

Electronic and optical properties of graphene and other 2D materials

Andrzej Wysmolek

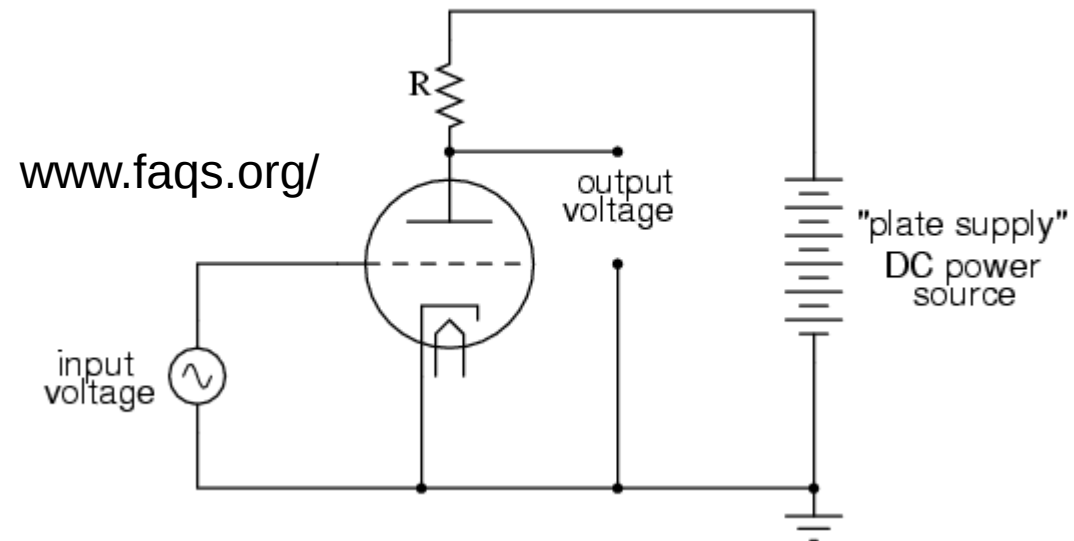
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Vacuum electron tubes



Triode amplifier circuit



First transistor...

Julius Edgar Lilienfeld (born in Lwów) – field effect transistor Canada, 1925



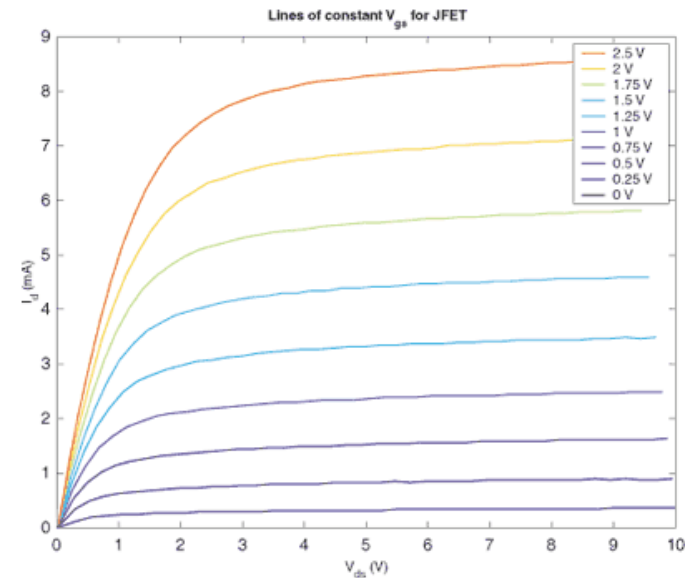
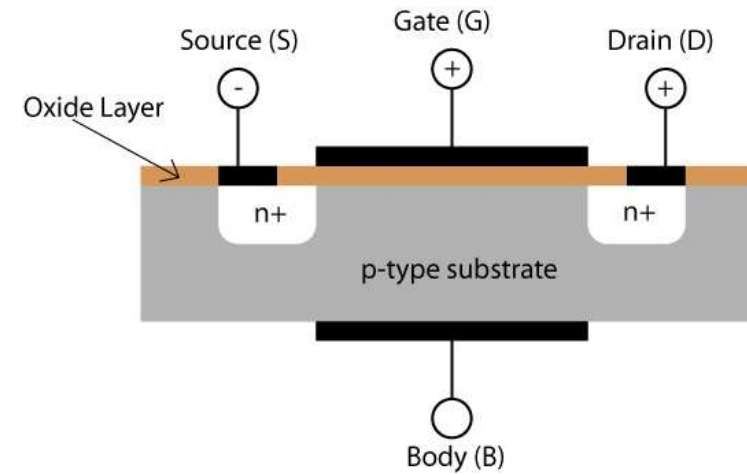
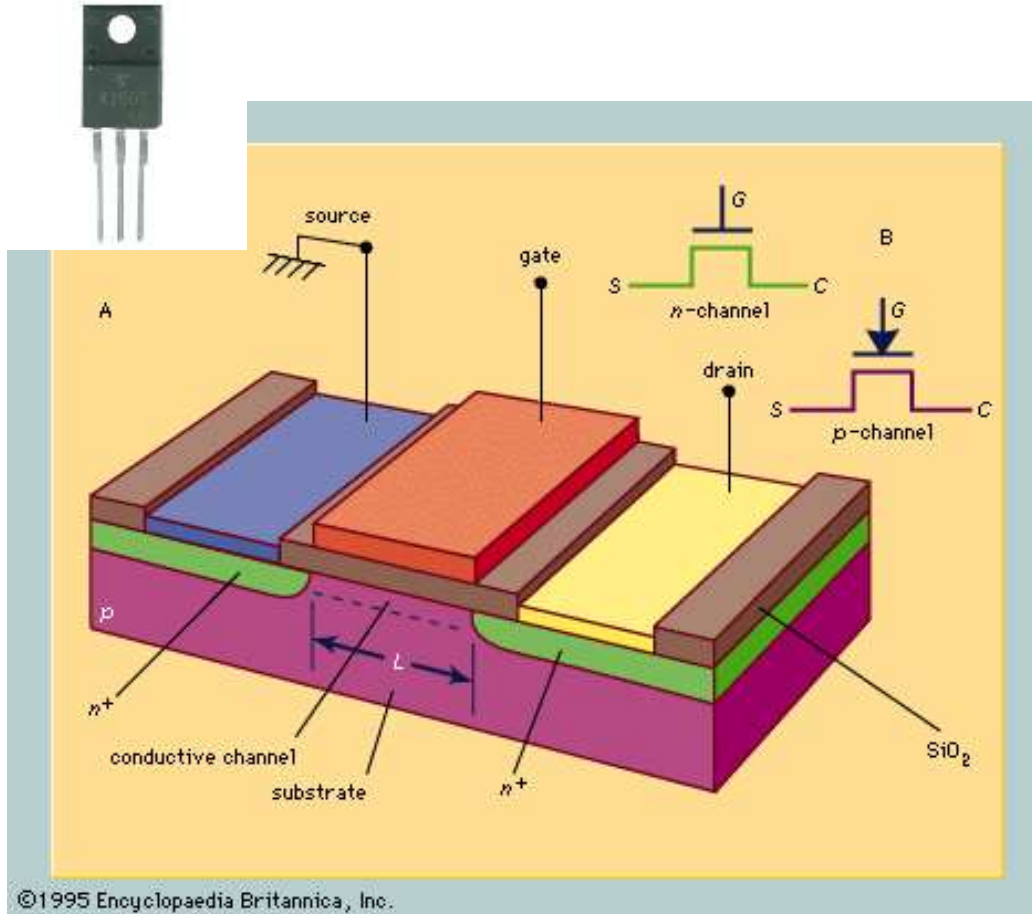
John Bardeen, William Shockley, Walter Brattain
Bell Labs, 1948
(Nobel Prize in Physics 1956)



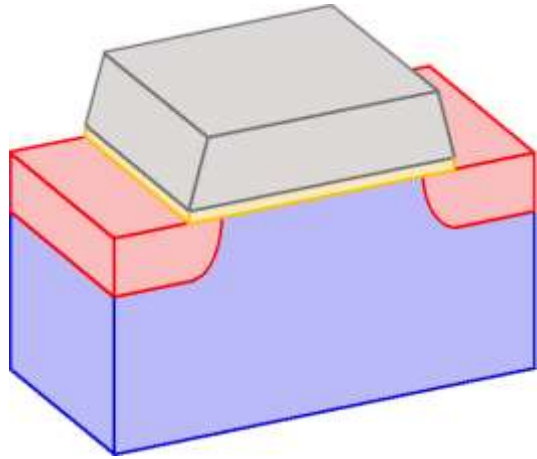
First point-contact transistor

<http://en.wikipedia.org/wiki/Transistor#History>

Field effect transistors



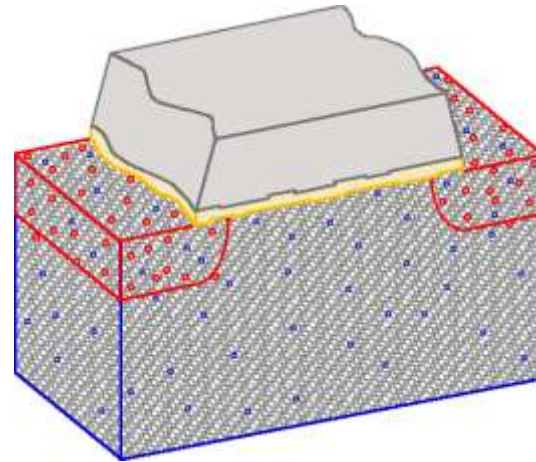
Miniaturization limits



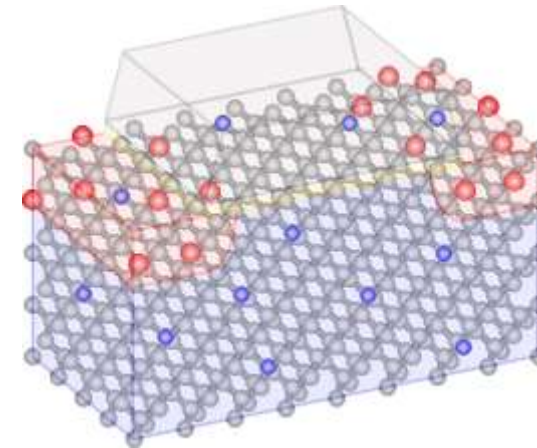
we think that single transistor looks like this

Asen Asenov, Glasgow

David Williams *Hitachi-Cambridge*



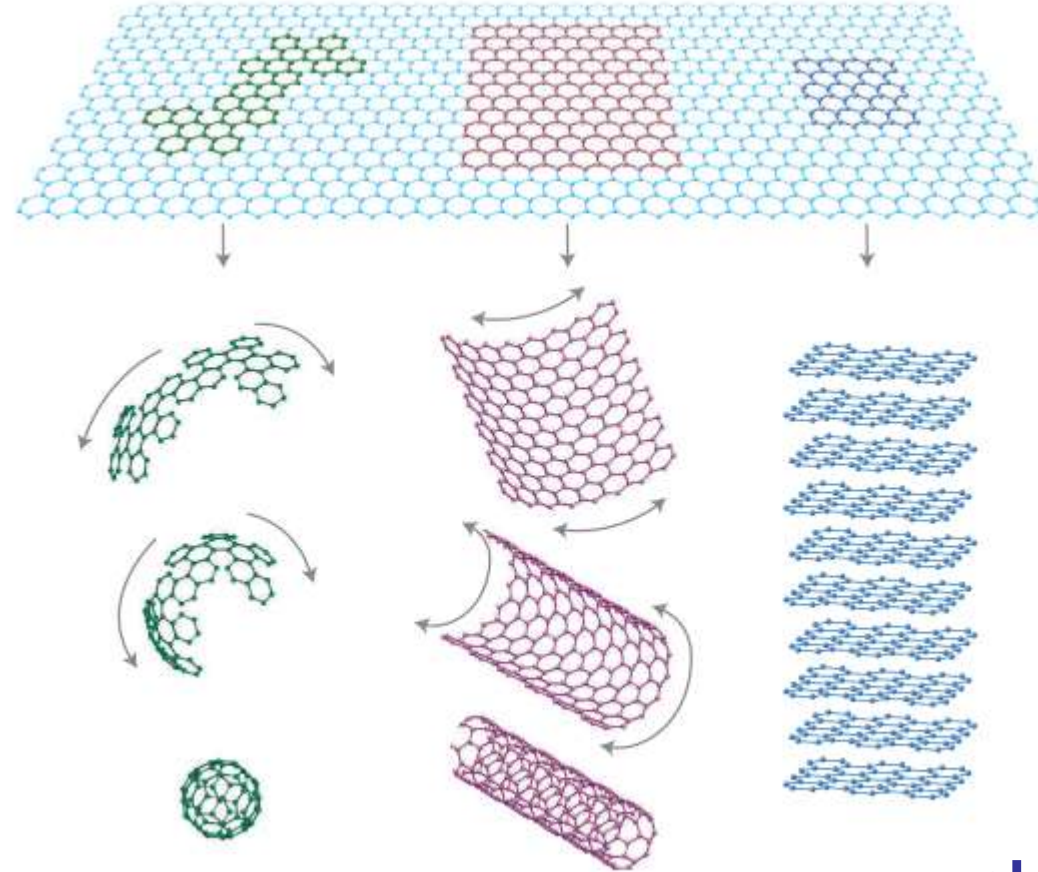
25 nm MOSFET
Production since 2008



4,2 nm MOSFET ?

New ideas?

Graphene – a single layer of graphite...



fullerenes (0D)

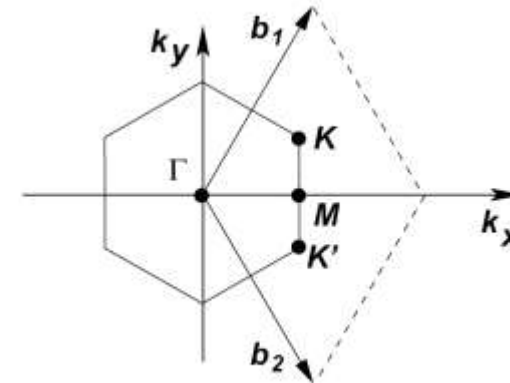
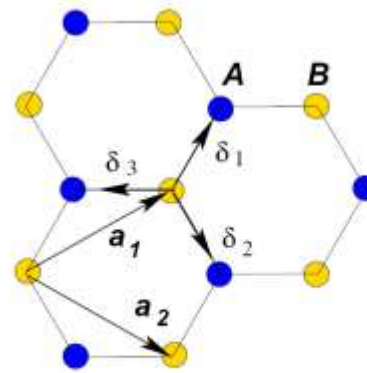
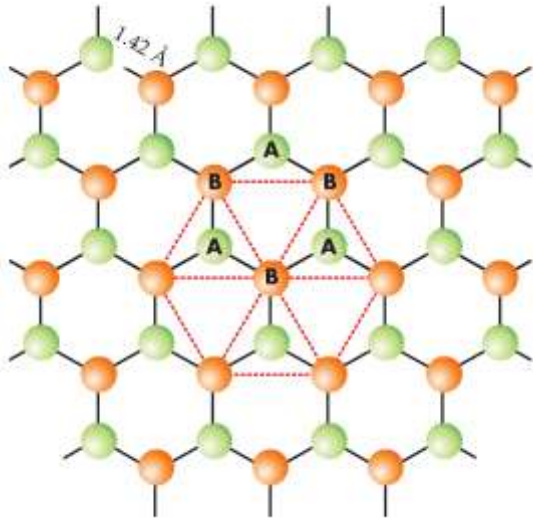
nanotubes (1D)

graphite (3D)

Basic block of different carbon allotropes....

