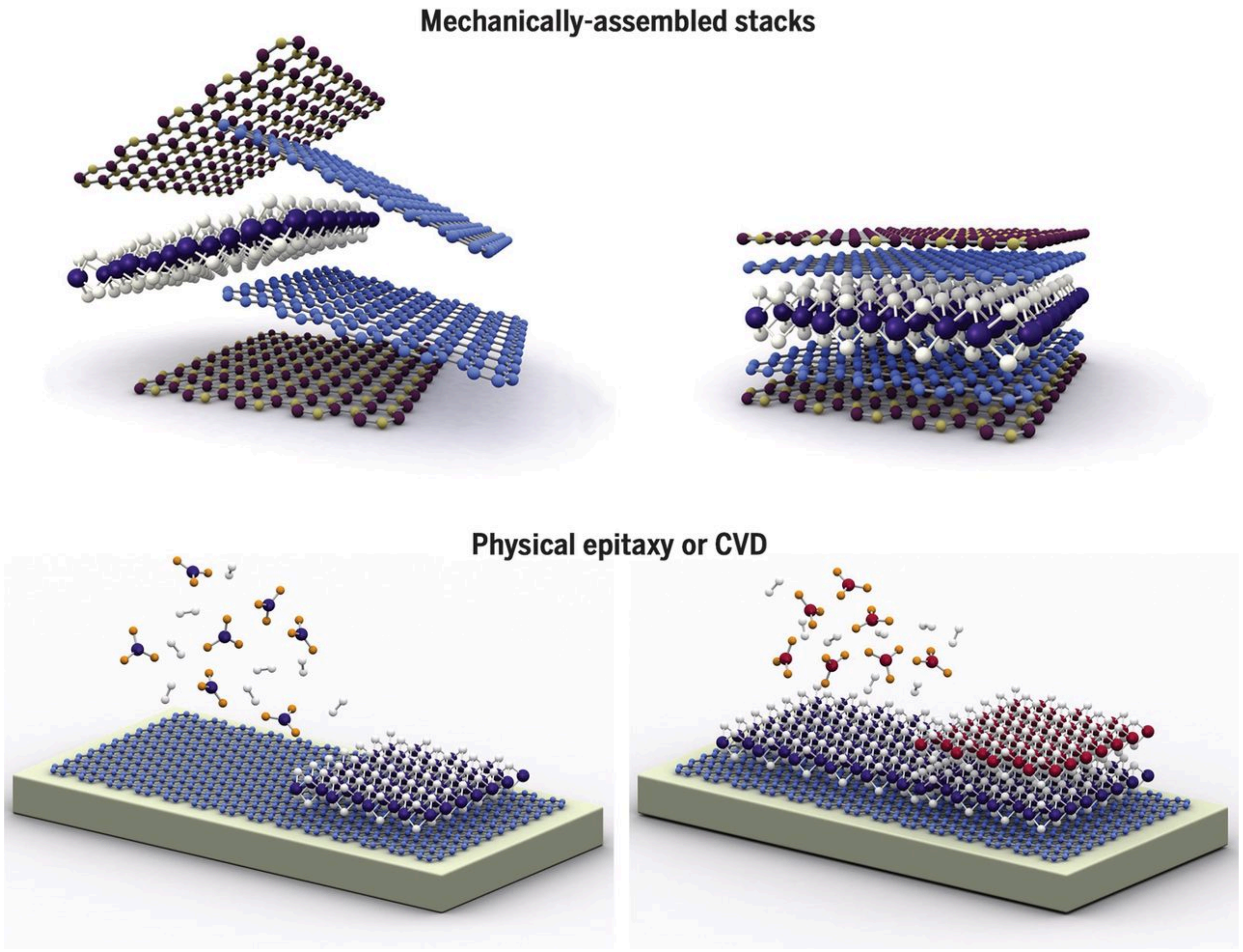


SCIENCE CHINA Physics, Mechanics & Astronomy, 2018.

Assembly Techniques

Assembly of 2D materials and heterostructures

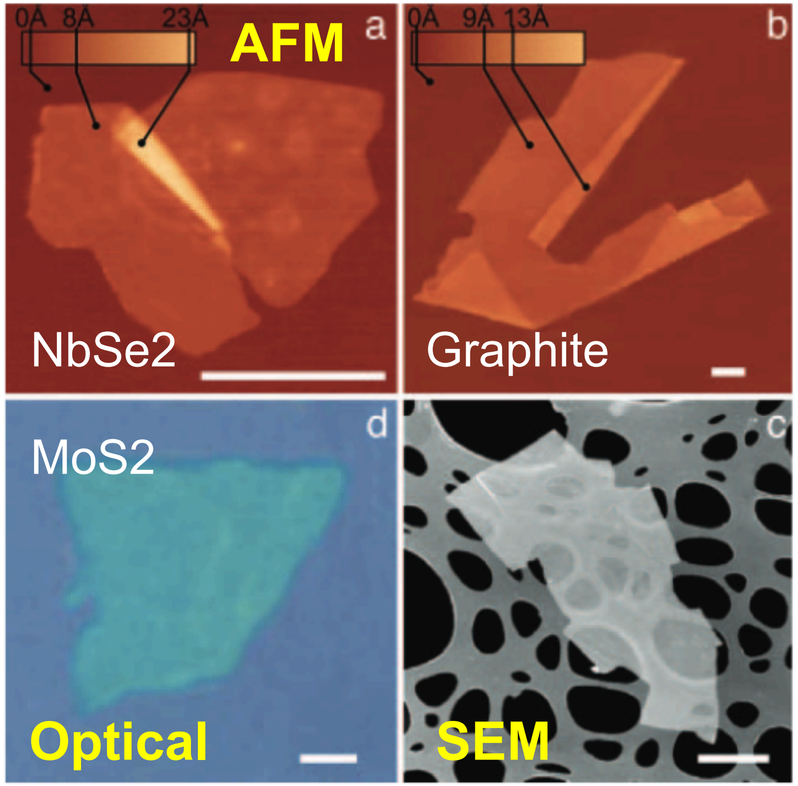
- Various assembly techniques
- Their Comparison
- Stacking with a twist



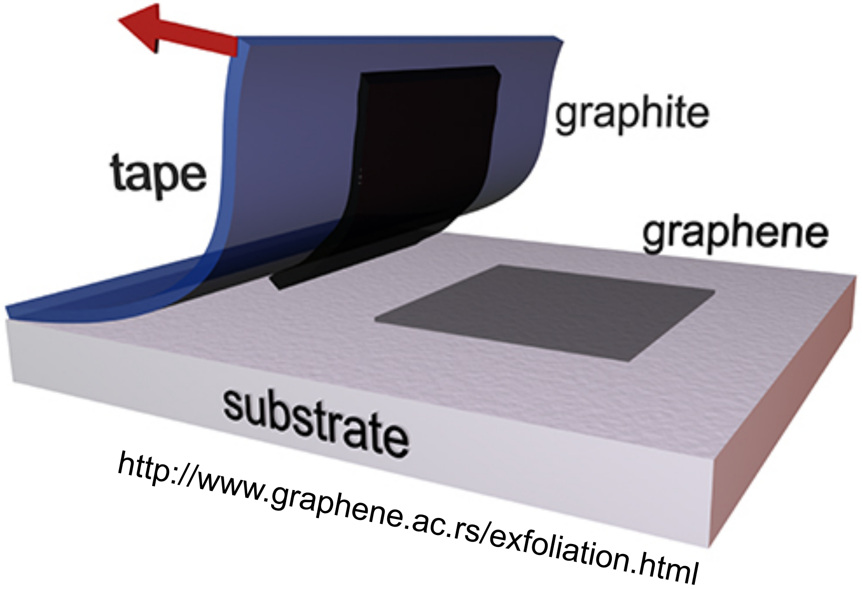
K. S. Novoselov *et. al.,* Science (2016), 353, 6298

Mechanical exfoliation

- *First demonstration of graphene in 2004
- Yields highest quality material
- Scalability is an issue (quantity and size of flakes)
- Nevertheless, fundamental studies



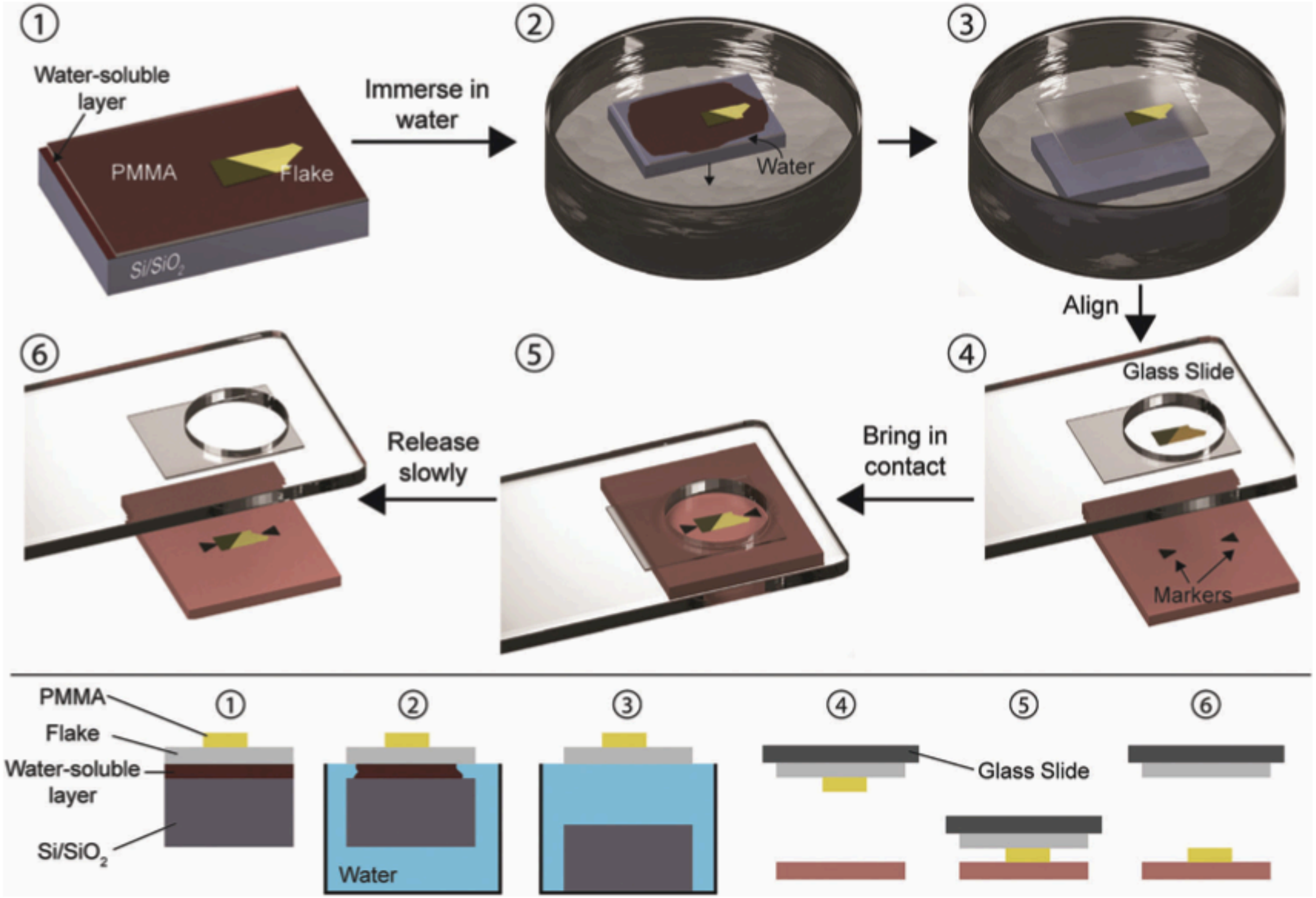
K. S. Novoselov *et. al.*, PNAS (2005), 102 (30) 10451-10453



