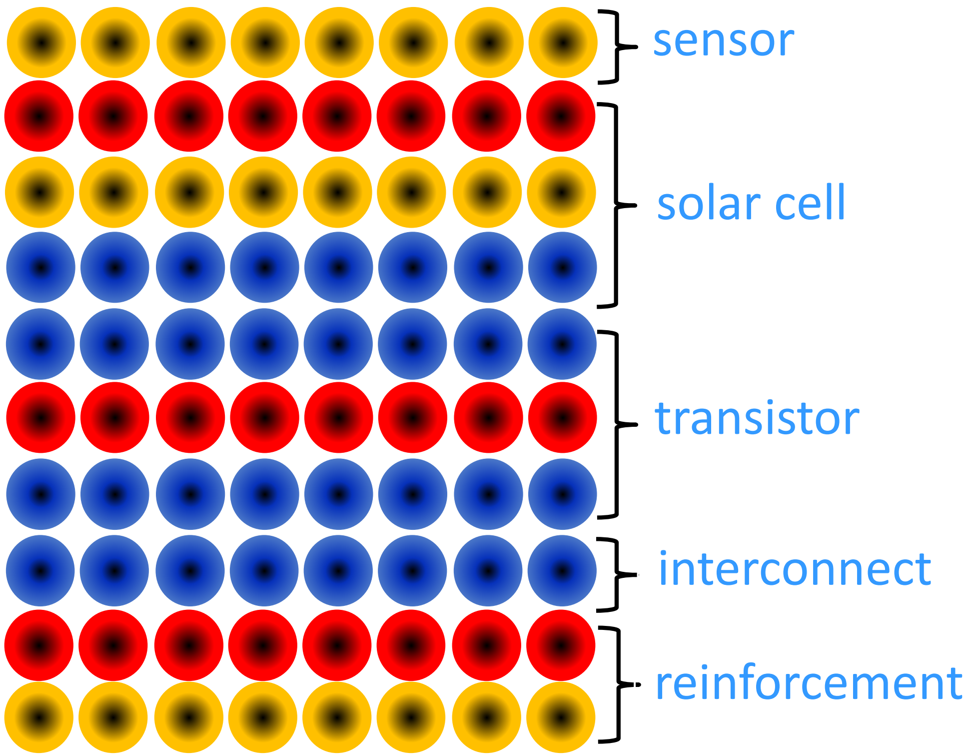
vdW heterostructures
Pt. 2

Roman Gorbachev

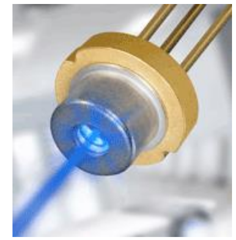
Layer by Layer Material Engineering

Building materials
atom by atom

Wide range of compositions -
wide range of functionalities



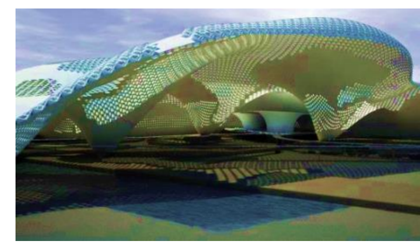
Composite materials &
Heterostructures



InGaN laser

AlInN HEMT

Plastics



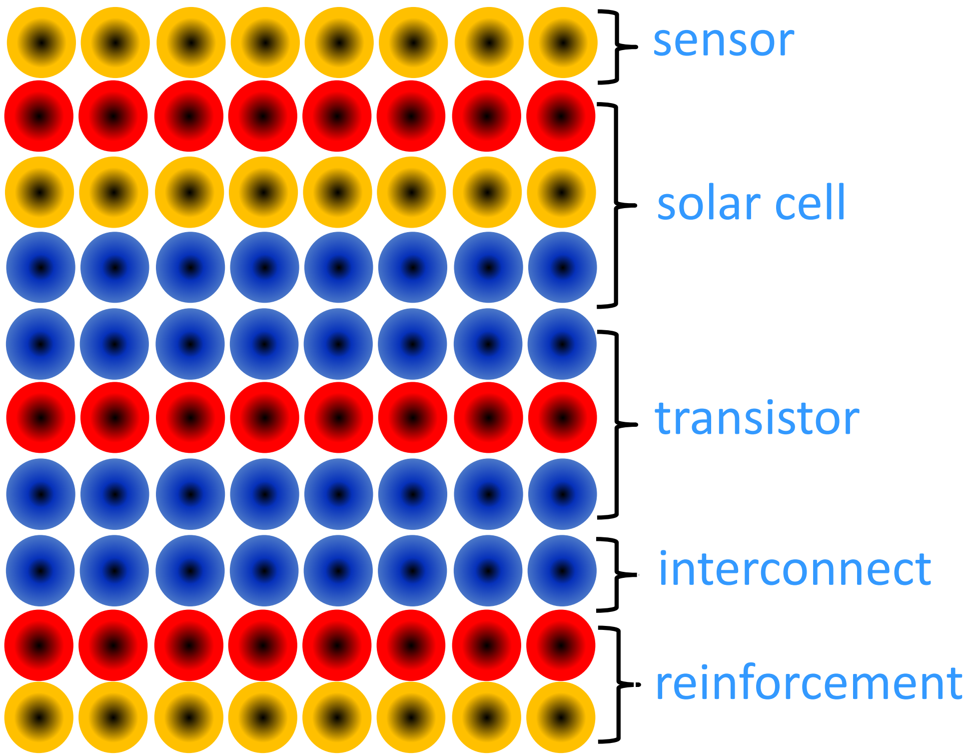
Fibres

Carbon Fibres

Layer by Layer Material Engineering

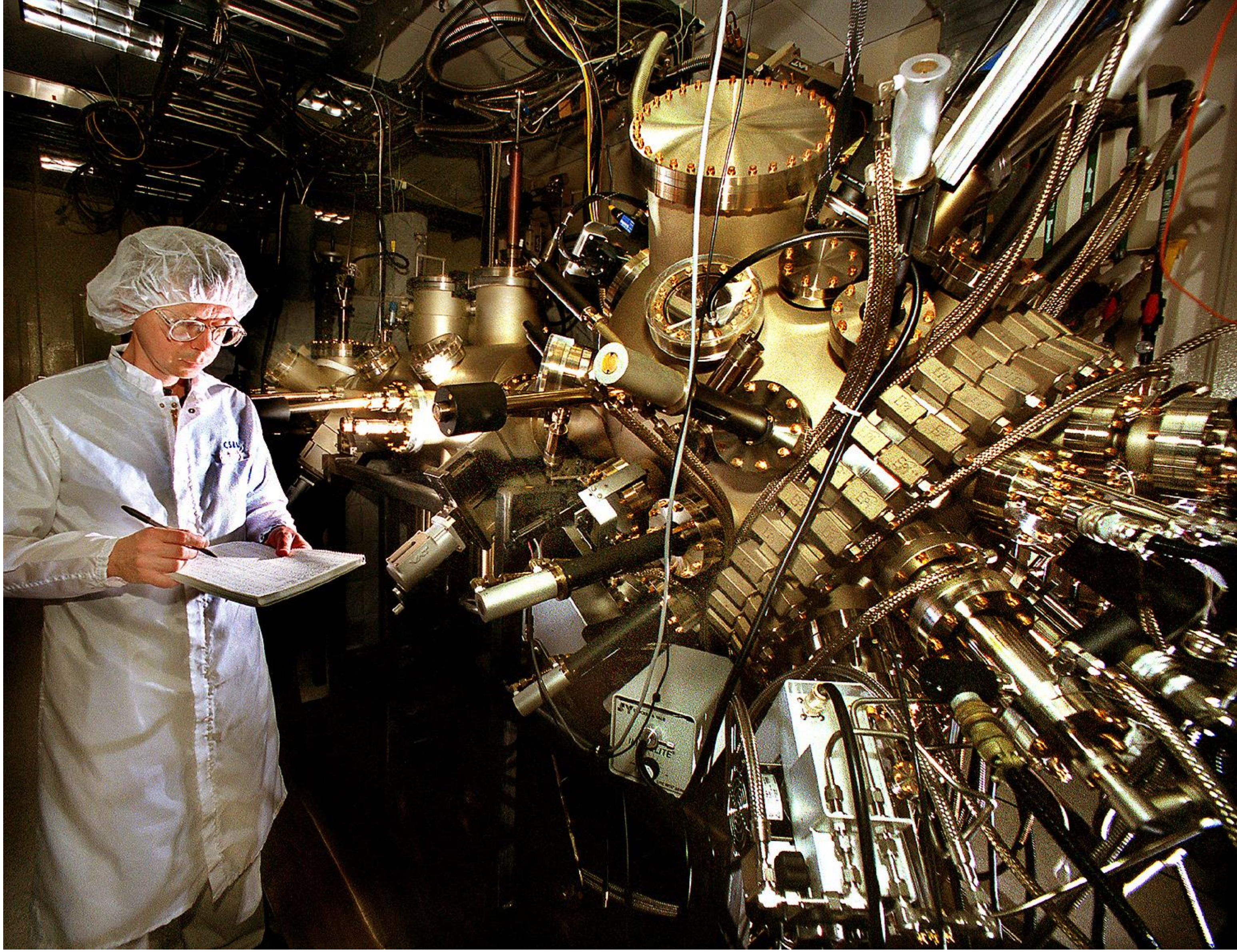
Building materials
atom by atom

Wide range of compositions -
wide range of functionalities



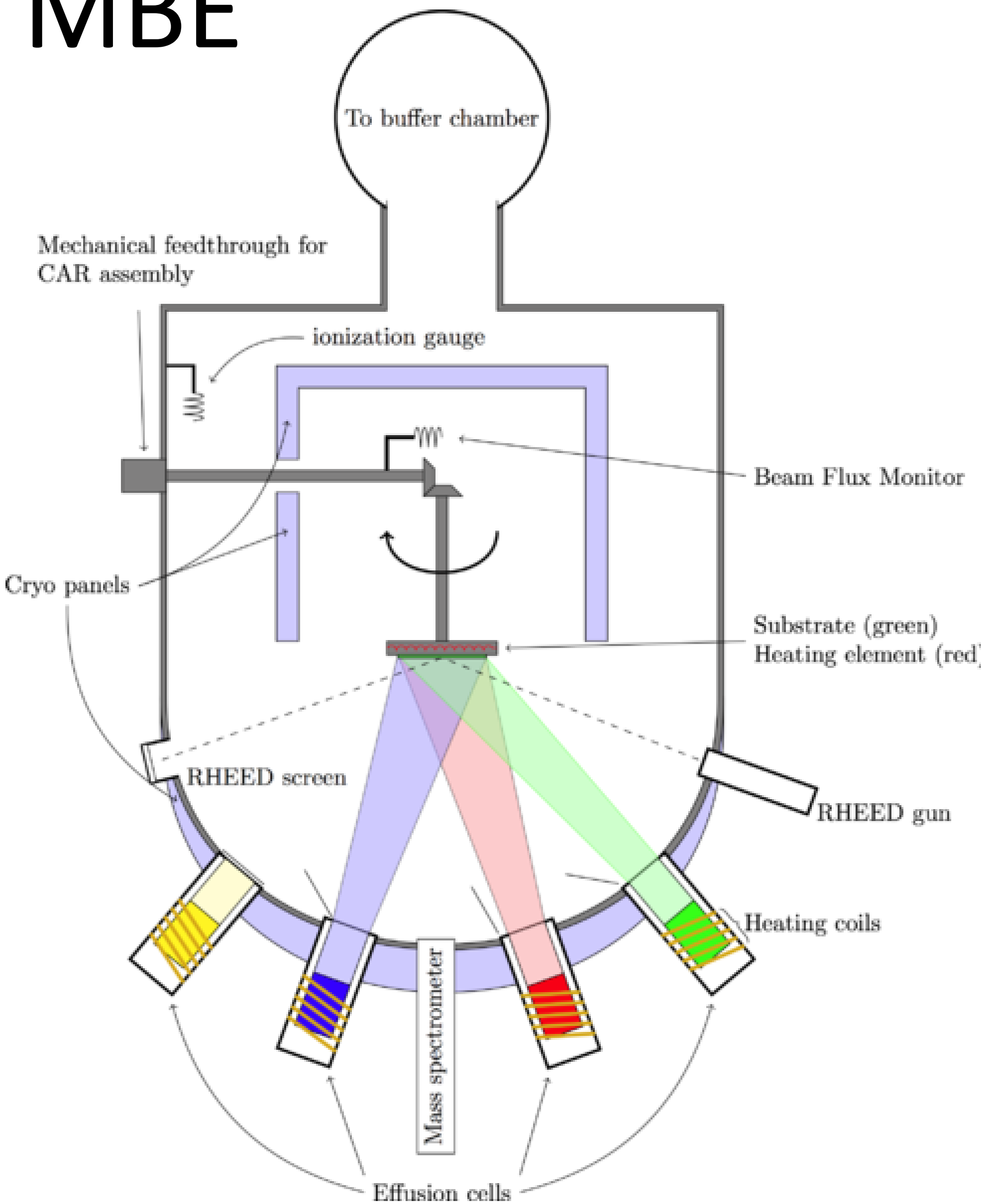
funding proposals vs real life

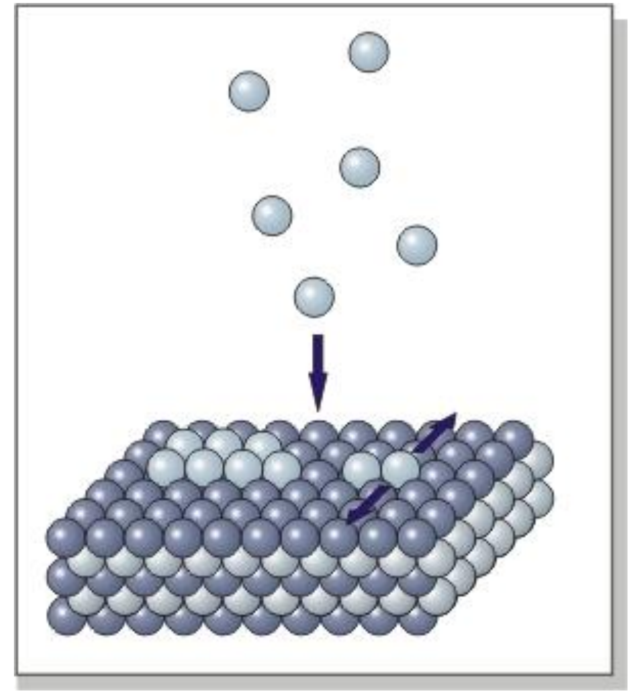
MBE

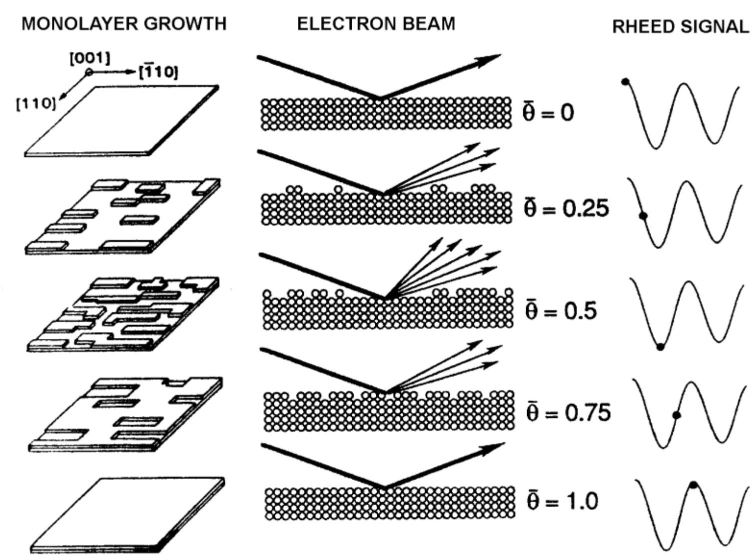


Molecular Beam Epitaxy - a versatile technique for growing thin epitaxial structures made of semiconductors, metals or insulators

MBE

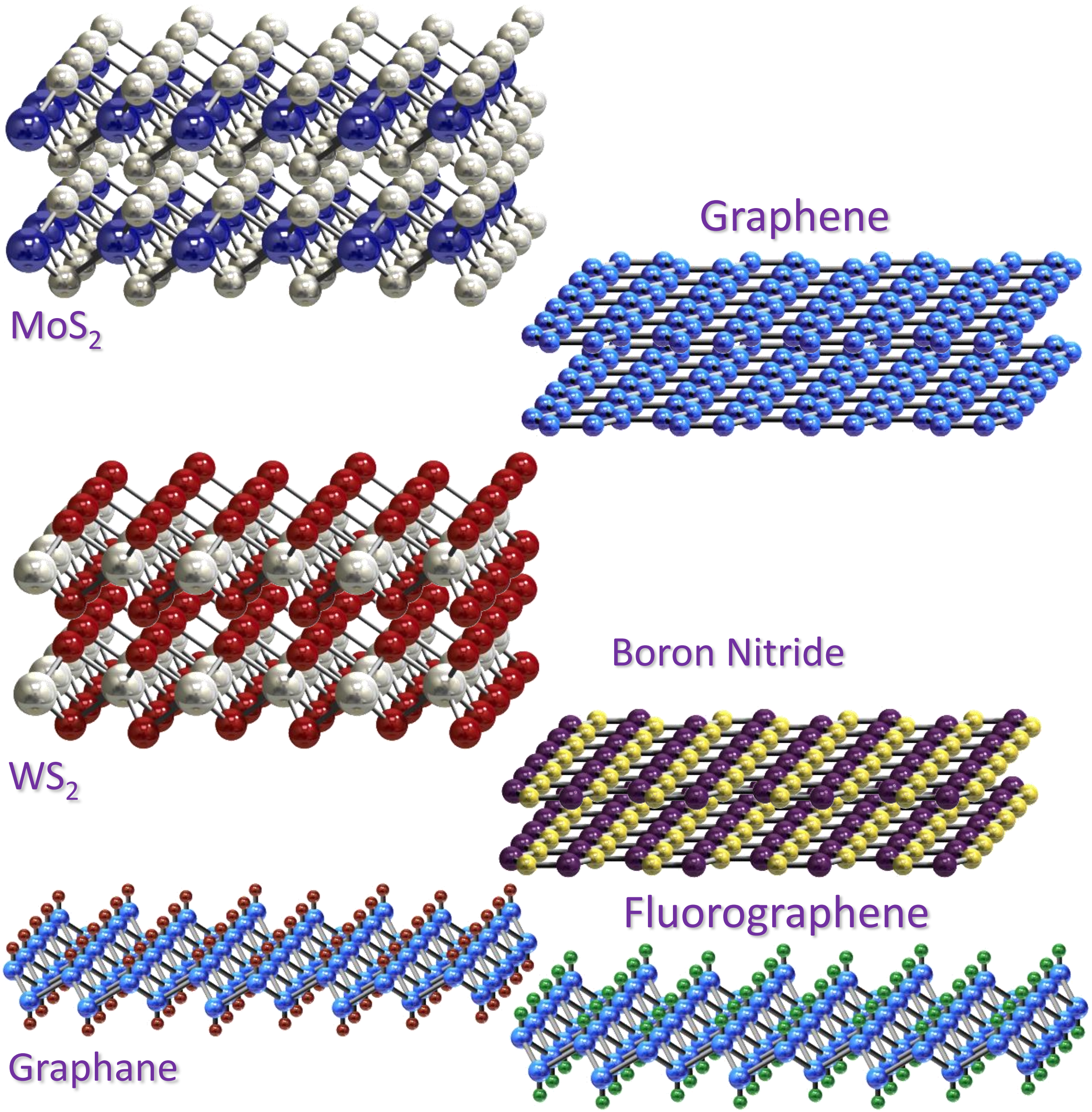

To buffer chamber
Mechanical feedthrough for
CAR assembly
ionization gauge
Beam Flux Monitor
Cryo panels
Substrate (green)
Heating element (red)
RHEED screen
RHEED gun
Heating coils
Mass spectrometer
Effusion cells

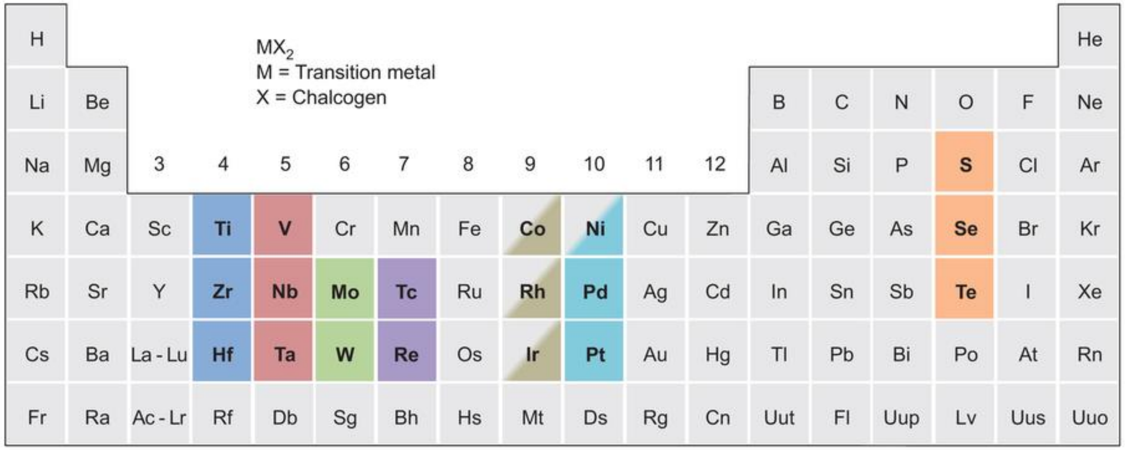


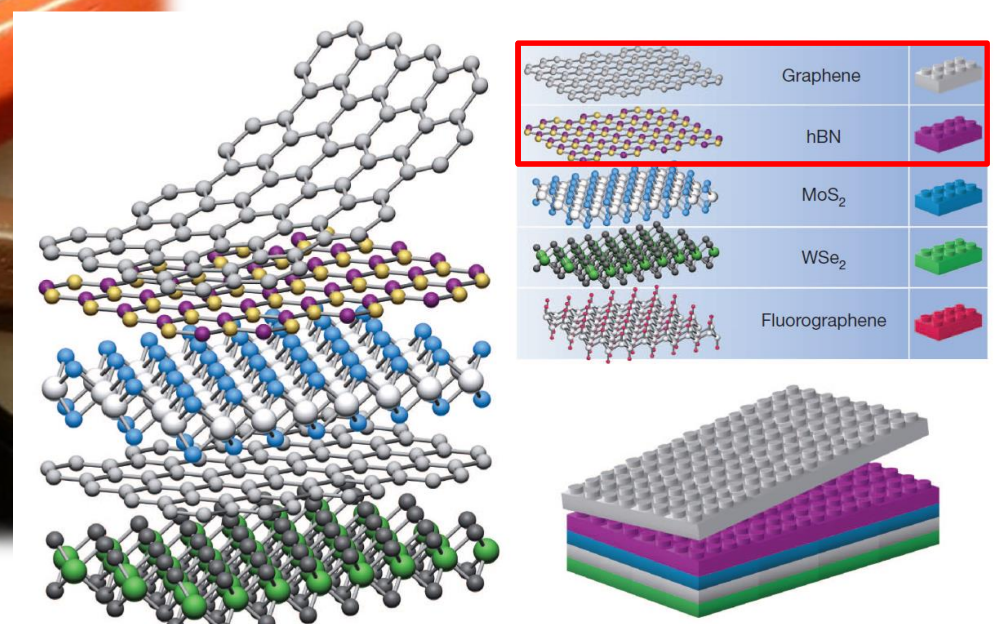

MONOLAYER GROWTH
ELECTRON BEAM
RHEED SIGNAL
[001]
[$\bar{1}$10]
[110]
$\bar{\theta}$ = 0
$\bar{\theta}$ = 0.25
$\bar{\theta}$ = 0.5
$\bar{\theta}$ = 0.75
$\bar{\theta}$ = 1.0

New Class of Crystalline Materials

Large Variety of Properties







Chhowalla, *Nat. Chem.* (2013)

Back in 1969

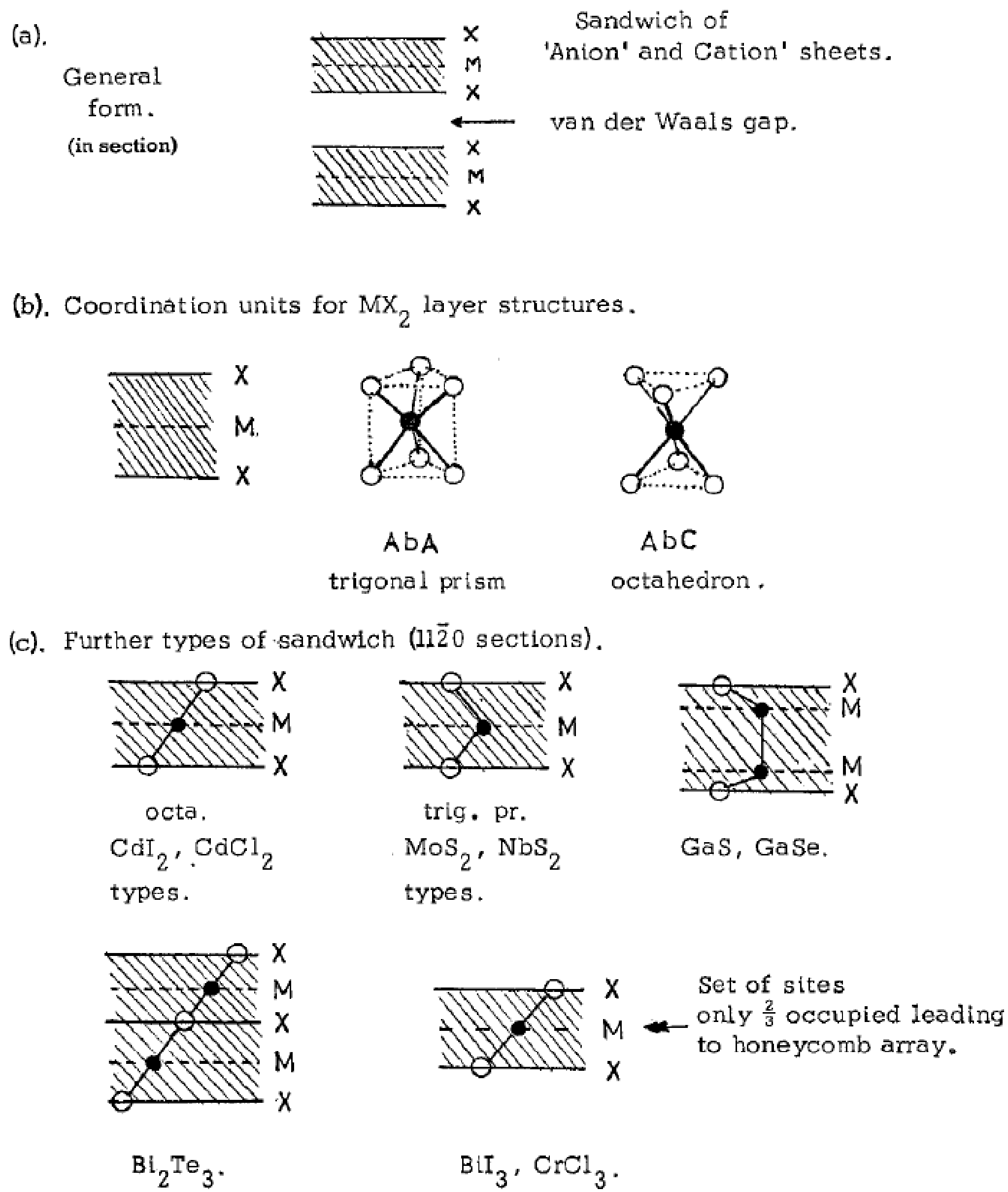
The Transition Metal Dichalcogenides

Discussion and Interpretation of the Observed Optical, Electrical and Structural Properties

By J. A. Wilson and A. D. Yoffe
Cavendish Laboratory, Cambridge

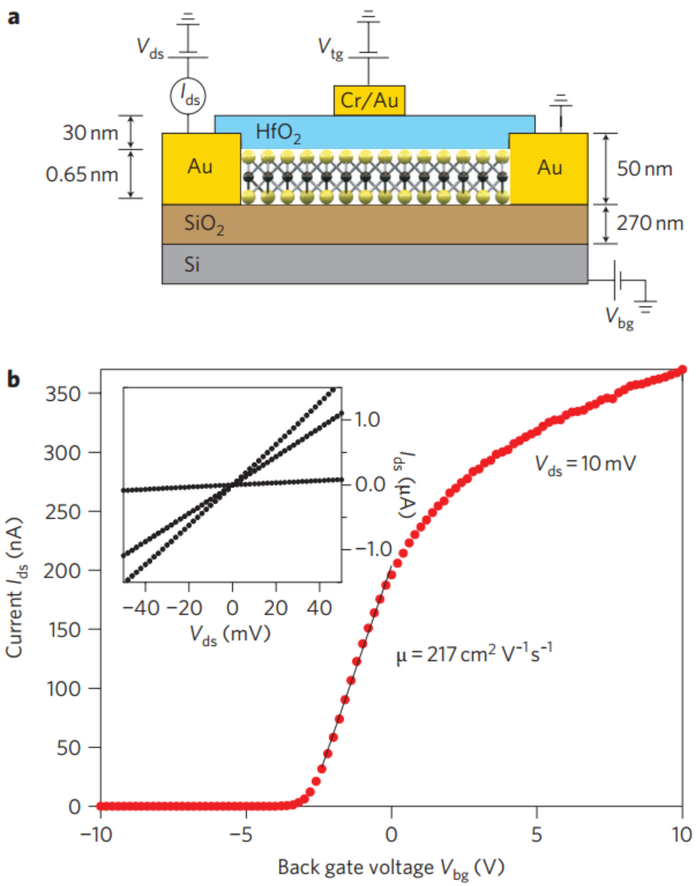
Abstract

The transition metal dichalcogenides are about 60 in number. Two-thirds of these assume layer structures. Crystals of such materials can be cleaved down to less than 1000 Å and are then transparent in the region of direct band-to-band transitions. The transmission spectra of the family have been correlated group by group with the wide range of electrical and structural data available to yield useful working band models that are in accord with a molecular orbital approach.