Band structure of graphene

...known since years: (P.R. Wallace, Phys. Rev. (1947))

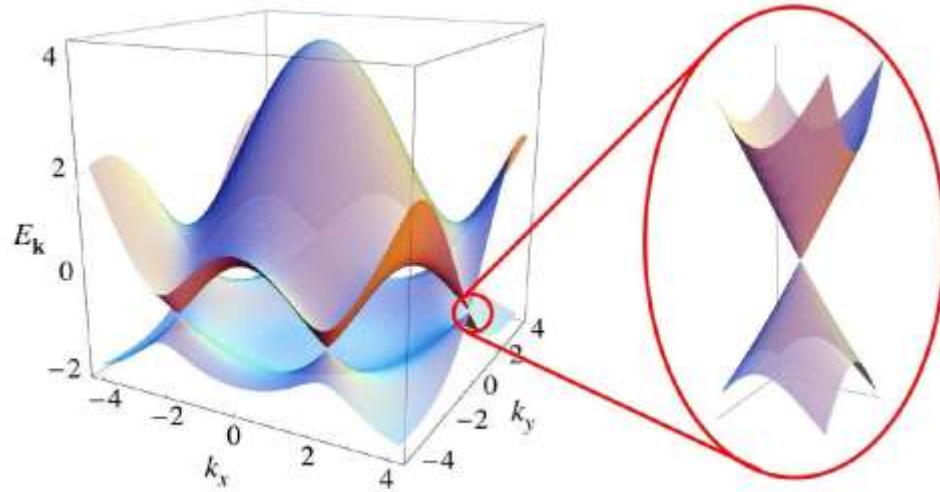


$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}),$$

$$\mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}),$$

$$\mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3})$$



$$E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k})}.$$

$$f(\mathbf{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right)$$

$$\mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right)$$

A.H. Castro Neto et al., Rev. Mod. Phys. (2009)



The Nobel Prize in Physics 2010

Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010

Andre Geim

Konstantin Novoselov



Photo: Sergeom, Wikimedia Commons

Andre Geim



Photo: University of Manchester, UK

Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

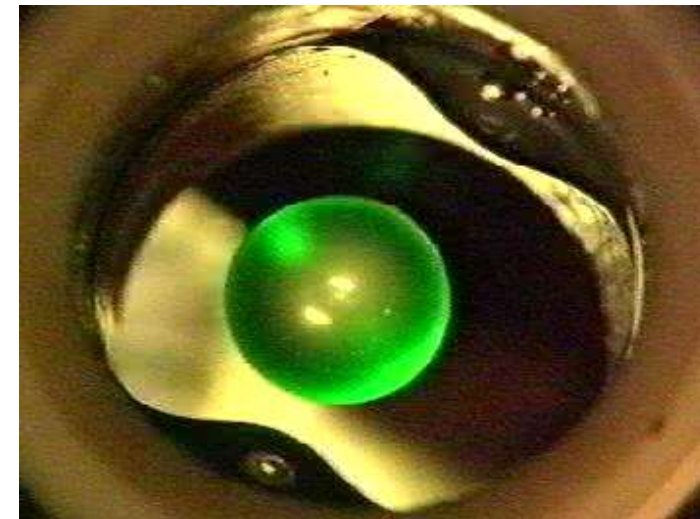
Ig Nobel Prize 2000

Andre Geim, University of Nijmegen (Netherlands)
Sir Michael Berry, Bristol University (UK),
„for using magnets to levitate a frog”



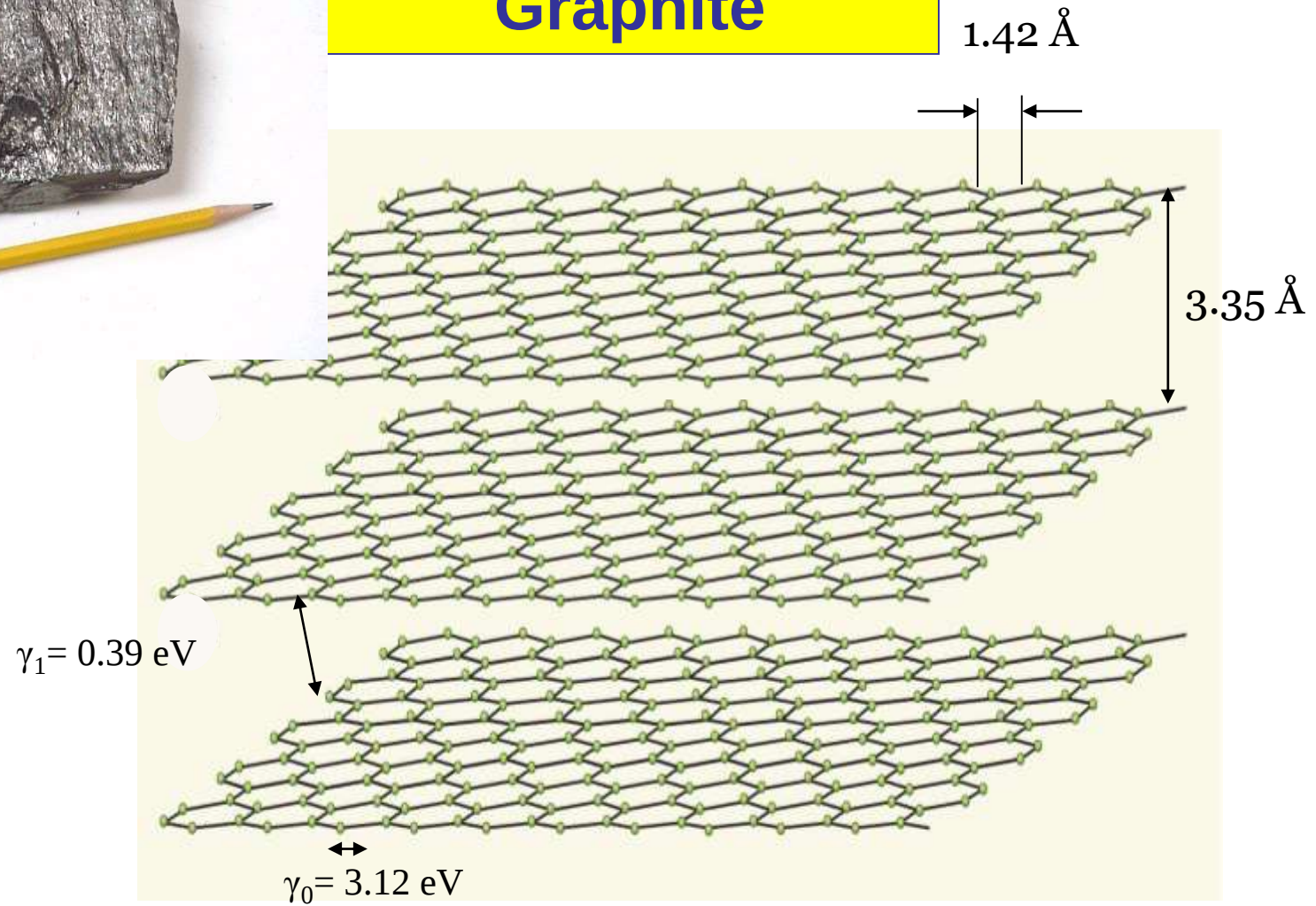
M.V. Berry and **A.K. Geim**,
"Of Flying Frogs and Levitrons"
European Journal of Physics, v. 18, 1997, p. 307-13.

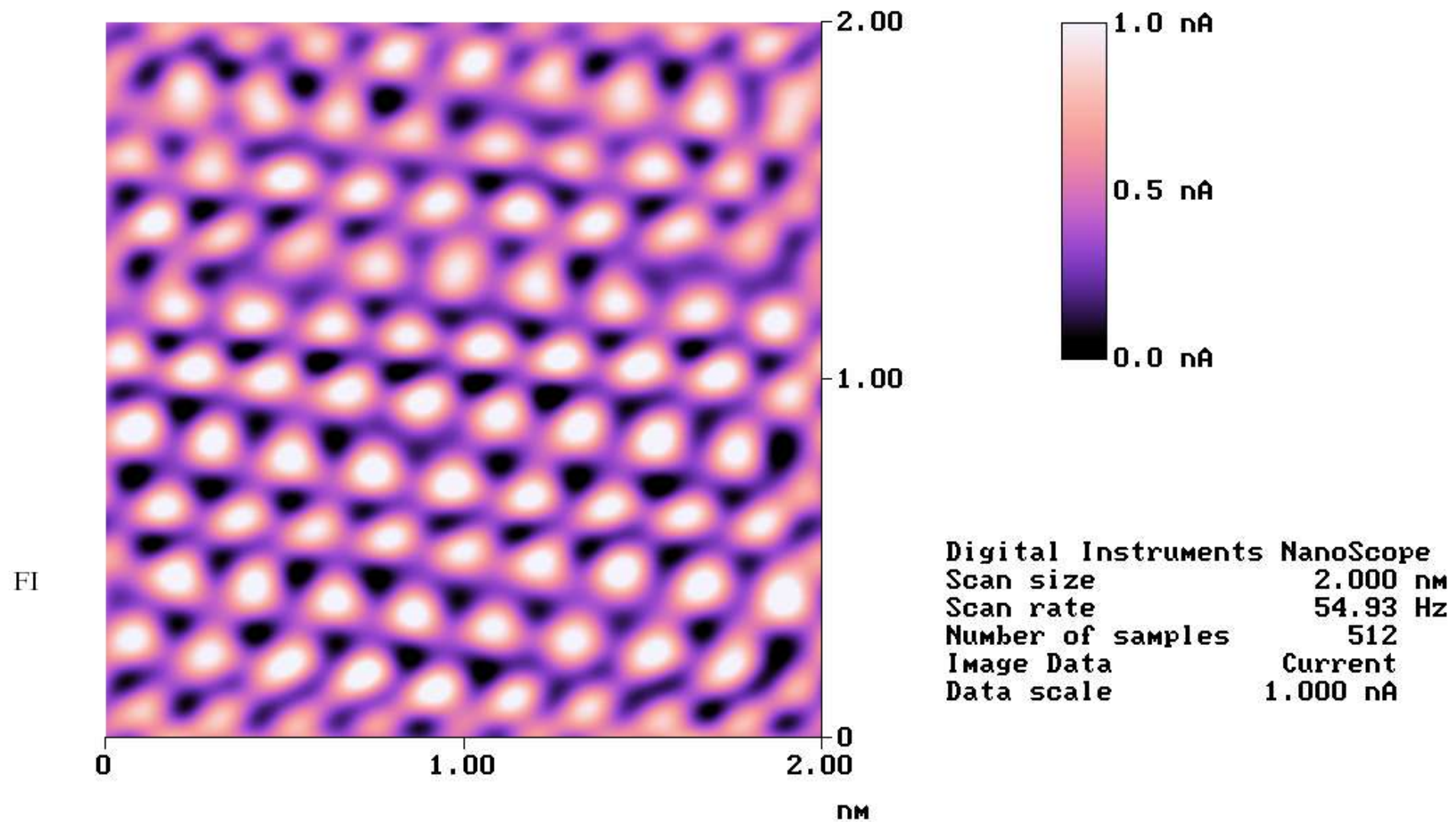
The motto of the Ig Nobel Prize
is to „honour the achievements
that first make people laugh,
and then think...”





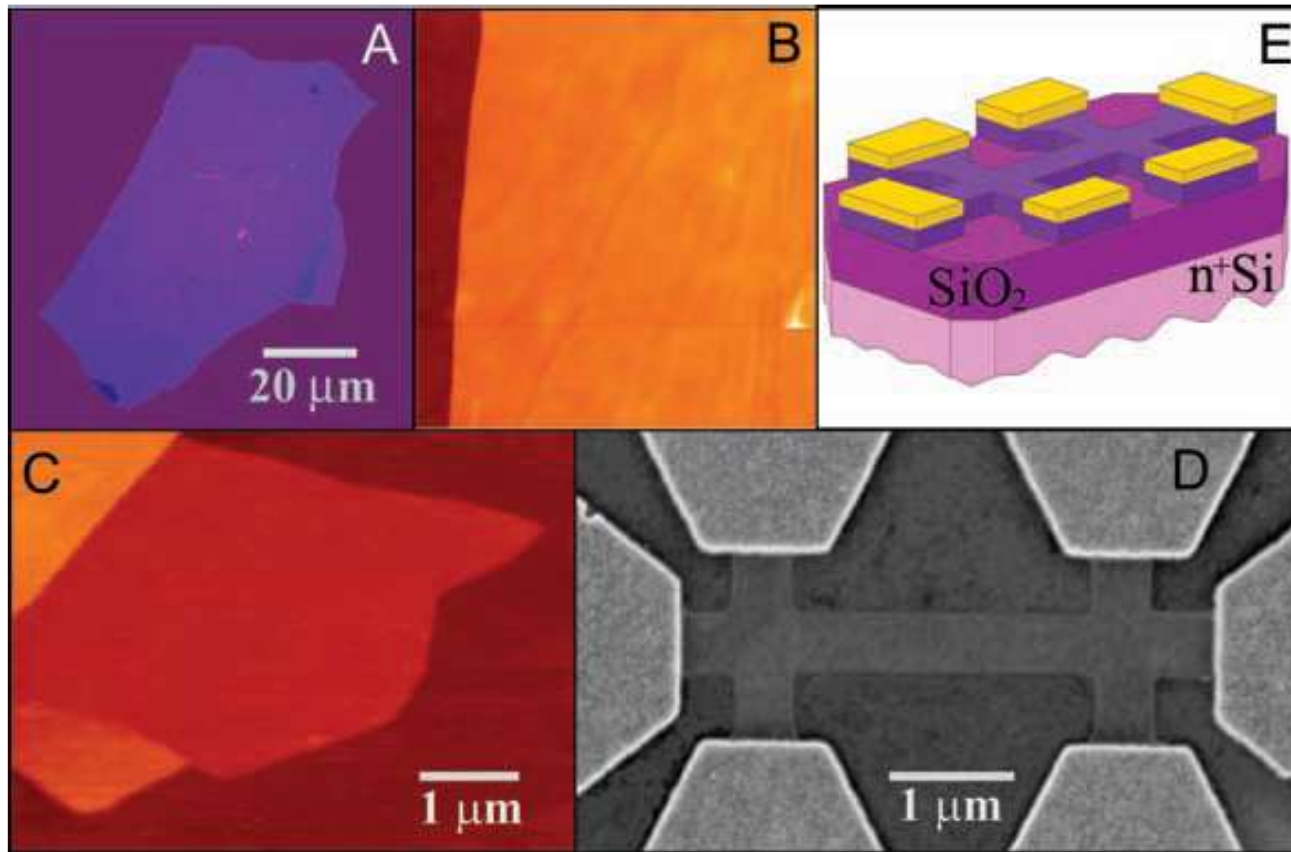
Graphite





grafit1.001

Mechanical exfoliation from graphite

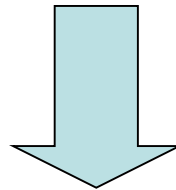


flake size ~10 μm

K. Novoselov, A. Geim *et al.* Science (2004)

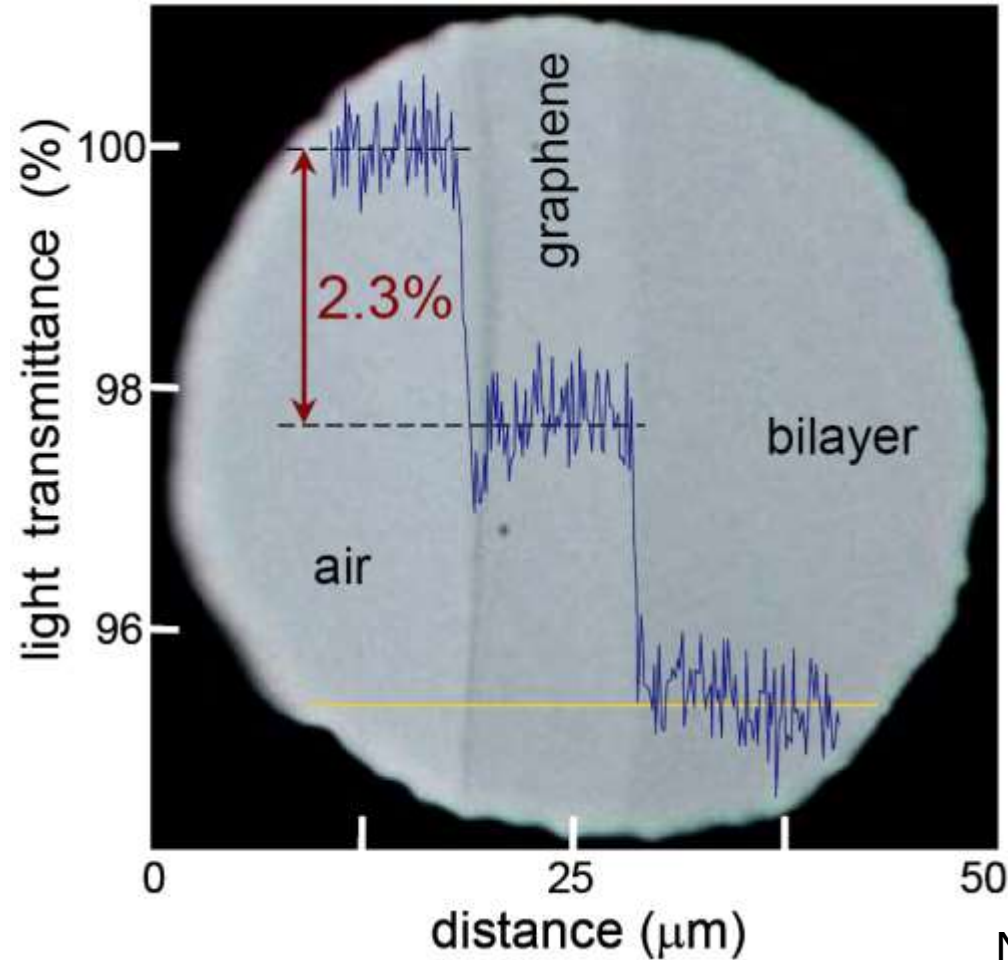
Graphene...

- high electron mobility ($200000 \text{ cm}^2/\text{Vs}$)
- high critical density of carriers $\sim 10^8 \text{ A/cm}^2$
- very high thermal conductivity
- excellent mechanical properties
- optical transparency...
-



... very promising for electronic and optoelectronic applications!

Graphene is transparent...