Another example:
Micromechanical cleavage: A fresh surface of layered crystal rubbed against another solid surface

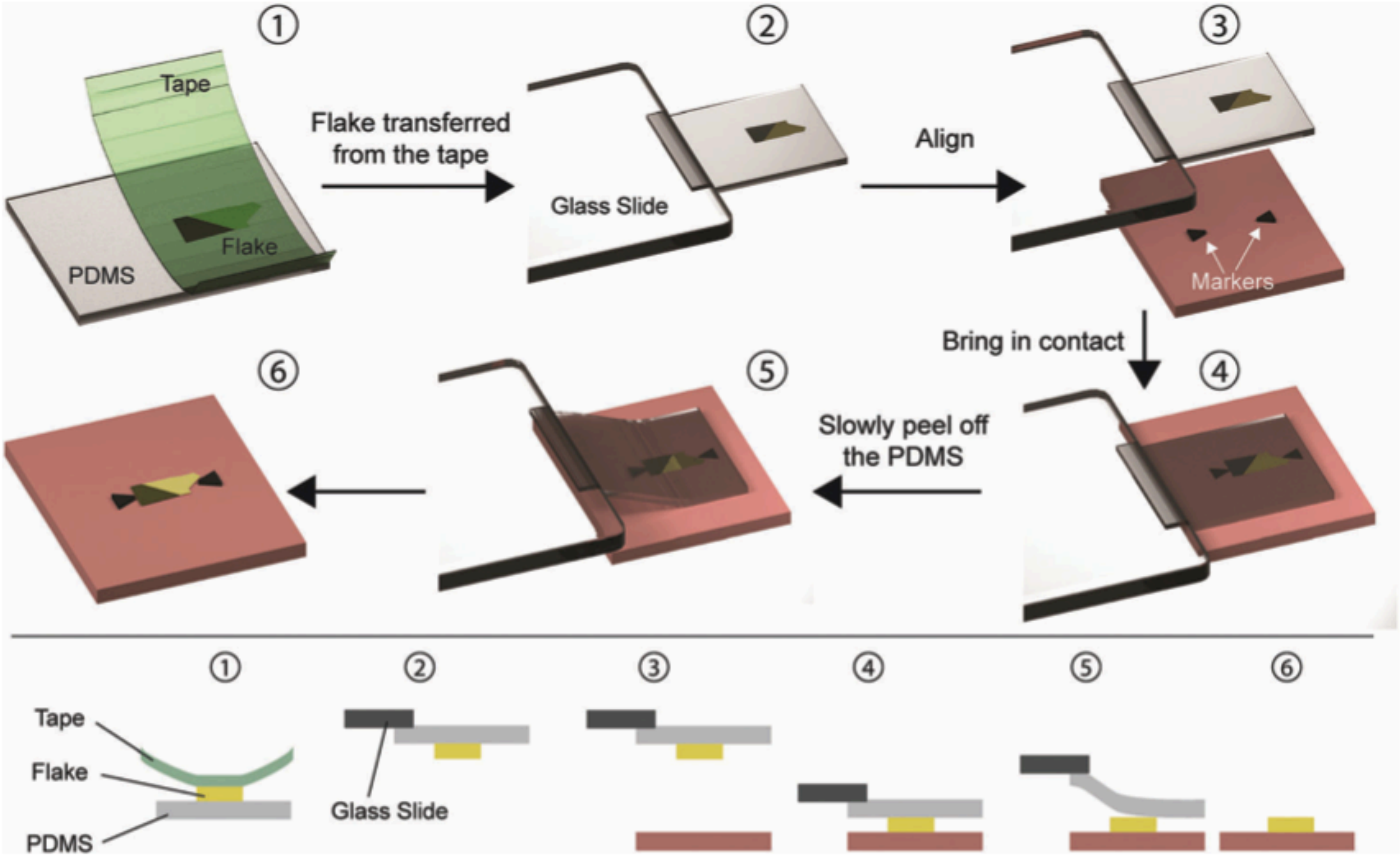
*K. S. Novoselov *et. al. Science* (2004), 666-669

PMMA carrying layer transfer



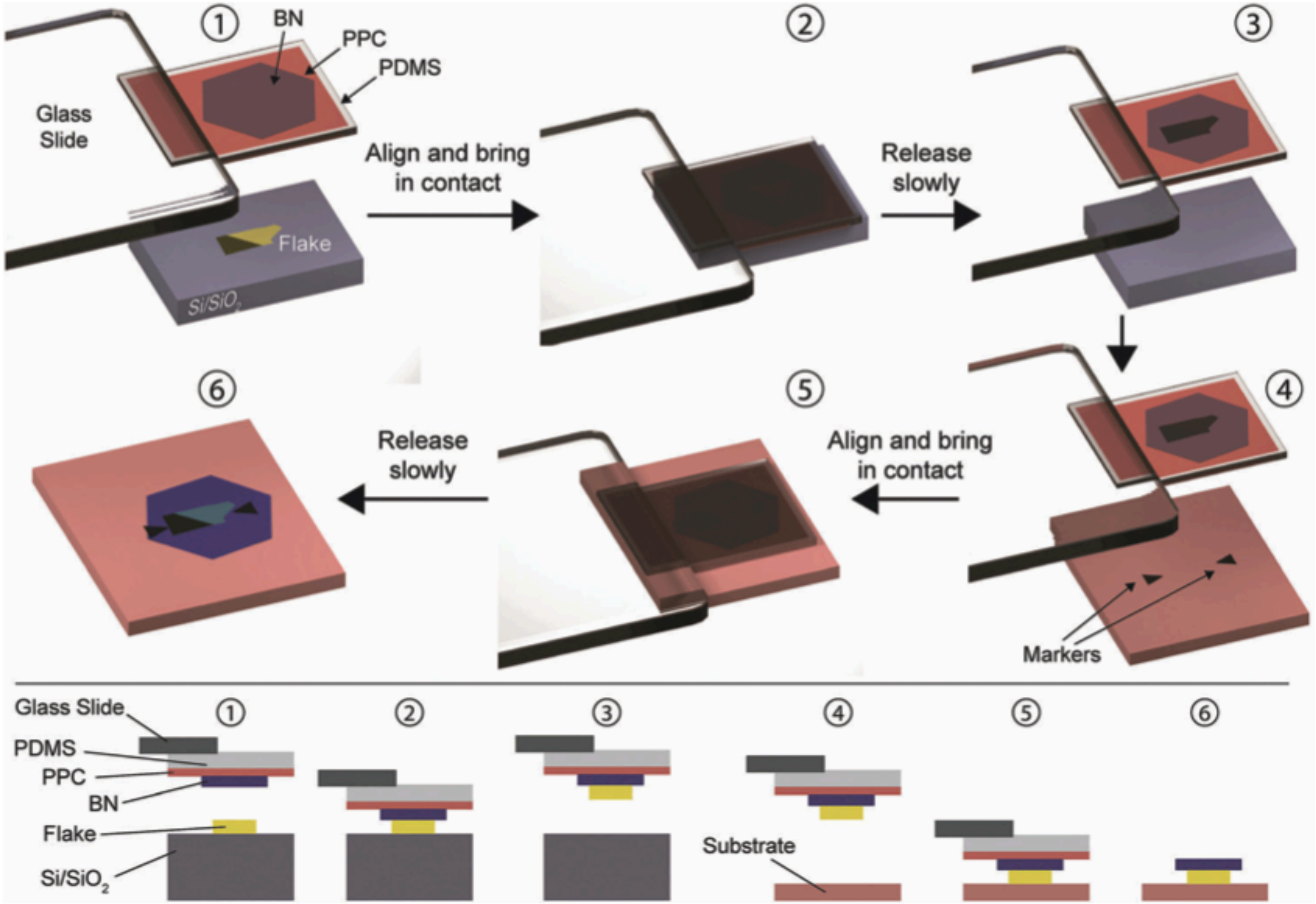
C. R. Dean *et. al.* Nat. Nanotechnol., 2010, 5, 722–726.

PDMS deterministic transfer method



A. Castellanos-Gomez *et. al.* 2D Mater., 2014, 1, 11002.

van der Waals pick-up method



L. Wang *et. al.* Science, 2013, 342, 614–617.

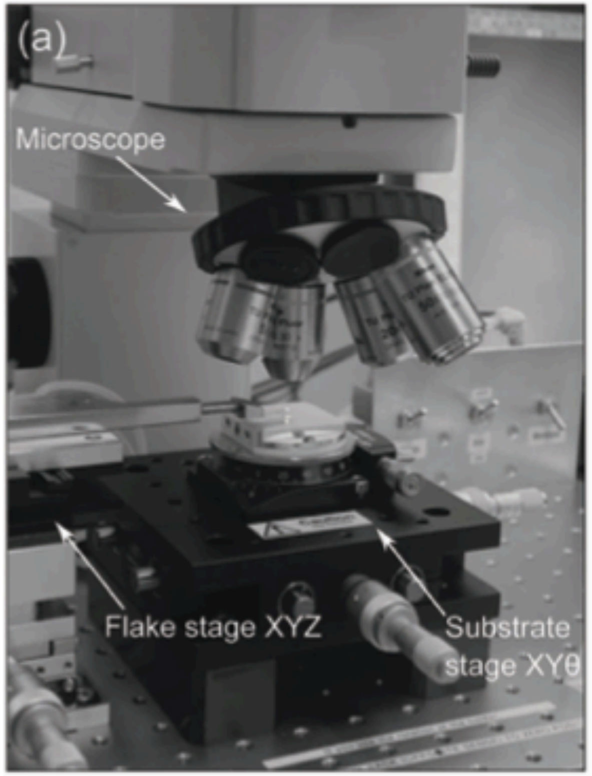
Comparison of various techniques

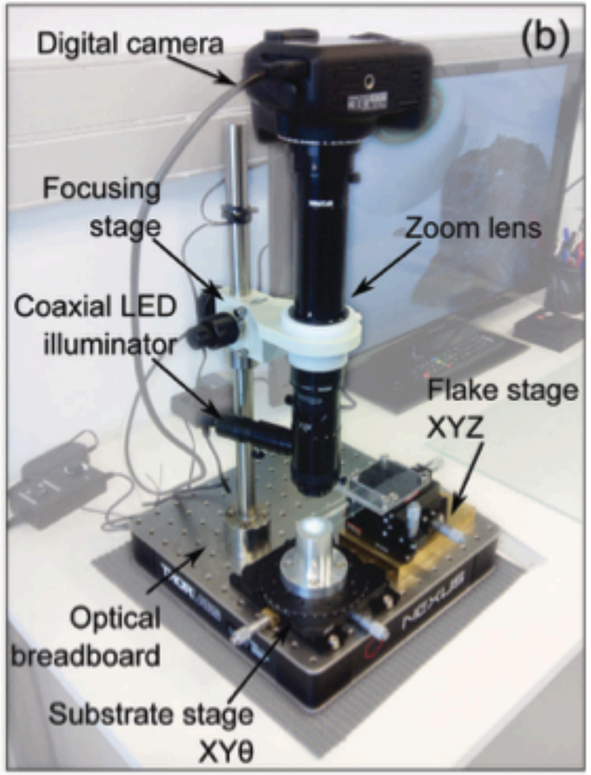
Table 1 Comparison between the different deterministic placement methods. Qualitative comparison in terms of cleanness, easiness and speed between the different deterministic placement methods described in the text. Comments about their main drawbacks are also included in the table