(a).
General form.
(in section)
X
M
X
Sandwich of 'Anion' and Cation' sheets.
van der Waals gap.
X
M
X
(b). Coordination units for MX2 layer structures.
X
M.
X
AbA
trigonal prism
AbC
octahedron.
(c). Further types of sandwich (1120 sections).
X
M
X
octa.
CdI2, CdCl2
types.
X
M
X
trig. pr.
MoS2, NbS2
types.
X
M
M
X
GaS, GaSe.
X
M
X
M
X
Bi2Te3.
X
M
X
Set of sites
only 2/3 occupied leading
to honeycomb array.
BiI3, CrCl3.

Single-layer MoS_2 transistors

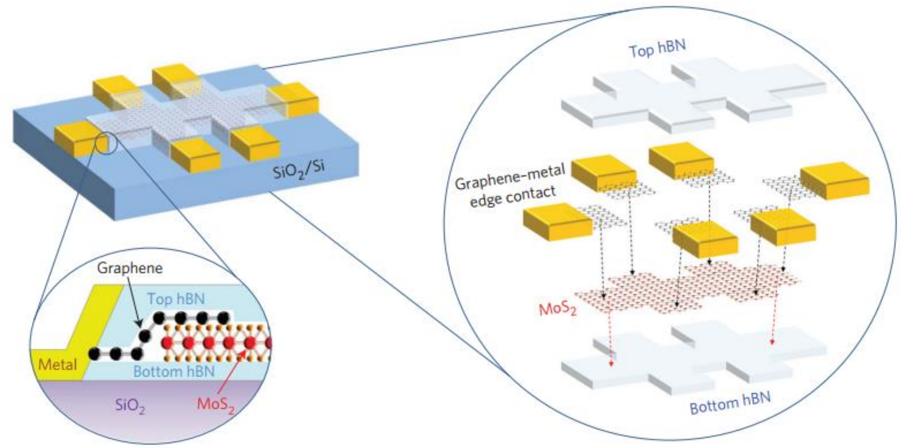
B. Radisavljevic[1], A. Radenovic[2], J. Brivio[1], V. Giacometti[1] and A. Kis[1]*

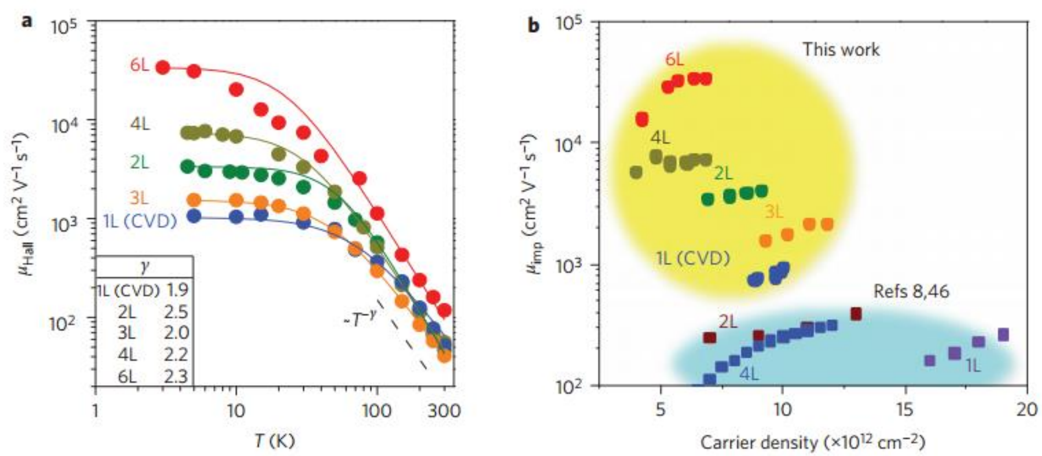


Nature Nanotech. 6, 147–150 (2011)

Multi-terminal transport measurements of MoS_2 using a van der Waals heterostructure device platform

Xu Cui[1†], Gwan-Hyoung Lee[2*†], Young Duck Kim[1†], Ghidewon Arefe[1], Pinshane Y. Huang[3], Chul-Ho Lee[4], Daniel A. Chenet[1], Xian Zhang[1], Lei Wang[1], Fan Ye[5], Filippo Pizzocchero[6], Bjarke S. Jessen[6], Kenji Watanabe[7], Takashi Taniguchi[7], David A. Muller[3,8], Tony Low[9], Philip Kim[10] and James Hone[1]*



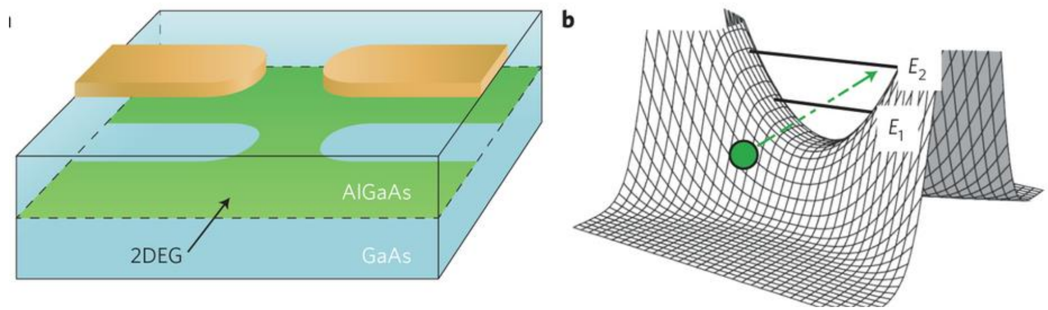


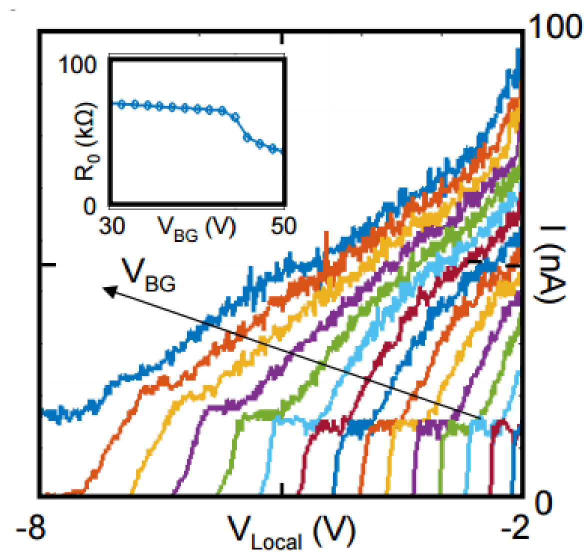
Nature Nanotechnology 10, 534–540 (2015)

Engineering Quantum Confinement in Semiconducting van der Waals Heterostructure

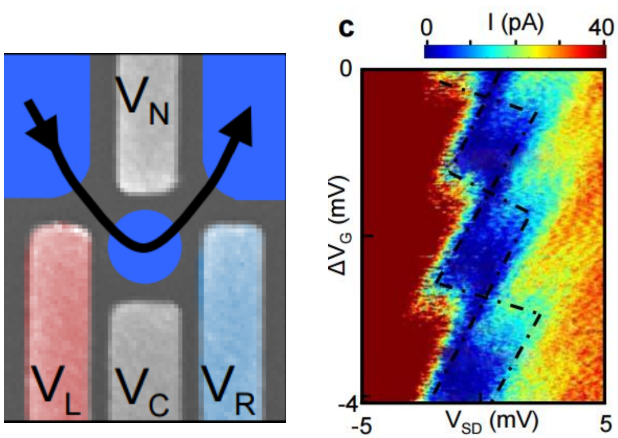
K. Wang[1], T. Taniguchi[2], K. Watanabe[2], P. Kim[1] *