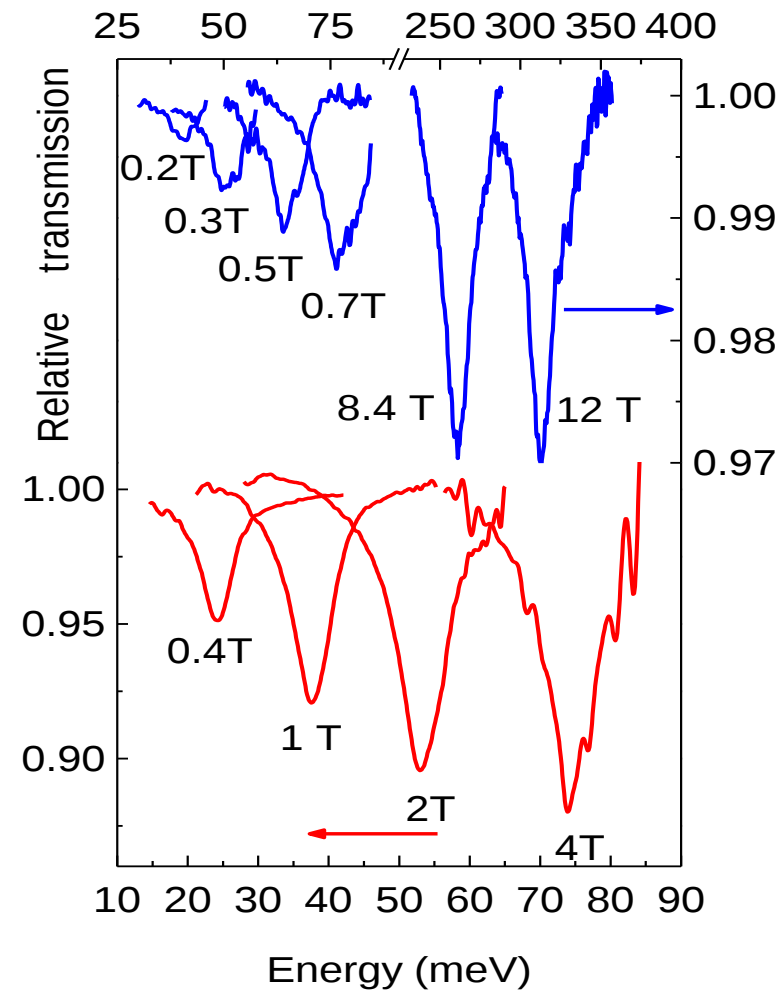
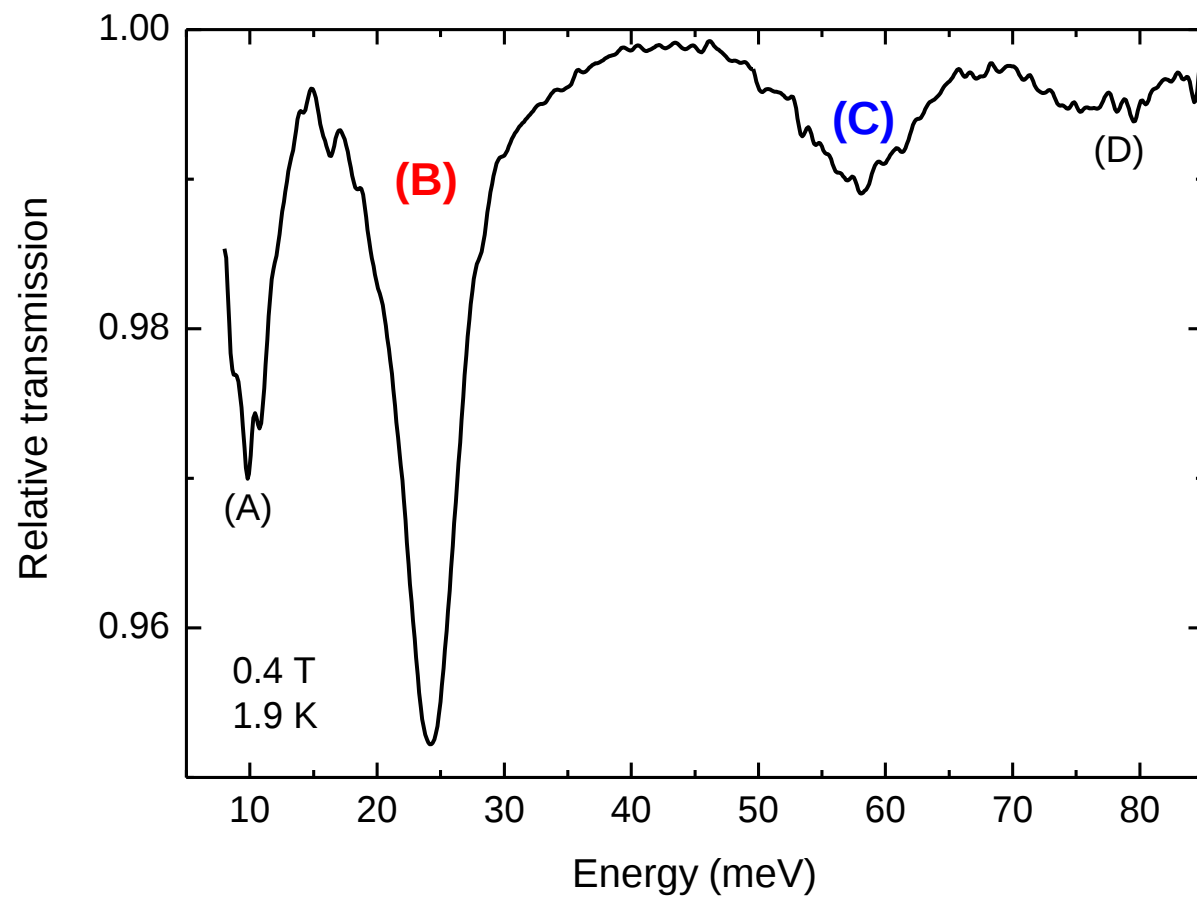
$$T = (1 + \frac{1}{2} \pi \alpha)^{-2}$$

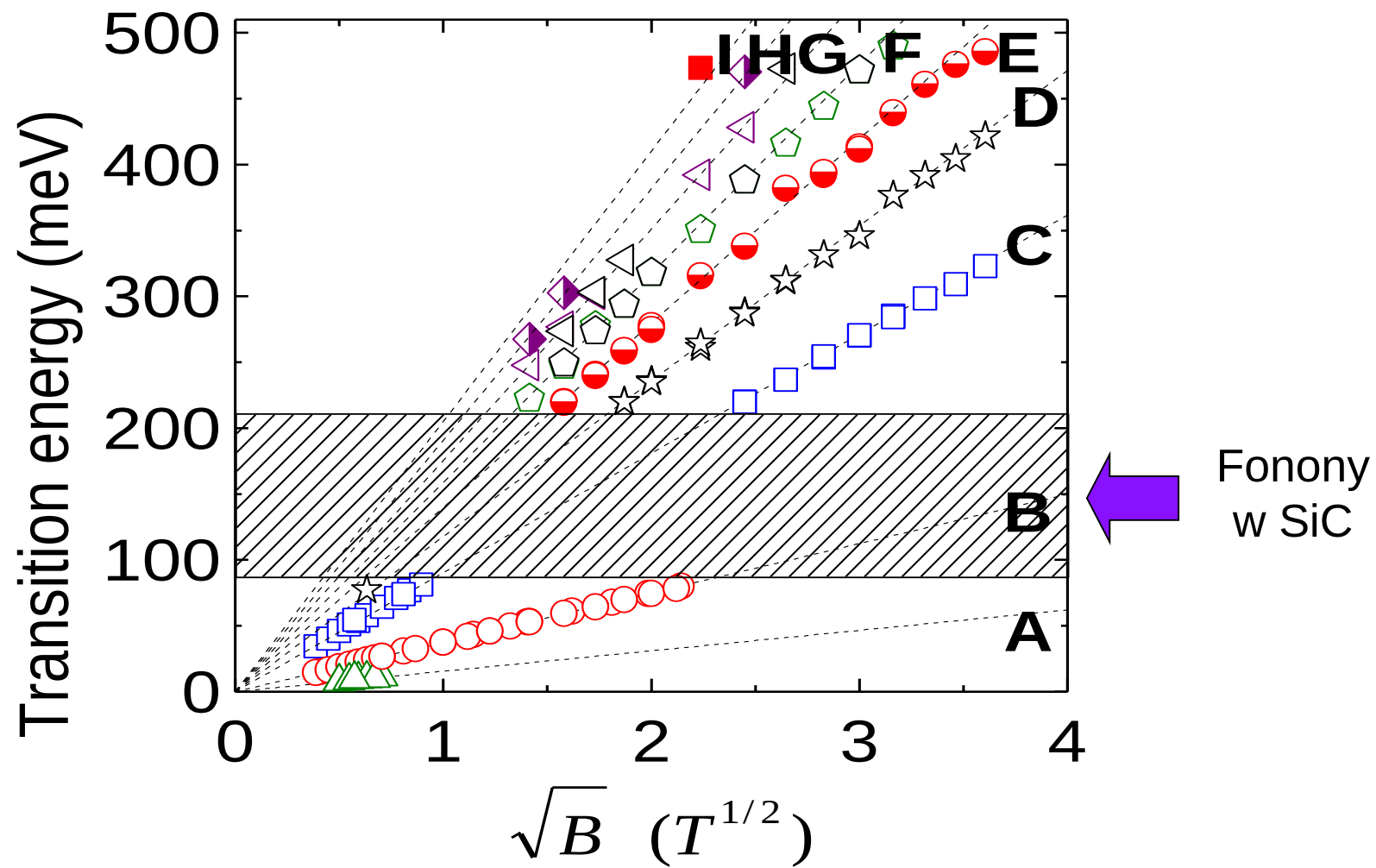
$$\alpha = e^2/\hbar c = 1/137,036 !$$

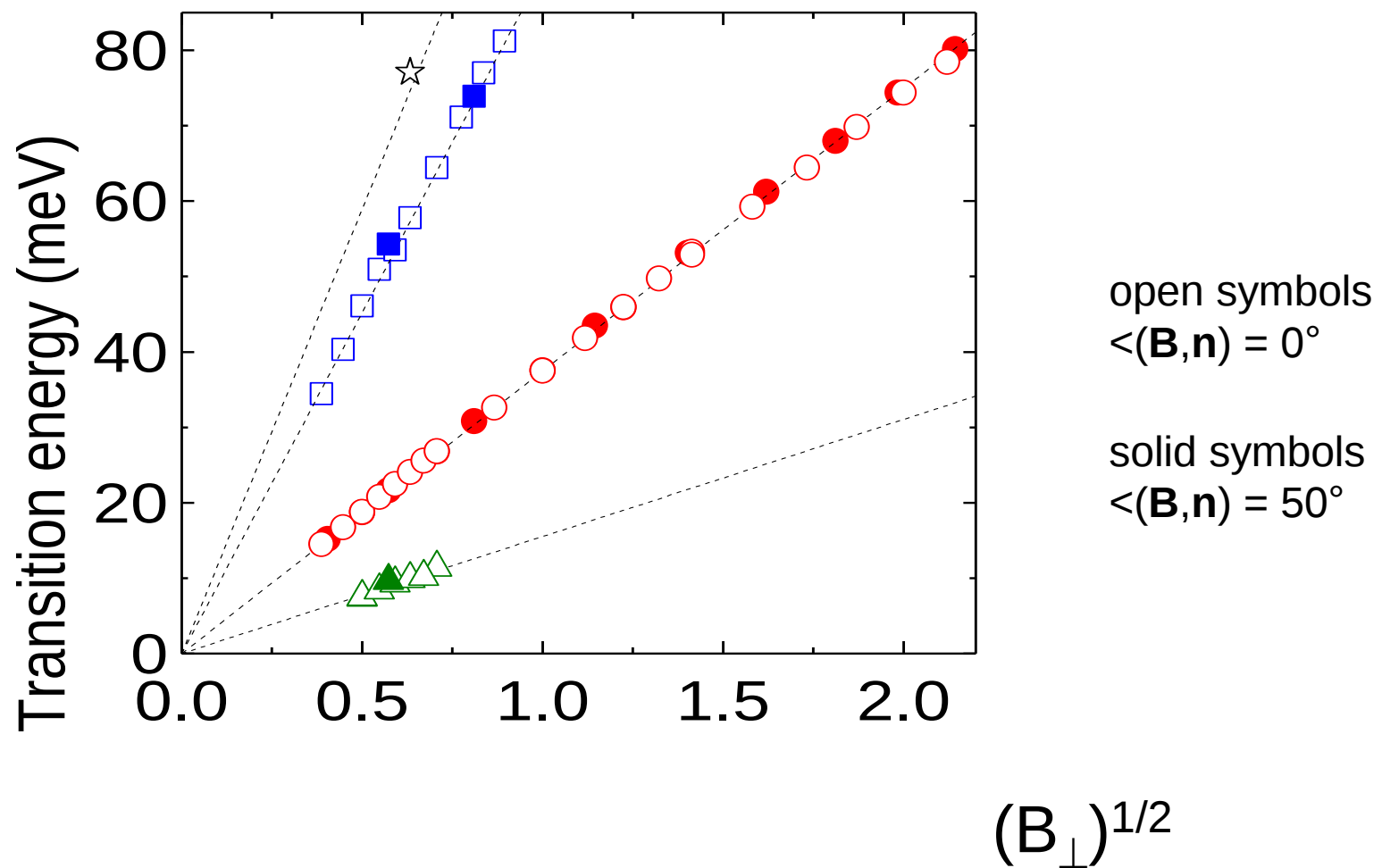
Nair *et al.*, *Science* **320**, 1308 (2008)

Applications: touch screens, solar cells...

Infrared magnetotransmission







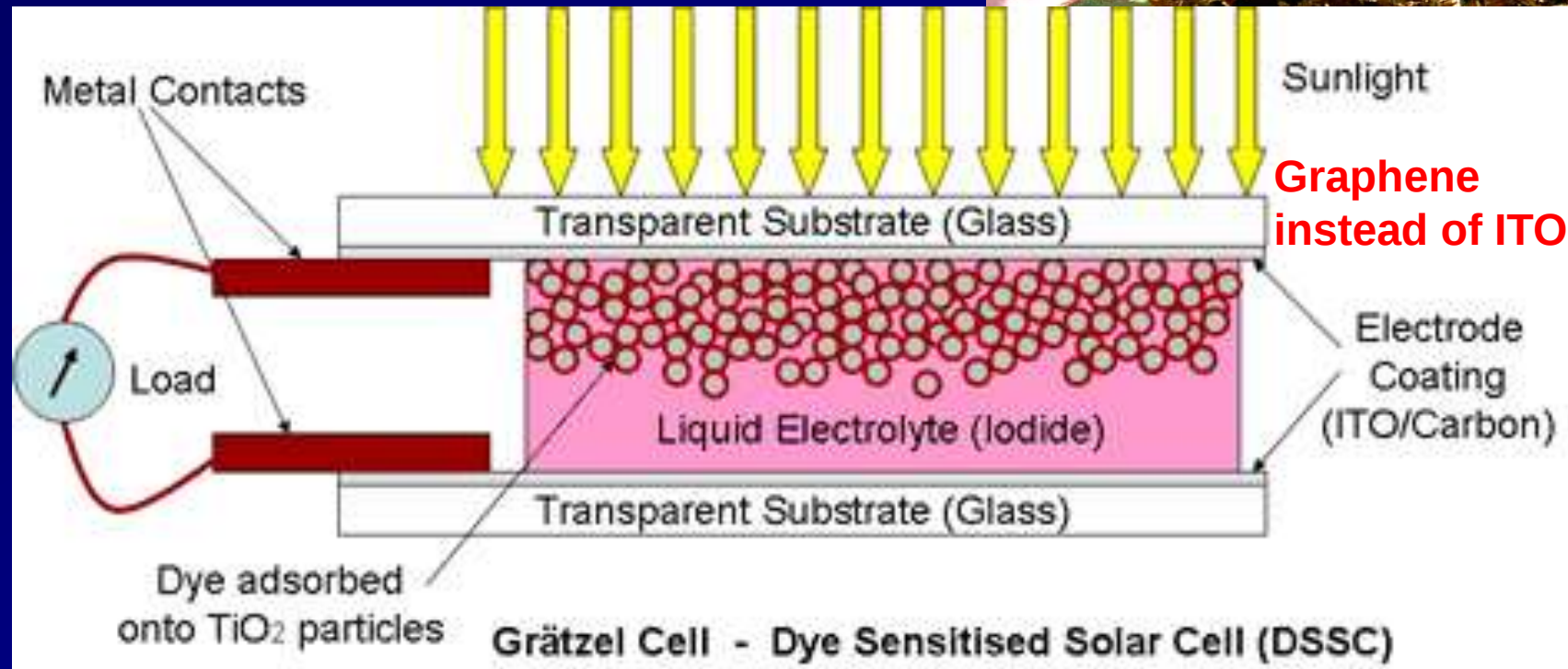
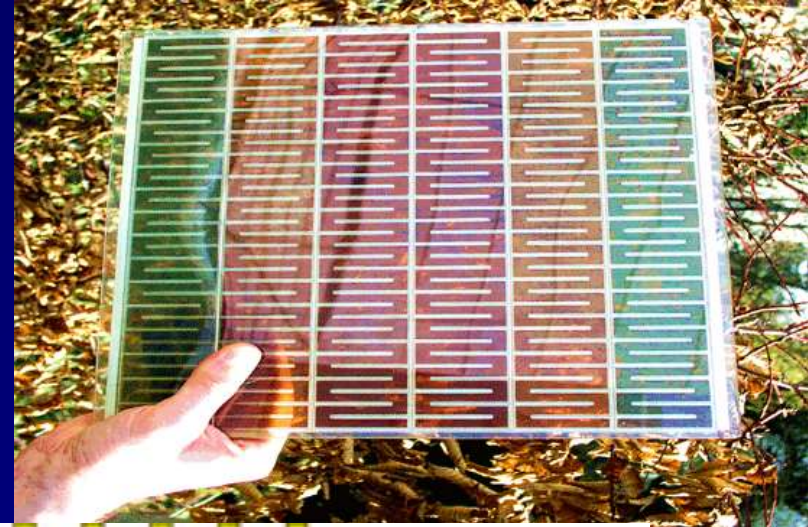
2D system !