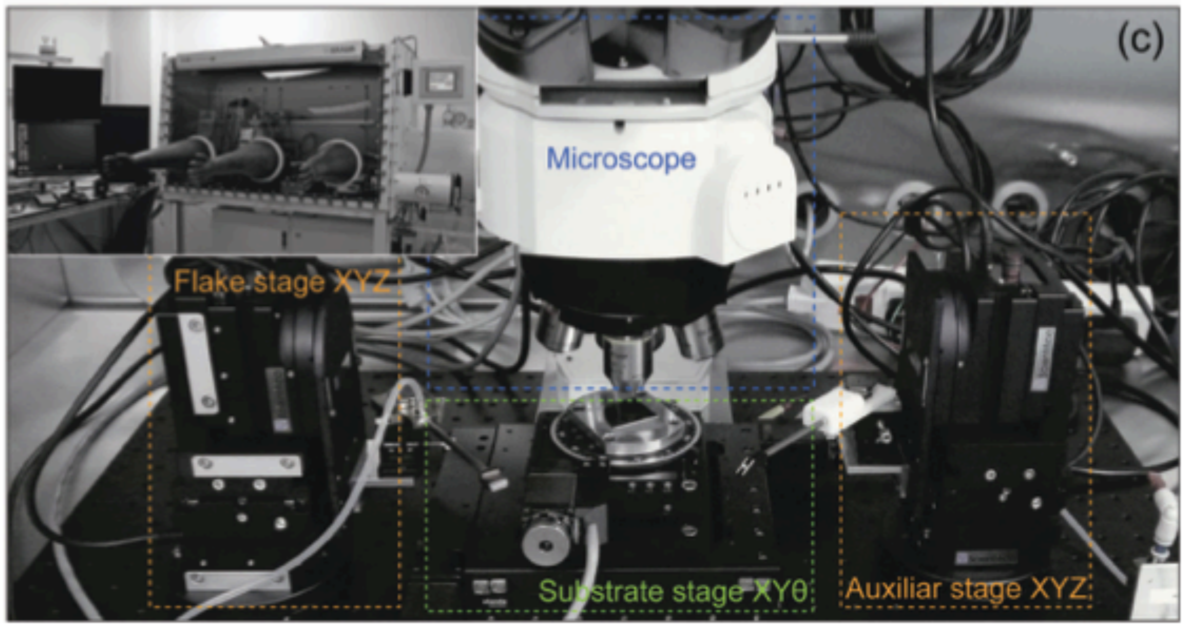
Method	Cleanness	Easiness	Speed	Notes
PMMA carrier layer	***	***	***	Spin-coating is needed, direct contact with polymer, it can transfer large-area flakes.
Elvacite sacrificial layer	*	***	***	Capillary forces, spin-coating is needed, direct contact with polymer.
Wedging	*	**	***	Capillary forces, dip-coating is needed, difficult alignment, direct contact with polymer, transfer over curved or uneven surfaces is possible.
PDMS dry transfer	***	*****	*****	Direct contact with polymer.
van der Waals pick-up	*****	*	**	Spin-coating is needed, several steps involved, only works to transfer heterostructures, direct contact with the polymer only for the topmost layer.

Frisenda R. *et. al.* Chem.Soc.Rev.,2018,47,53--68

Transfer setups in the lab



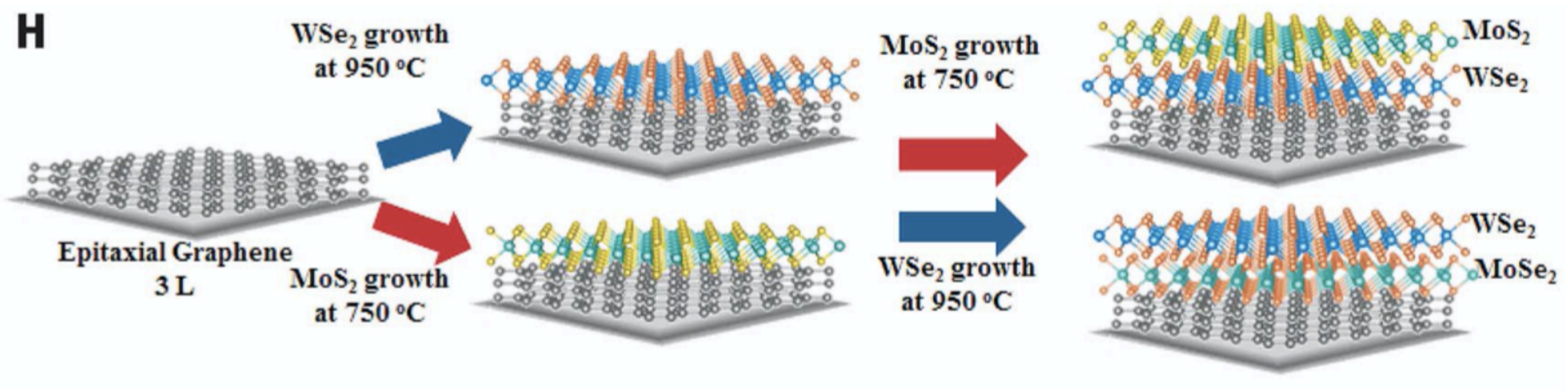




Frisenda R. *et. al.* Chem.Soc.Rev.,2018,47,53--68

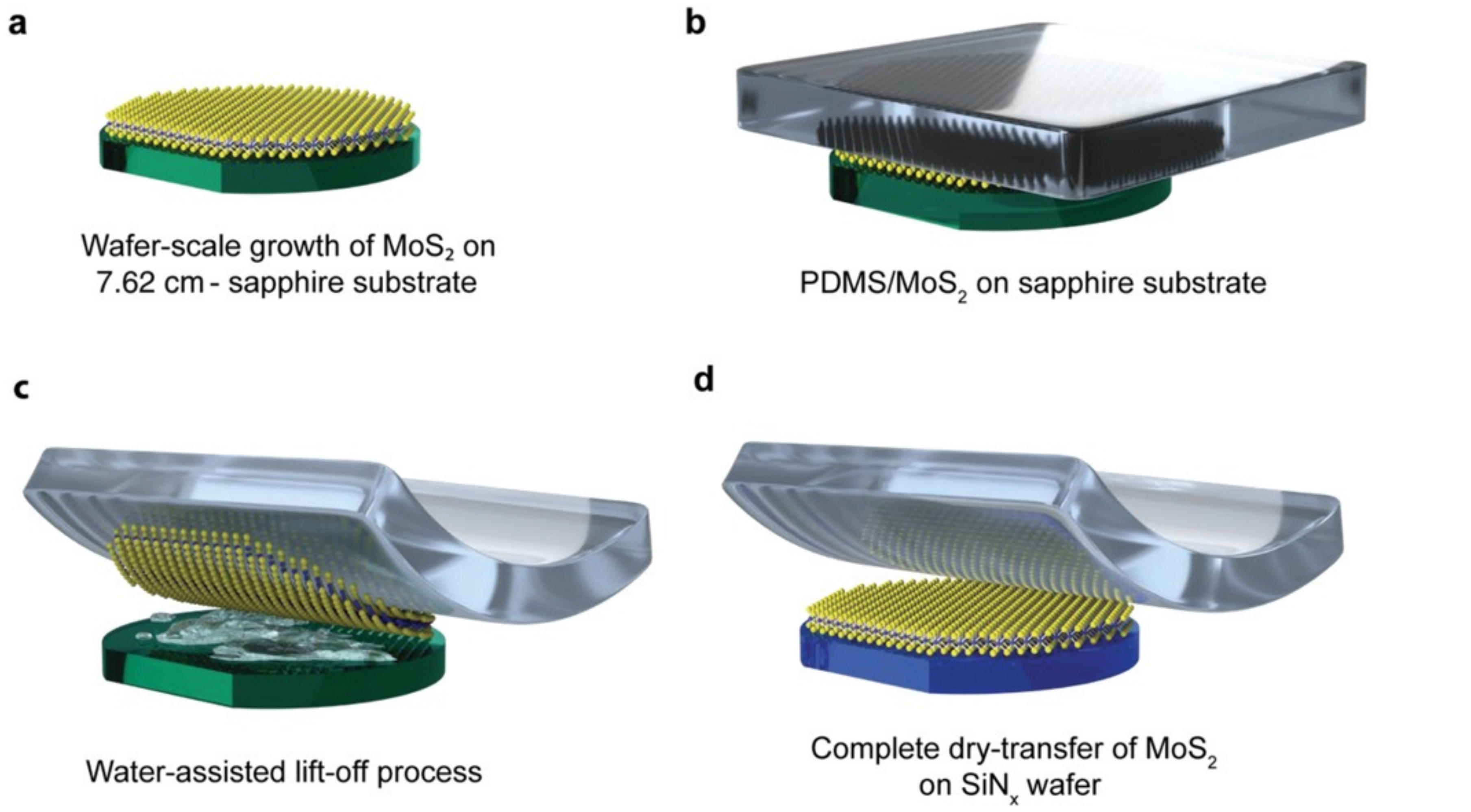
CVD growth

- Growth of individual layers
- Different deposition conditions for different layers