Quantum point contact





Electrostatically defined Quantum dot

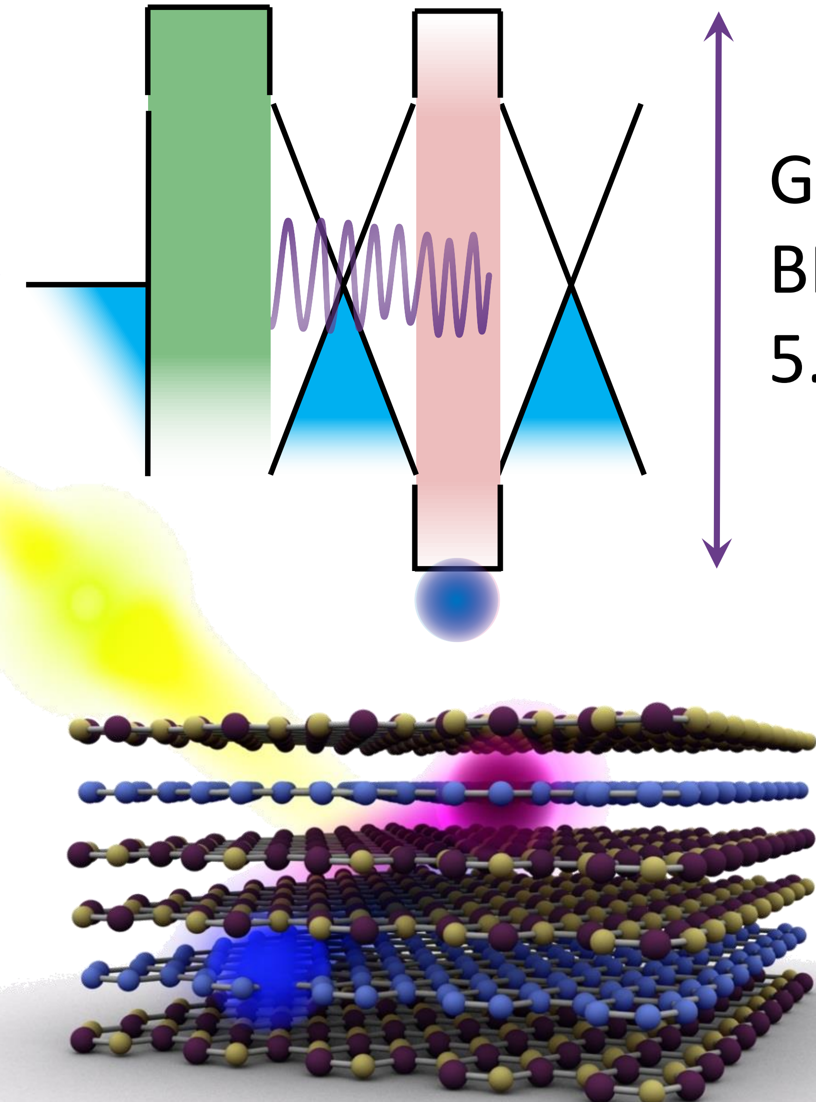


arXiv:1610.02929

Metal
TM(D)C
Metal

Photovoltaics

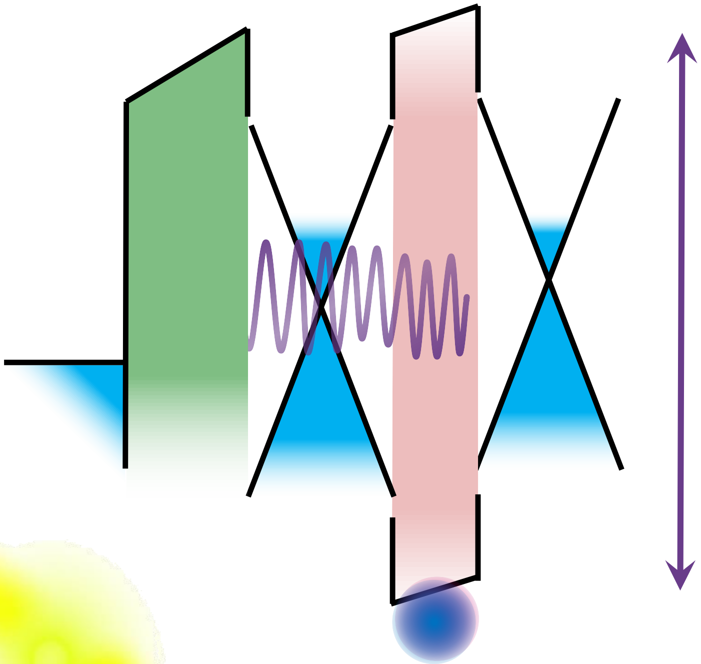
Illuminated Tunnelling



Gap in BN: 5.9 eV

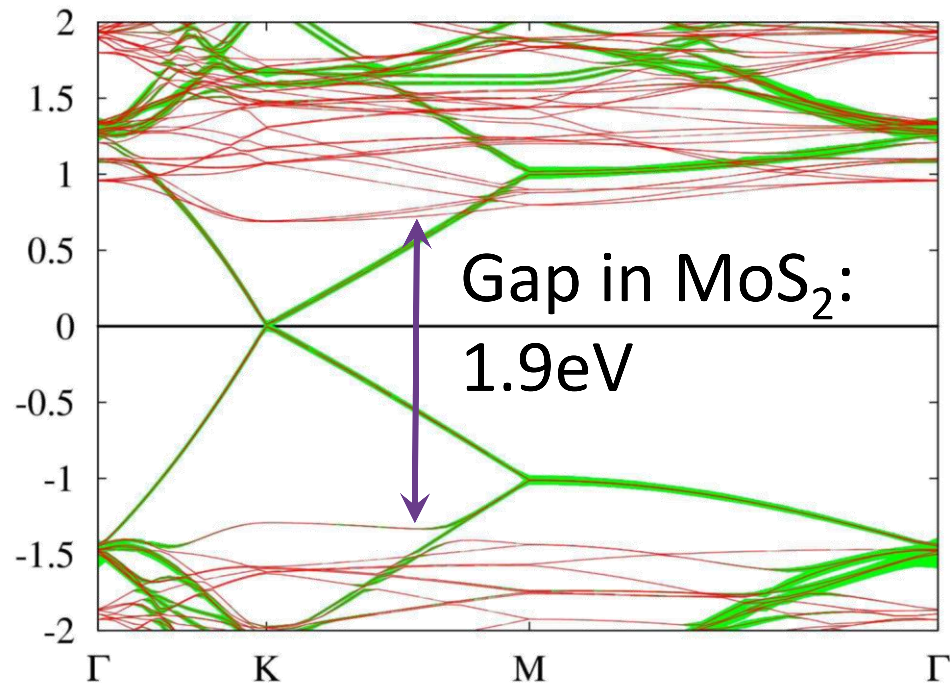
Photogenerated charge carriers

Britnell et al Science'13

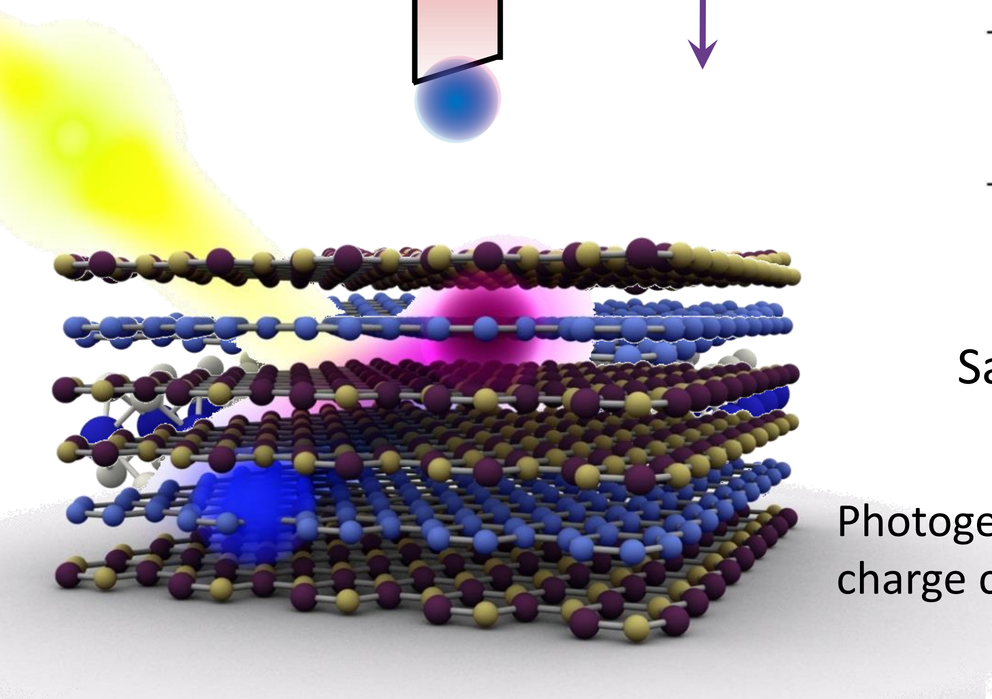


Gap in BN: 5.9 eV

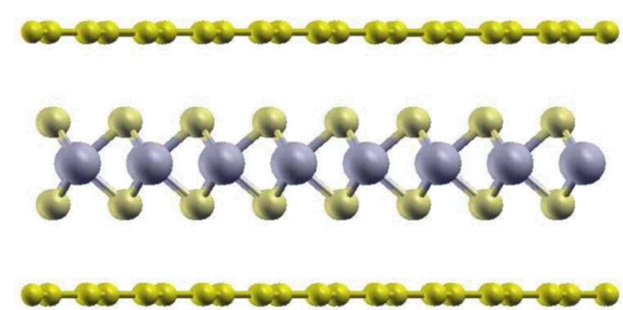
Other semiconducting TMDCs



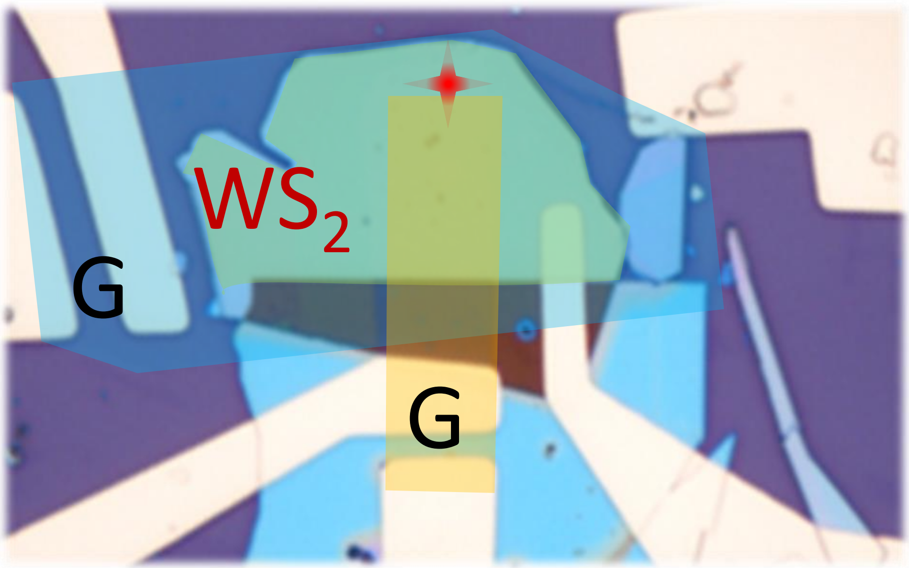
Sachs 2013

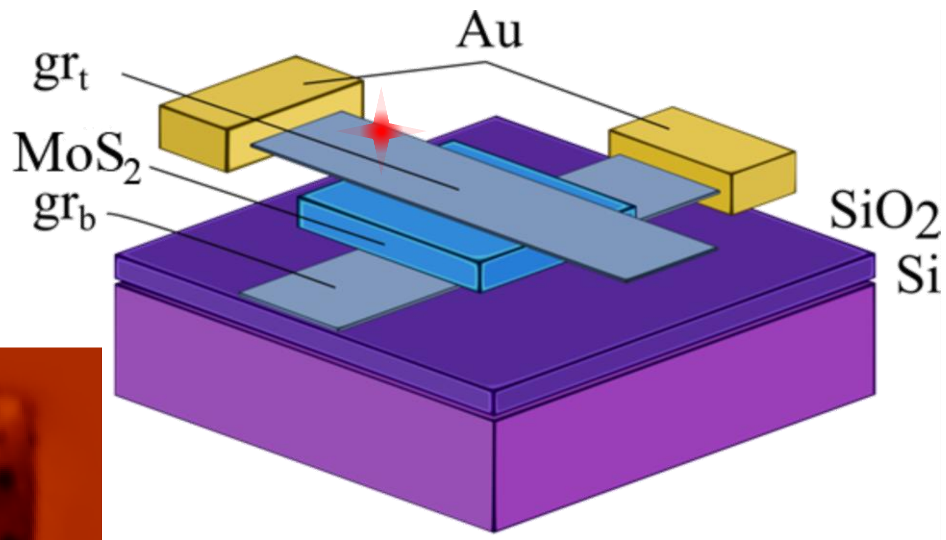


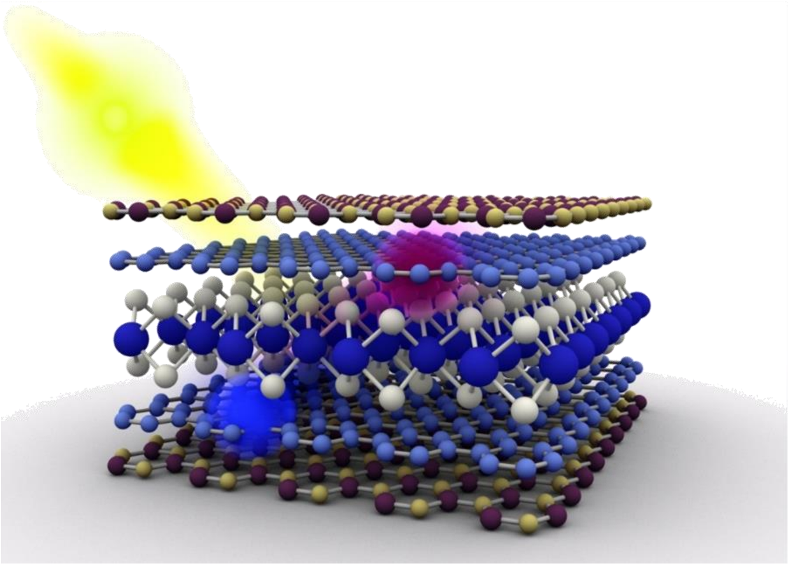
Photogenerated charge carriers



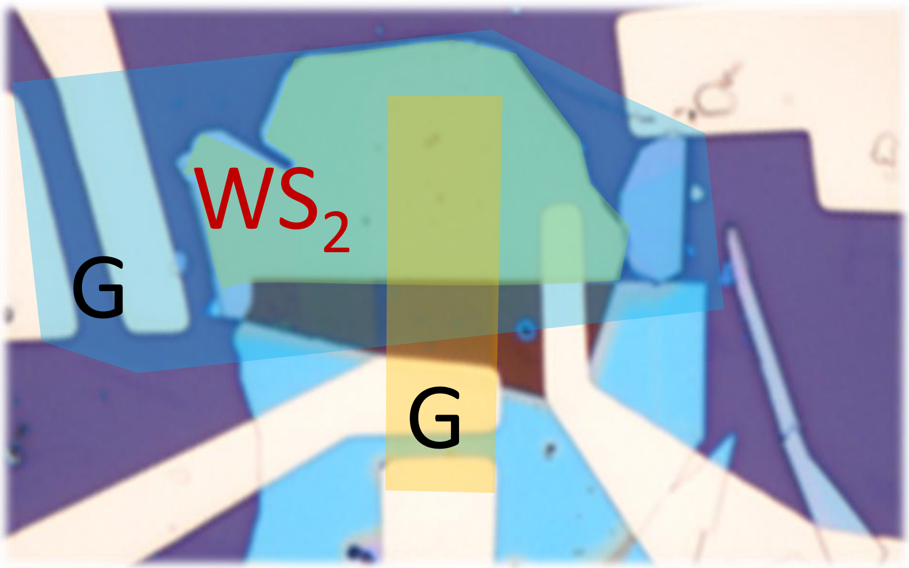
MoS_2 photodiode

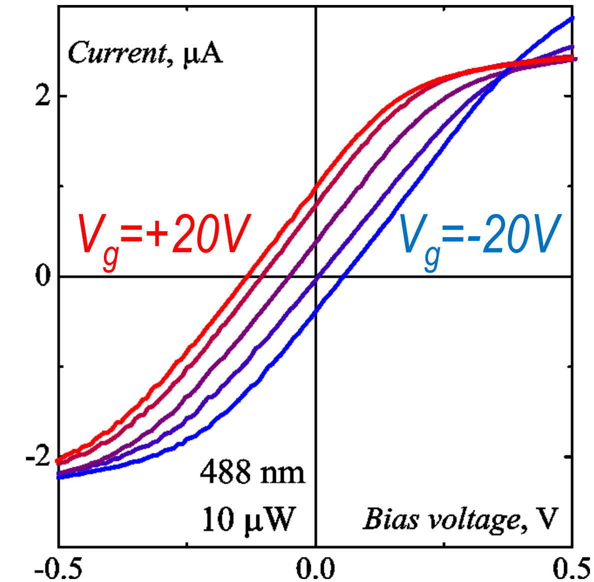


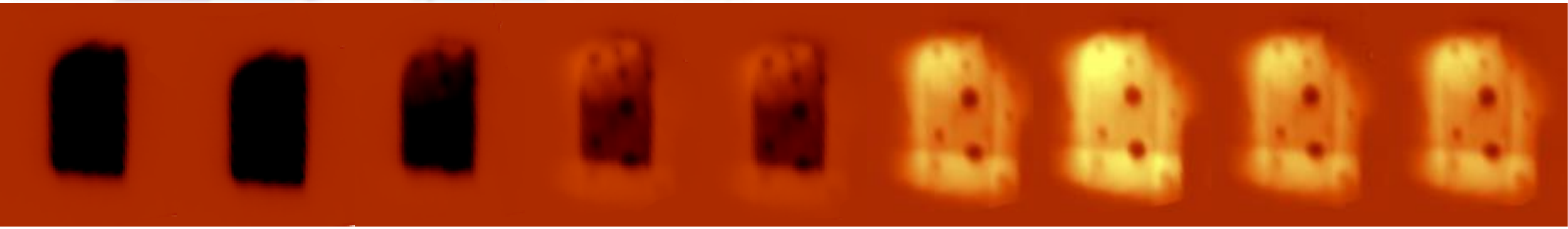




WS_2 photodiode





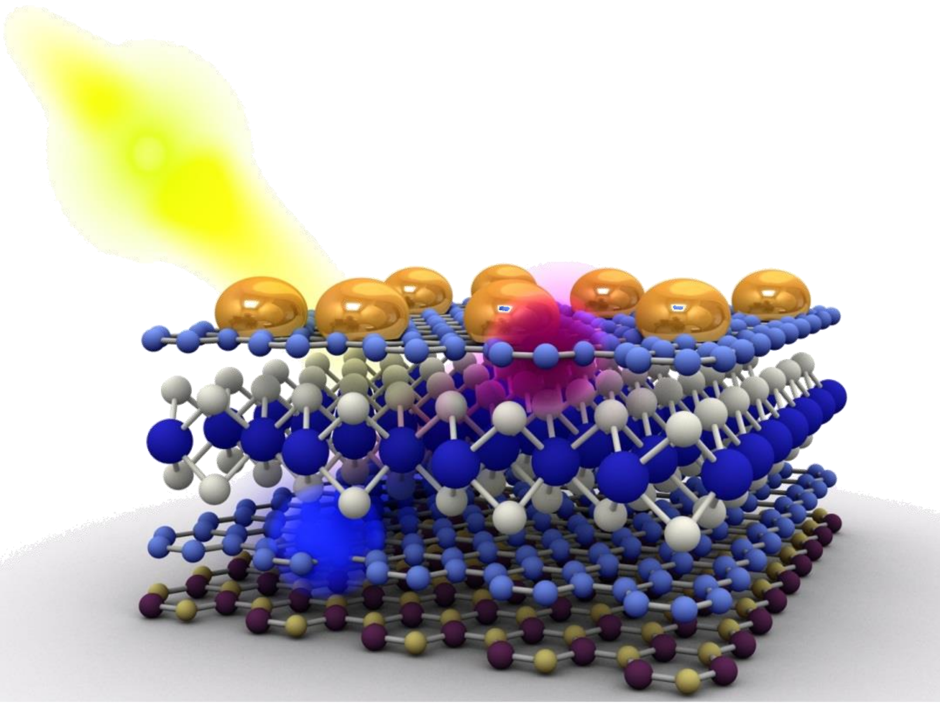


Plasmonics

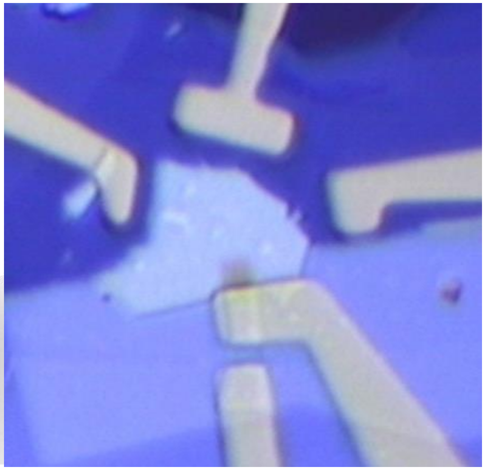
Nanostructured gold:

Strongly enhanses absorbtion

Dopes graphene (p-type)