M. Potemski et al. (Grenoble)

Solar cells



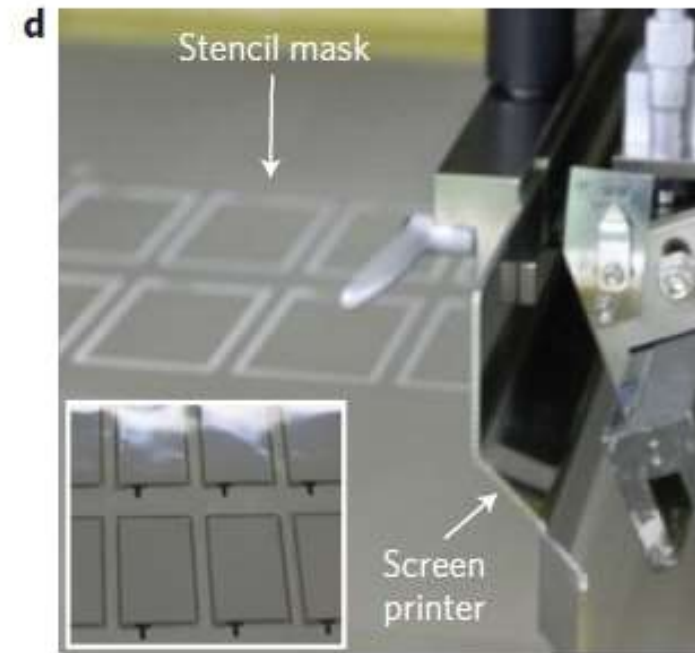
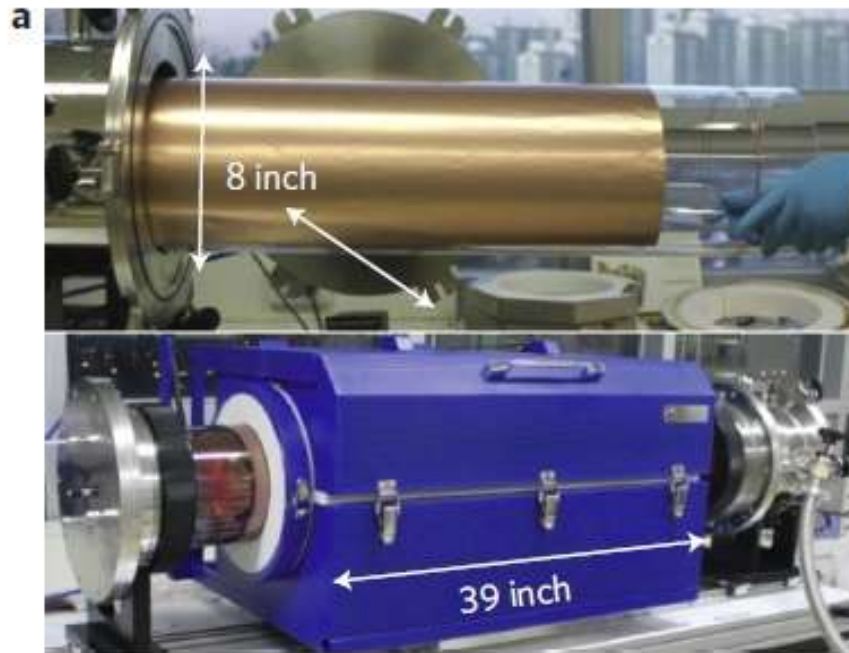
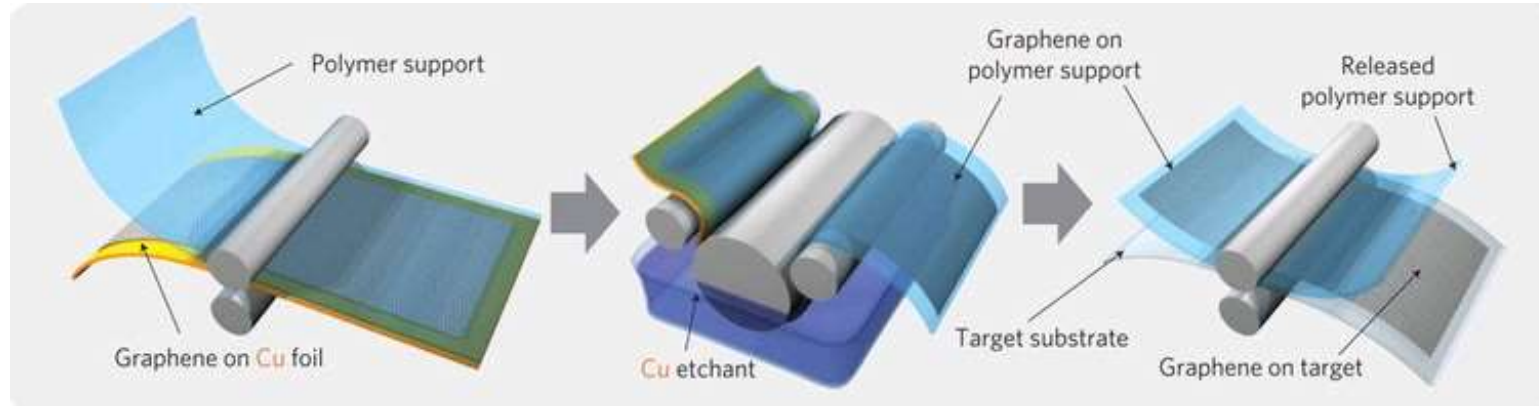
Improved Grätzel cells...



<http://www.solarisnano.com/>

<http://www.mpoweruk.com/semiconductors.htm>

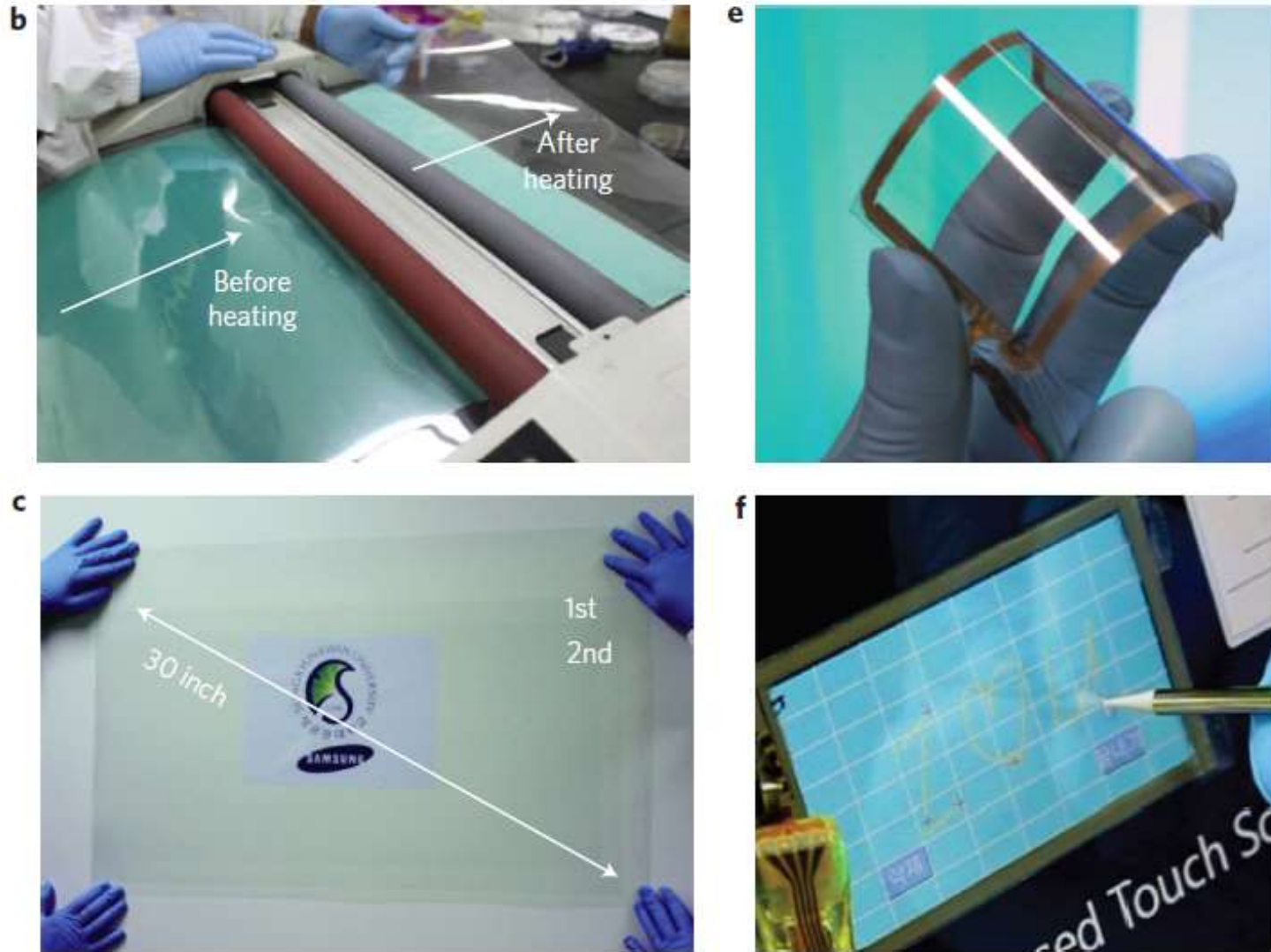
Graphene „roll-to-roll”



Bae et al. NATURE NANOTECHNOLOGY 5,574 (2010)

NATURE NANOTECHNOLOGY

Transparent and elastic touch screens



Bae et al. NATURE NANOTECHNOLOGY 5,574 (2010)

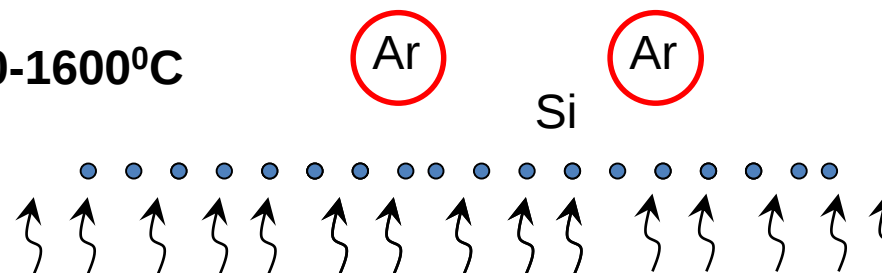
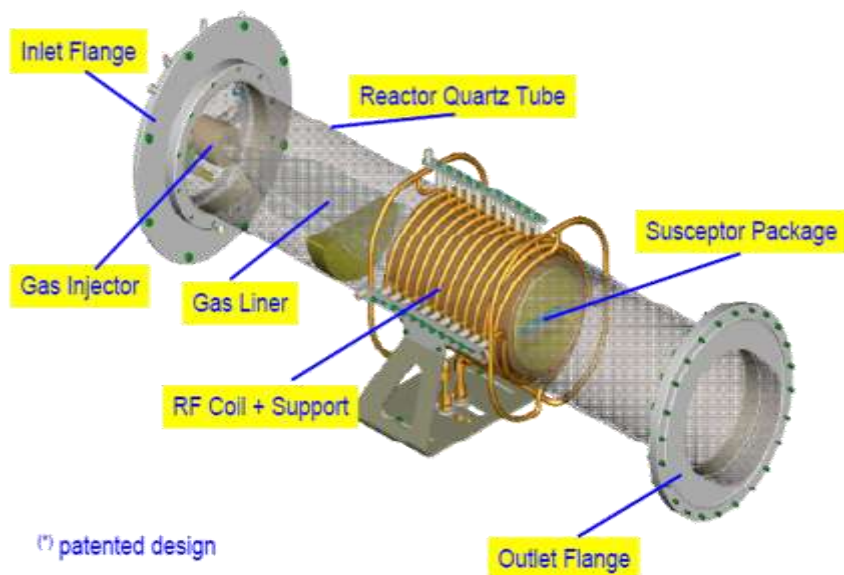
Sublimation method

(in Warsaw ~2006/2007)

First step: etching in H_2 at $1300-1600^{\circ}C$



Graphitization at $1300-1600^{\circ}C$

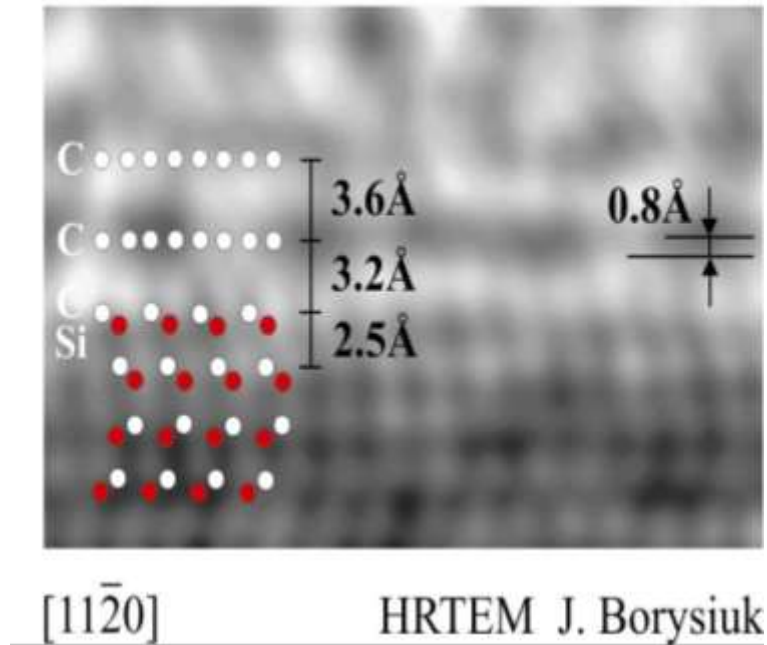


Silicon carbide

Graphite susceptor

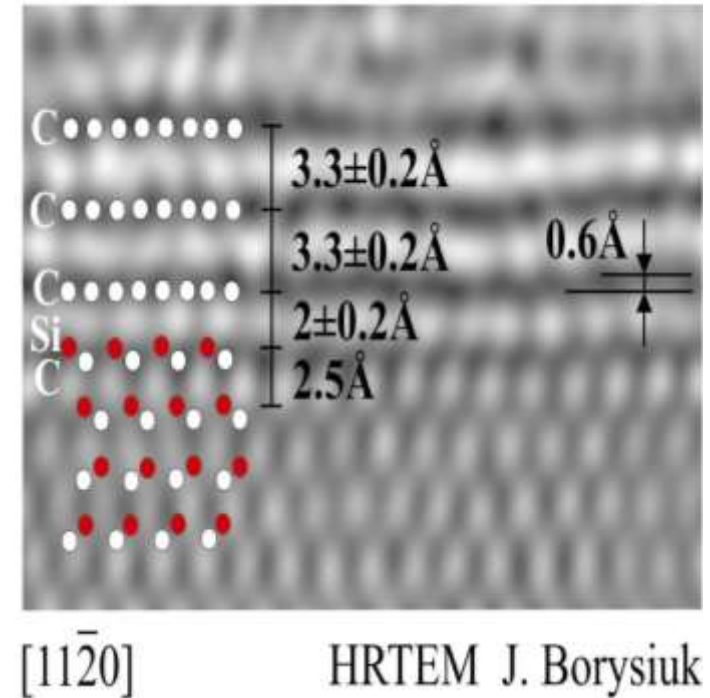
Aixtron VP508 CVD reactor (for SiC growth)

Graphene on SiC



Carbon face

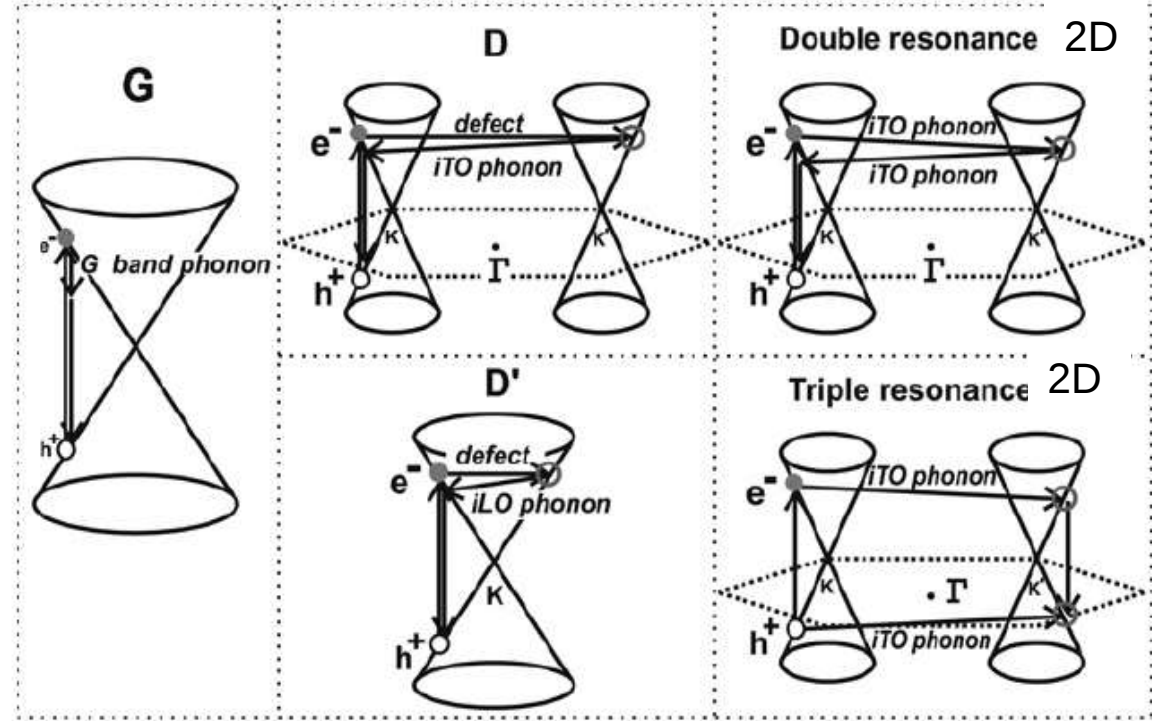
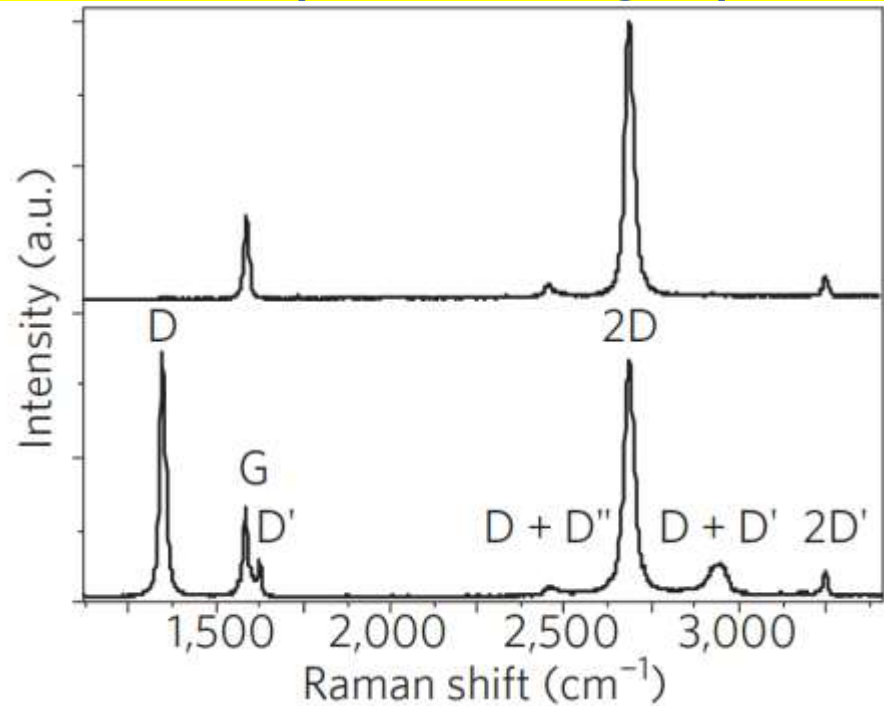
(usually low p-type)