K. S. Novoselov *et. al.*, Science (2016), 353, 6298

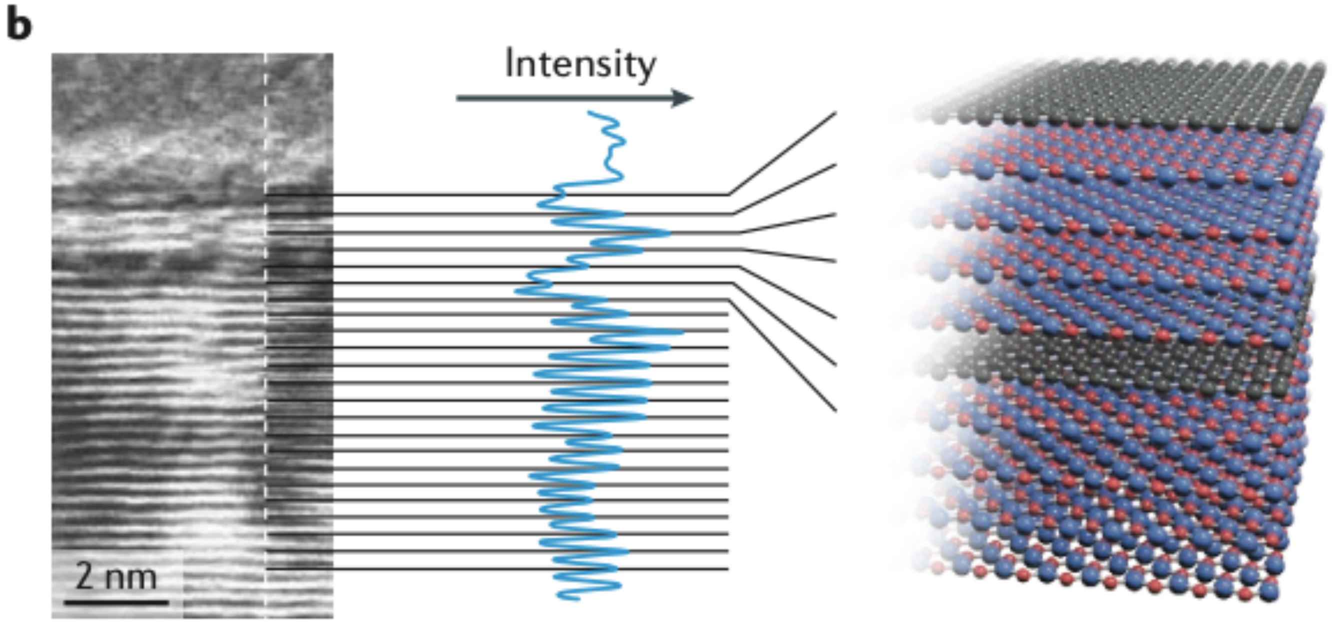
Example of a wafer-scale technique



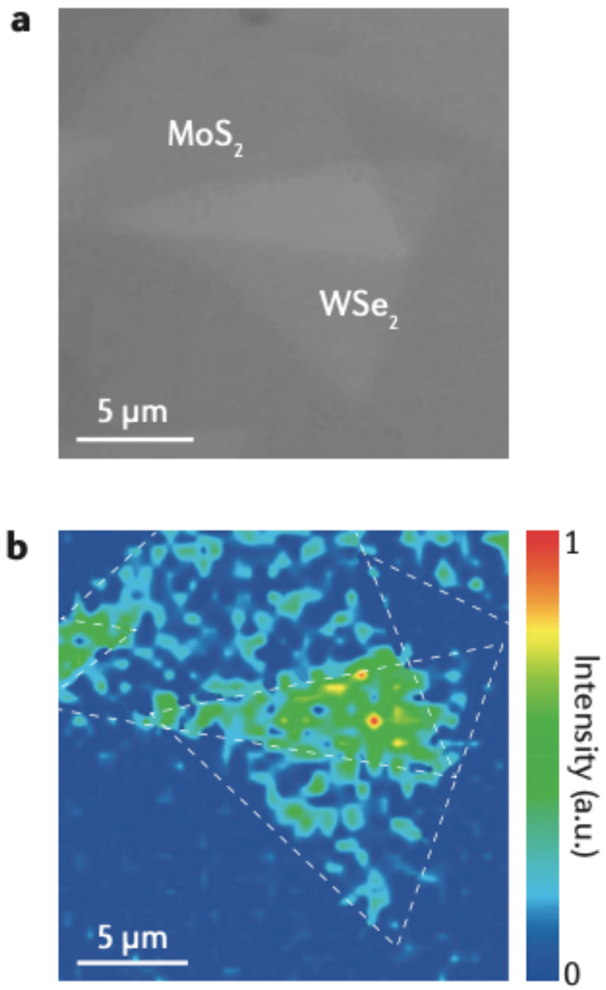
Thakur, M. *et. al.*, *Small Methods* 2020, 2000072.

Example heterostructure: Multilayer stacks

BN-graphene stacks



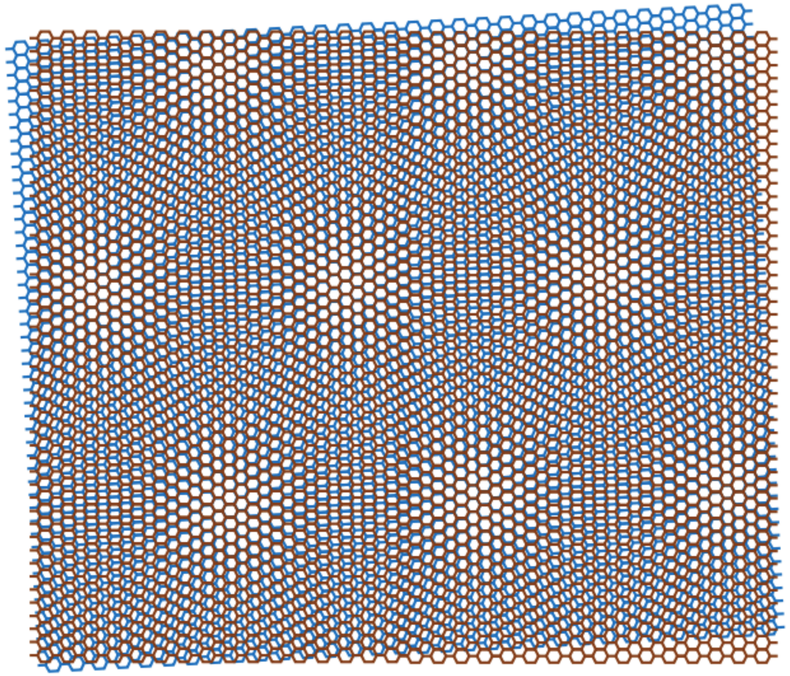
MoS_2-WSe_2

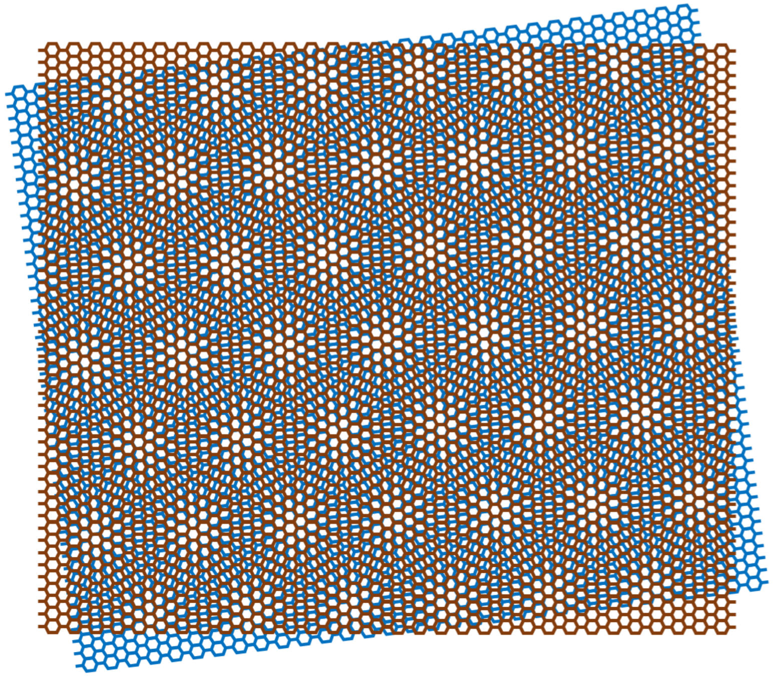


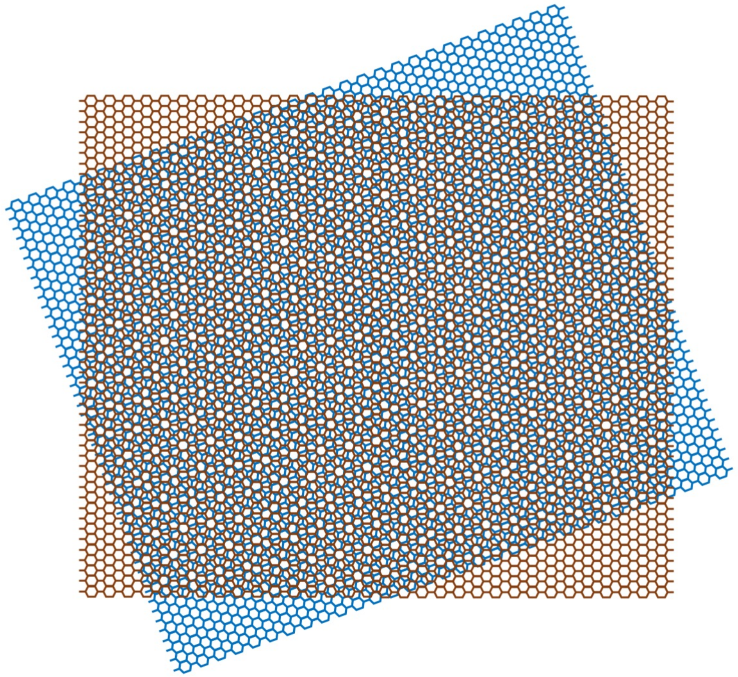
Coupling of A_{1g} Raman mode

Liu, Y., Weiss, N., Duan, X. *et al. Nat Rev Mater* **1,** 16042 (2016).