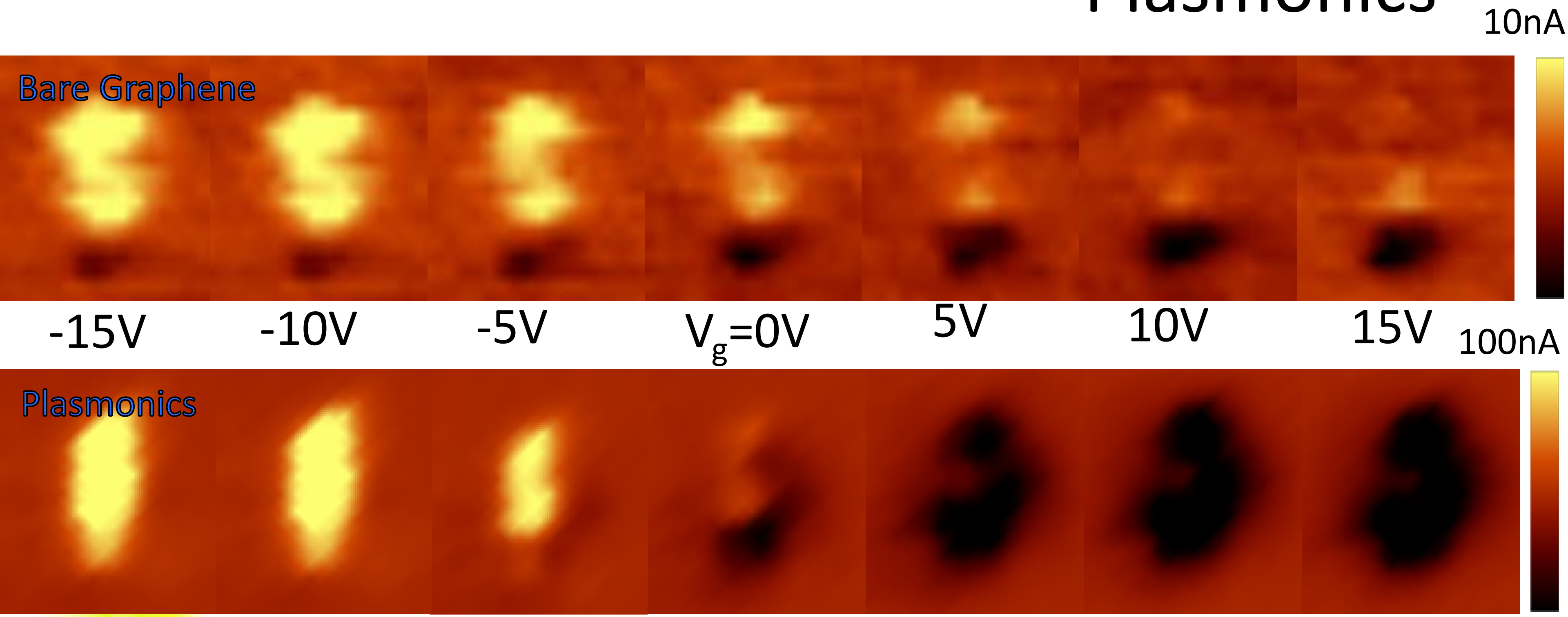


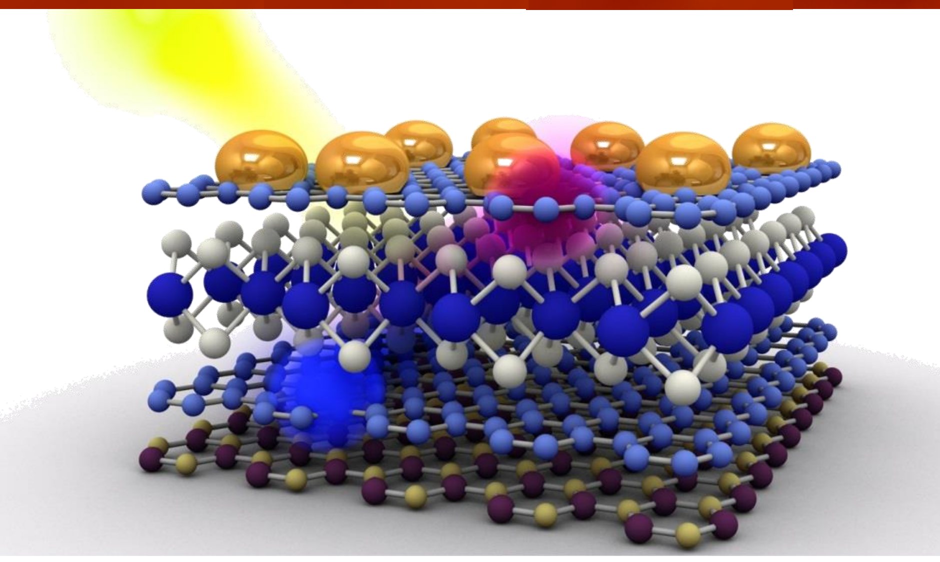
Bare Graphene



With Au droplets

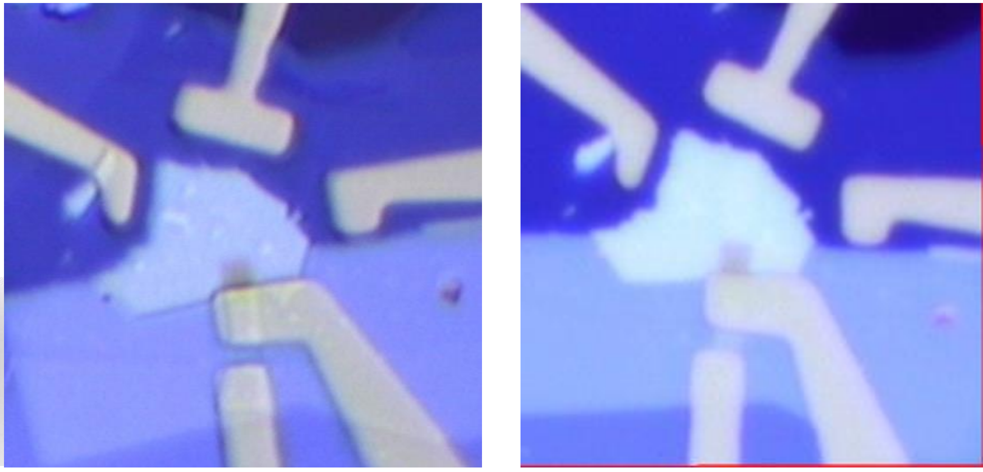
Plasmonics



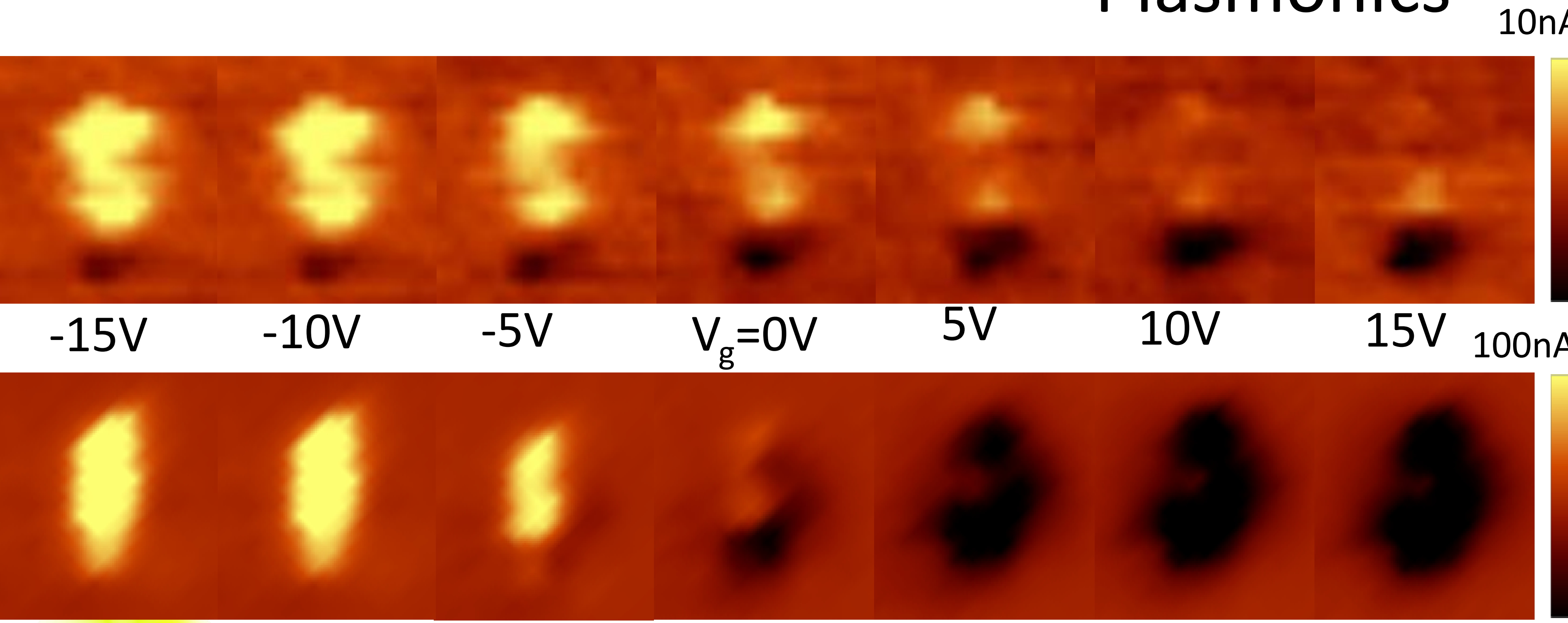


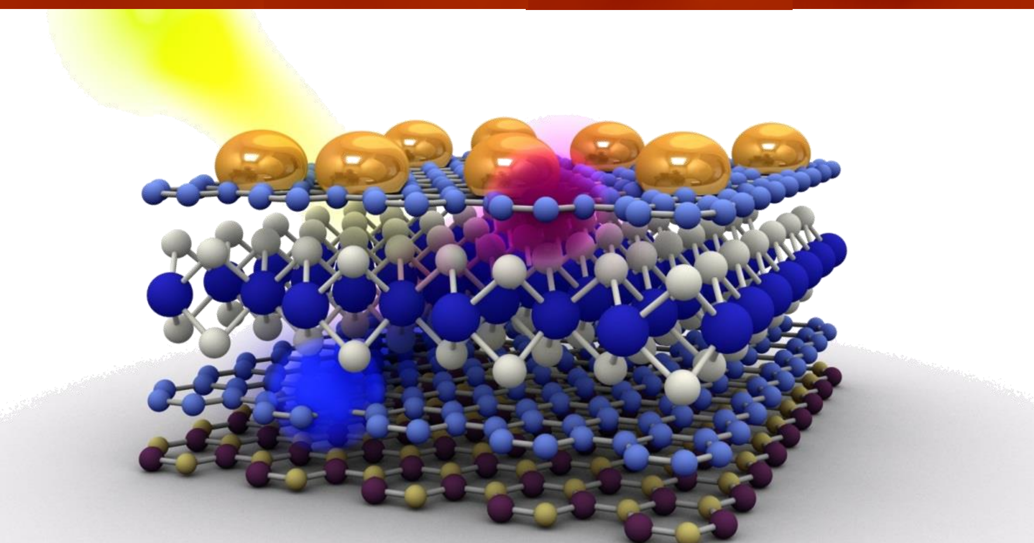
Bare Graphene

With Au droplets



Plasmonics

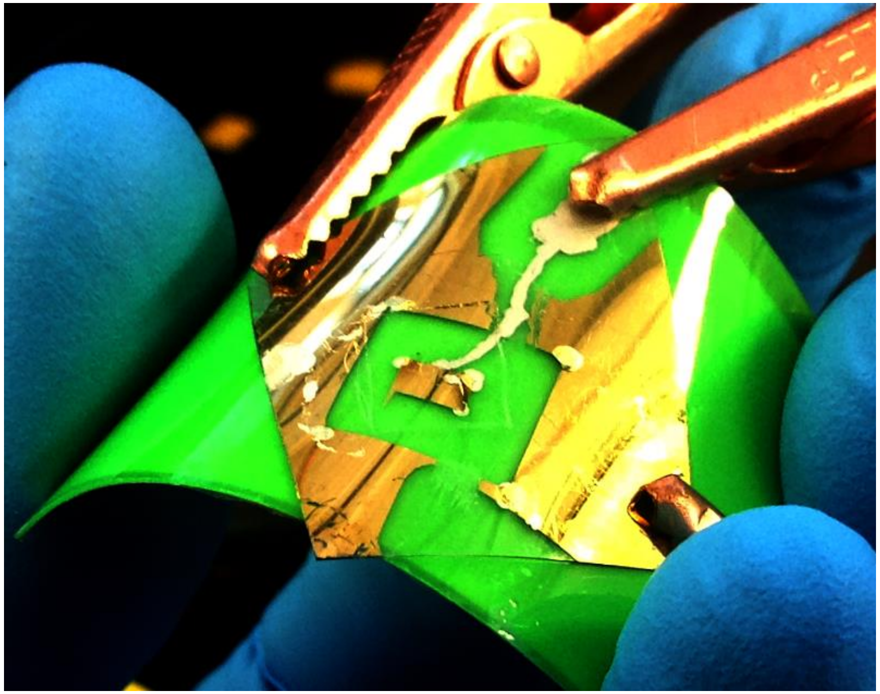




Order of Magnitude improvement in performance

Flexible Electronics

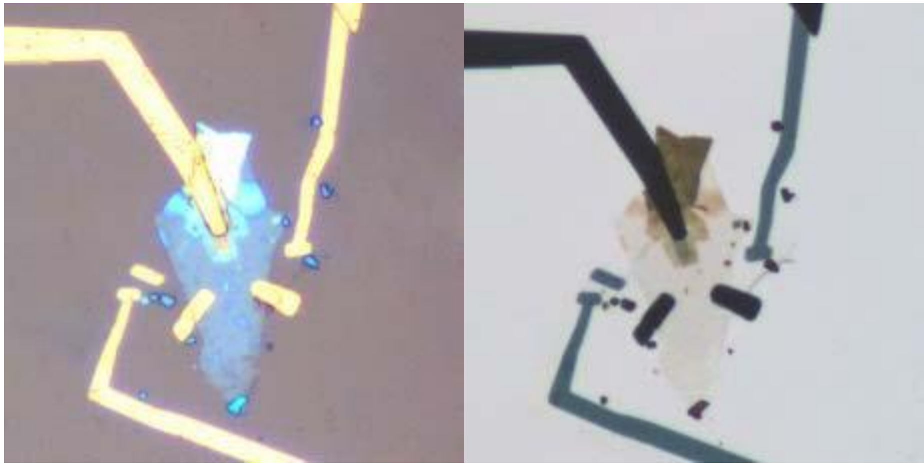
WS_2 photovoltaic device



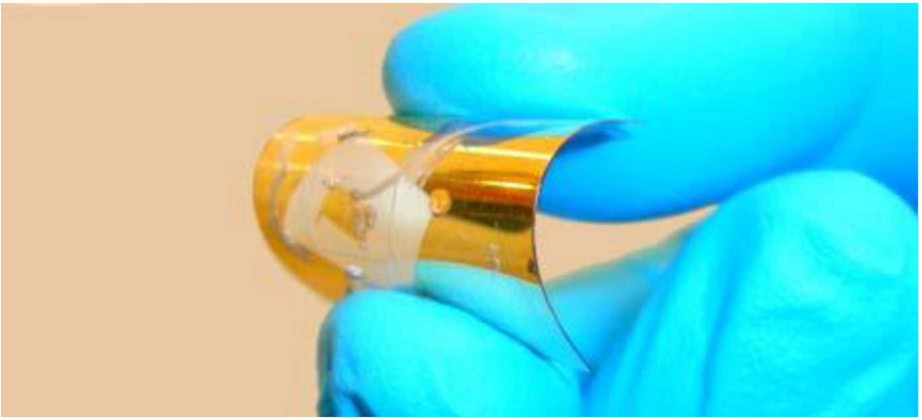
Can be prepared on a flexible substrate

Britnell et al Science'13

WS_2 tunnelling transistor



transparent



flexible

Georgiou et al Nature Nano'13

Metal

Insulator

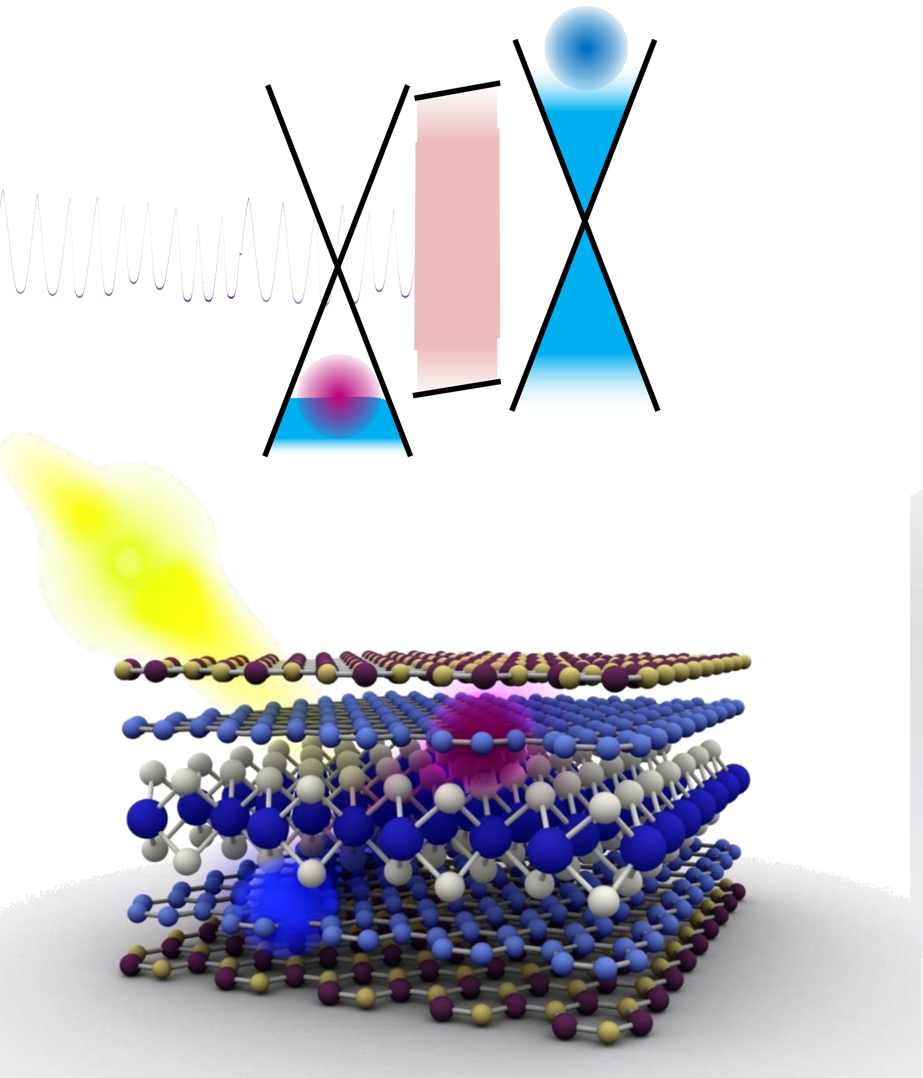
TM(D)C

Insulator

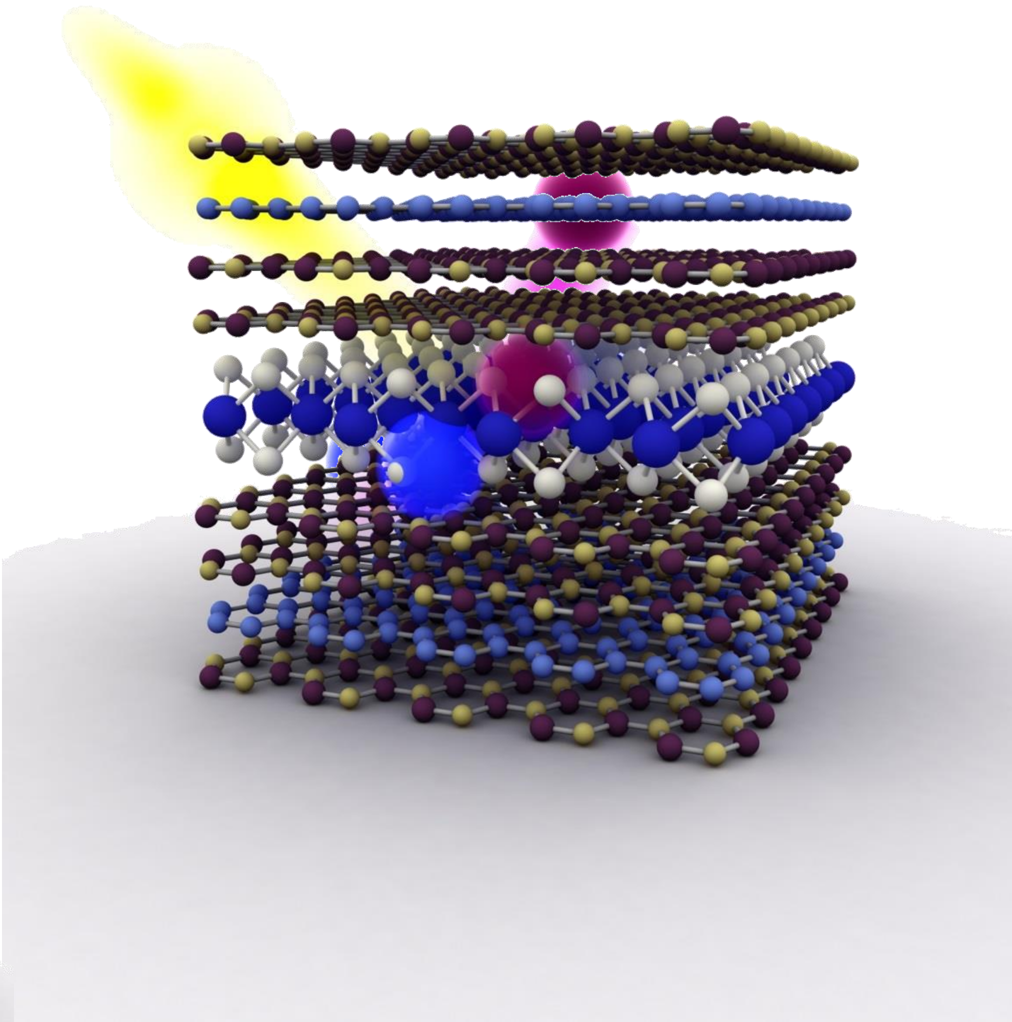
Metal

Light emission

Electron Injection



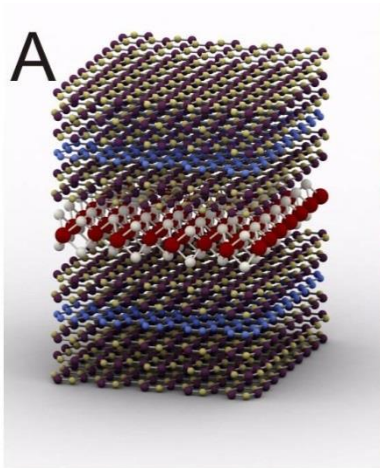
Withers et al Nature Materials ‘15

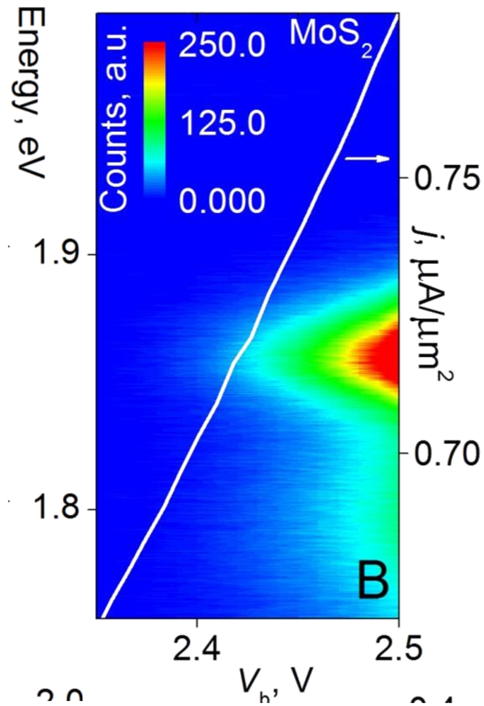


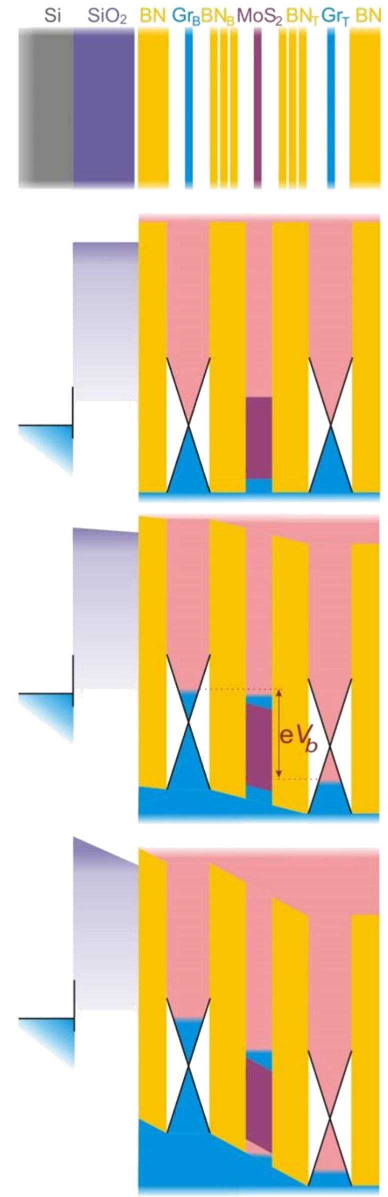
Light emitting recombination of electron-hole pair

Photoemission

Electroluminescence



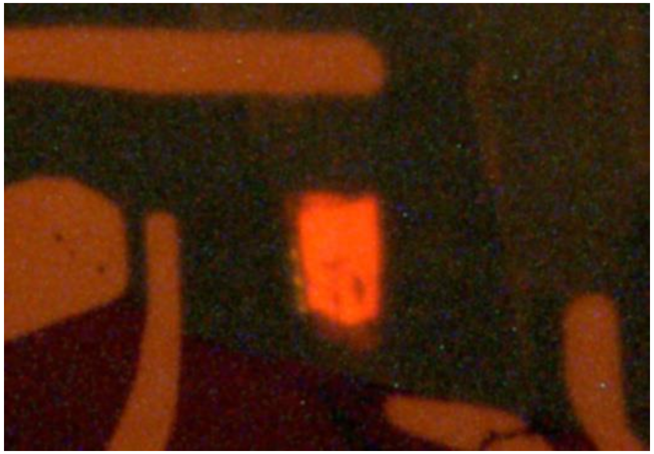




Many materials would luminesce:
MoS_2, WS_2, $MoSe_2$, WSe_2...

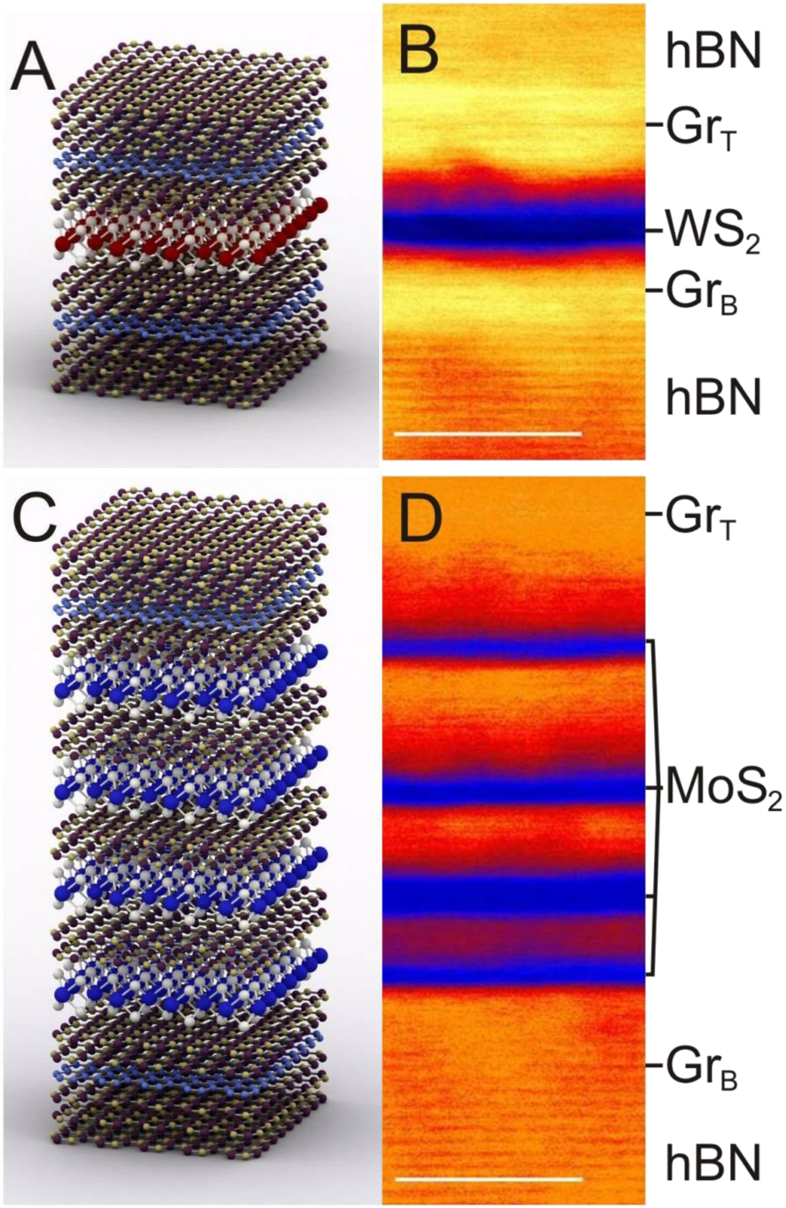
LED Based on 2D Crystals

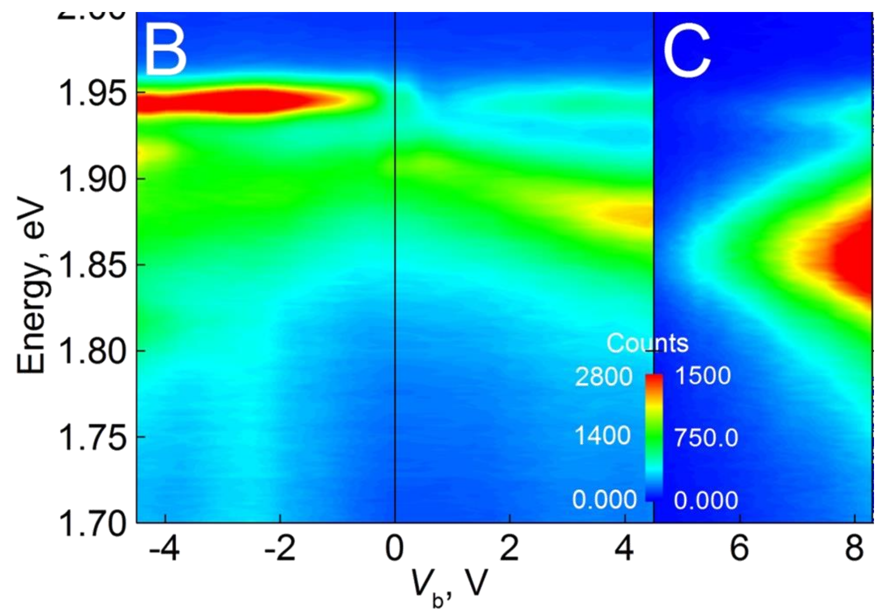
LED based on MoS_2, WS_2, WSe_2



Withers et al Nature Materials'15

Enhancing Emission



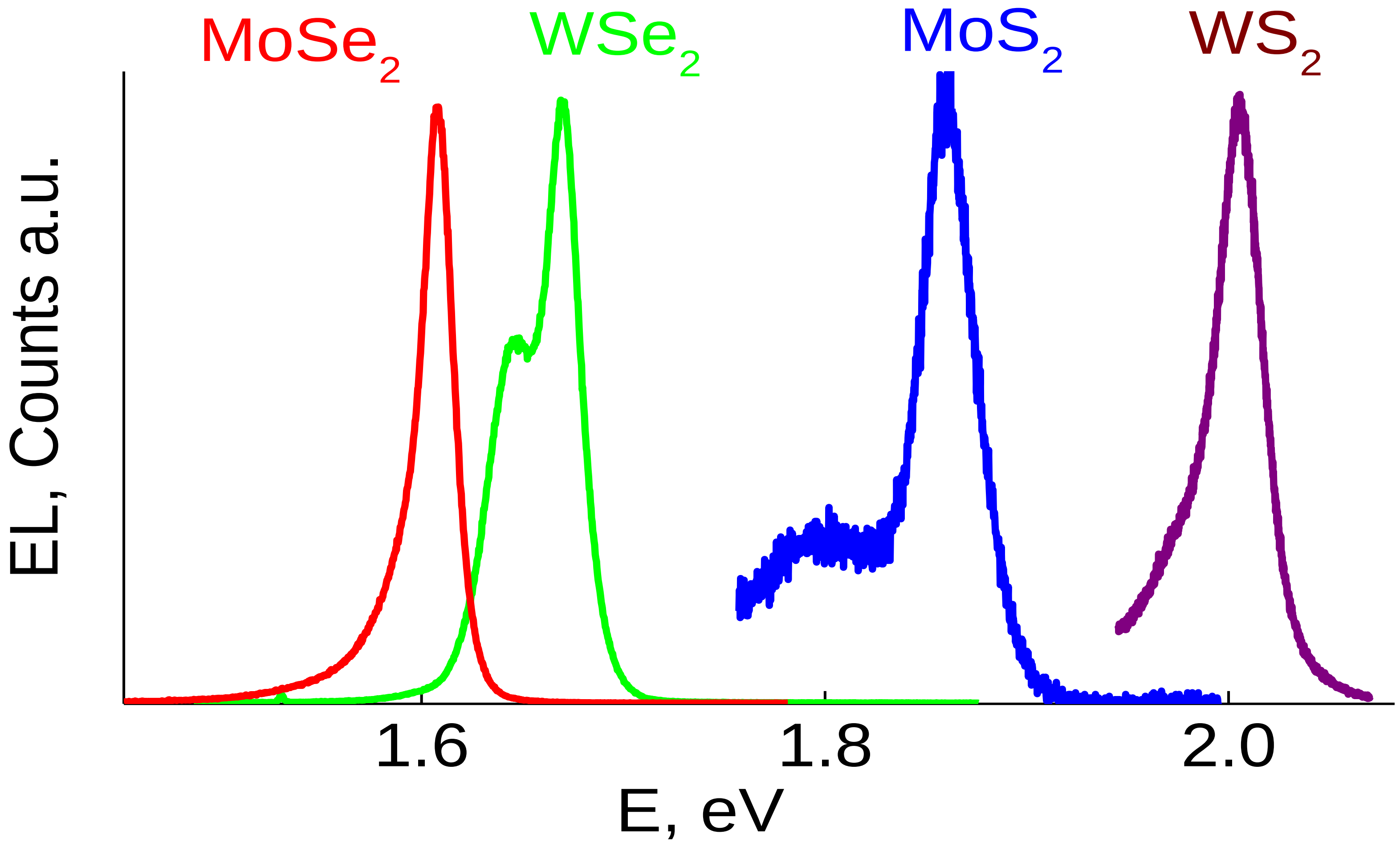


multiple quantum wells

the magic of persistence

Withers et al Nature Materials'15

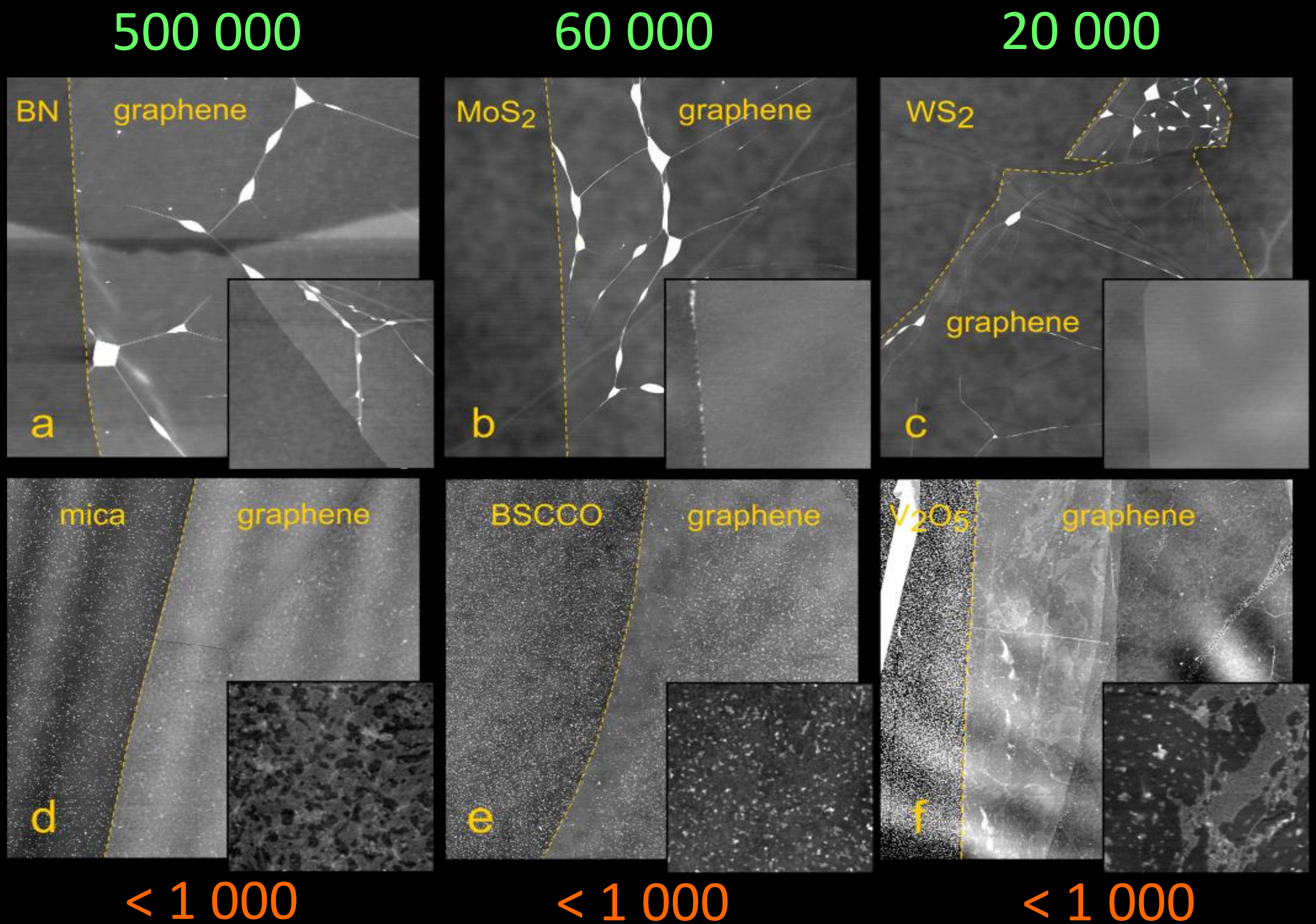
Light emitting quantum wells from different materials



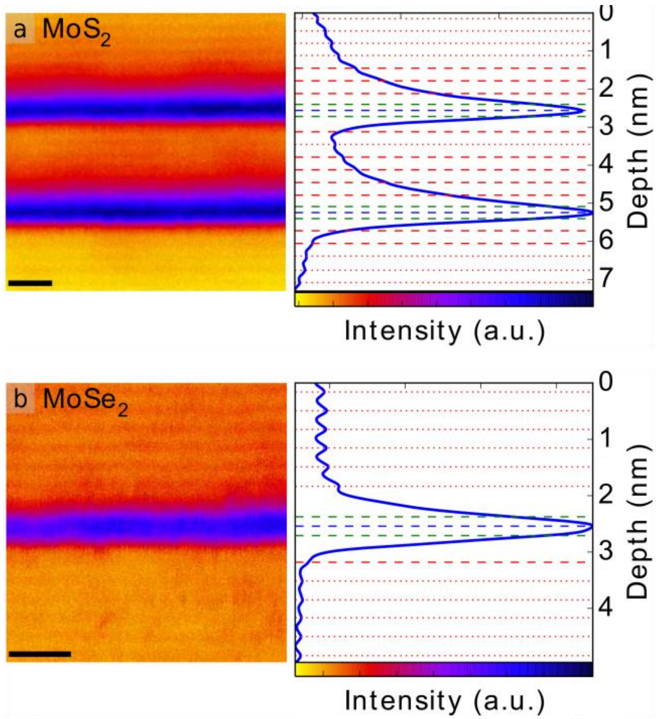
Collectively various TMDC cover a large portion of spectrum

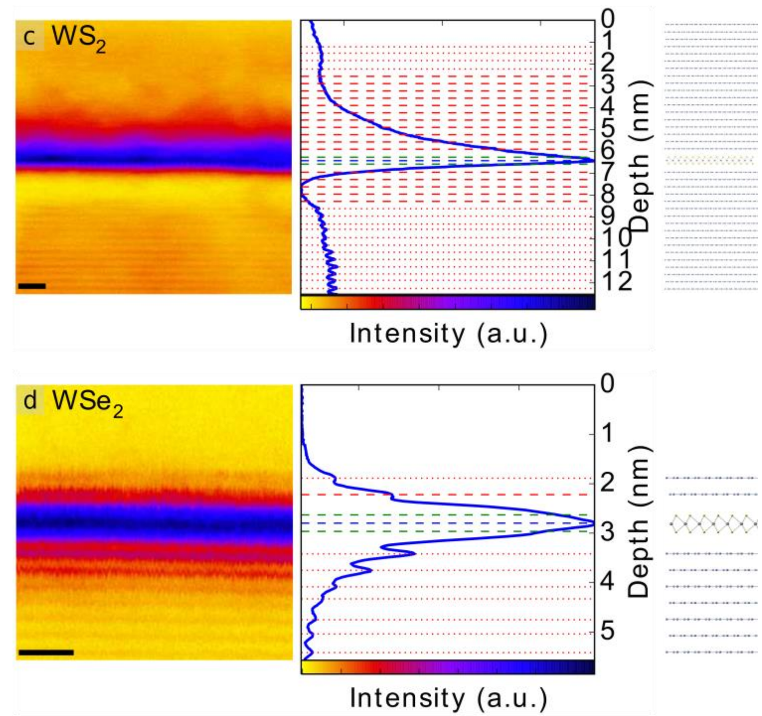
New materials and the chemical stability

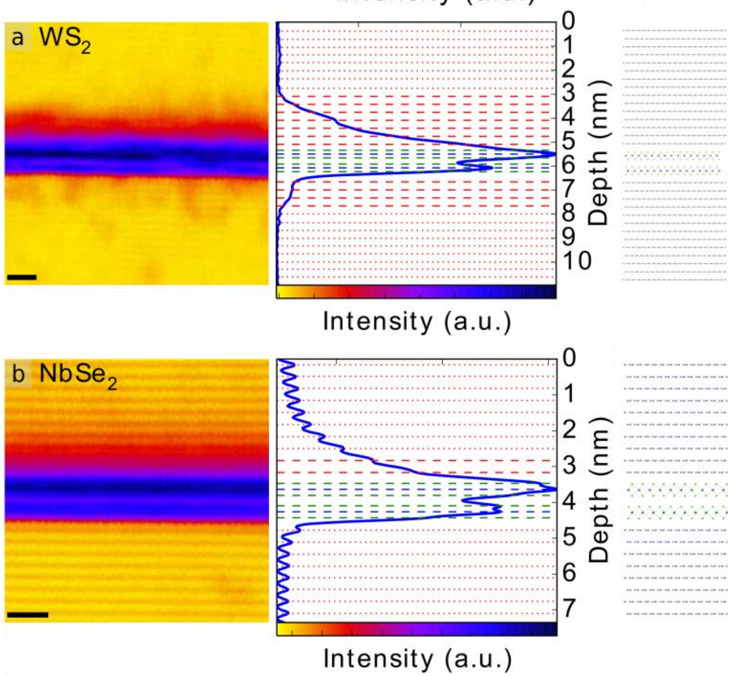
self-cleaning of the interface

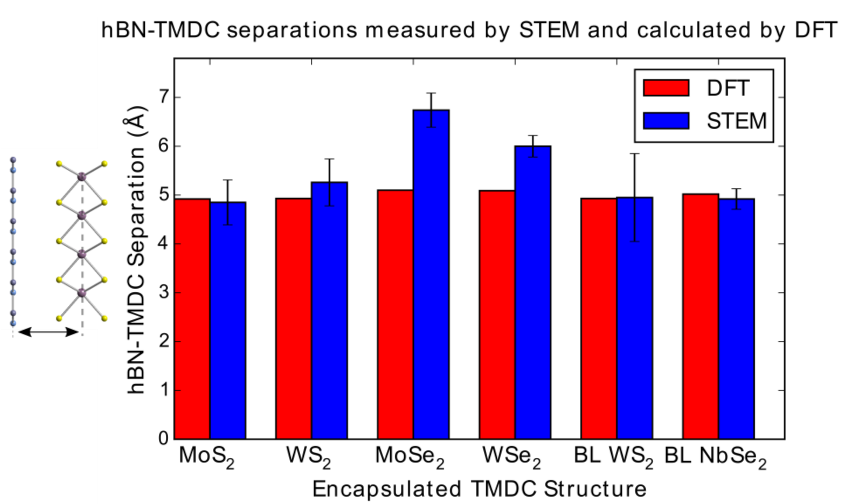


Nano Lett., *14* (6), 3270, 2014

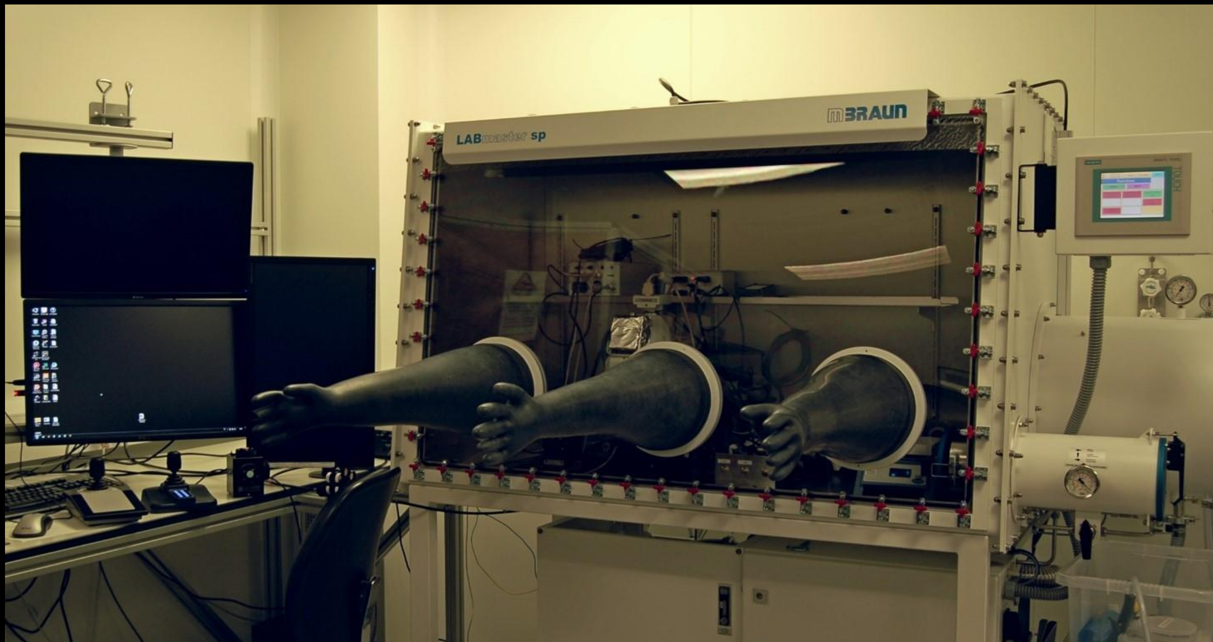

a MoS$_2$
Depth (nm)
Intensity (a.u.)
b MoSe$_2$
Depth (nm)
Intensity (a.u.)