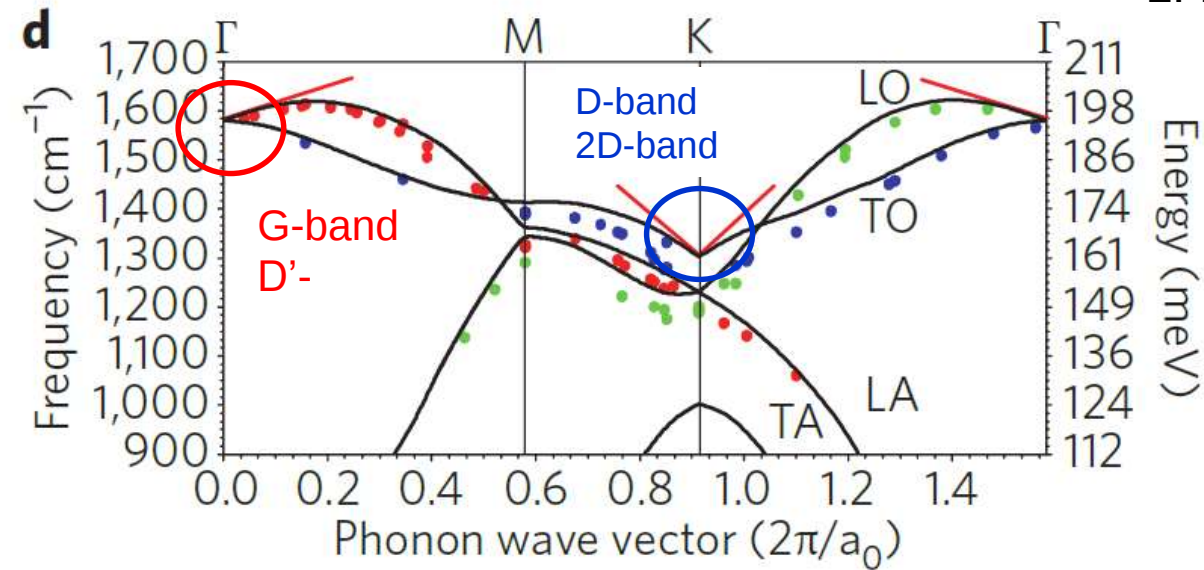
Silicon face

(usually highly n-type)

Raman spectra of graphene



L. M. Malard et al. Phys. Rep. 473, 51 (2009)



A. C. Ferrari and D. M. Basco,
Nature Nanotechnology 8, 235–246 (2013)

Defects in Graphene

D peak is produced only in a small region near a defect or an edge...

„Ideal” crystallites (flakes):

$$\begin{aligned} I(D) &\propto L_a \\ I(G) &\propto L_a^2 \end{aligned} \Rightarrow \boxed{\frac{I(D)}{I(G)} \propto 1/L_a}$$

L_a – flake size

Flakes with rare defects

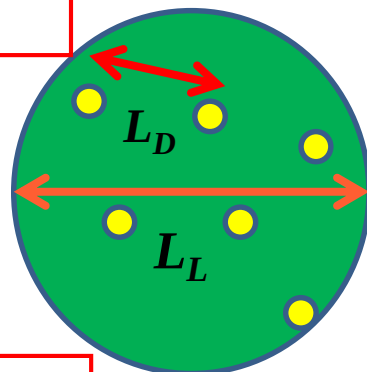
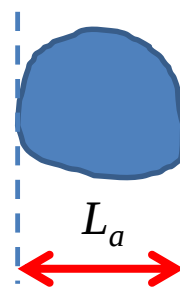
$I(D) \propto$ number of defects within the laser spot...

$$\begin{aligned} I(D) &\propto (L_L/L_D)^2 \\ I(G) &\propto L_L^2 \end{aligned} \Rightarrow \boxed{\frac{I(D)}{I(G)} \propto 1/L_D^2}$$

High disorder

$I(D) \propto$ number of sp^2 rings
 $I(G) \cong$ constant ($\propto$ relative motion of sp^2 carbons)

$$\boxed{\frac{I(D)}{I(G)} \propto L_D^2}$$



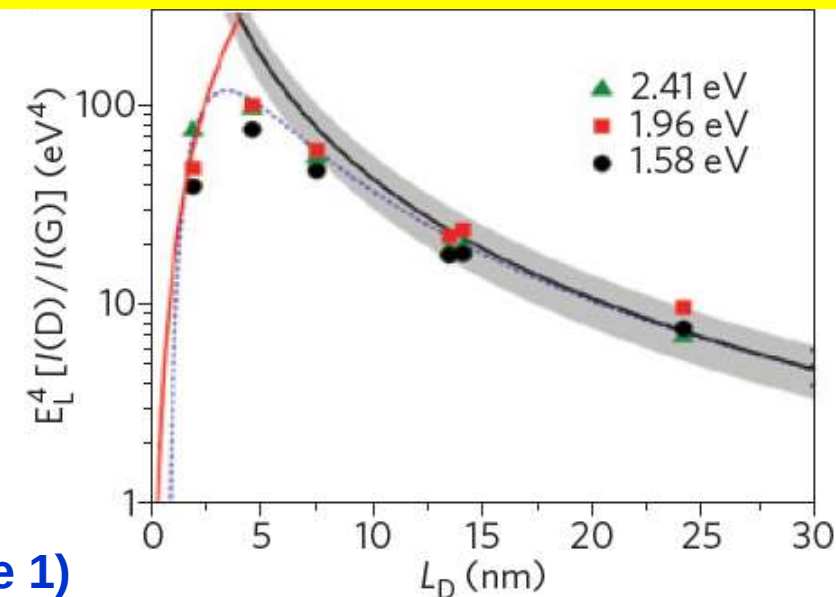
Low disorder (Stage 1)

$$\boxed{n_D(cm^{-2}) = 7.3 \times 10^{-9} E_L^4(eV^4) \frac{I(D)}{I(G)}}$$

High disorder (Stage 2)

$$\boxed{L_D^2(nm^2) = 5.4 \times 10^{-2} E_L^4(eV^4) \frac{I(D)}{I(G)}}$$

$$\boxed{n_D(cm^{-2}) = \frac{5.9 \times 10^{14}}{E_L^4(eV^4)} \left(\frac{I(D)}{I(G)} \right)^{-1}}$$

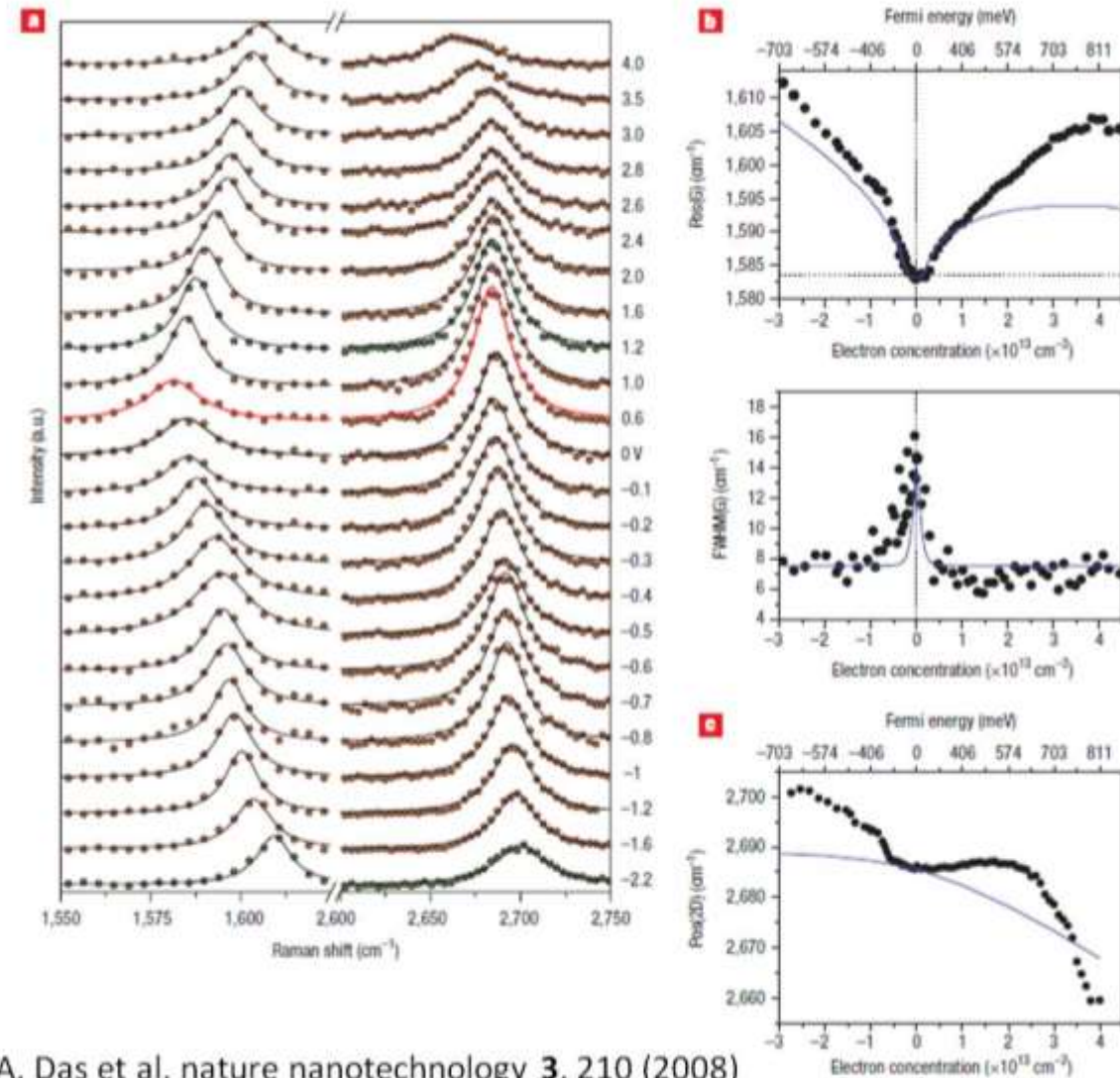
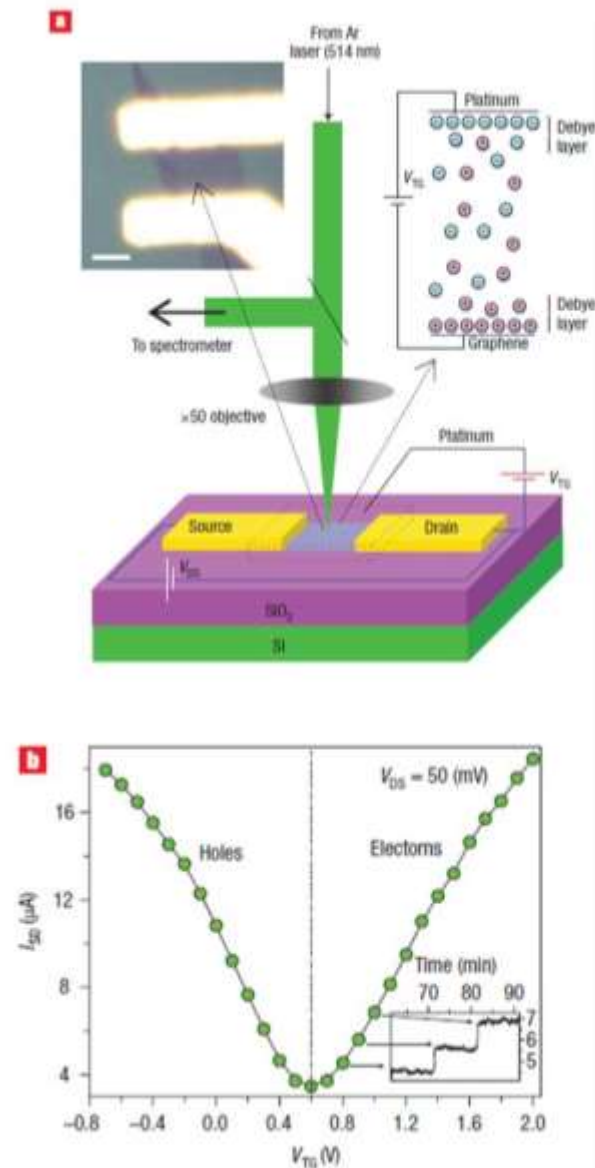


F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126 (1970)

L. G. Cancado et al., Nano Lett. **11** 3190 (2011)

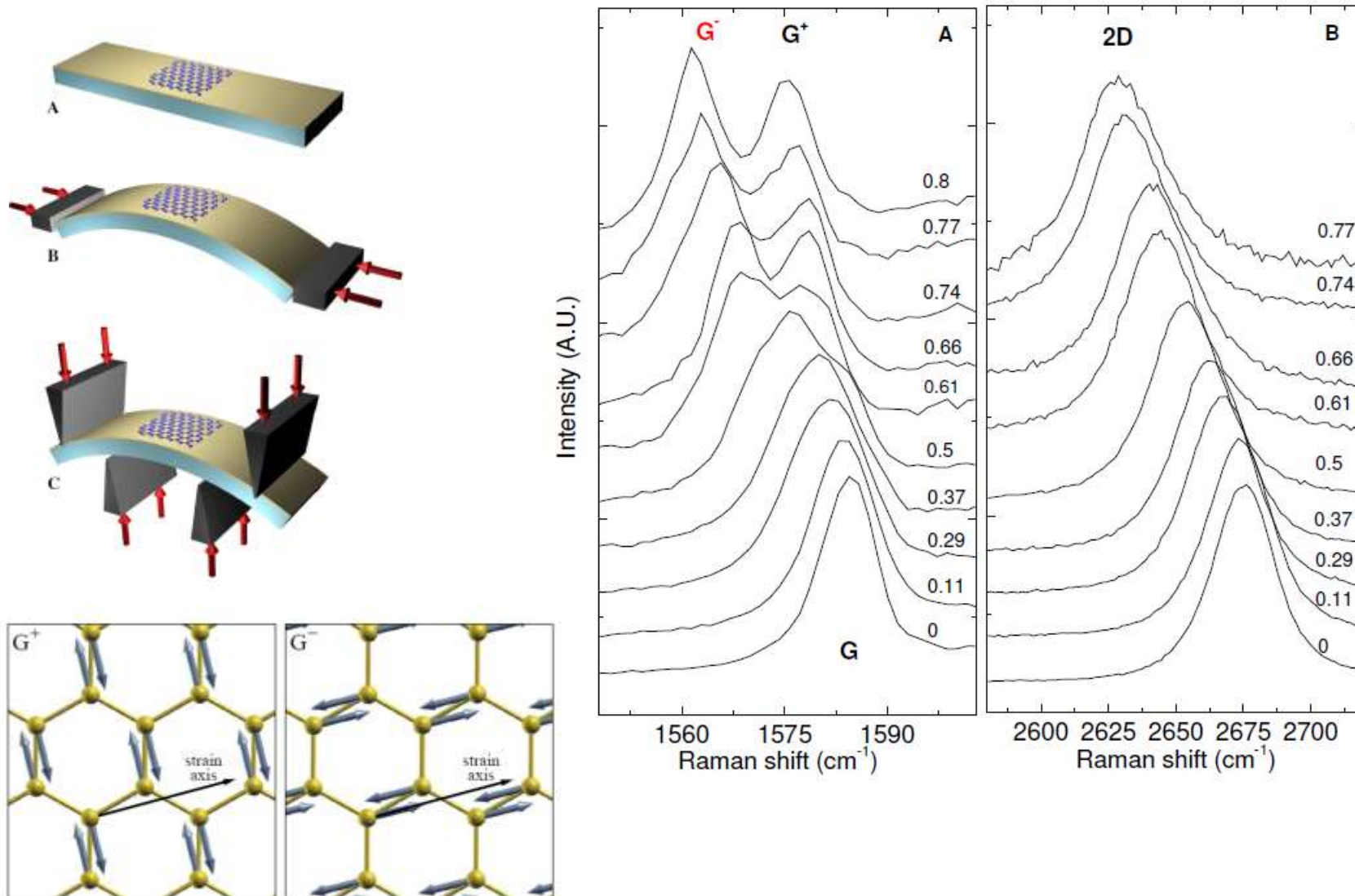
A. C. Ferrari and D. M. Basco, Nature Nanotechn. **8**, 235 (2013)