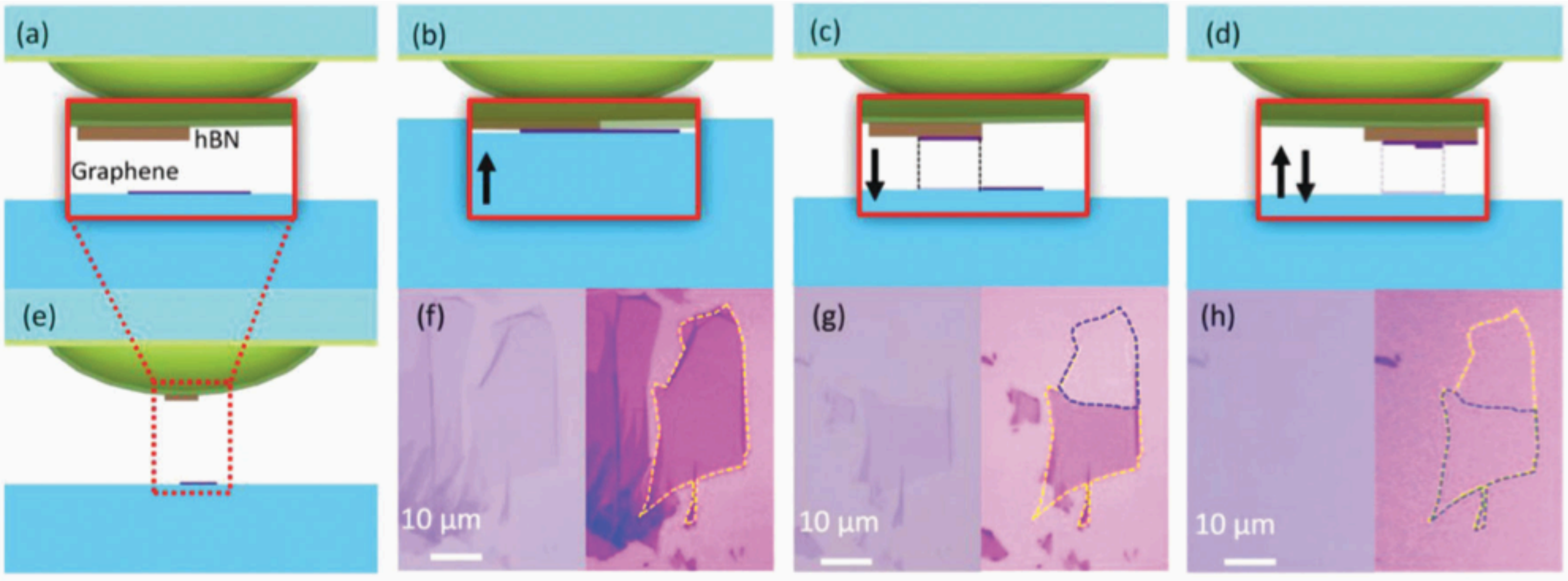
Stacking with a twist ☺







Control of twist angle

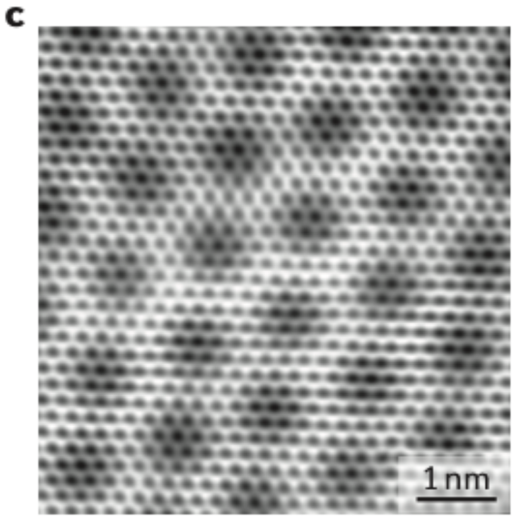


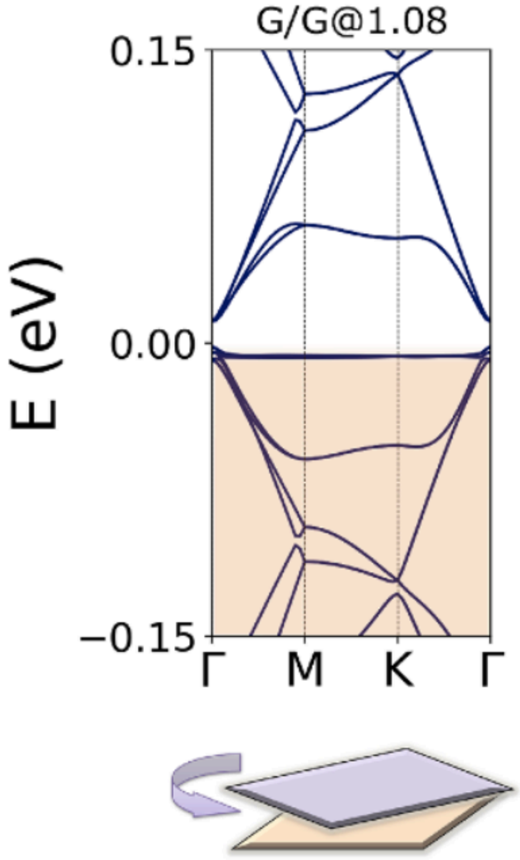
- One layer is rotated w.r.t. another
- New control knob
  - Removes symmetry restrictions (imposed by thermodynamic stacking)
- Fabrication using variation of vdW pick-up method

Frisenda R. *et. al.* Chem.Soc.Rev.,2018,47,53--68

Twistronics

Moiré pattern in graphene





Band structure in twisted bilayer graphene

- Hosts exotic Moiré physics
- Quantum tunnelling of electrons between layers
  - Emergence of superconductivity
  - “Magic angle” (1.1°)

1. Liu, Y., Weiss, N., Duan, X. *et al. Nat Rev Mater* **1,** 16042 (2016).
2. Georgios A Tritsaris et al 2020 2D Mater.7 035028

Some examples of 2D heterostructures

A quick overview

2D heterostructures and applications.

Heterojunction type	Layer structure	Application	Device performance	Ref
Semi-metal/ semiconductor	Graphene/MoS_2	DNA biosensor	Detection DNA concentration 1 atto mole	Loan et al. [60].
	Graphene/WS_2	Solar cells	Power conversion efficiency 3.3%	Shanmugam et al. [67]
	Graphene/WS_2/graphene/ h-BN	Vertical FETs	ON/OFF ratio $>1 \times 10^6$	Georgiou et al. [75]
	Graphene/MoS_2	Vertical FETs	Current density 5000 A cm^{-2} ON/OFF ratio $>10^3$	Yu et al. [76]
	Graphene/MoS_2	Vertical FETs	Current density $\sim 10^4$ A cm^{-2} ON/OFF ratio $\sim 10^5$	Moriya et al. [77]
	Graphene/h-BN/MoS_2/ graphene	FETs	Electron mobility ~ 33 cm^2/V s. ON/OFF current ratio $>10^6$	Roy et al. [68]
	Graphene/MoS_2/graphene	Photodetector	External quantum efficiency 55% Internal quantum efficiency 85% Photoresponsivity 0.22 A/W	Yu et al. [80]
	Graphene/WS_2/graphene	Photodetector	External quantum efficiency $\sim$30% Photoresponsivity 0.1 A/W	Britenall et al. [79]
	Graphene/MoS_2	Photodetector	Photogain $>10^8$ Internal quantum efficiency $\sim$15% Photoresponsivity $>10^7$ A/W	Zhang et al. [89]
	Graphene/MoS_2	Photodetector	Gain ~ 5–10×10^{10} Quantum efficiency $\sim$32% Photoresponsivity 1×10^{10} A/W at 130 K, 5×10^8 A/W at room temperature	Roy et al. [90]
	Graphene/h-BN/MoS_2(WS_2)/ h-BN/graphene	Electroluminescence	Extrinsic quantum efficiency $\sim$10%	Withers et al. [88]
Semi-metal/insulator	Graphene/h-BN	FETs	Mobility 60,000 cm^2/V s	Dean et al. [42]
	h-BN/Gra./h-BN/Gra./h-BN; h-BN/Gra./MoS_2/Gra./h-BN	Vertical FET	B/G/B/G/B: ON/OFF ratio 50 B/G/M/G/B: ON/OFF ratio 1×10^4	Britnell et al. [74]
	Graphene/h-BN/graphene	Thermoelectrical power	Seebeck coefficient -99.3 µV/K $ZT = 1.05 \times 10^{-6}$	Chen et al. [92]
Semiconductor/ semiconductor	WSe_2/MoS_2	Solar cells	Power conversion efficiency 0.2% External quantum efficiency 1.5%	Furchi et al. [63]
	p-WSe_2/n-WSe_2	CMOS	Full logic swing voltage gain up to 38	Yu et al. [76]
	p-MoS_2/n-MoS_2	Solar cells	Power conversion efficiency 2.8%	Wi et al. [65]
	MoS_2/p-Si	Solar cells	Power conversion efficiency 5.23%	Tsai et al. [66]
	WSe_2/MoS_2 Gra./WSe_2/MoS_2/Gra.	Solar cells	Photoresponsivity is $\sim$2 mA W^{-1} Photoresponsivity is $\sim$10 mA W^{-1} External quantum efficiency 2.4%, 12% and 34% for monolayer, bilayer and multi-layer TMDs	Lee et al. [64]
	WSe_2/MoS_2	p–n diode Photodetector Electroluminescence	Current rectification factor 1.2 External quantum efficiency 12%	Cheng et al. [81]
	Black phosphorus/MoS_2	p–n diode Photodetector	Current rectification factor 10^5 External quantum efficiency 0.3% Photoresponsivity 418 mA/W	Deng et al. [82]
	MoS_2/WS_2	Charge transfer	Ultrafast hole transfer time $<$50 fs.	Hong et al. [93]
	WS_2/MoS_2	Solar cells	Open-loop voltage 0.12 V Close-loop current 5.7 pA	Gong et al. [49]
	WSe_2/WS_2	Solar cells	Open-loop voltage $\sim$0.47 V Close-loop current $\sim$1.2 nA	Duan et al. [53]
	WSe2/MoS2	Solar cells	Open-loop voltage $\sim$0.22 V Close-loop current $\sim$7.7 pA	Li et al. [55]
	WSe2/MoSe2	Solar cells	Power conversion efficiency 0.12%	Gong et al. [56]
	MoS_2/p-Ge	Band-to-band tunneling FET	Subthreshold swing minimum of 3.9 mV/decade, average 31.1 mV/decade	Sarkar et al. [78]
	MoS2/p-Si	Solar cells Electroluminescence	External quantum efficiency 4%	Lopez-Sanchez et al. [83]
Semiconductor/ insulator	MoS_2/h-BN/graphene	FETs	Mobility >45 cm^2/V s ON/OFF ratio 10^4–10^6	Lee et al. [94]