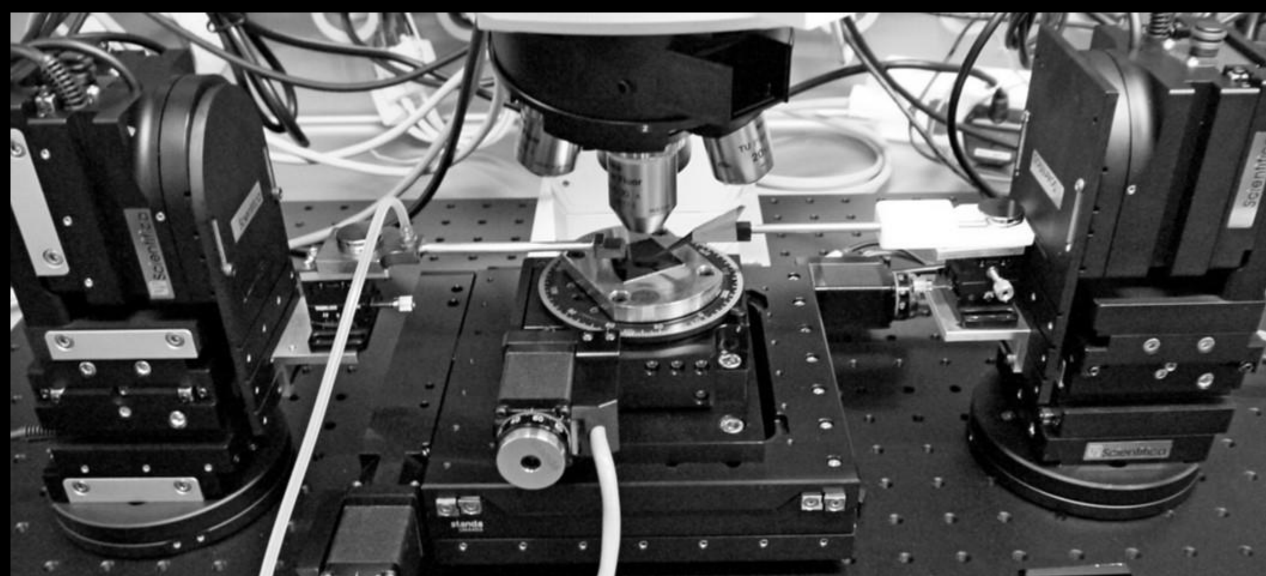

c WS$_2$
Depth (nm)
Intensity (a.u.)
d WSe$_2$
Depth (nm)
Intensity (a.u.)


a WS$_2$
Depth (nm)
Intensity (a.u.)
b NbSe$_2$
Depth (nm)
Intensity (a.u.)


hBN-TMDC separations measured by STEM and calculated by DFT
DFT
STEM
hBN-TMDC Separation (Å)
MoS$_2$
WS$_2$
MoSe$_2$
WSe$_2$
BL WS$_2$
BL NbSe$_2$
Encapsulated TMDC Structure

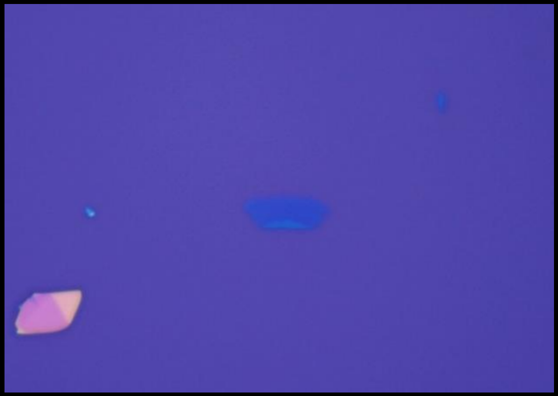
Remotely controlled assembly of heterostructures in argon chamber



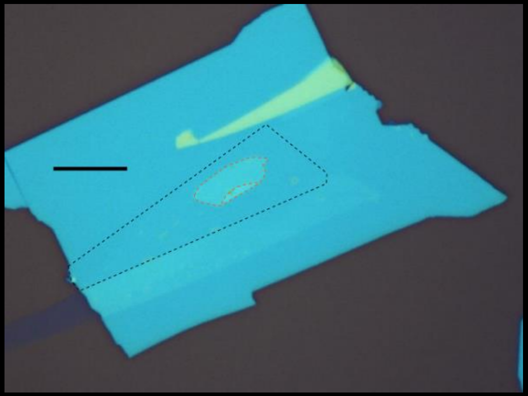


Device fabrication

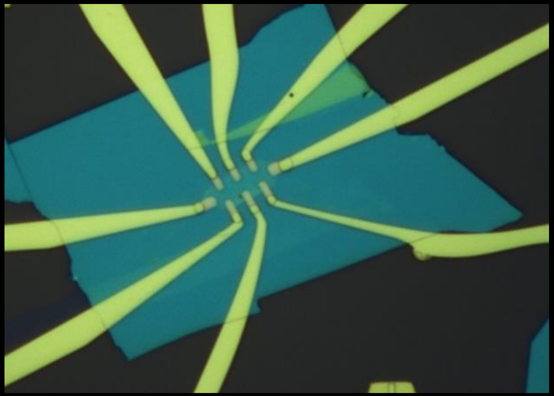
Argon chamber



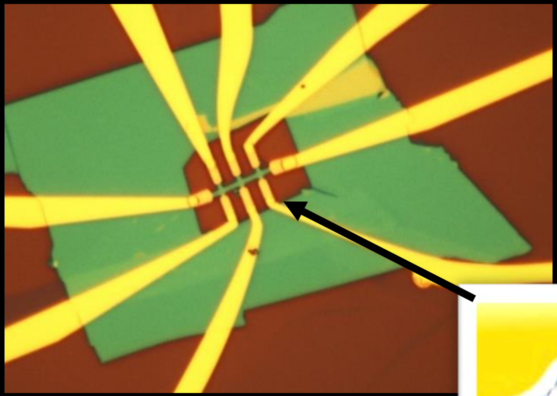
Exfoliation



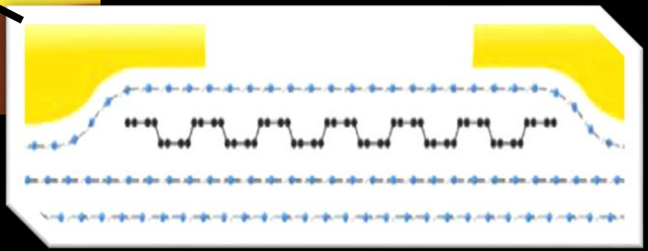
Encapsulation



Contacts

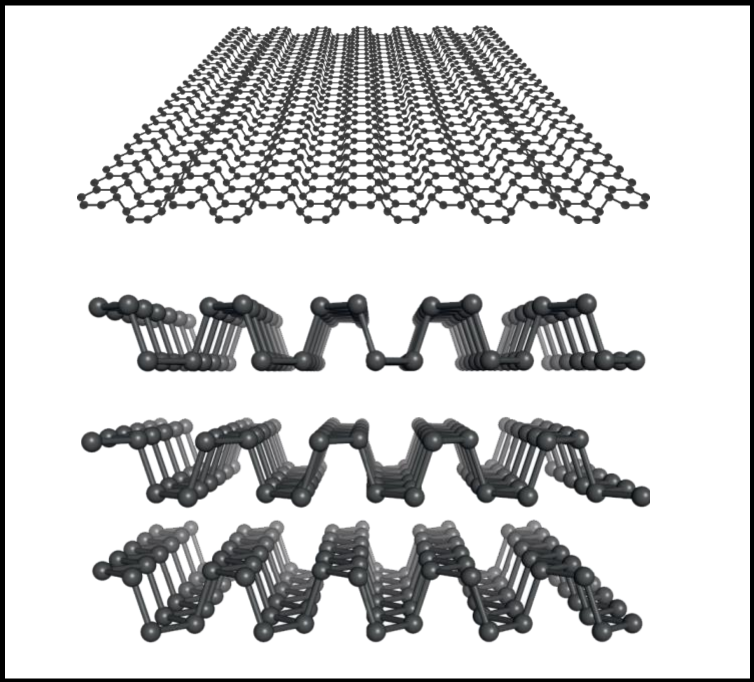


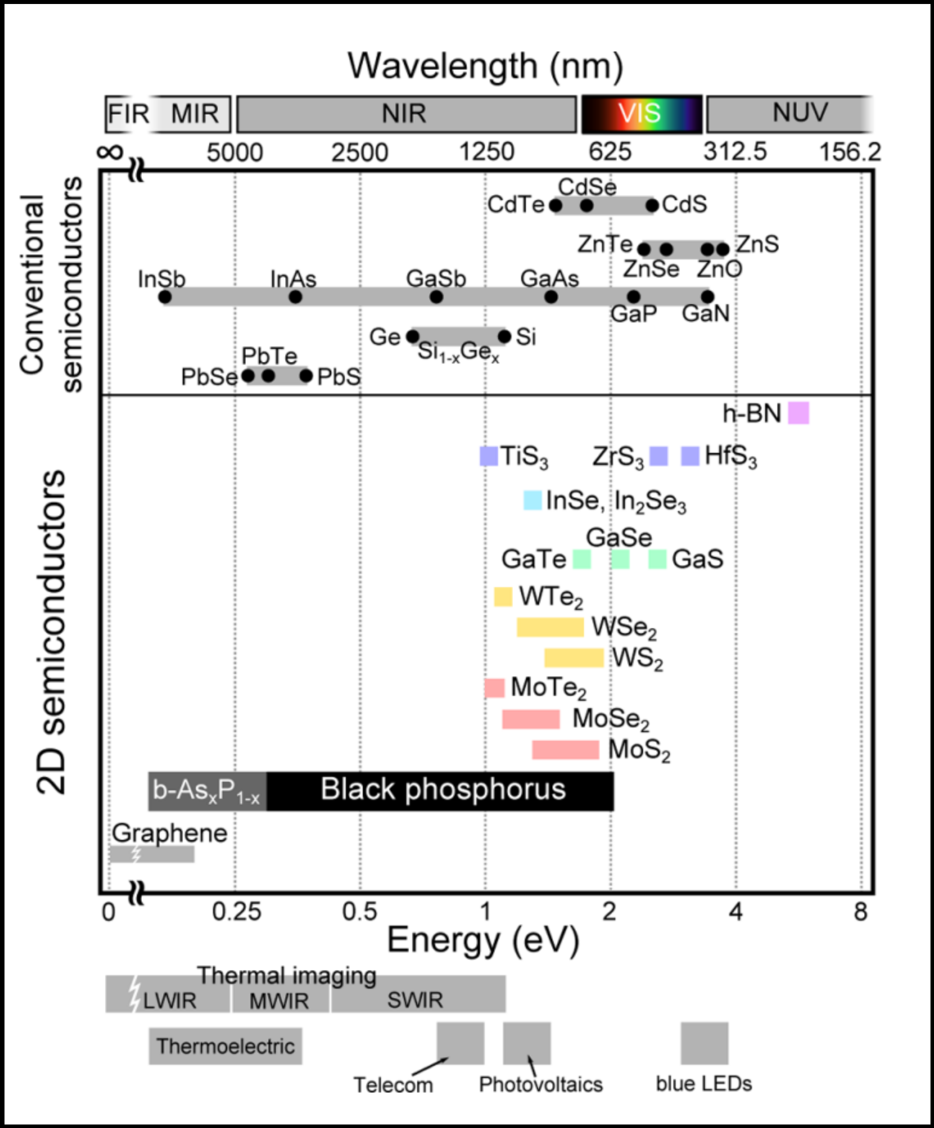
Etching



Black Phosphorus

BP



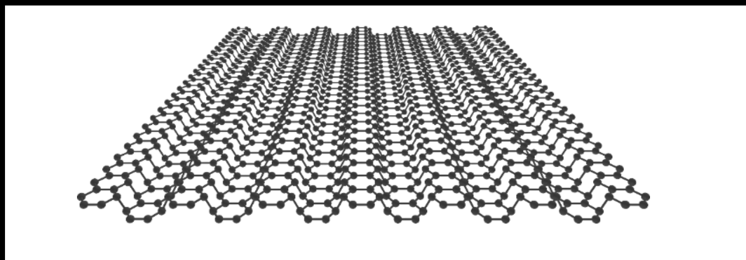


- RT μ=1000cm^{-2}V^{-1}s^{-1} , on/off ratios 100-10 000
- Thickness dependent direct bandgap 0.35eV (bulk) -> 1.88eV (1L)
- Anisotropy in electron, optical, mechanical properties.

A. Castellanos-Gomez, *J. Phys. Chem. Lett.*, **2015**, *6* (21), pp 4280–4291

Black Phosphorus

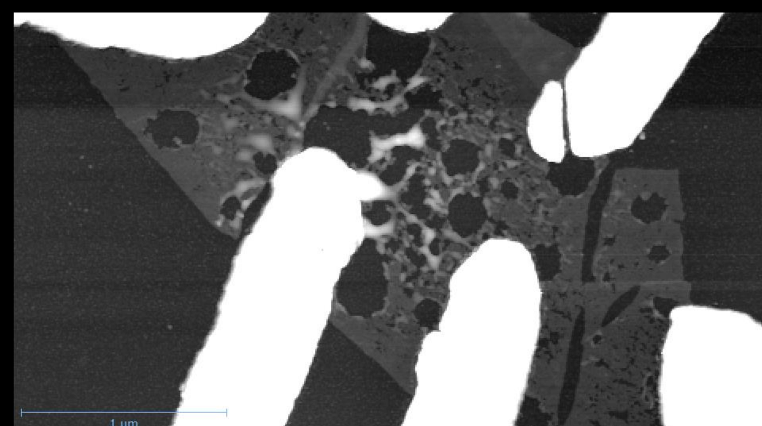
BP



- air sensitive
- heat sensitive
- e-beam sensitive
- light sensitive

Bulk devices - 2DEG survives in the lowest layers
Phys Rev Lett **2014,** 113, (10), 106802

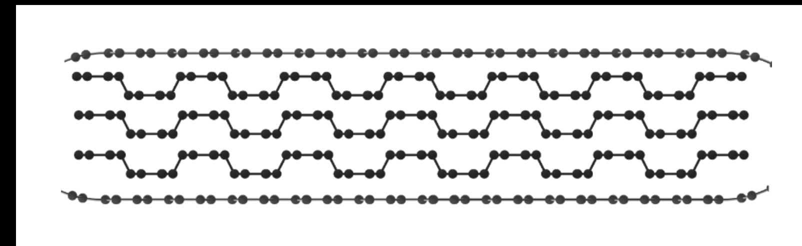
10 layers

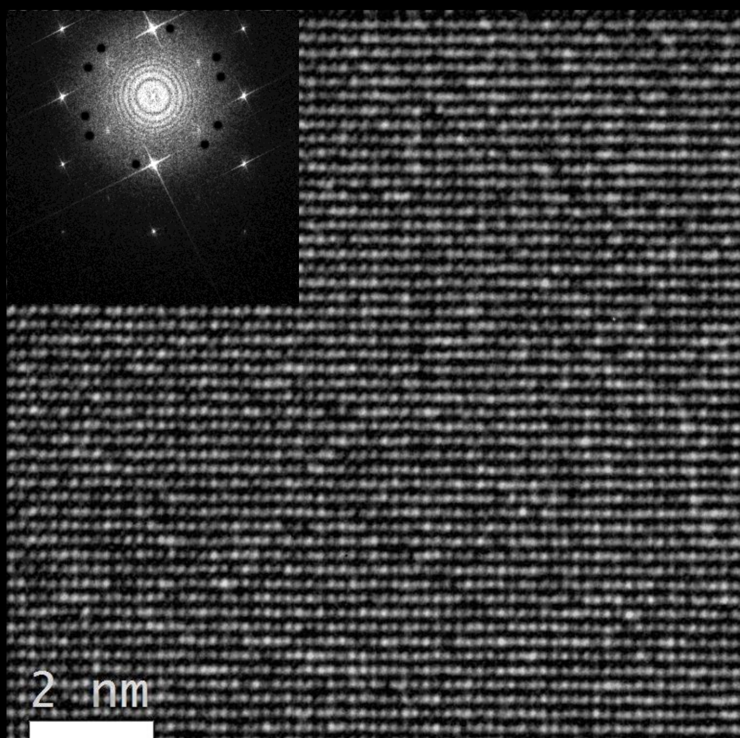


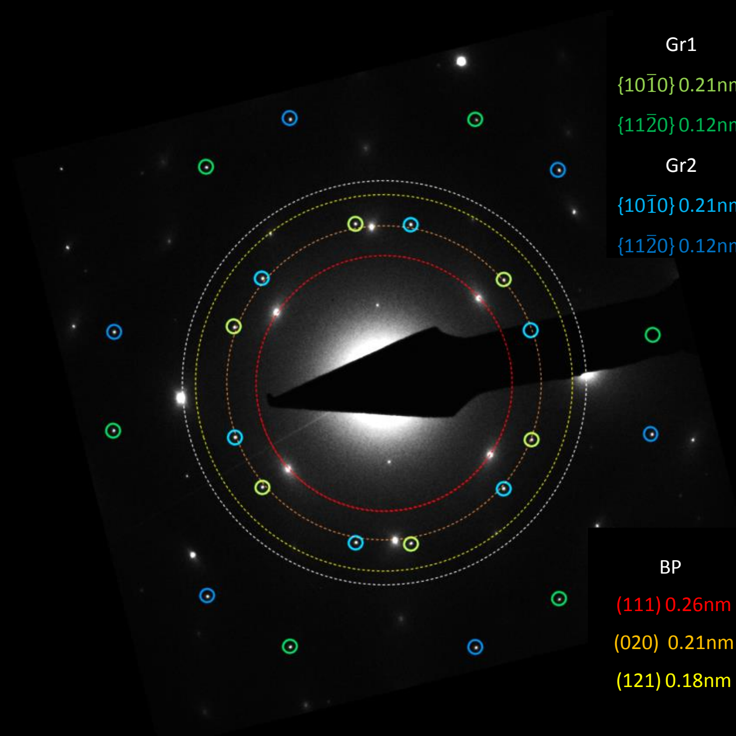
5 layers

Encapsulated BP - TEM

BP

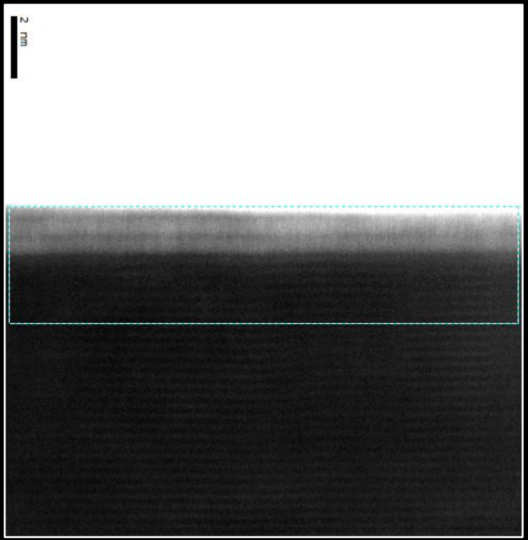


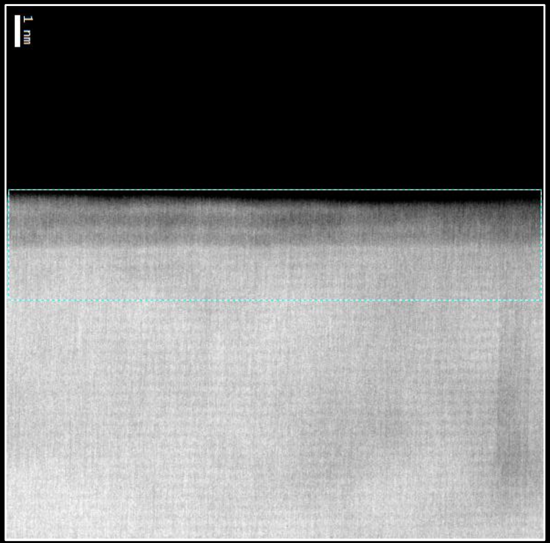


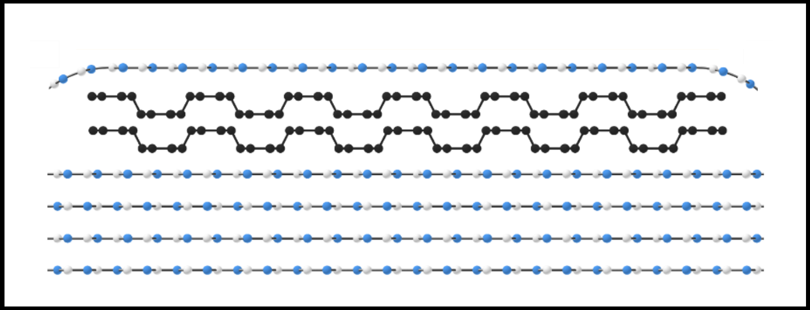


BP – TEM: cross-sections

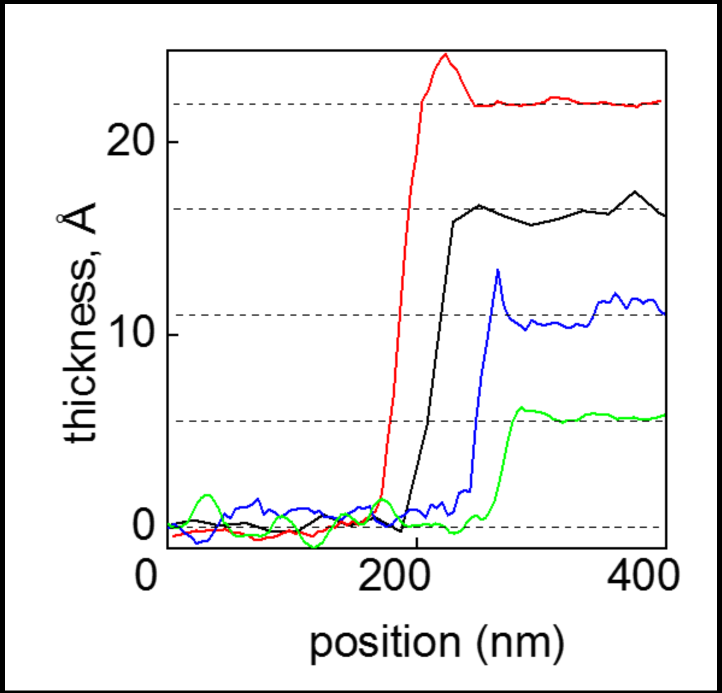
BP







AFM step-height

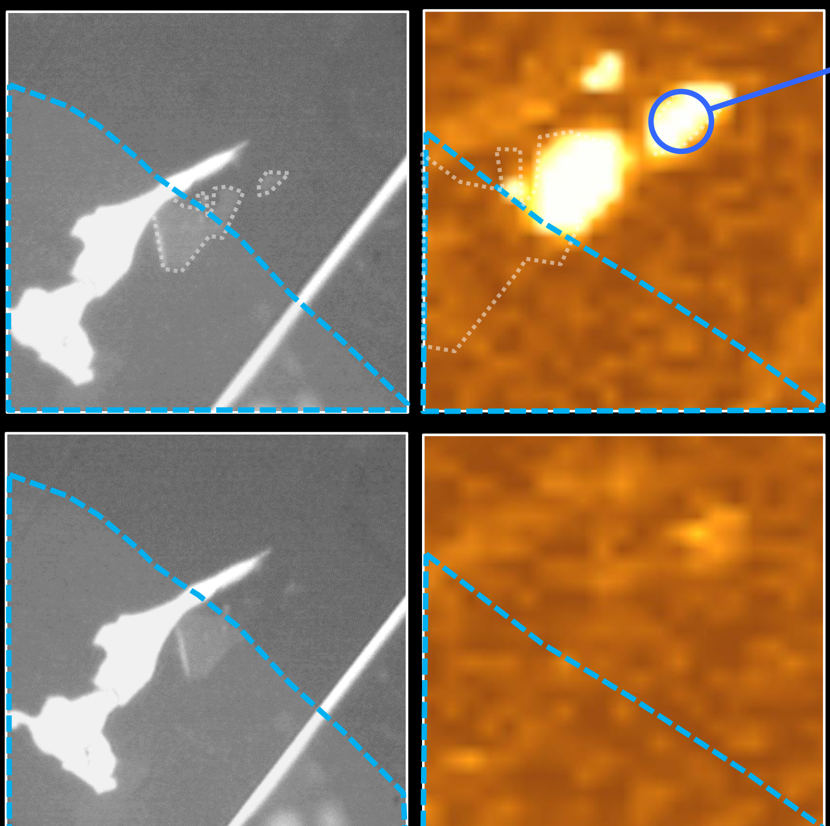


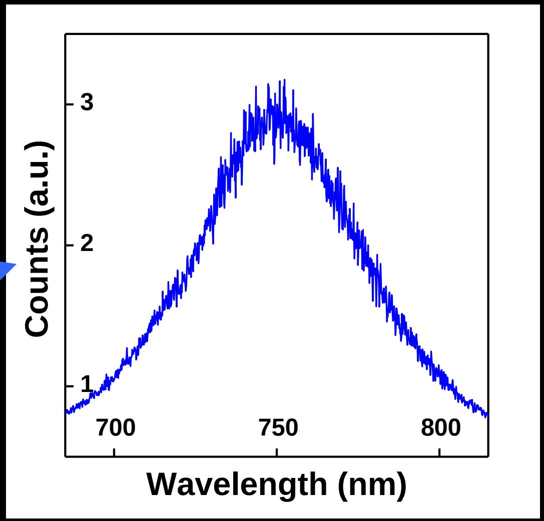
Black Phosphorus - Photoluminescence

BP

2D Mater. **1,** 025001 (2014)