Doping reference - solid electrolyte top gated exfoliated graphene

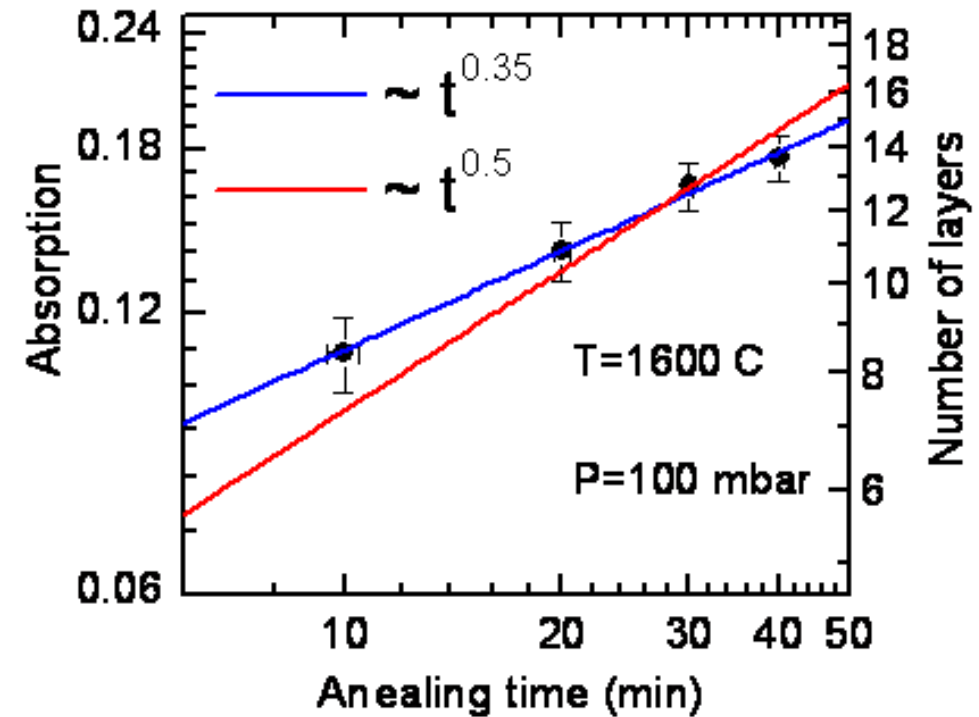
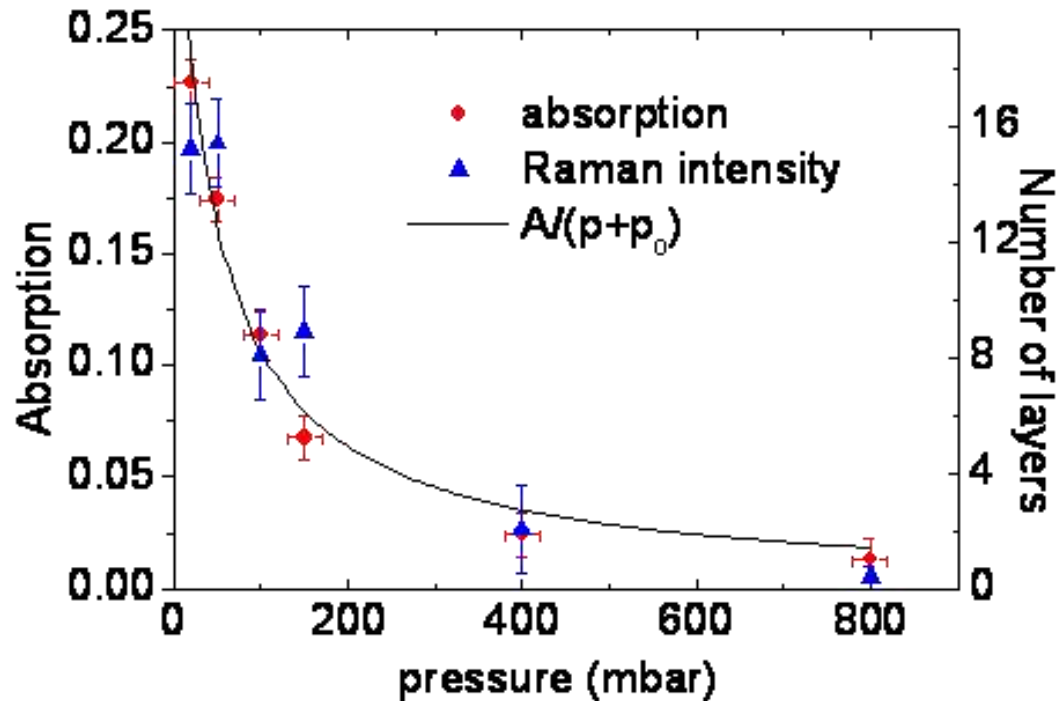


A. Das et al. nature nanotechnology 3, 210 (2008)

Uniaxial strain influence on Raman spectra



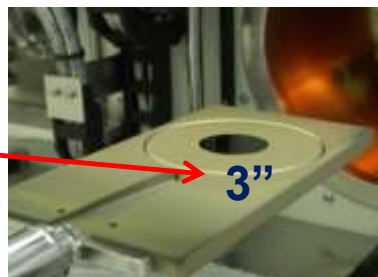
Graphene on SiC - sublimation growth kinetics (C-face)



Growth kinetics driven by 2D – diffusion of Si!

A.Drabińska et al., Phys. Rev. B **81**, 245410 (2010)

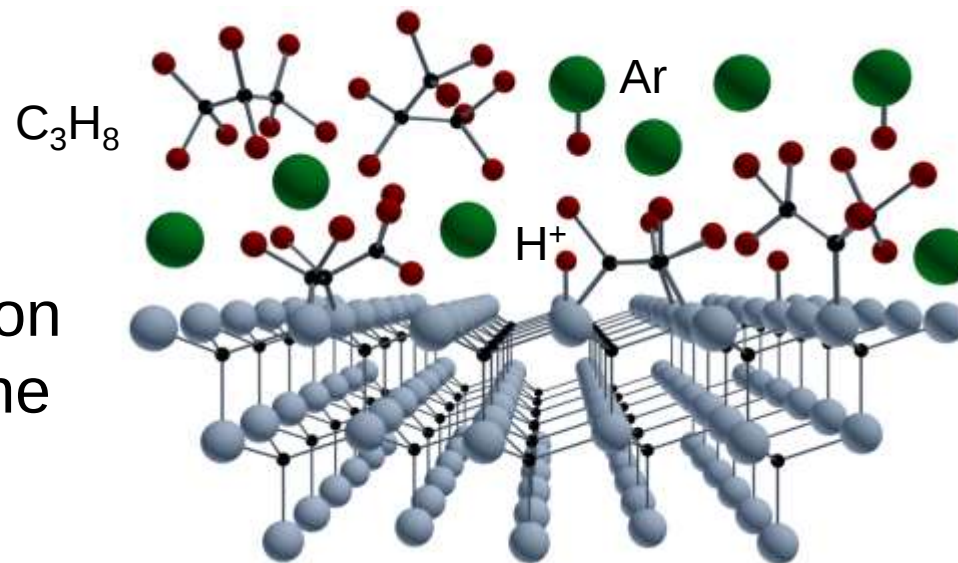
Chemical Vapour Deposition



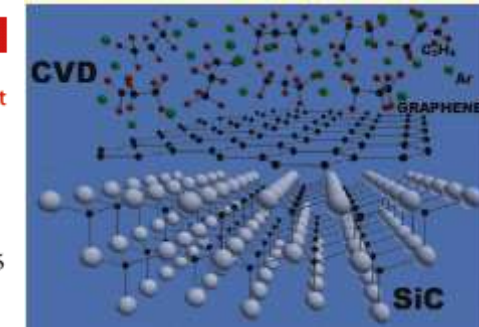
- suppression of sublimation
- decomposition of propane in Ar atmosphere



Standard CVD

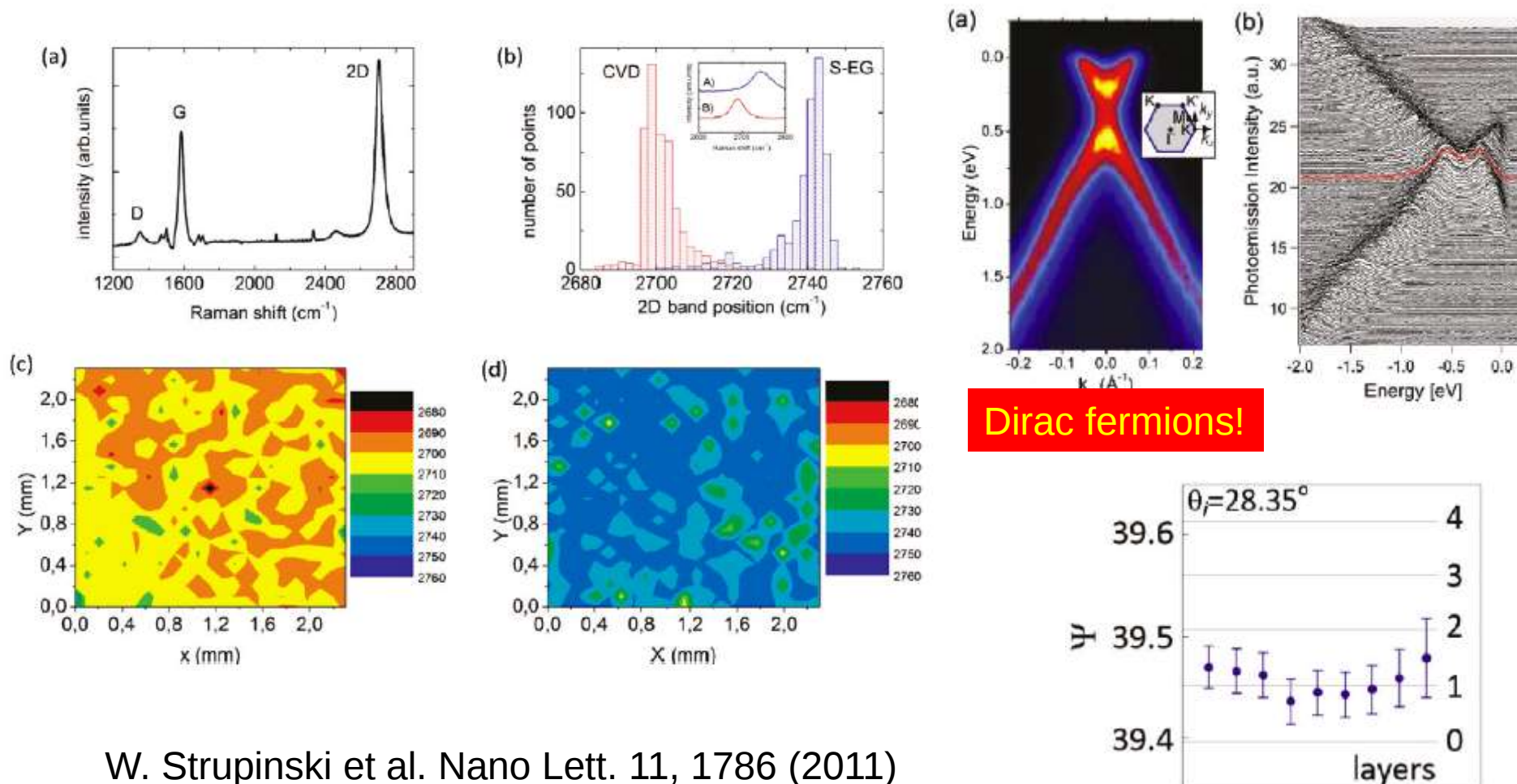


W. Strupinski et al. Nano Lett. 11, 1786 (2011)



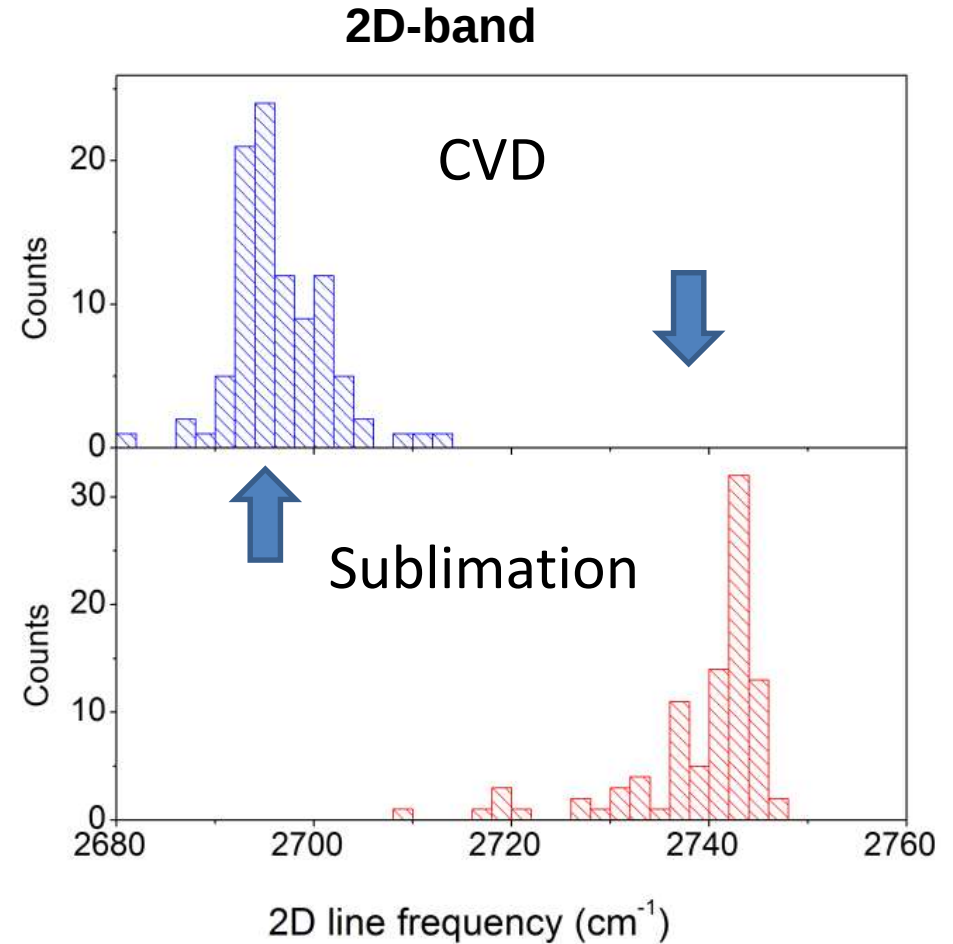
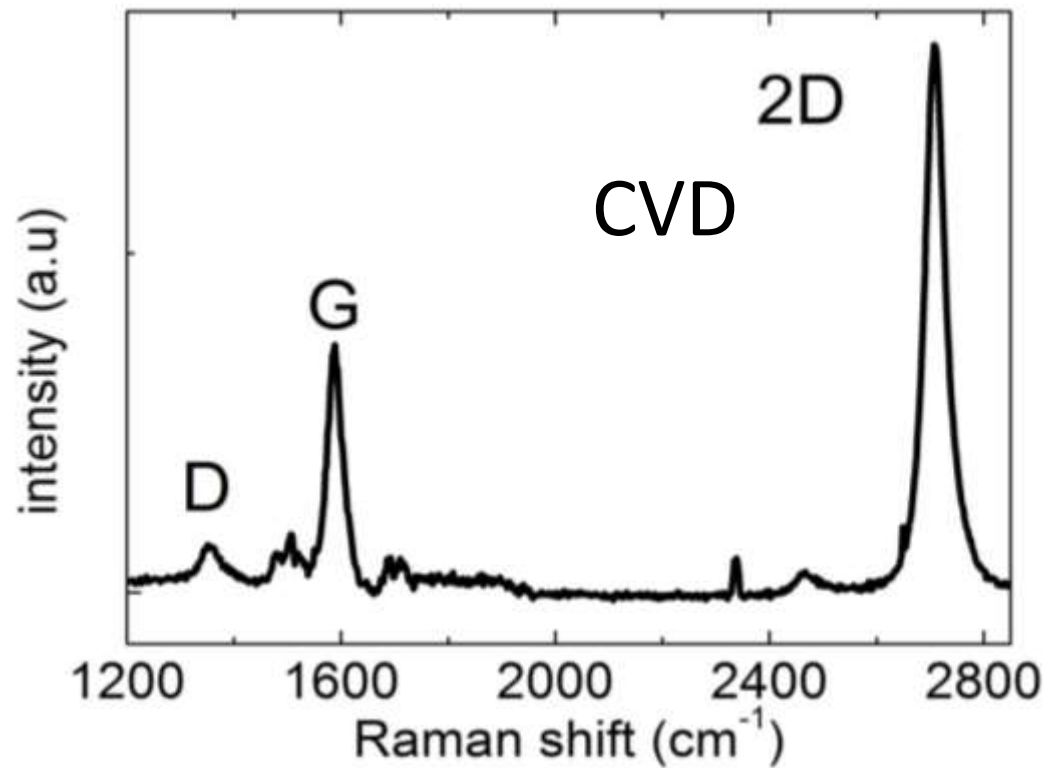
Graphene Epitaxy by Chemical Vapor Deposition on SiC

W. Strupinski,^{*,1} K. Grodecki,^{1,2} A. Wyszomolek,² R. Stepniewski,² T. Szkopek,³ P. E. Gaskell,³ A. Grüneis,^{4,5} D. Haberer,⁴ R. Bozek,² J. Krupka,⁶ and J. M. Baranowski^{1,2}