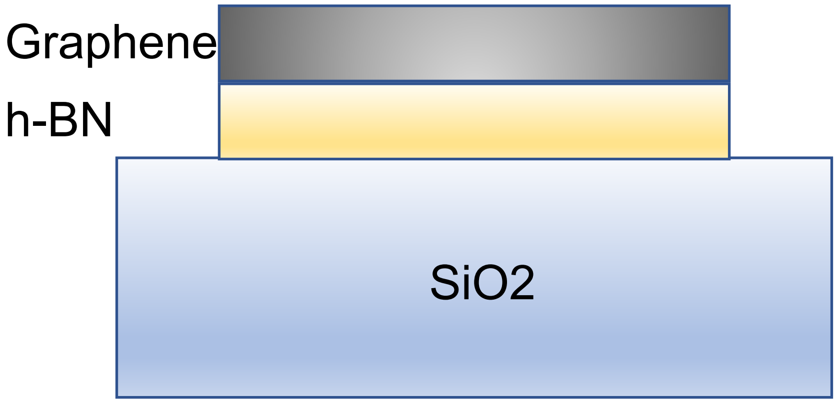
10.1016/j.mattod.2015.11.003

Example 1a: High quality substrate

- SiO2 is an inferior substrate for graphene

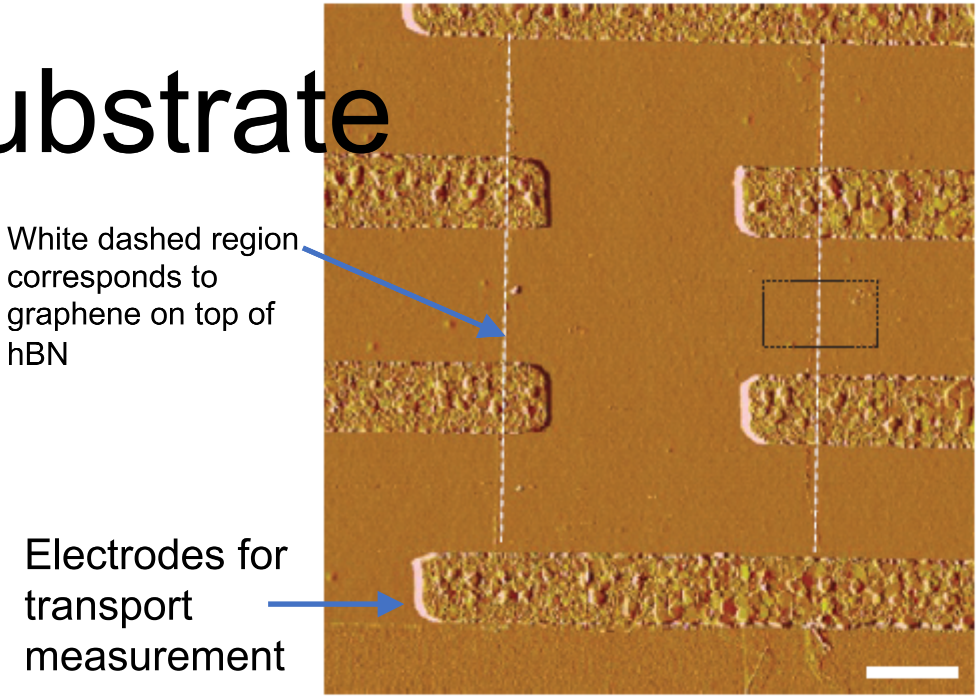
Example 1a: High quality substrate

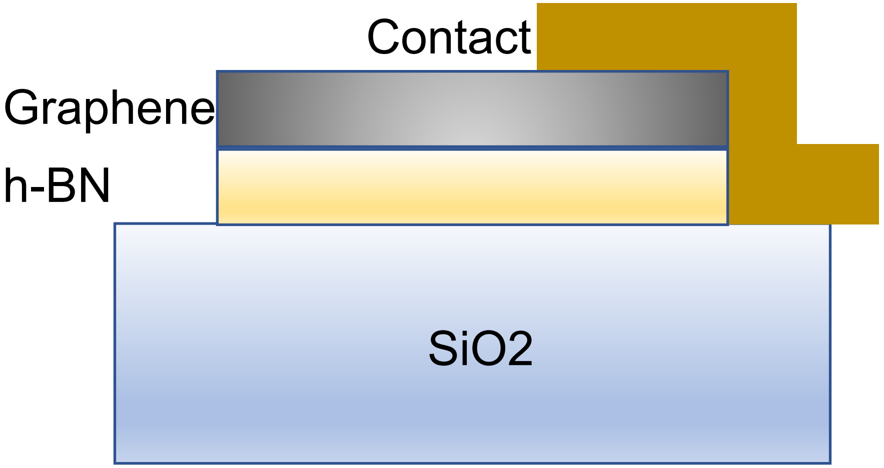
- SiO_2 is an inferior substrate for graphene
- Solution: few layers of h-BN as substrate



Example 1a: High quality substrate

- SiO2 is an inferior substrate for graphene
- Solution: few layers of h-BN as substrate
- Structures assembled by exfoliation





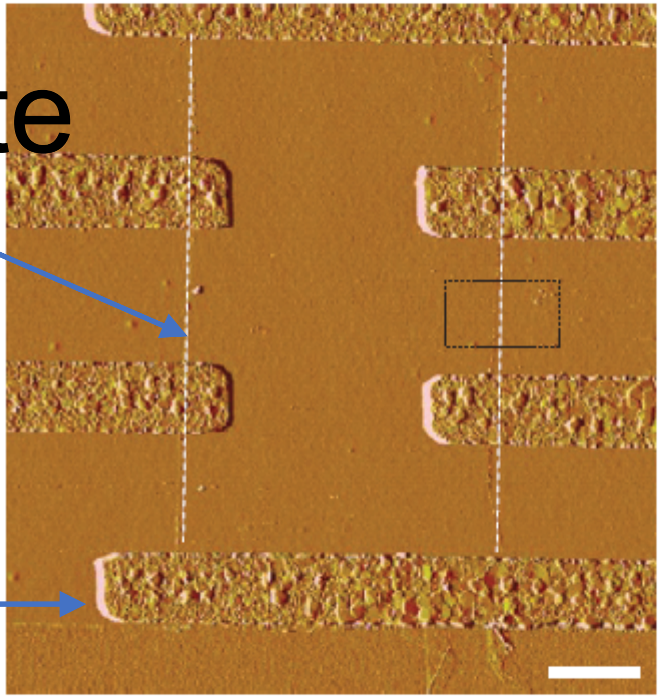
DOI: 10.1038/NNANO.2010.172

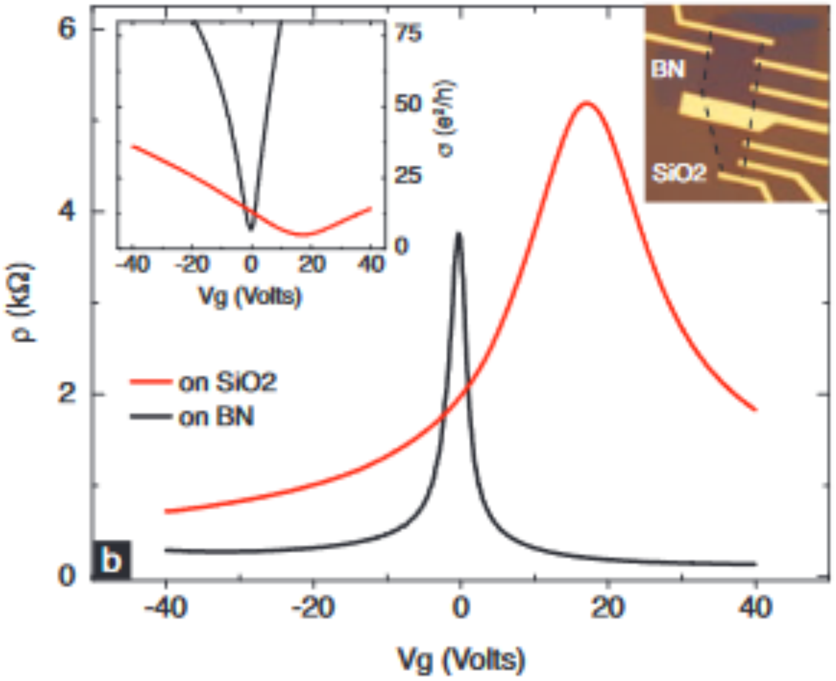
Example 1a: High quality substrate

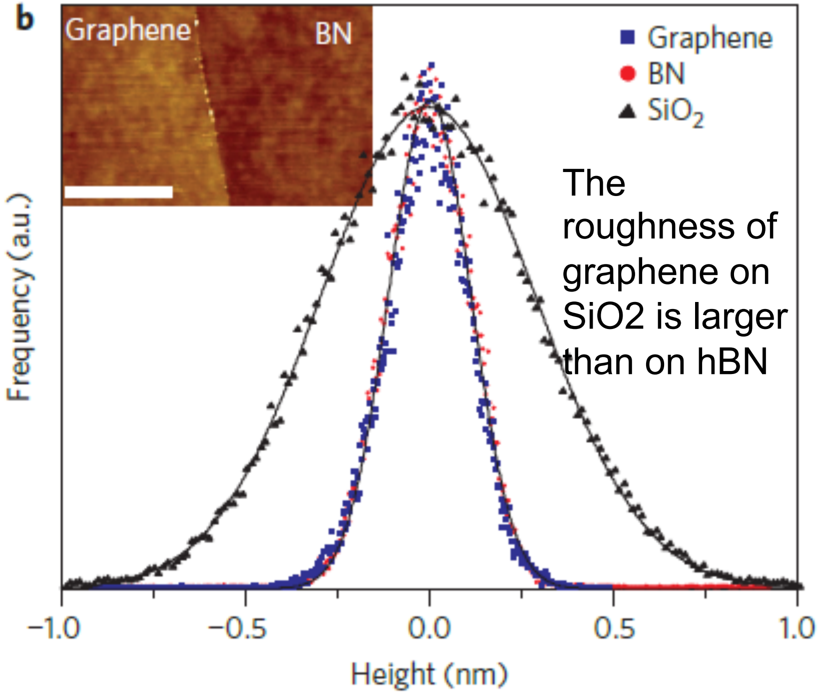
- SiO2 is an inferior substrate for graphene
- Solution: few layers of h-BN as substrate
- Structures assembled by exfoliation
- Improvement in performance

White dashed region corresponds to graphene on top of hBN

Electrodes for transport measurement







The roughness of graphene on SiO2 is larger than on hBN

DOI: 10.1038/NNANO.2010.172

Example 1b: High quality substrate (CVD)

- Challenge example 1a: size and thickness

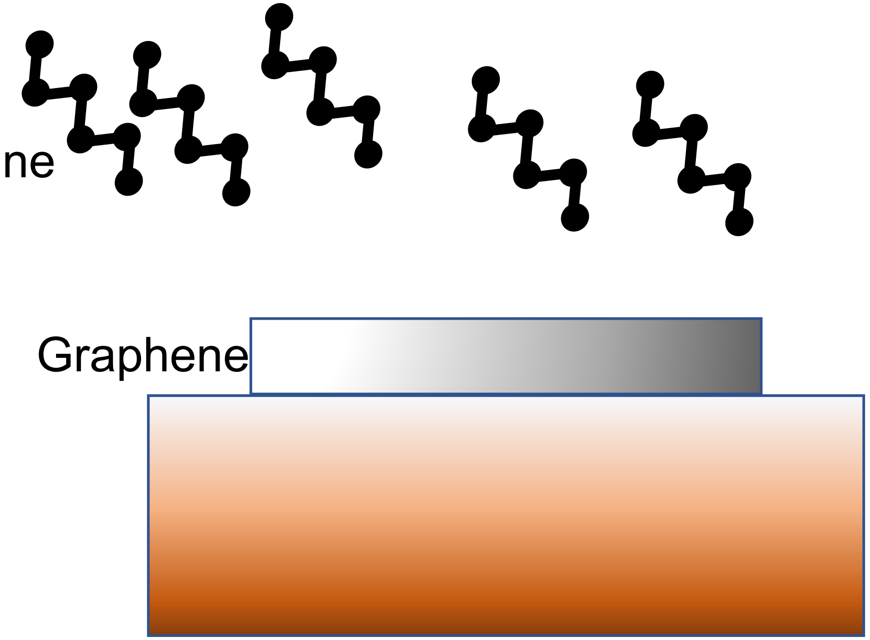
Example 1b: High quality substrate (CVD)