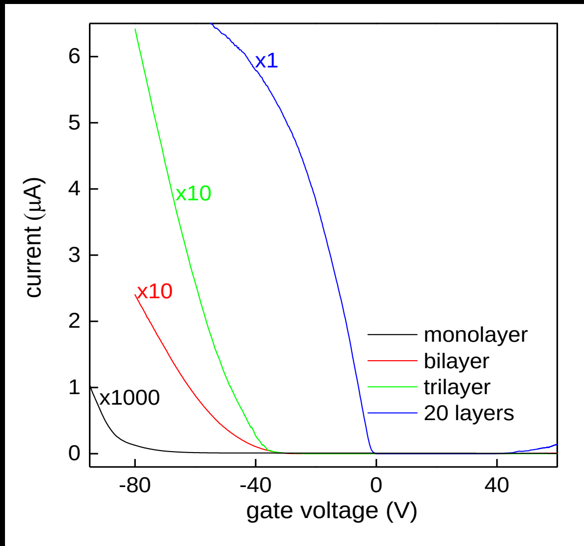
ACS Nano **8 (4),** 4033 (2014)



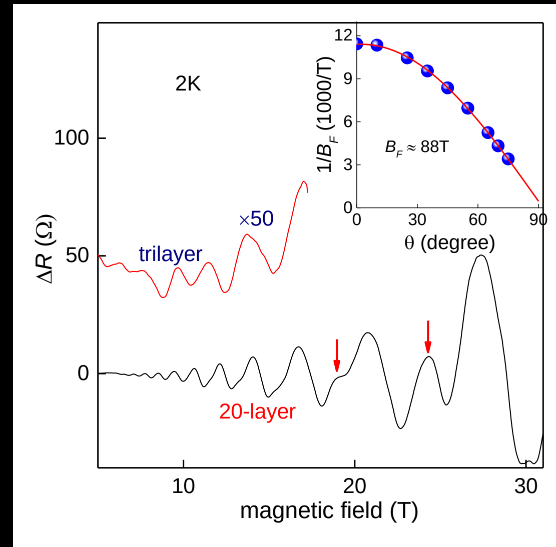


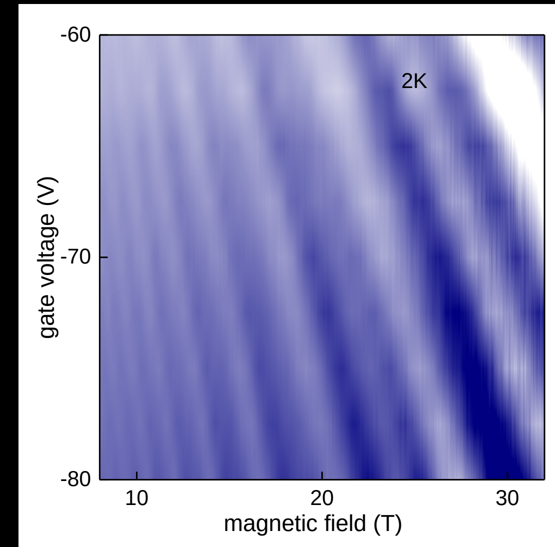
PL from defect

photo- assisted decomposition of open regions

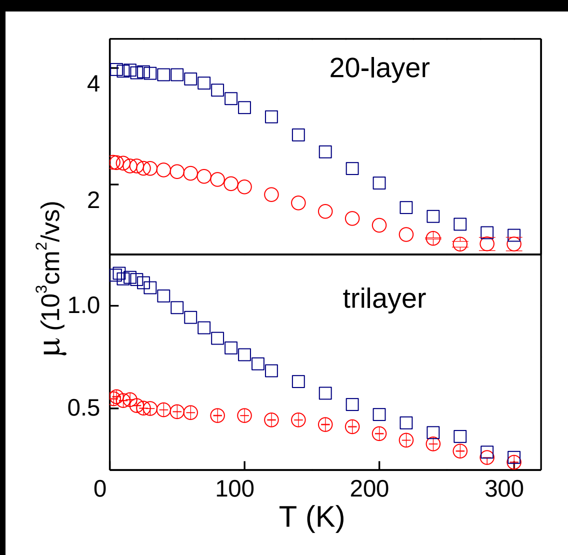


B





T



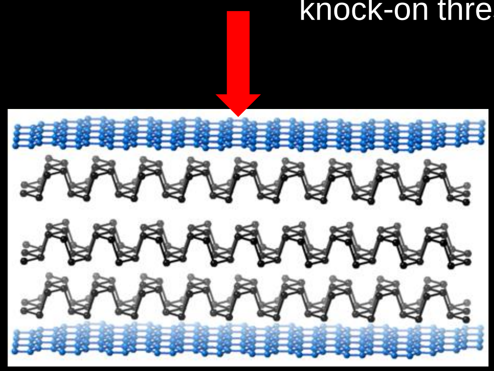
- Third highest mobility among 2D materials so far.
- μ, $cm^{-2}V^{-1}s^{-1}$: 4000 (20 L) 1200 (3 L) 80 (2 L) 1 (1 L)
- SdH oscillations in 3+ layers
- LL spin degeneracy lifted in high B (20 layers)
- $m_h = 0.24 \pm 0.02\, m_0$
- $g = 2.3 \pm 0.2$

Nano Letters 15 (8), p 4914 (2015)

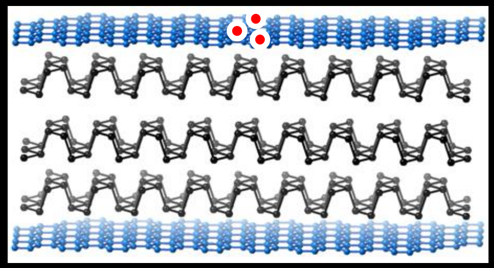
BP: local oxidation at nanometre resolution

BP

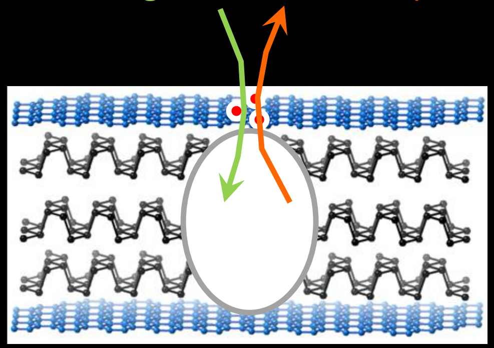
e⁻ energies above knock-on threshold



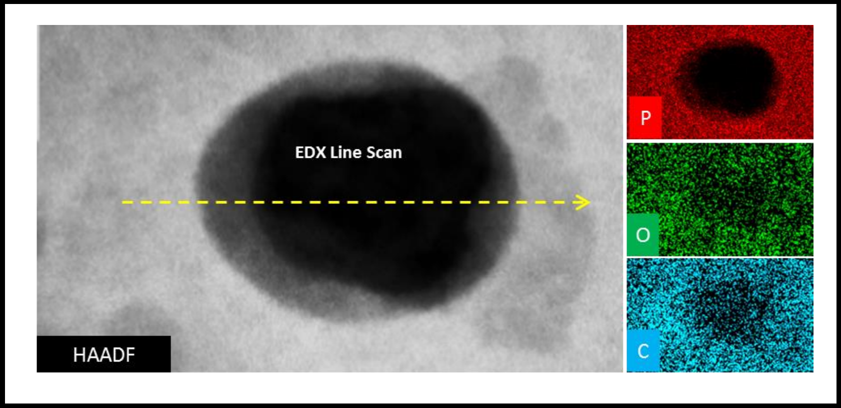
Atomic scale defects in hBN



Oxidation agent IN Reaction products OUT



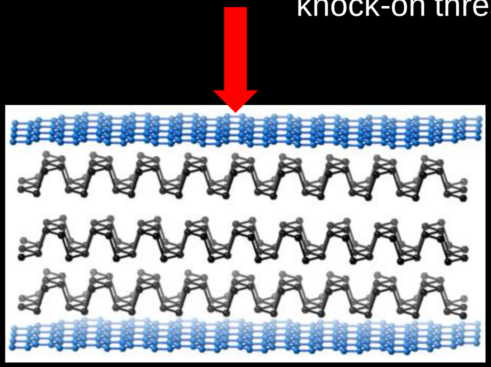
Energy-dispersive X-ray spectroscopy



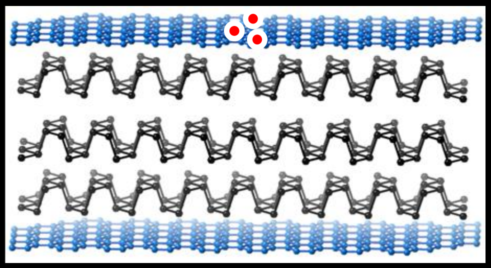
BP: local oxidation at nanometre resolution

BP

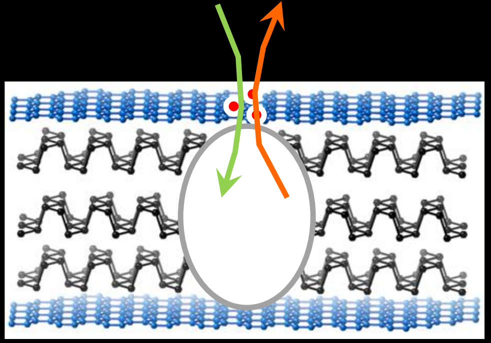
e^- energies above knock-on threshold

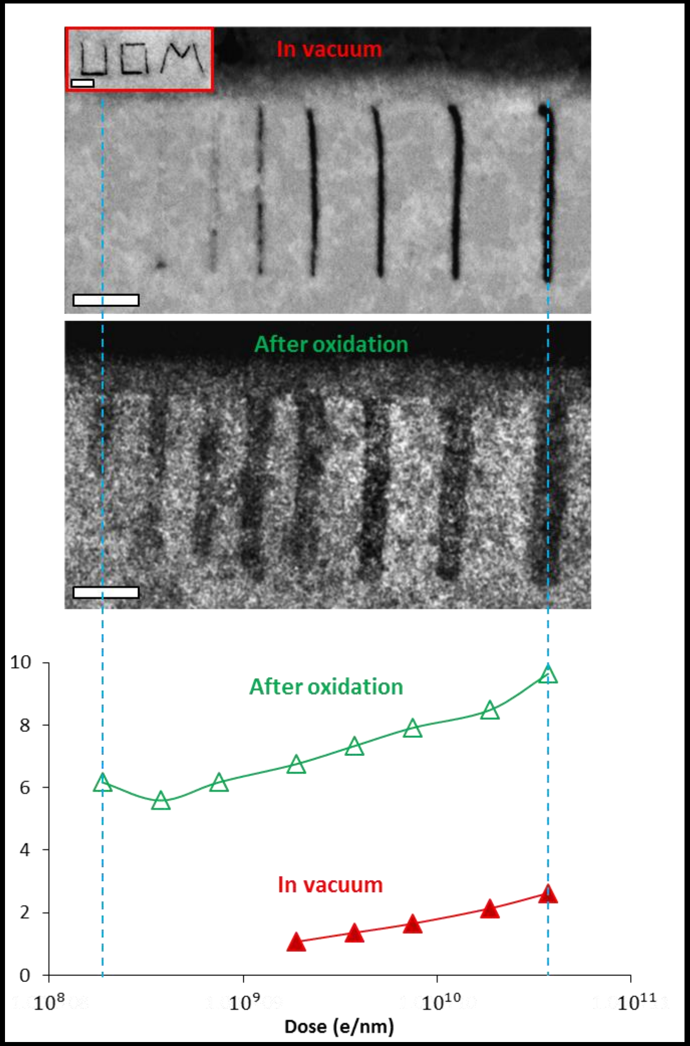


Atomic scale defects in hBN



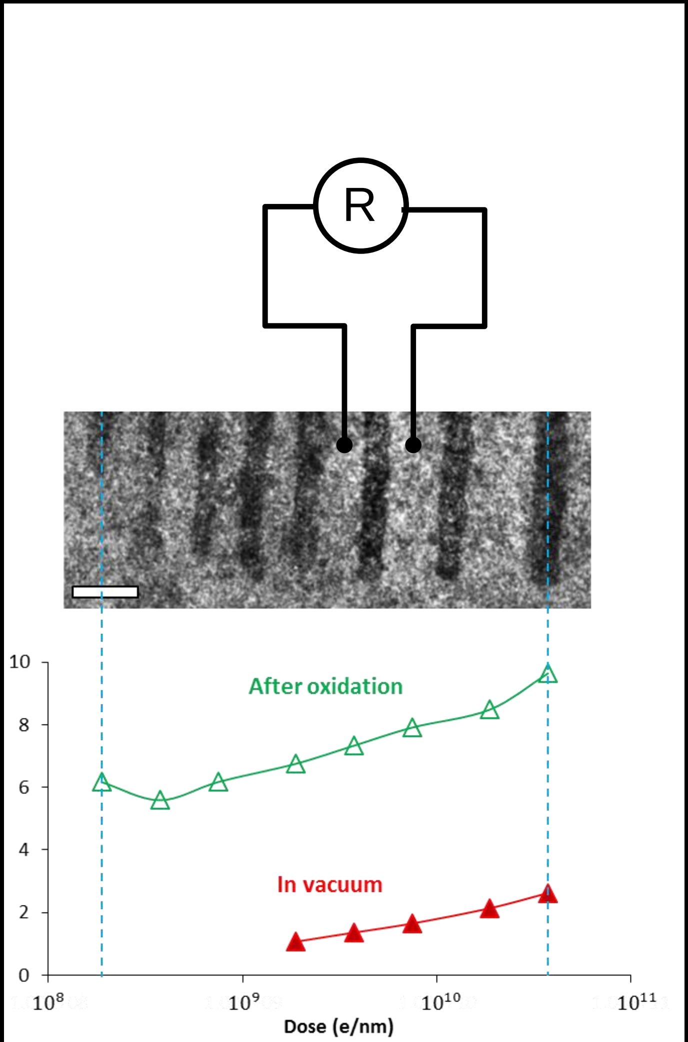
Oxidation agent IN Reaction products OUT

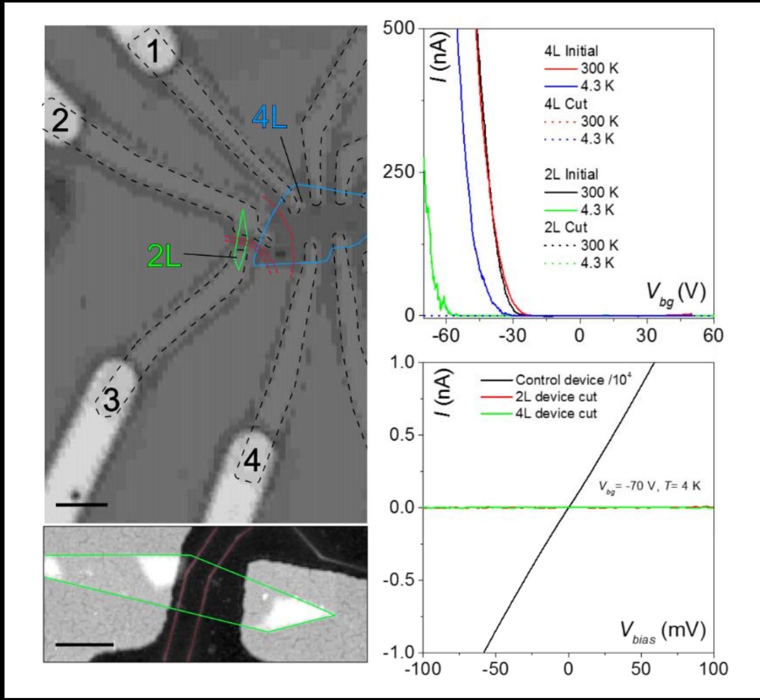


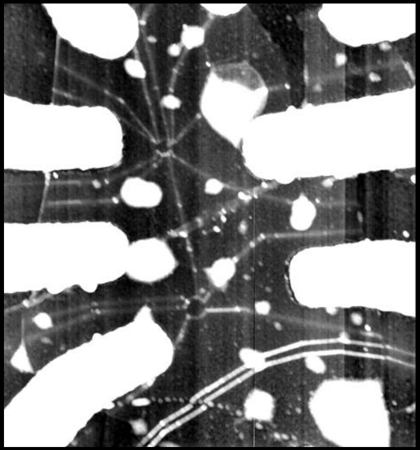


BP: local oxidation at nanometre resolution

BP



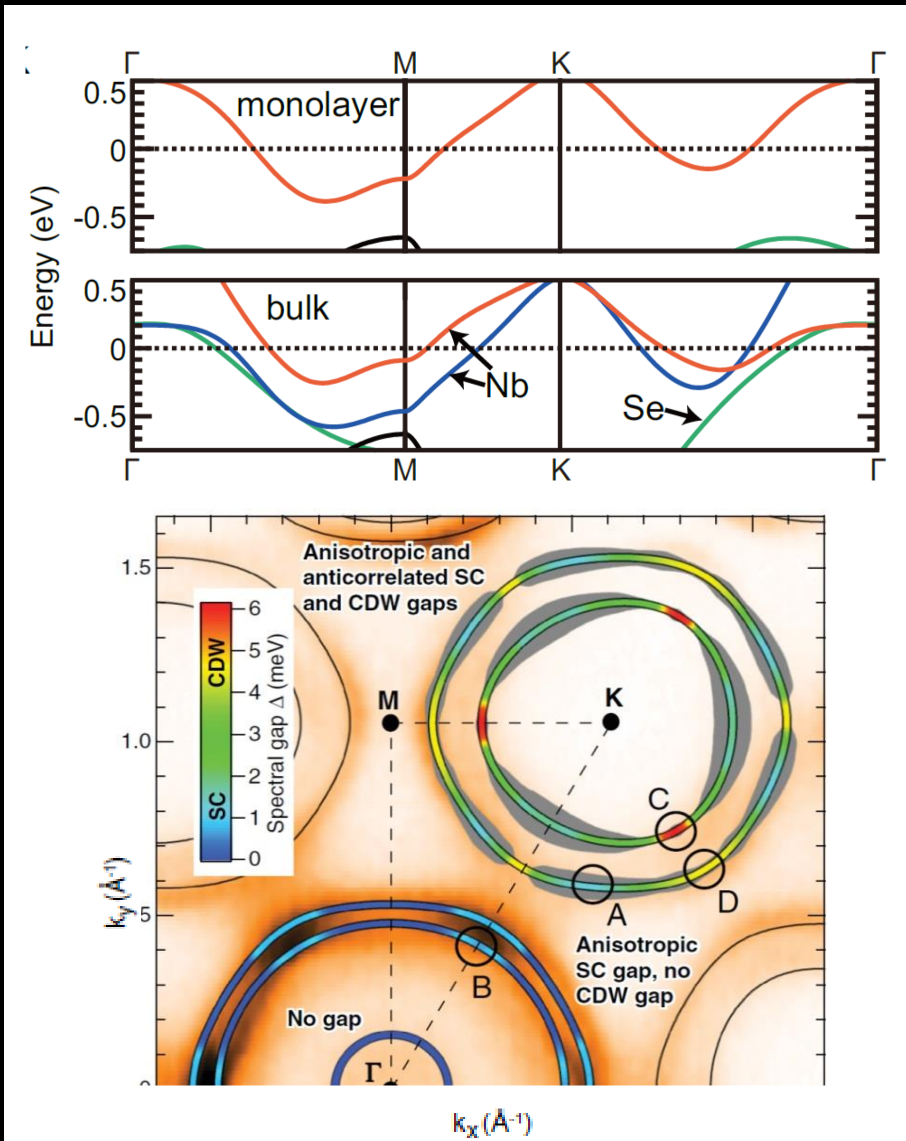




degradation is first avoided
and then used to our advantage

$NbSe_2$

$NbSe_2$



- Band structure changes with thickness
- Complex Fermi – Surface -> superconductivity and charge density waves at low T
- Ultrathin devices can give better insight into SC and CDW at 2D limit

Bulk ground states

Charge order	T_c (K)	Δ (meV)
SC	7.2	0.6 - 1.2
CDW	33.5	5.1

M.M.Ugeda, Nat.Phys, 12, 92–97 (2016) D.J. Rahn, *PRB 85*, 224532(2012)

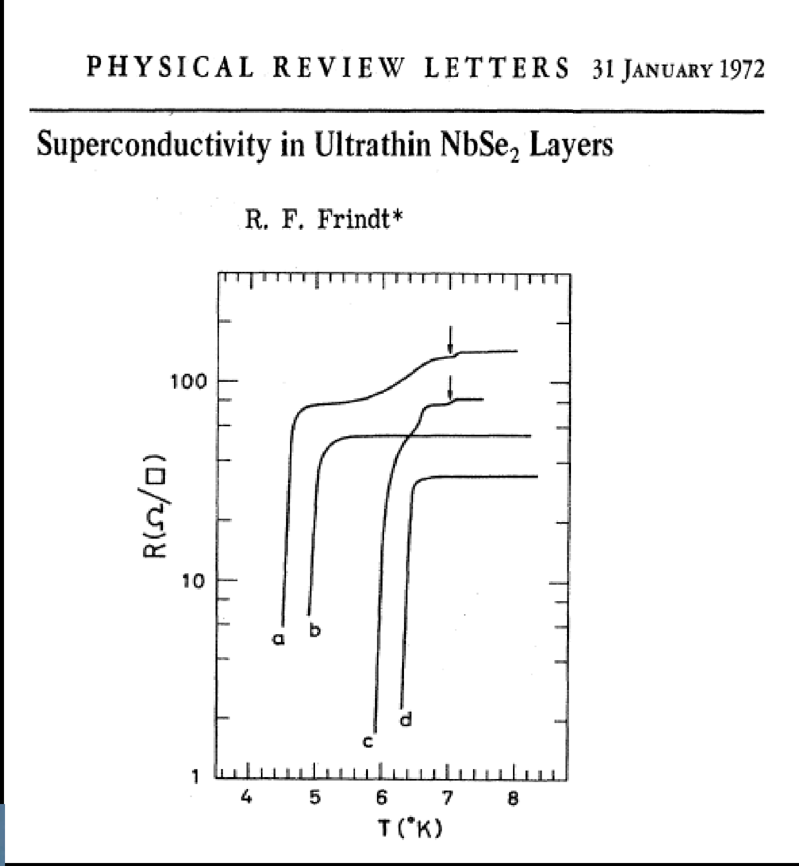
Instability of $NbSe_2$

$NbSe_2$

Previous reports:

lithography free contact fabrication
- superconductivity in >3 layers

Conventional electron beam lithography
- superconductivity in >6 layers

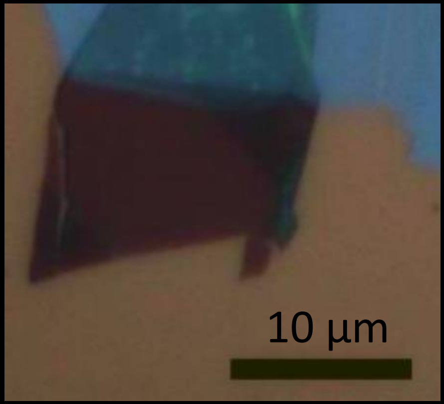

PHYSICAL REVIEW LETTERS 31 January 1972

Superconductivity in Ultrathin $NbSe_2$ Layers

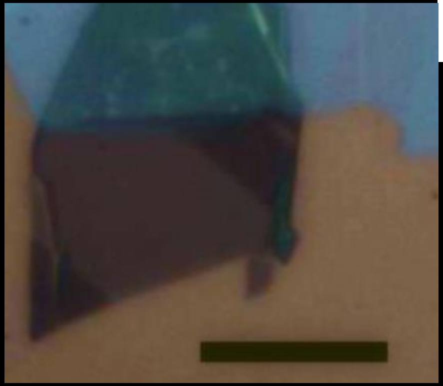
R. F. Frindt*

Air

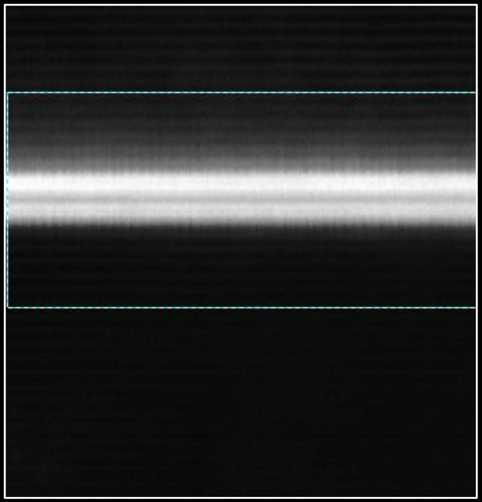
as exfoliated

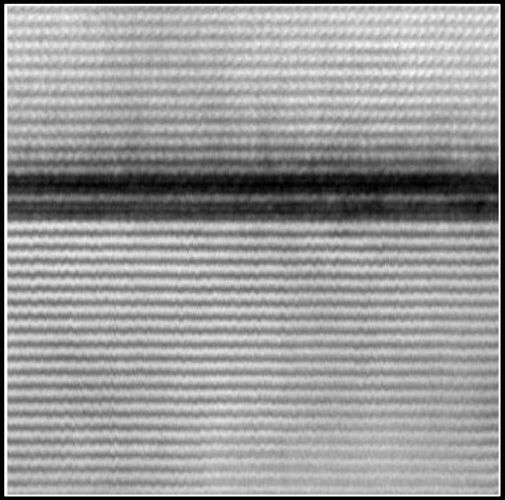


24h in air

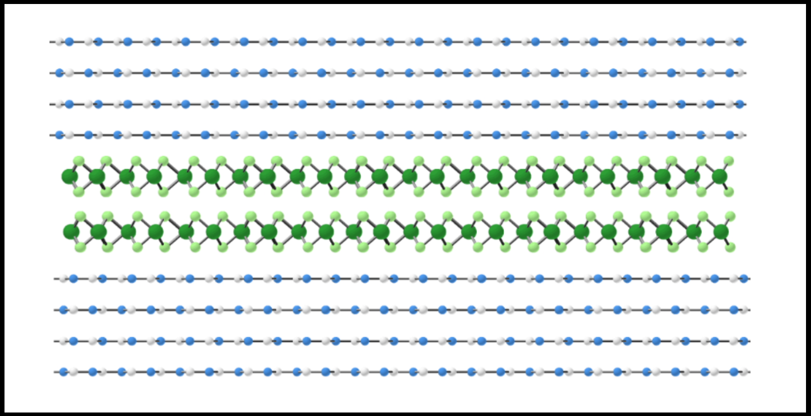


$NbSe_2$ - TEM

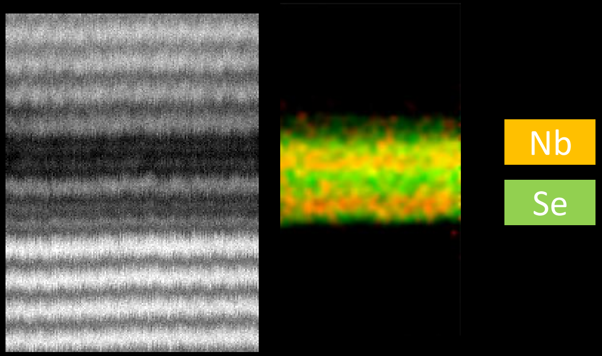




$NbSe_2$



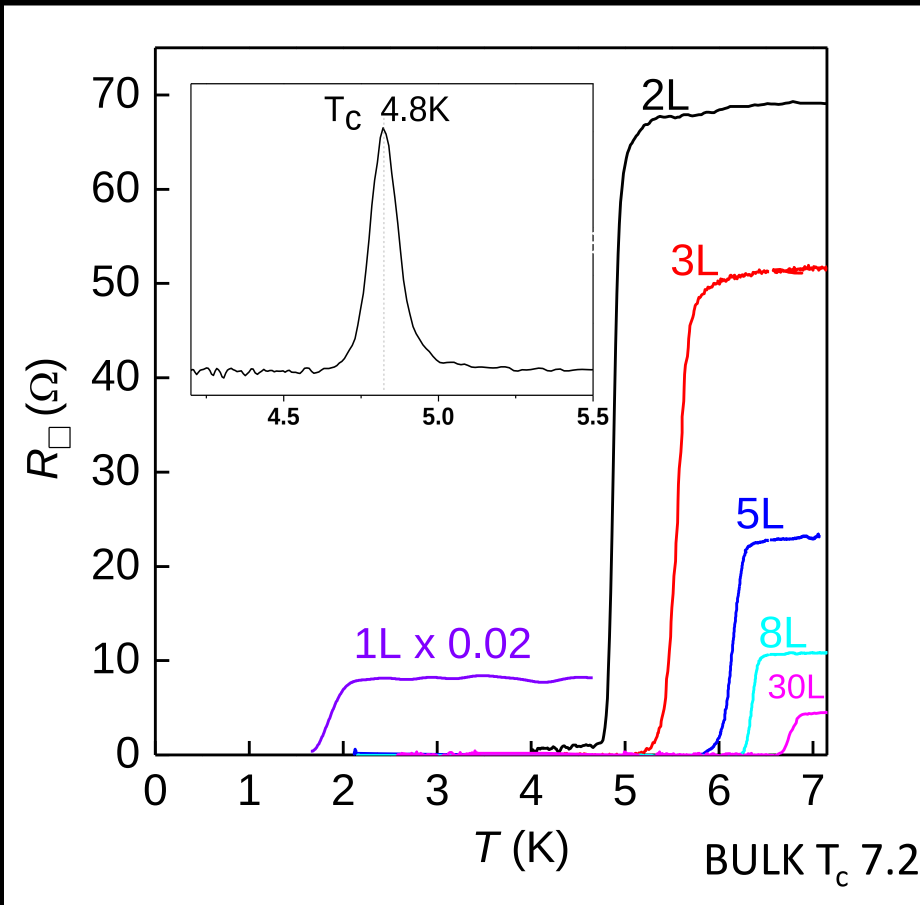
EELS elemental mapping

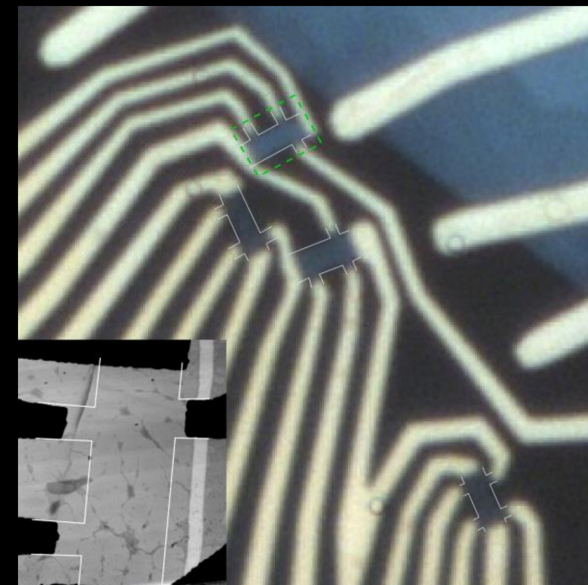


$NbSe_2$: superconductivity

$NbSe_2$

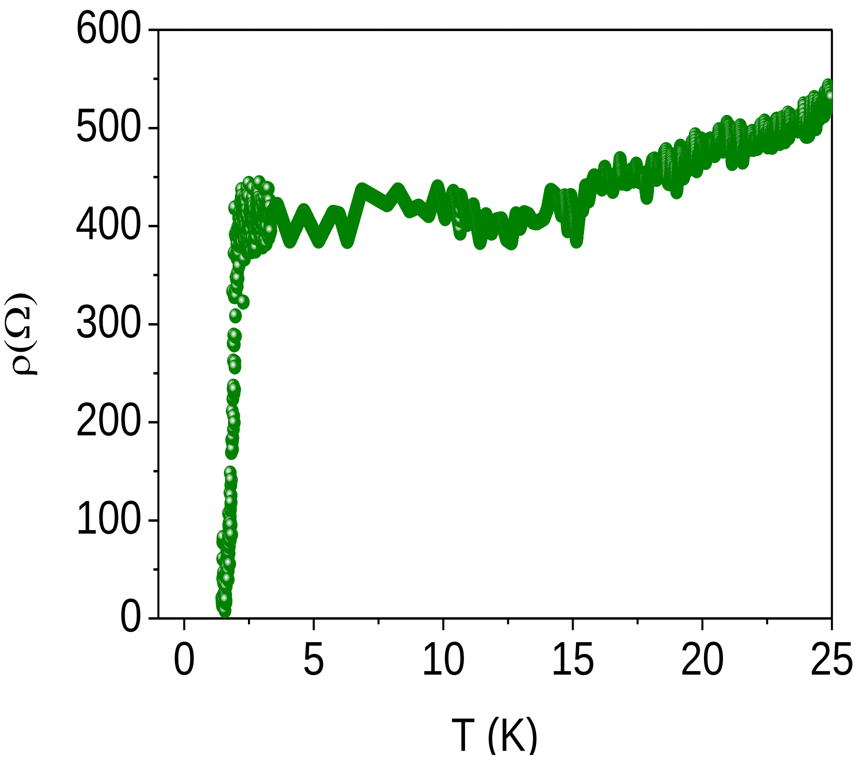
Resistivity vs temperature

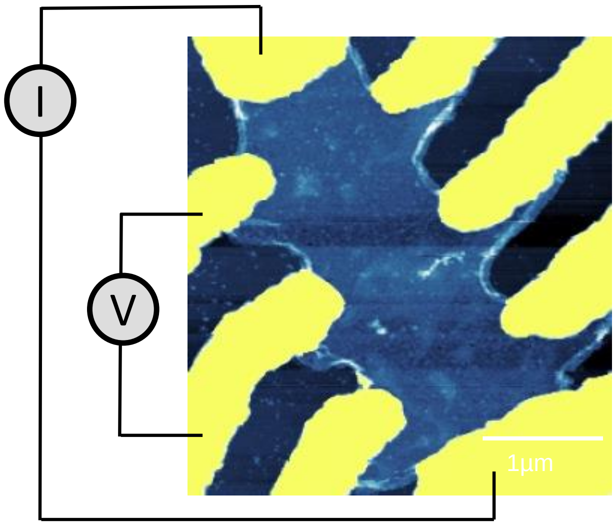




- Single peak on first derivative dR/dT indicates homogeneity of samples
- Observed superconducting transitions down to 1L thickness
- Transition temperatures defined as position of the peak on derivative

$NbSe_2$: superconductivity in monolayer

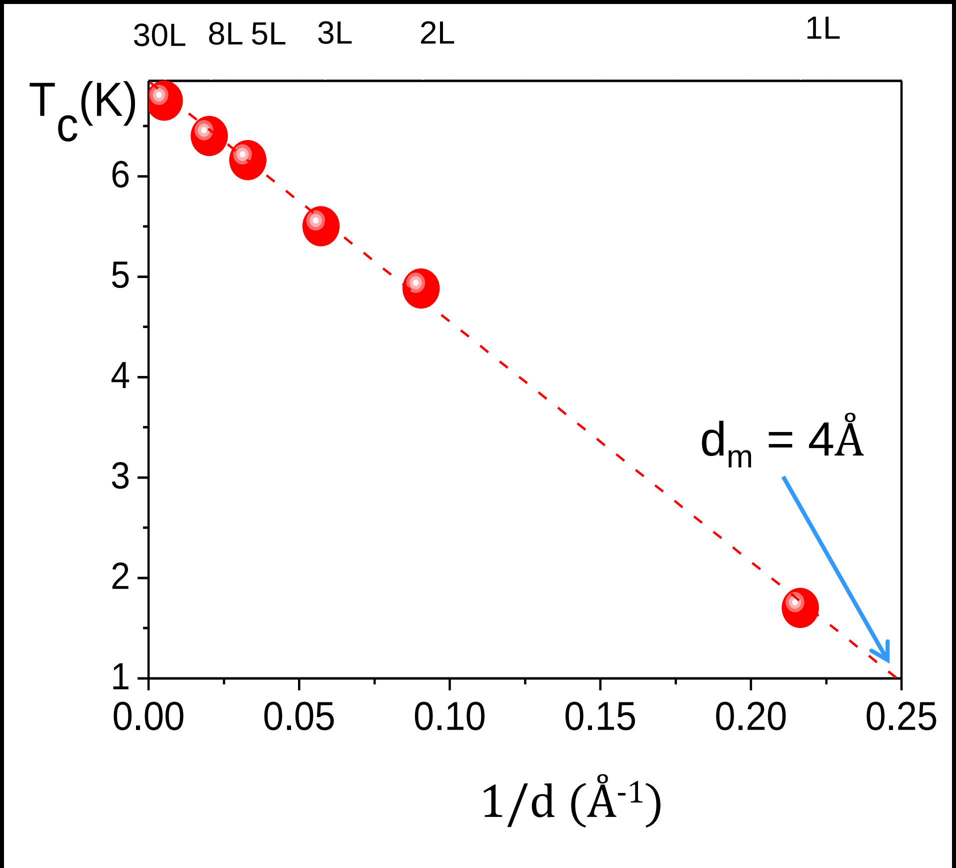




$NbSe_2$: superconductivity

For thin films with $d \ll \xi$ (T)

d - film thickness
ξ (T) - temperature dependent coherence length (~nm)



Ginzburg – Landau equations give:

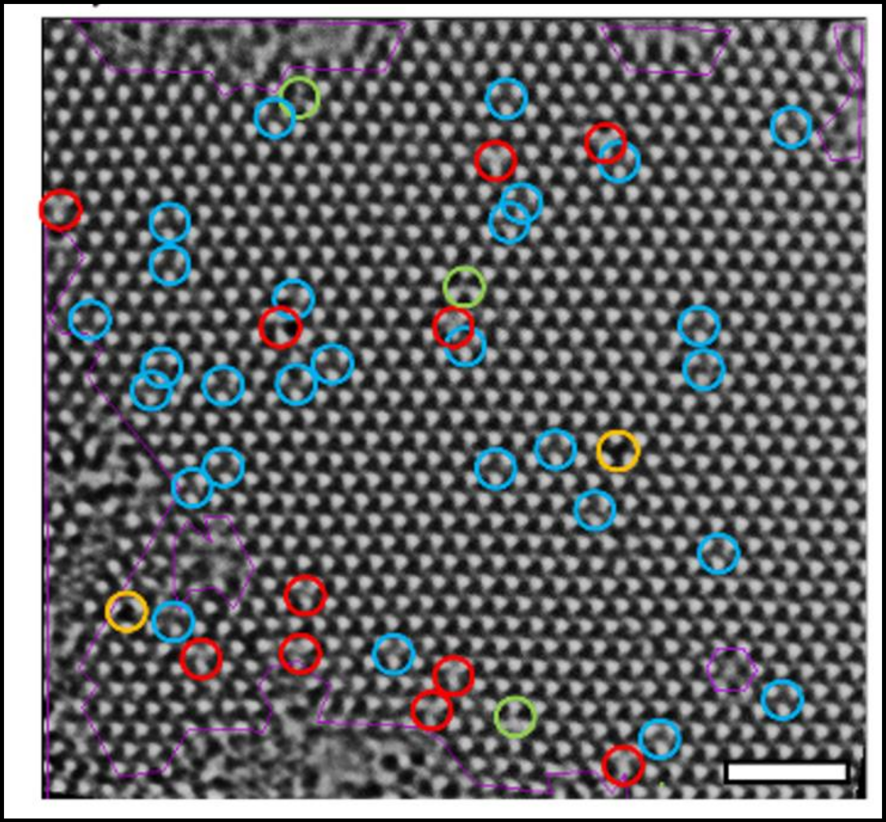
$$T_c = T_{c(bulk)} * (1 - \frac{d_m}{d})$$

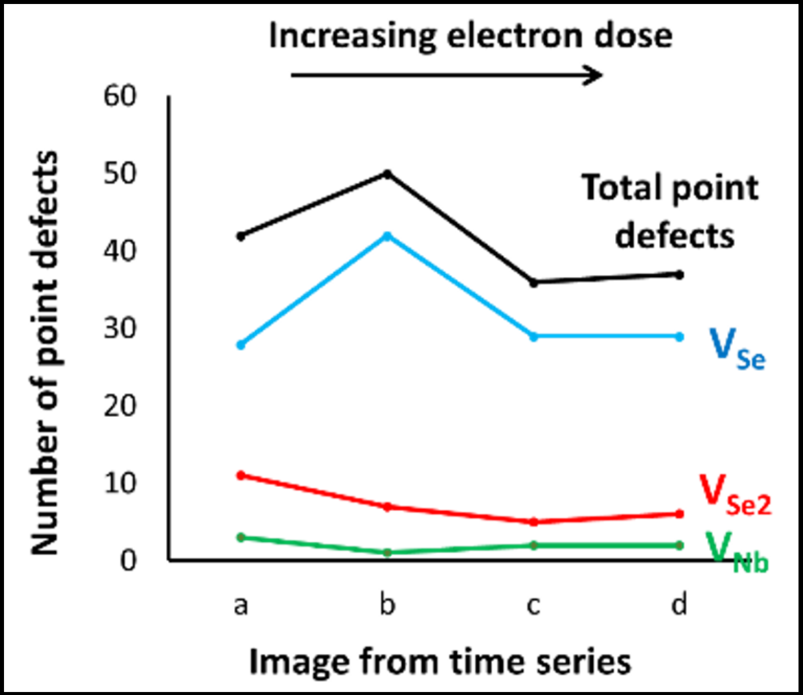
d – flake thickness
d_m – critical thickness, for which Tc=0

d_m < 1L thickness

J. Simonin, PRB, 33 (11) (1986)

Defects ?



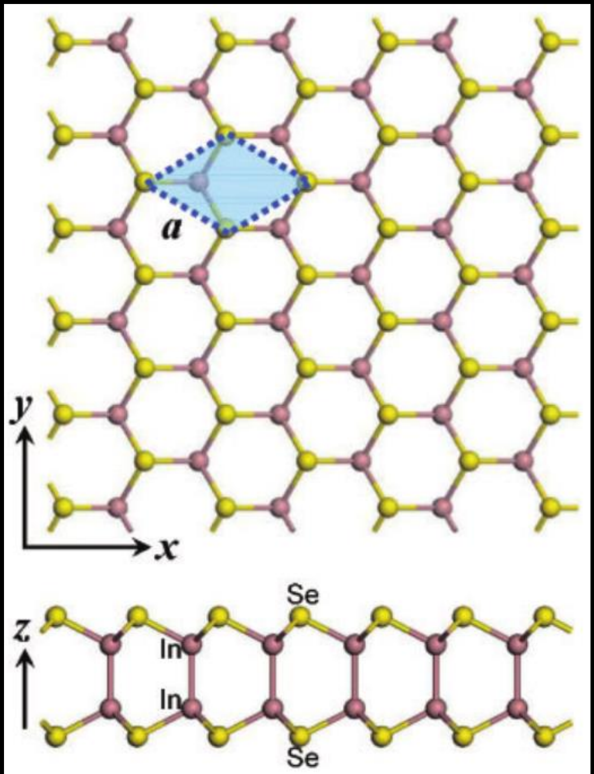


Most common defect:

Se mono- or divacancy filled with C or O

Still unclear if defects form before or after exfoliation

Indium and Gallium Selenides



PL in thick crystals changes during air exposure due to progression of degradation

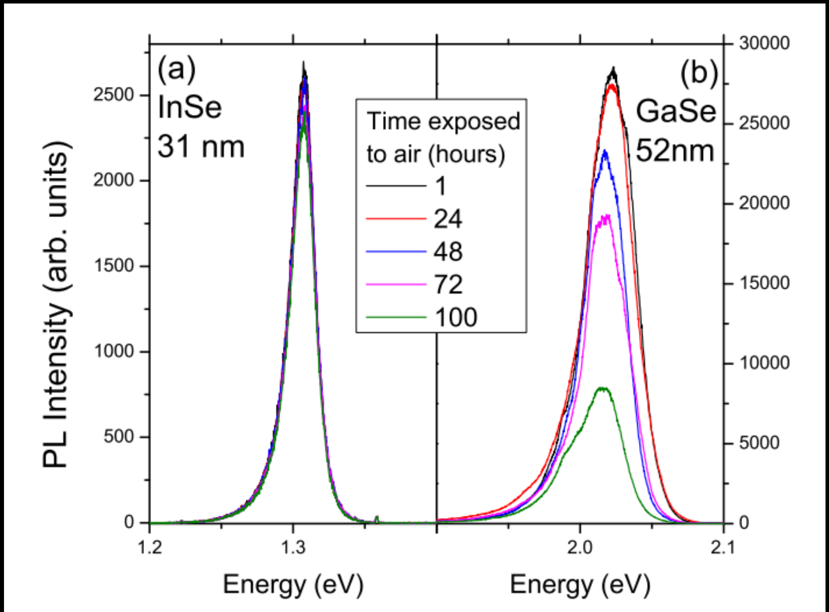
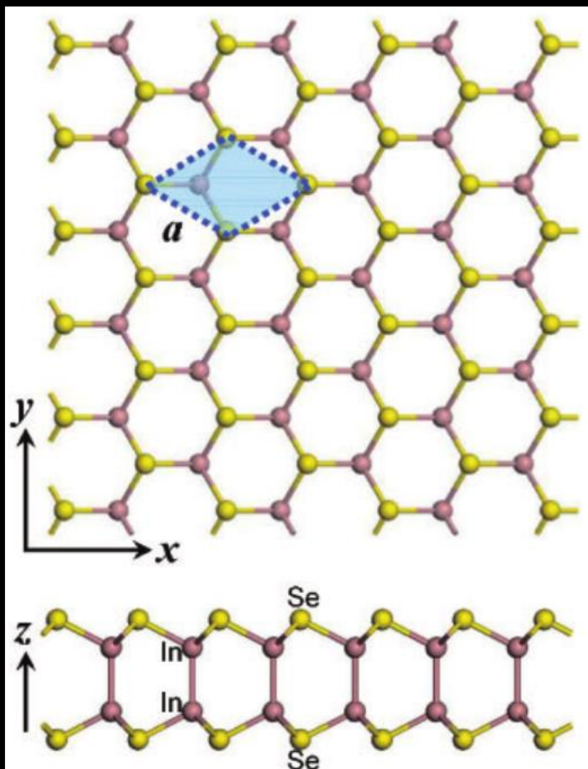


FIG. 2. Micro-photoluminescence spectra measured at low temperature of 10 K for (a) a 31 nm InSe film and (b) a 52 nm GaSe film after exposure to air from 1 to 100 hours.

arXiv:1506.05619

Indium Selenide

InSe



High bulk RT mobility **μ**$=10^3$ cm^2/Vs

Light electron effective mass $m=0.14m_0$

Direct band gap of 1.25 eV (bulk)

ADVANCED MATERIALS
www.advmat.de
Materials Views
www.MaterialsViews.com

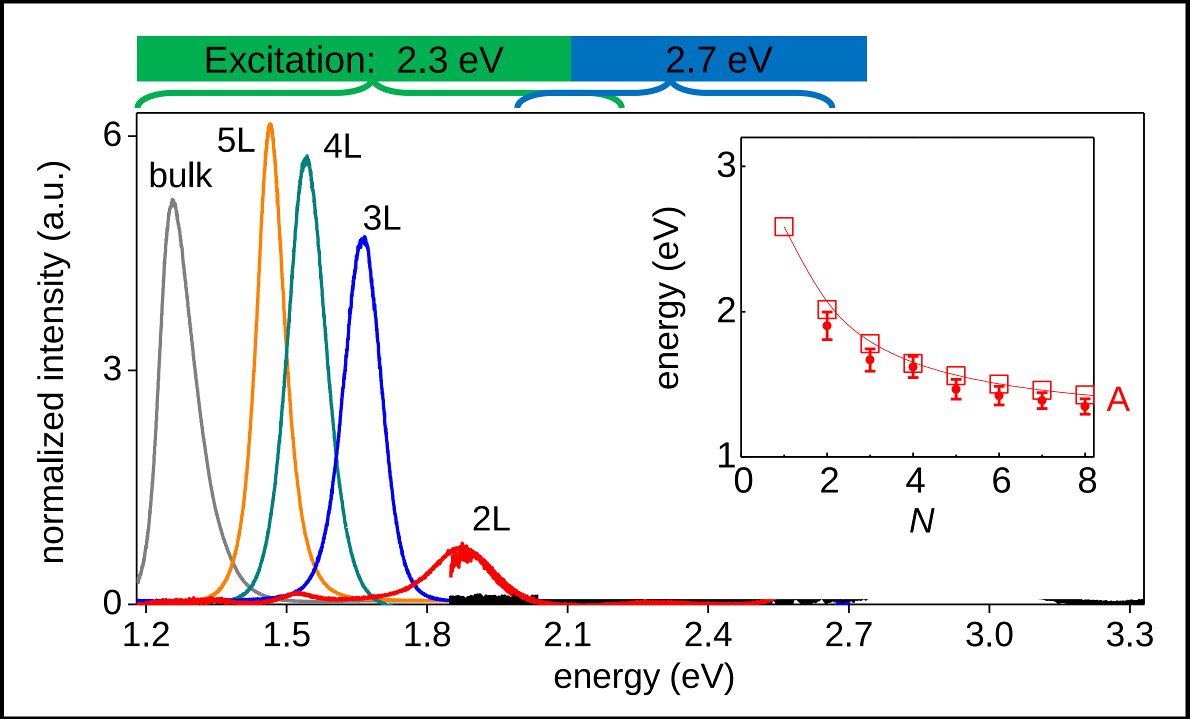
Tuning the Bandgap of Exfoliated InSe Nanosheets by Quantum Confinement

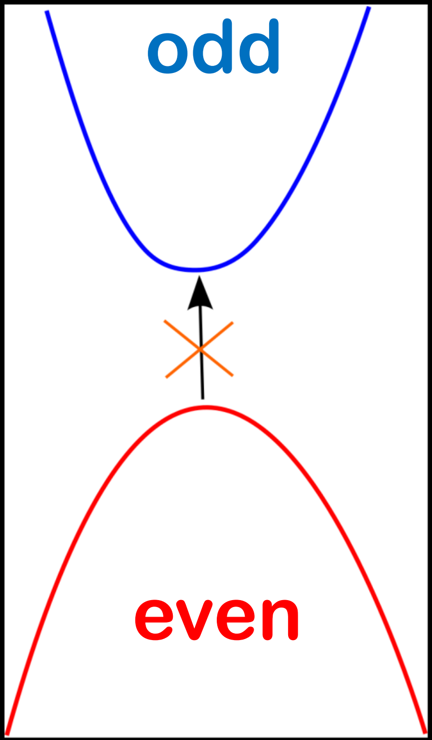
Garry W. Mudd, Simon A. Svatek, Tianhang Ren, Amalia Patanè, Oleg Makarovsky, Laurence Eaves, Peter H. Beton, Zakhar D. Kovalyuk, George V. Lashkarev, Zakhar R. Kudrynskyi, and Alexandr I. Dmitriev*