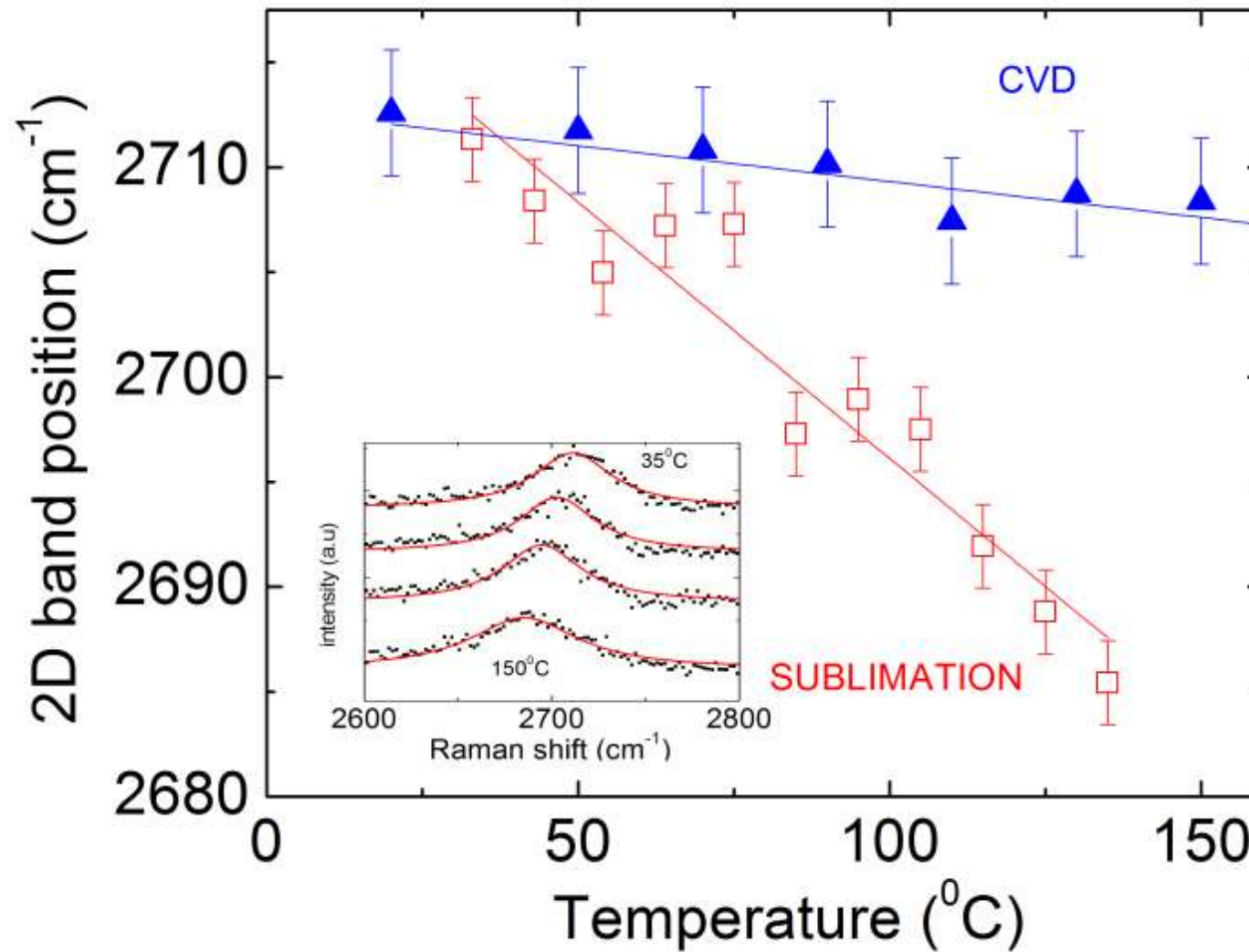
W. Strupinski et al. Nano Lett. 11, 1786 (2011)

Interaction with the substrate

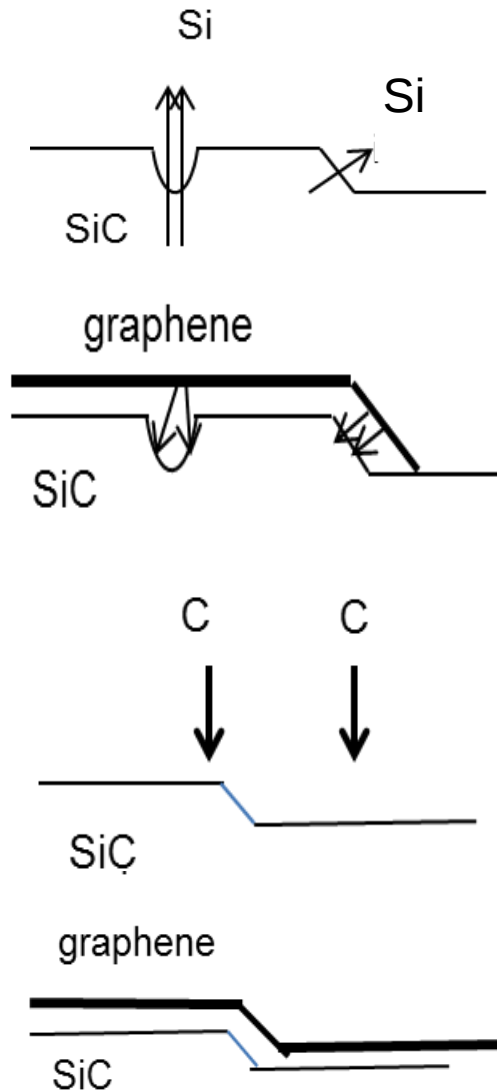


W. Strupinski et al. Nano Lett. 11, 1786 (2011)
K. Grodecki et al., J. Appl. Phys. 111, 114307 (2012)

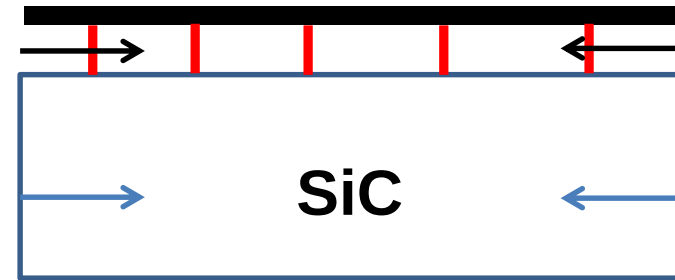
Temperature dependence of 2D-band position



Interaction with the substrate

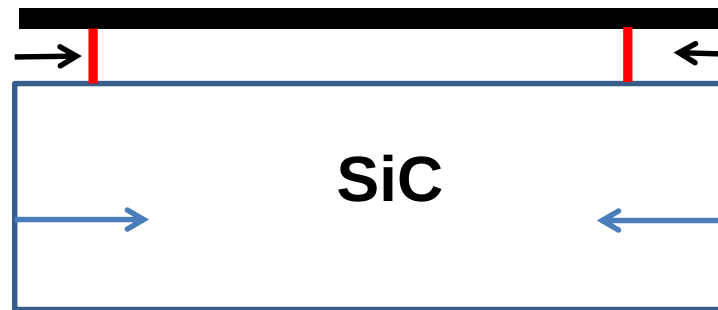


Sublimation



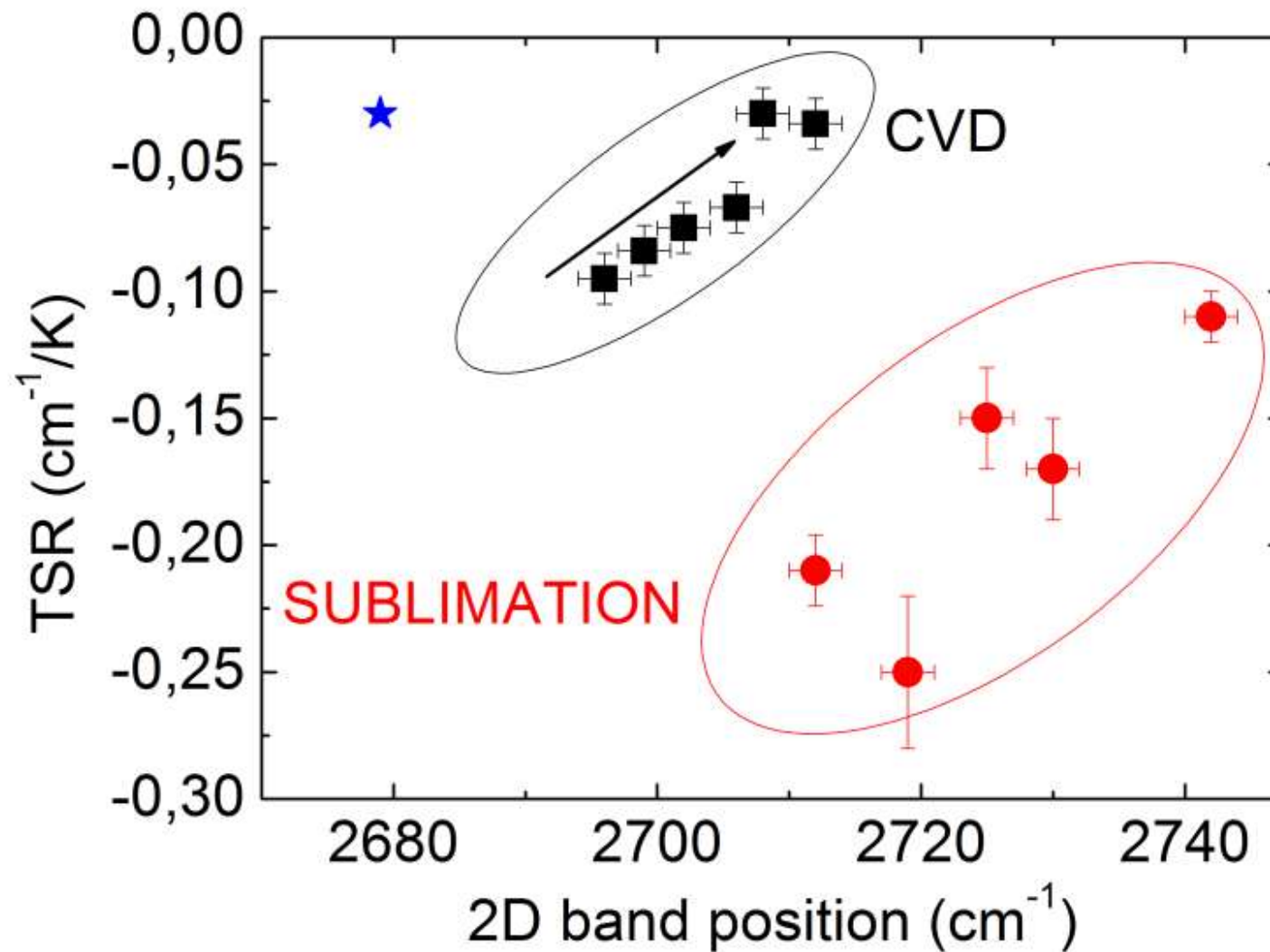
Graphene strongly **pinned** to the substrate
(**defects**, step edges...)

CVD



Graphene can slide over the substrate...

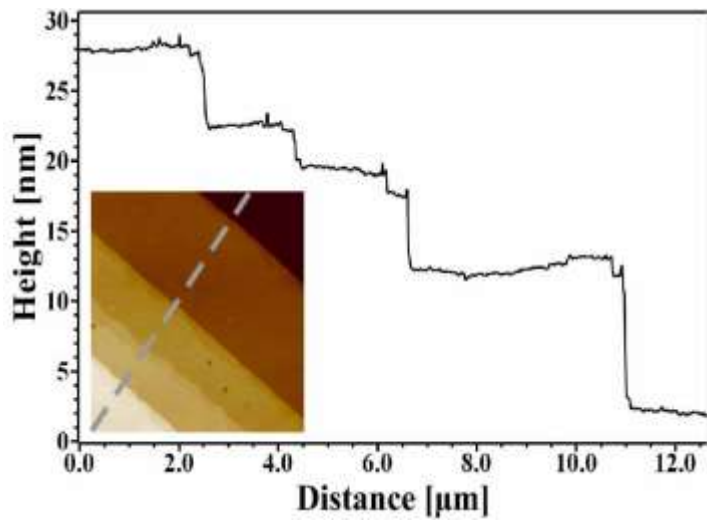
„Phase diagram”



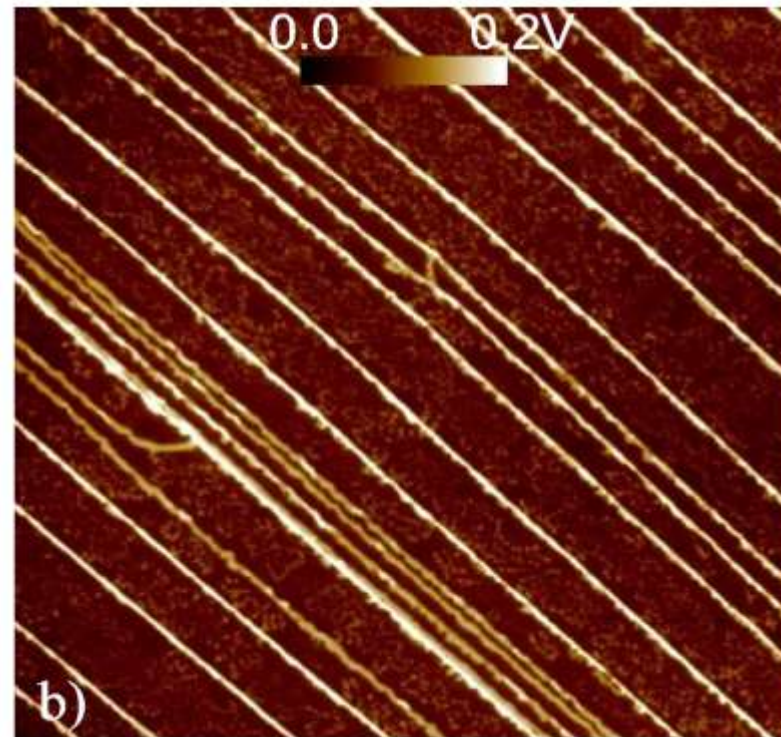
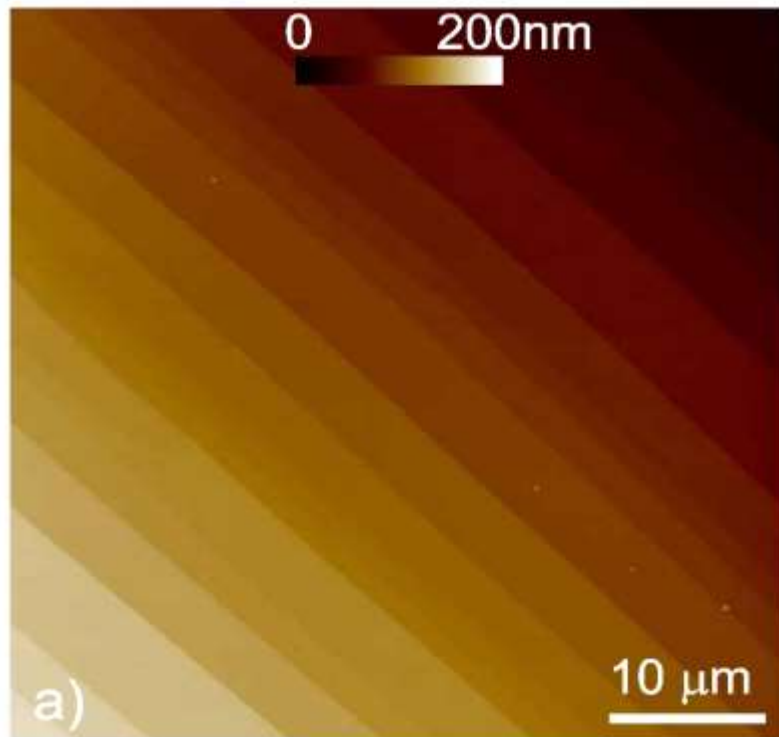
Microscale Raman experiments



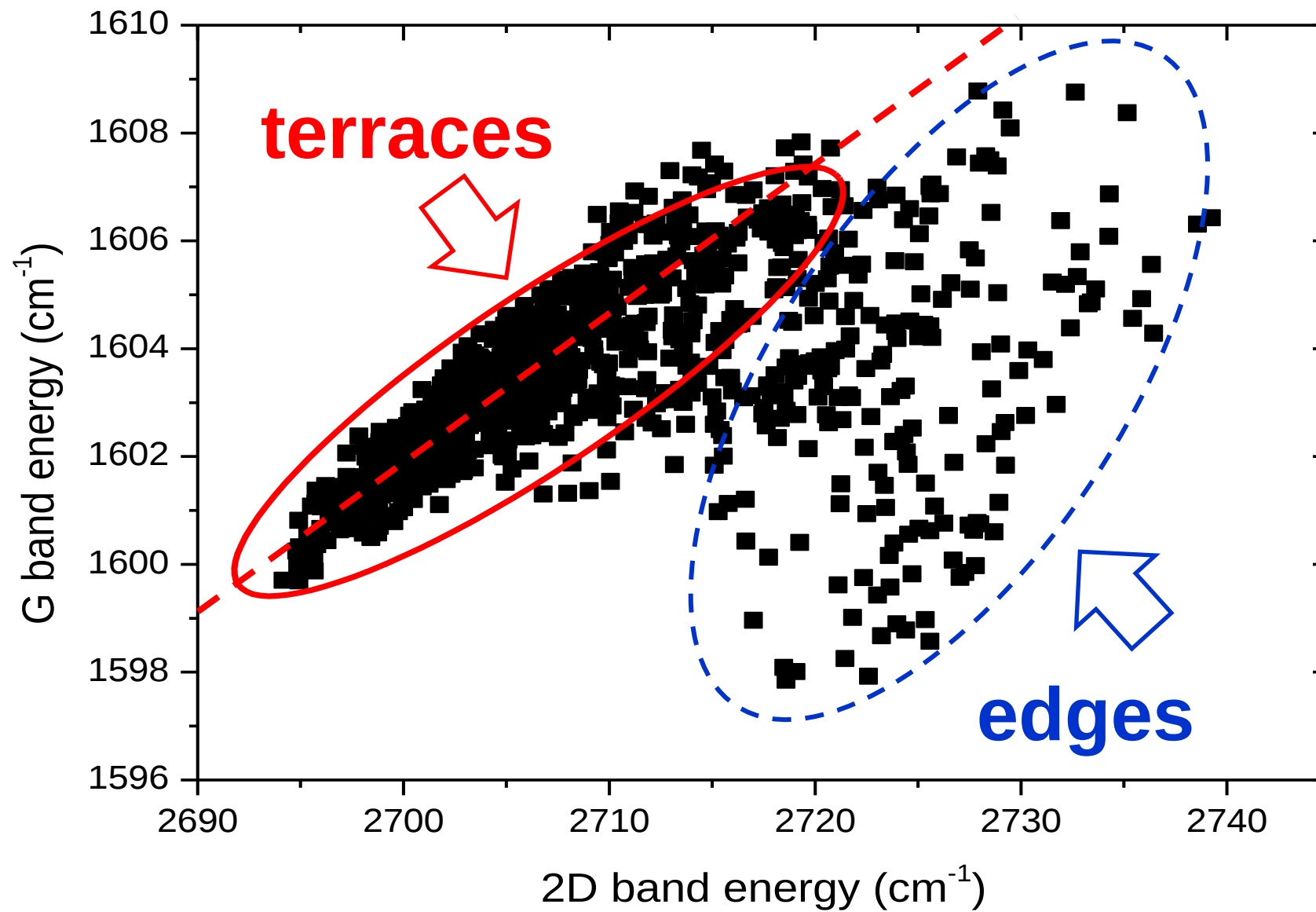
steps play a role...