- Challenge example 1a: size and thickness
- Solution: layer by layer growth

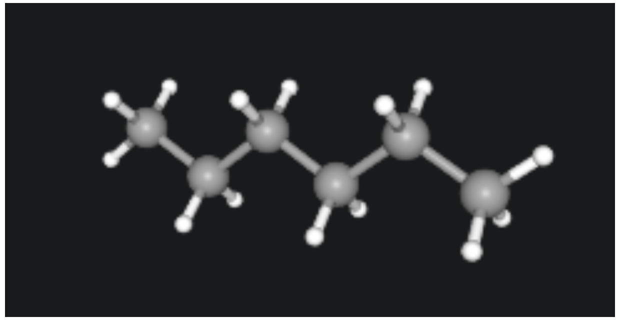
Example 1b: High quality substrate (CVD)

- Layer 1
  - High temperature and low pressure
  - n-hexane precursor
  - Growth of graphene on Cu foil

n-hexane
vapor

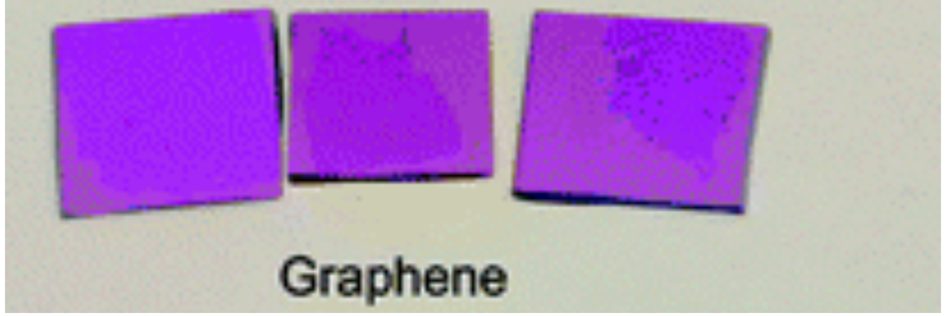


Copper



n-hexane molecule (PubChem)

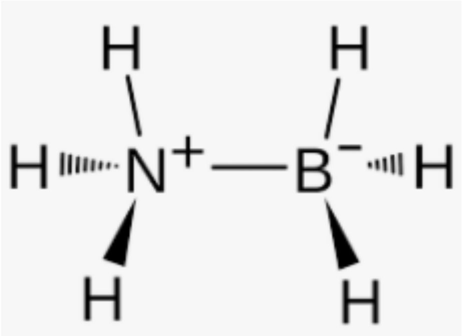
Graphene transferred to SiO2/Si stack



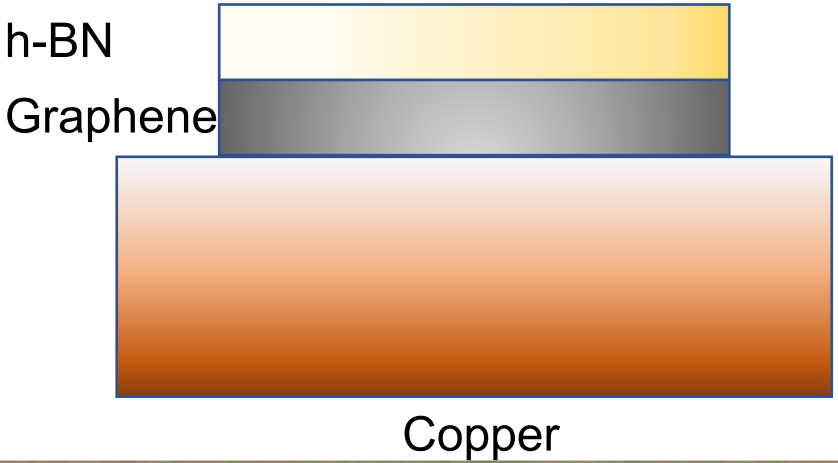
Nano Lett. 2011, 11, 5, 2032–2037

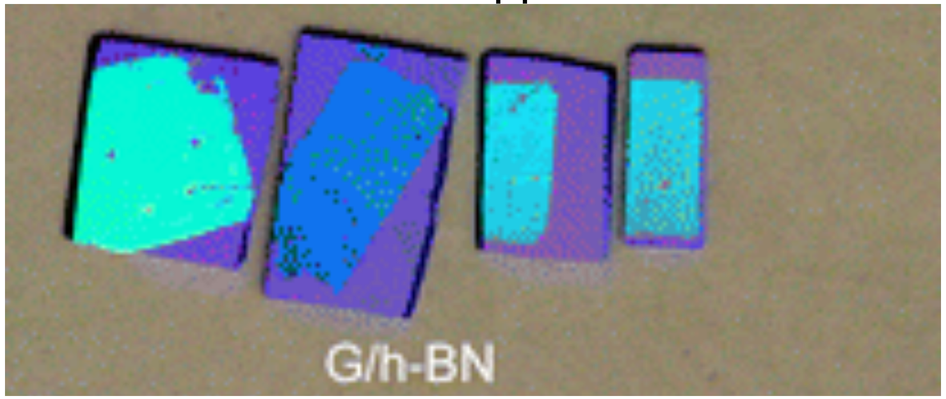
Example 1b: High quality substrate (CVD)

- Layer 2
  - High temperature and low pressure
  - Ammonia borane precursor
  - Growth of h-BN on graphene
  - Transfer to SiO2/Si substrate



Ammonia borane (wikipedia)

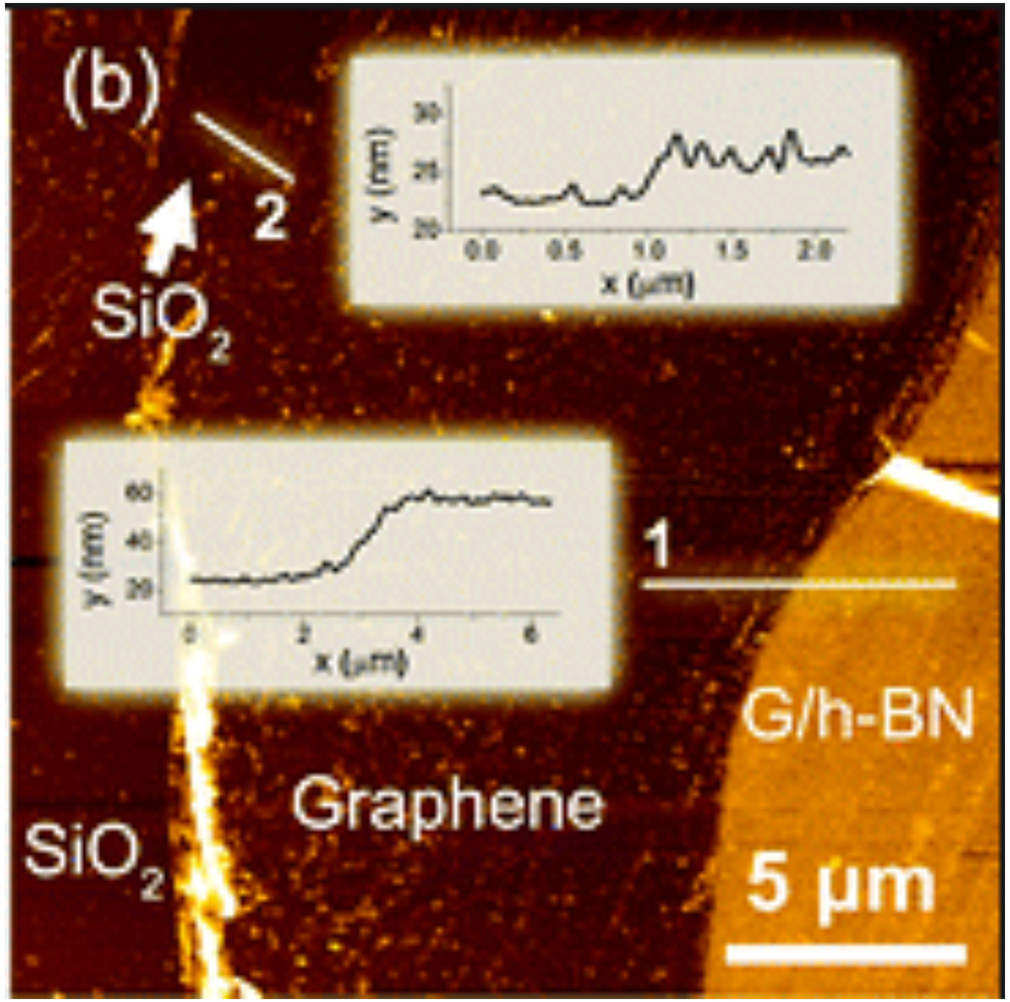




Nano Lett. 2011, 11, 5, 2032–2037

Example 1b: High quality substrate (CVD)

- Final results



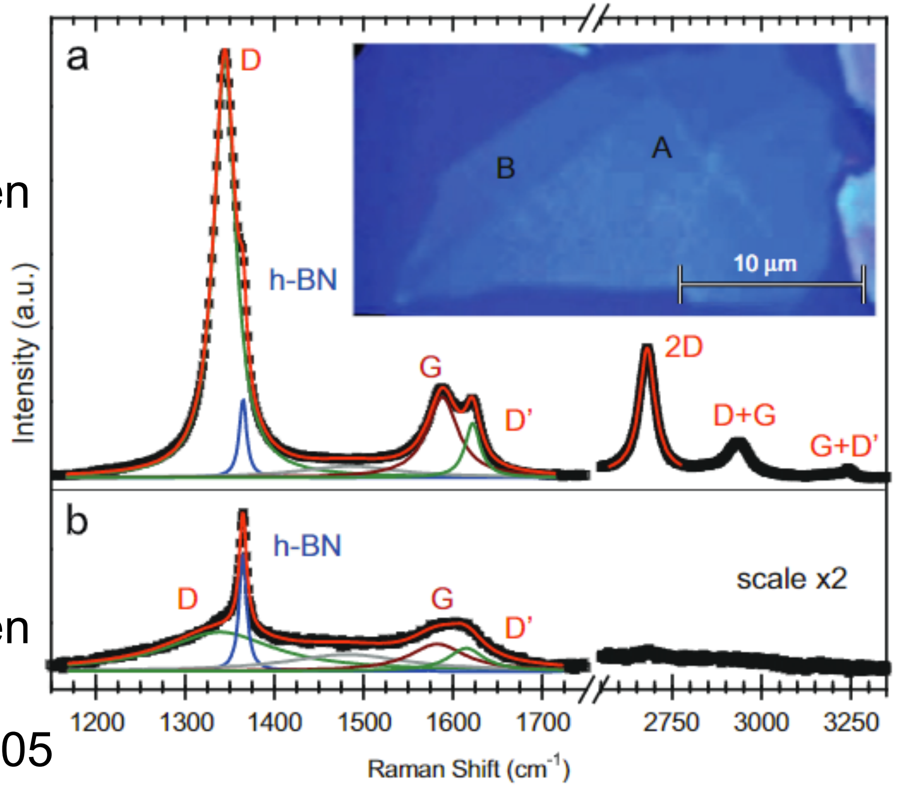
Nano Lett. 2011, 11, 5, 2032–2037

Example 1c: High quality substrate (MBE)