C. Sun et al, Appl. Phys. Express 2016

Photoluminescence of thin InSe

InSe

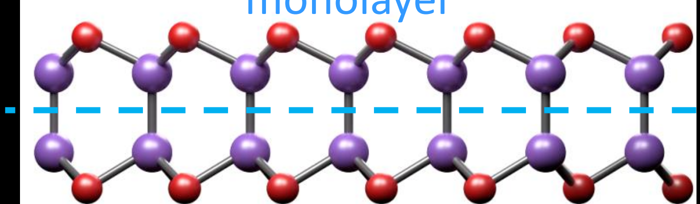




Tuneable band gap

No primary PL peak for monolayer while transport persists

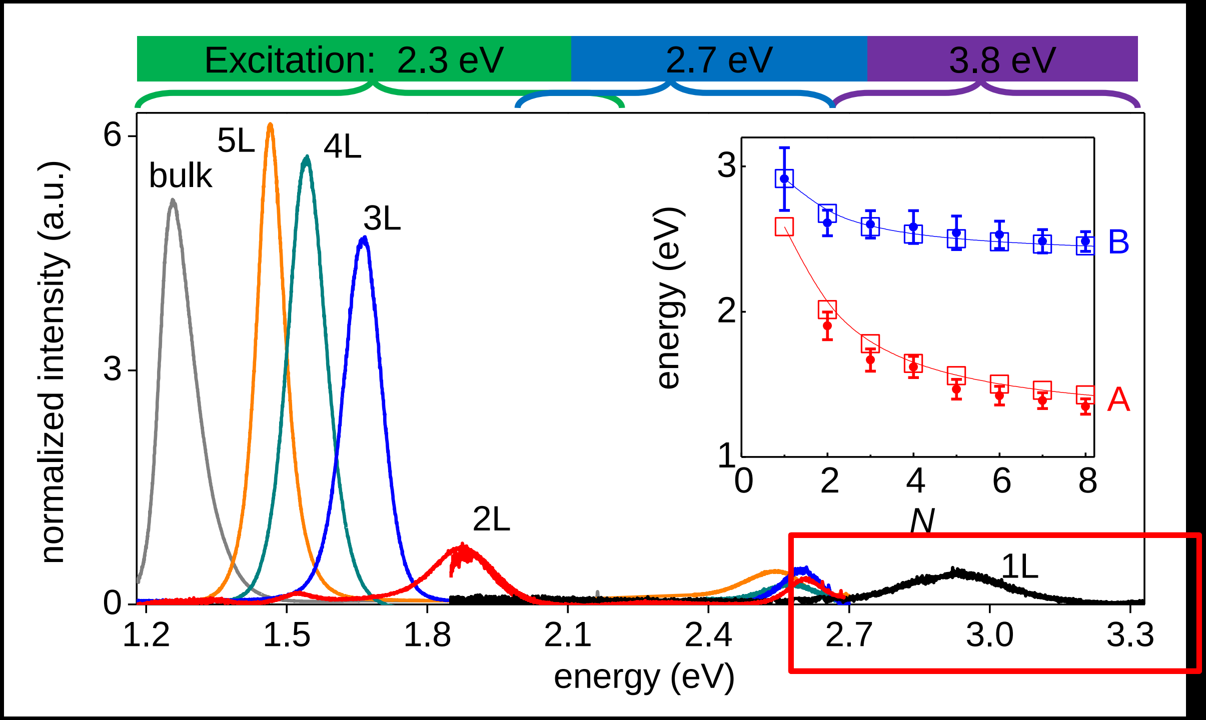
Mirror-plane symmetry of monolayer

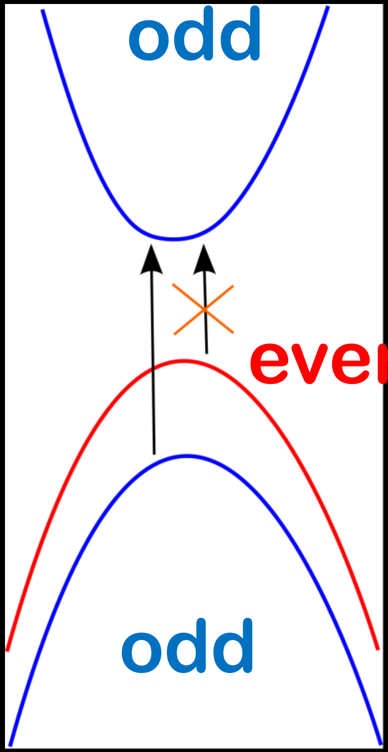


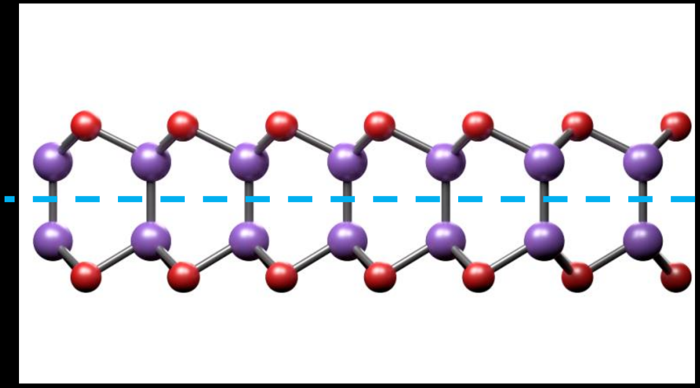
V. Zolyomi and V. Fal'ko

Photoluminescence of thin InSe

InSe

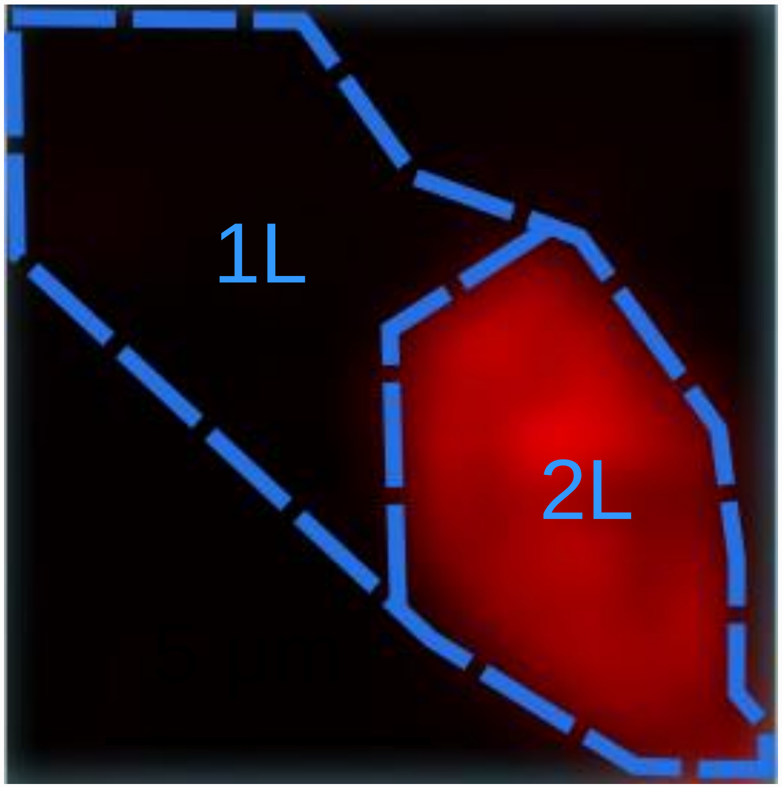






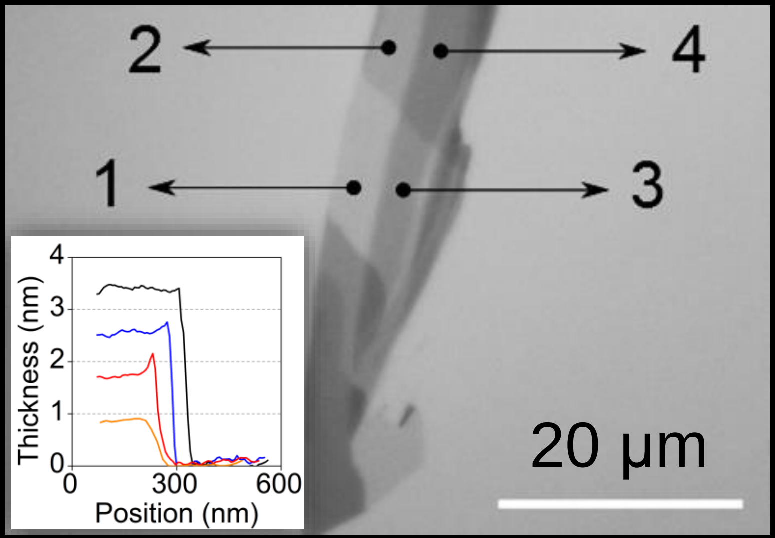
Hot photoluminescence from deeper states

InSe

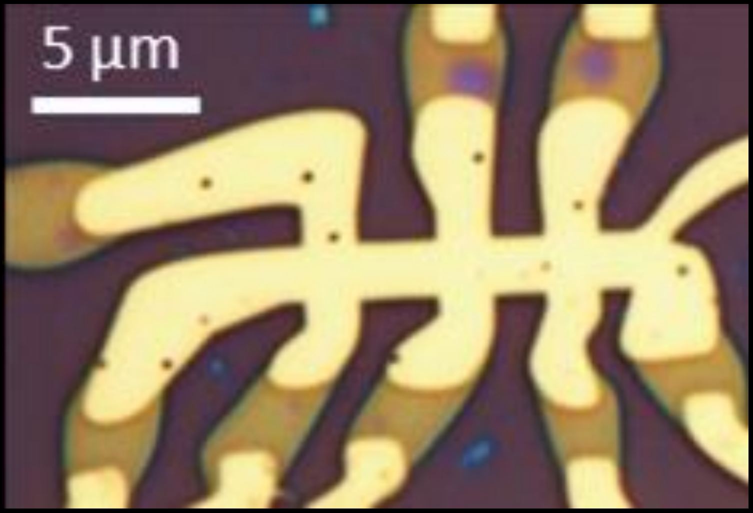


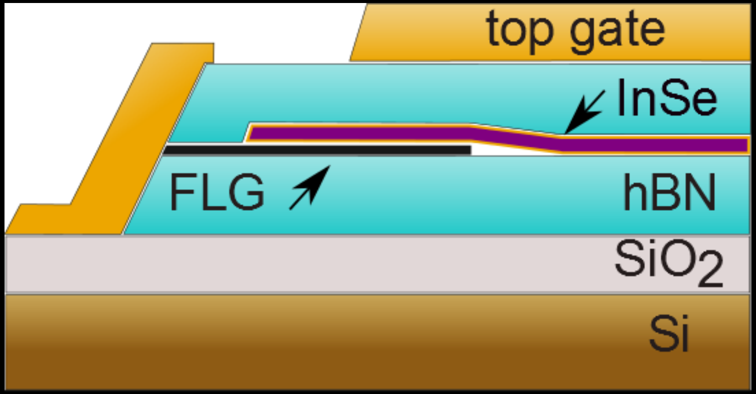
Coupling with in-plane polarized light is forbidden by crystal symmetry

InSe

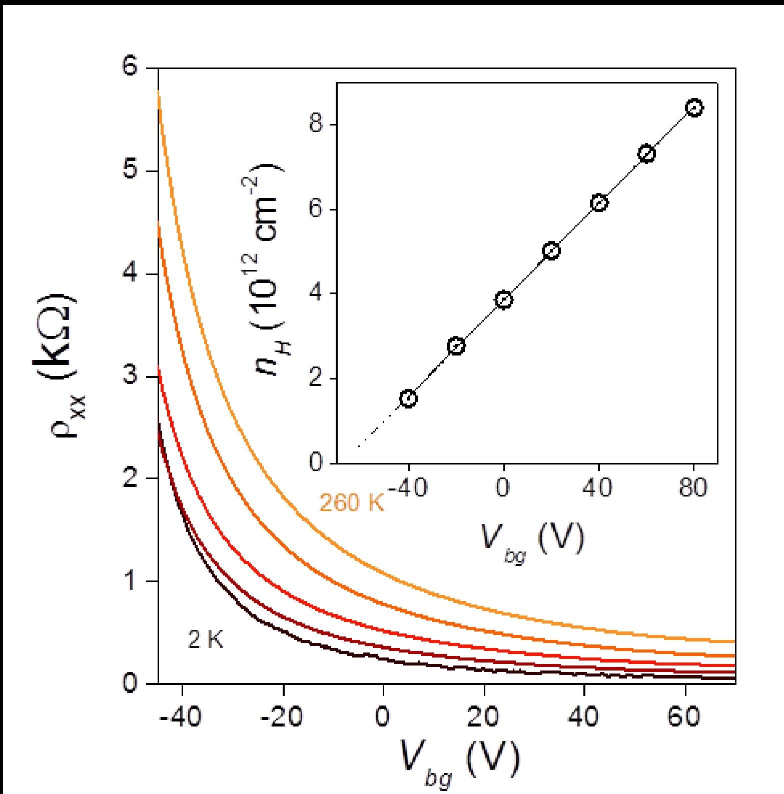


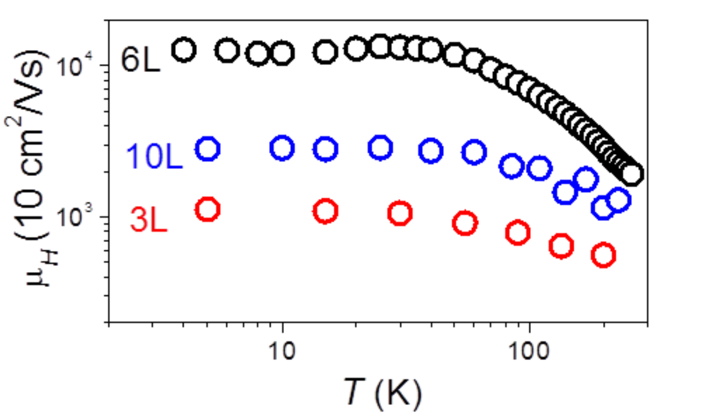
Gate-tuneable graphene contacts

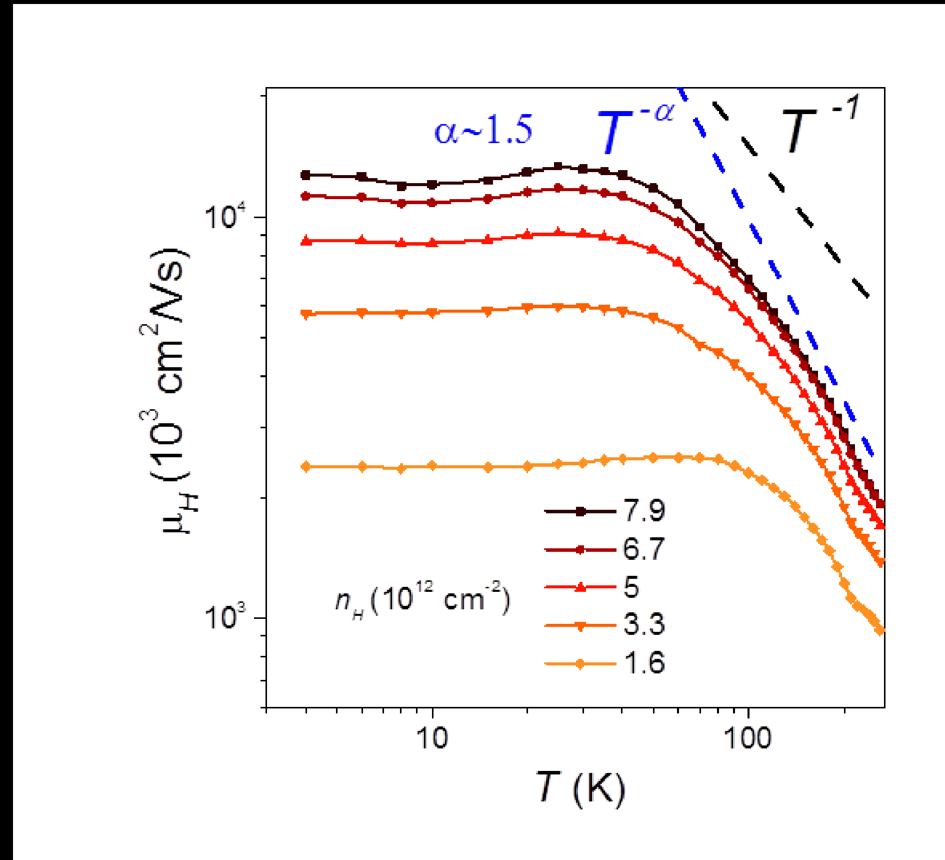




Transport properties of InSe FET





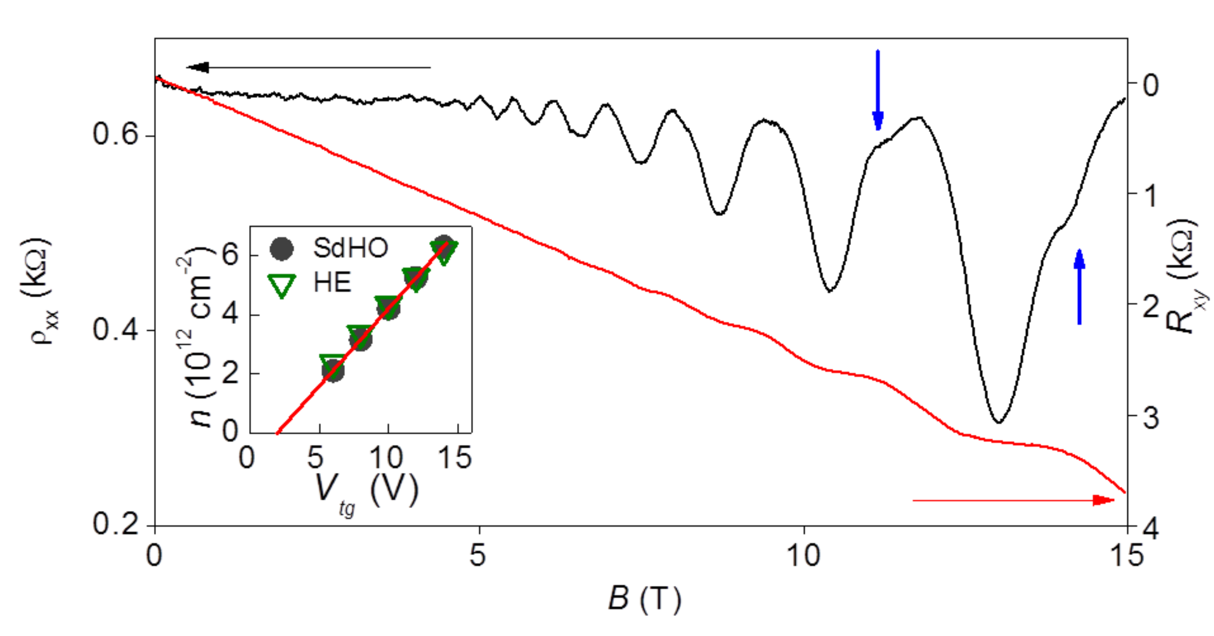


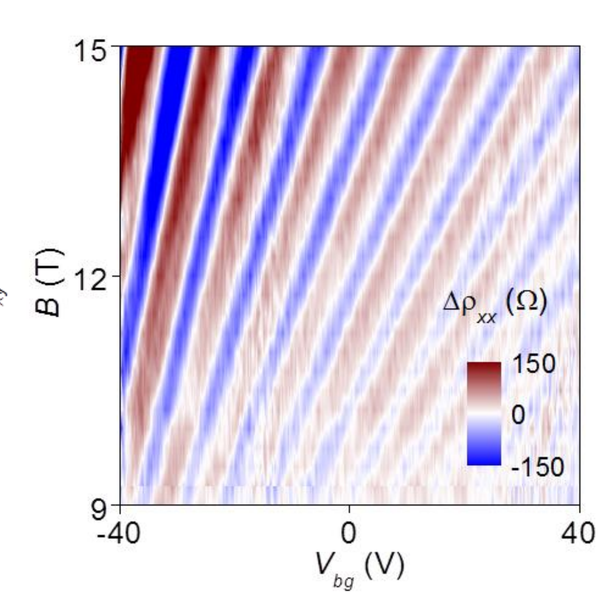
6L – the highest quality

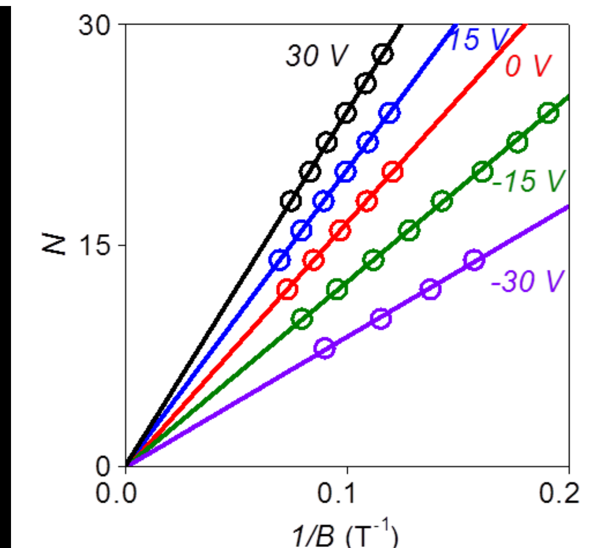
RT mobility	LT mobility
$2x10^3$ cm^2/Vs	$13x10^3$ cm^2/Vs

Quantum oscillations in 6L InSe

InSe







Start of oscillations at B=5 T

One sub-band

SdHO phase = 0

Light effective mass

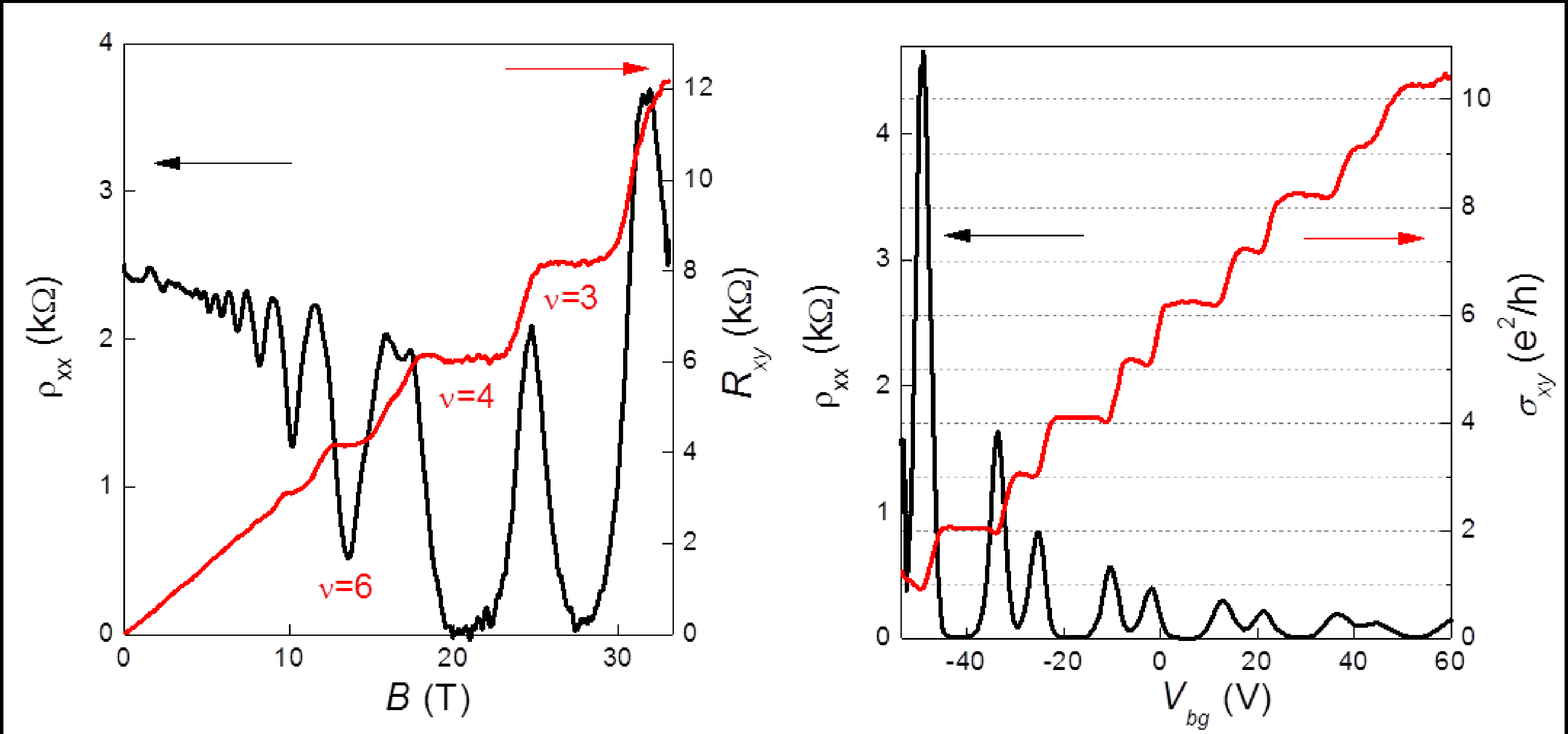
$m_c=0.14m_0$

BP: $m_c=0.3m_0 - 0.5m_0$

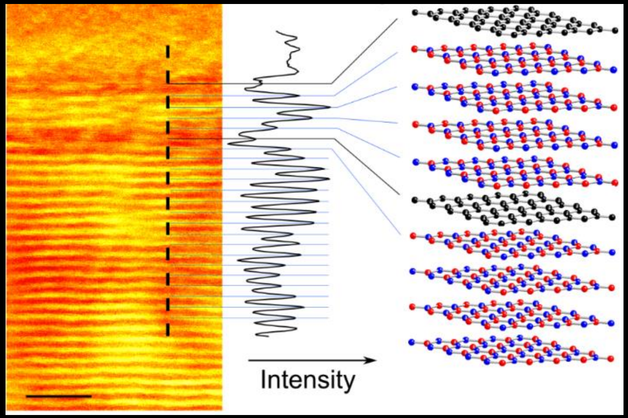
MoS_2: $m_c=0.45m_0$

QHE in 6L InSe

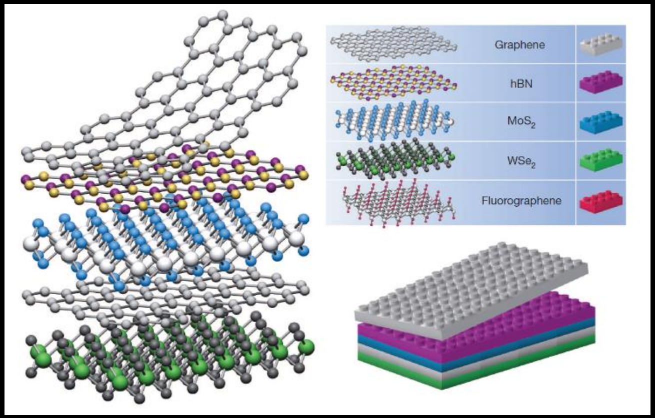
InSe



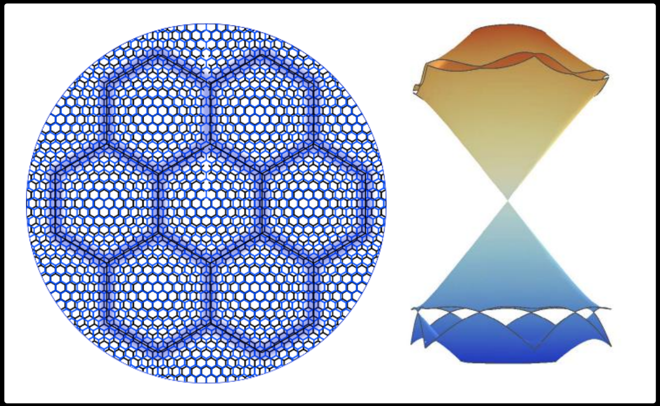
Lifting of the spin-degeneracy @ B>15 T



Atomically sharp and clean interfaces



Functionality from the layer sequence



Properties controlled by mutual crystal orientation

Many new materials with exotic properties

Thank you