- Challenge example 1b: low performance of graphene
- Solution: van der Waal epitaxy of heterostructures
  - hBN exfoliation and transfer to SiO2/Si
  - Graphene grown on hBN flakes
  - Solid carbon source
  - No dependence of Raman peaks on C atom flux
  - High D band: nanoscale domains of graphene

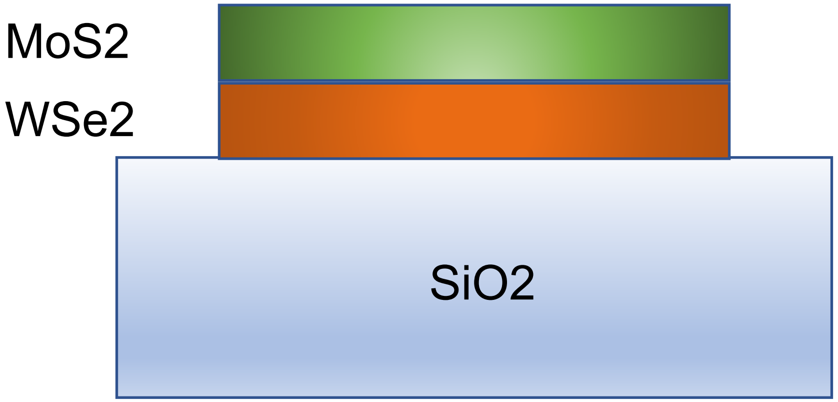
High quality graphene

Low quality graphene

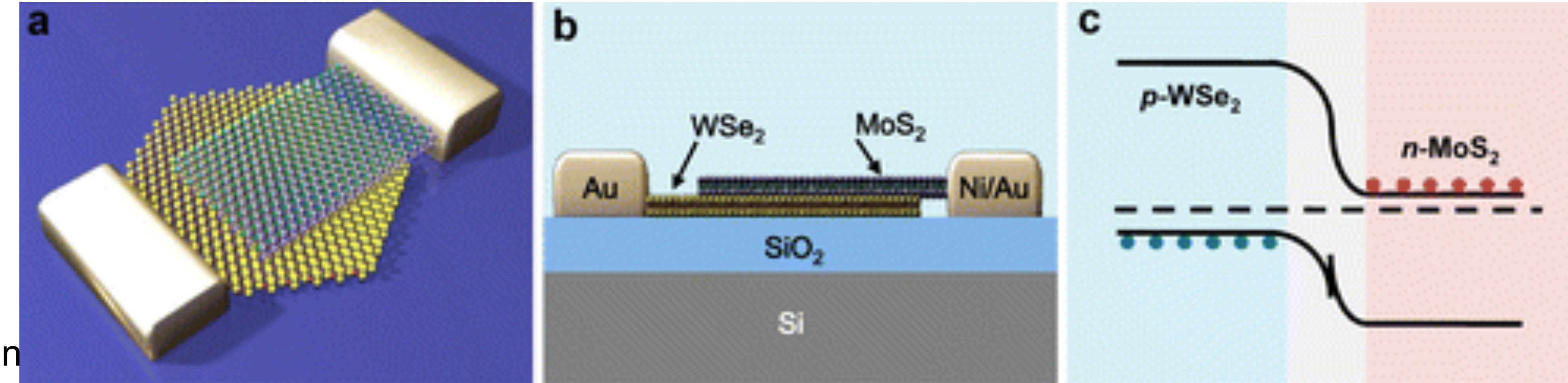


10.1016/j.ssc.2012.04.005

Example 2: 2D heterostructure based electronics



- Challenge for atomic scale electronic is selective doping
- Solution: Vertically stacking separately doped 2D layers
- Assembled using exfoliation and transfer



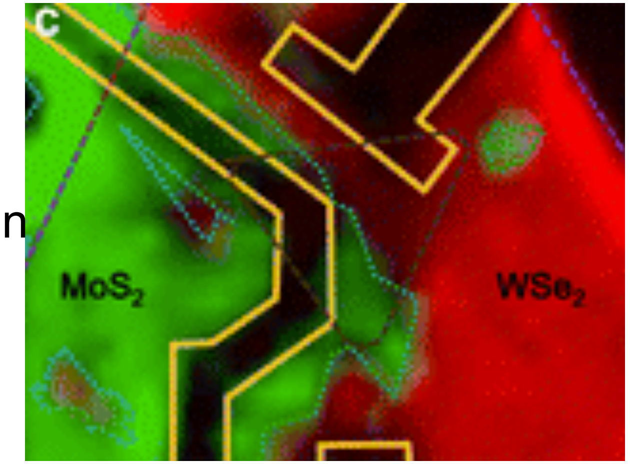
Schematic
10.1021/nl502075n

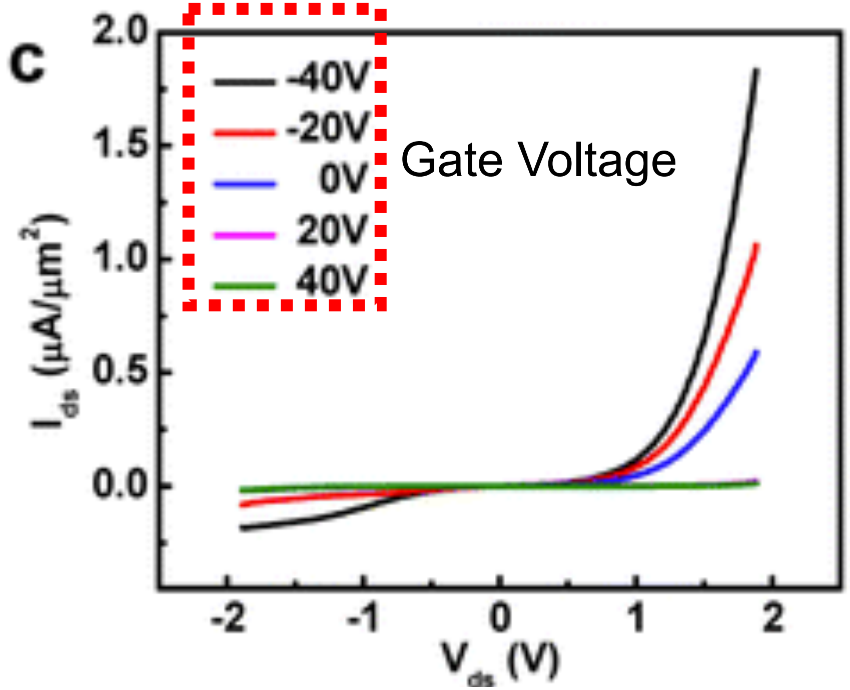
Example 2: 2D heterostructure based electronics

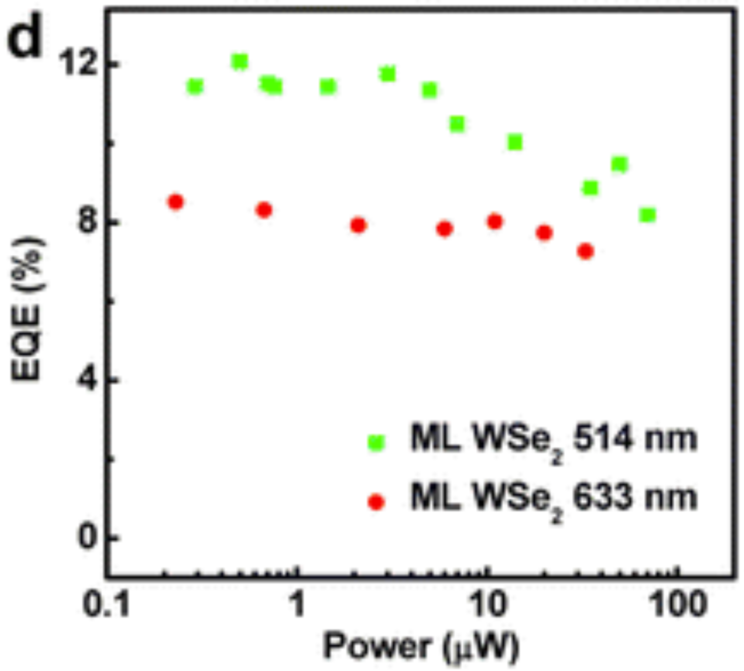
- Results
  - Ideal diode rectification
  - Photosensitive
  - Electroluminescent at high bias

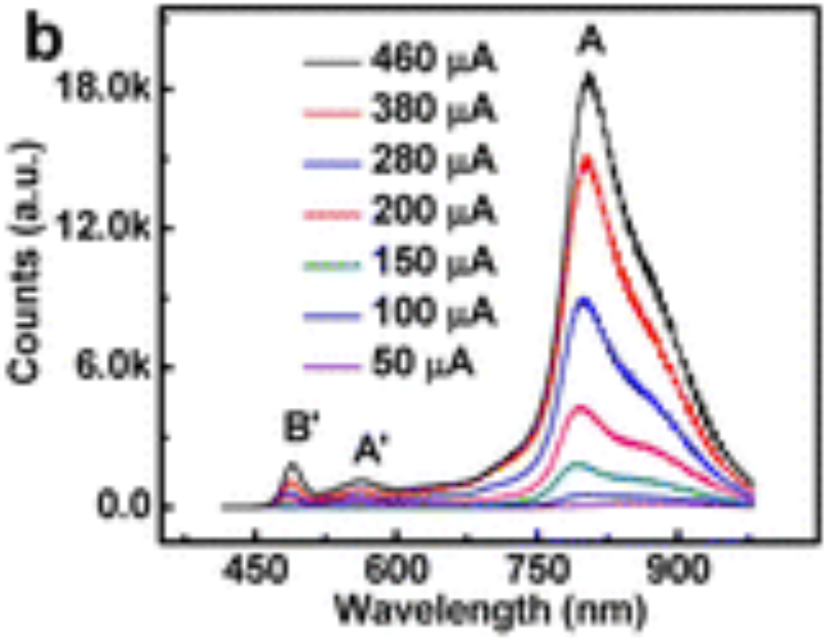
PL mapping of MoS_2 flake on WSe_2

10.1021/nl502075n









Summary

- Introduction to 2D heterostructures
- Assembly techniques
- Some practical examples