AFM &
Kelvin Probe Microscopy
CVD graphene
4H-SiC Si-face

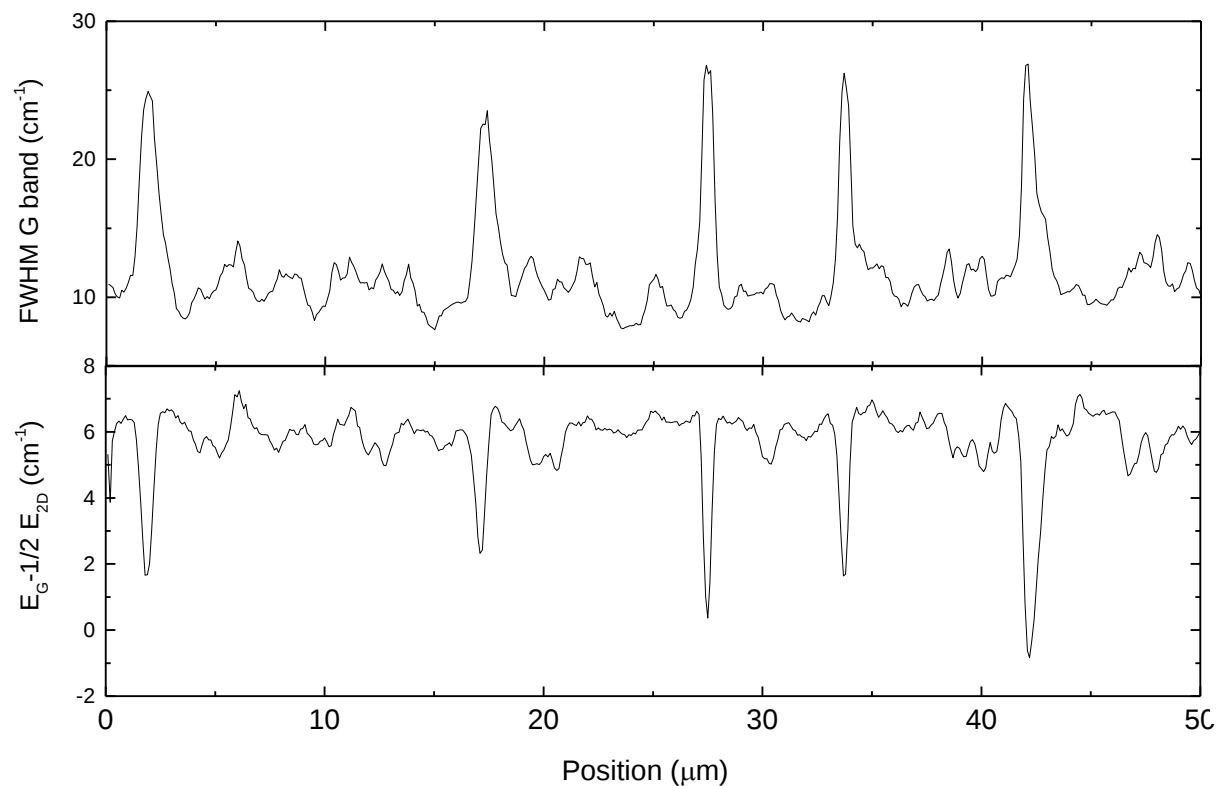


R. Božek (2012)

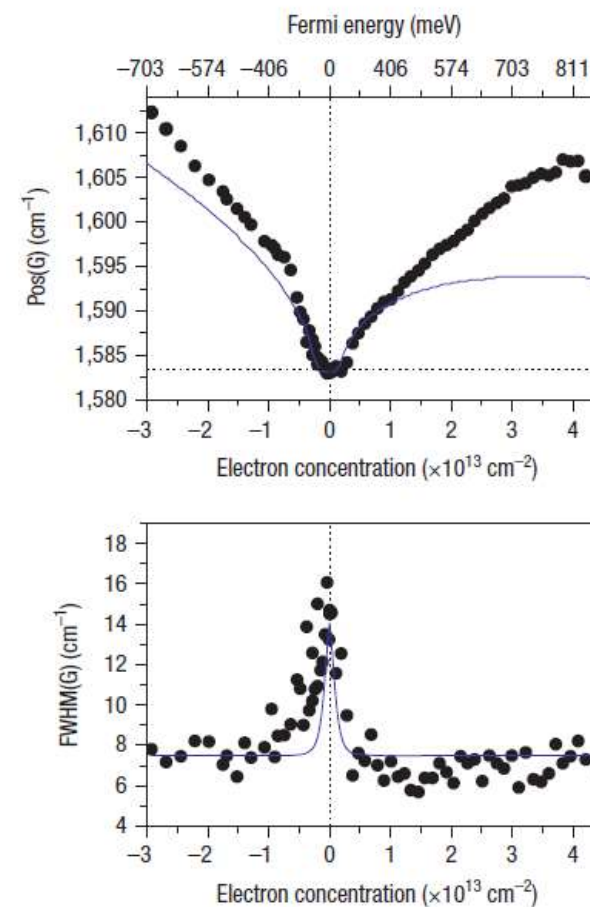


FWHM vs. G-band position

CVD



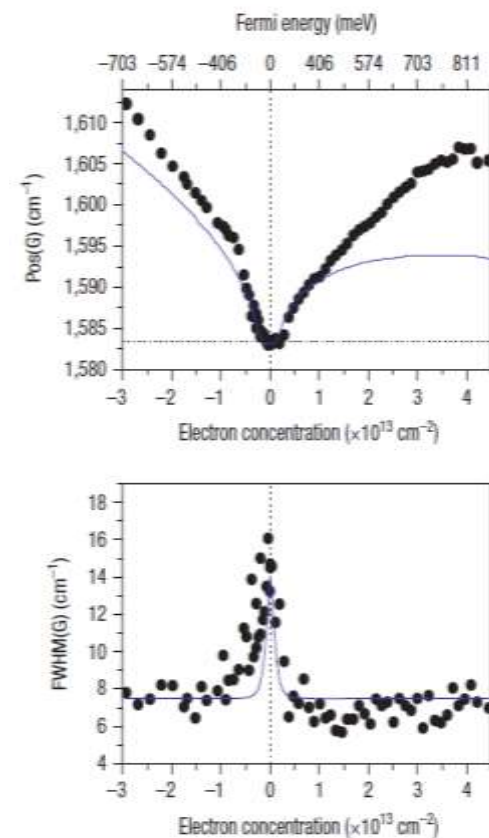
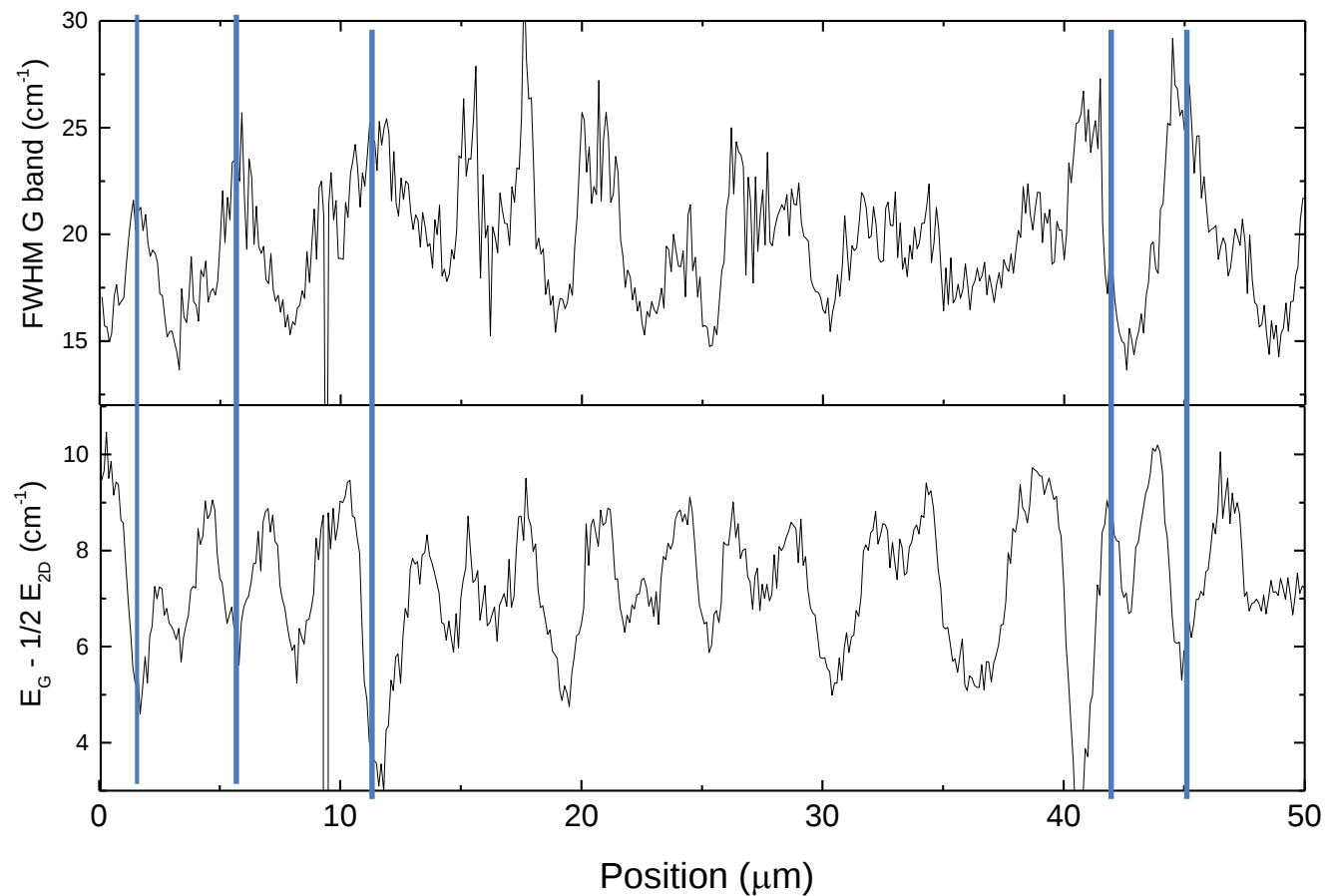
Well defined terraces!



A. Das et al.
Nature Nan. 3, 210 (2008)

G-band - FWHM vs. position

Sublimation

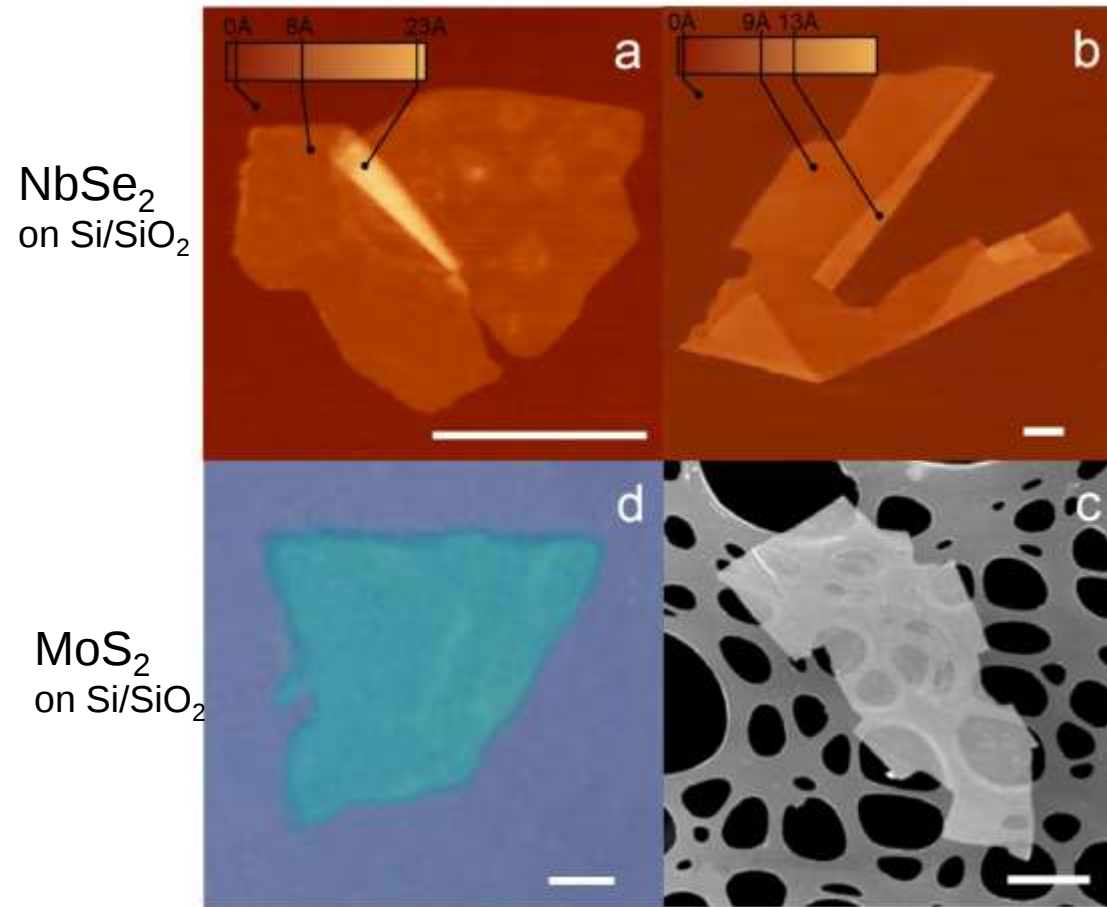


A. Das et al.
Nature Nan. 3, 210 (2008)

Erosion of steps...

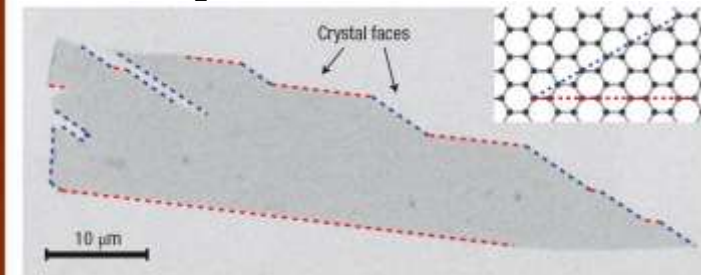
Other 2D materials

Single layers



graphite
on Si/SiO_2

graphene "big flake"



$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$
on carbon

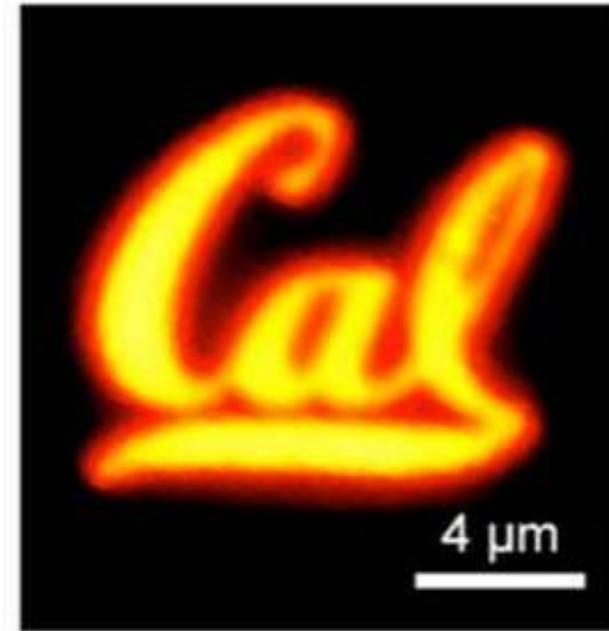
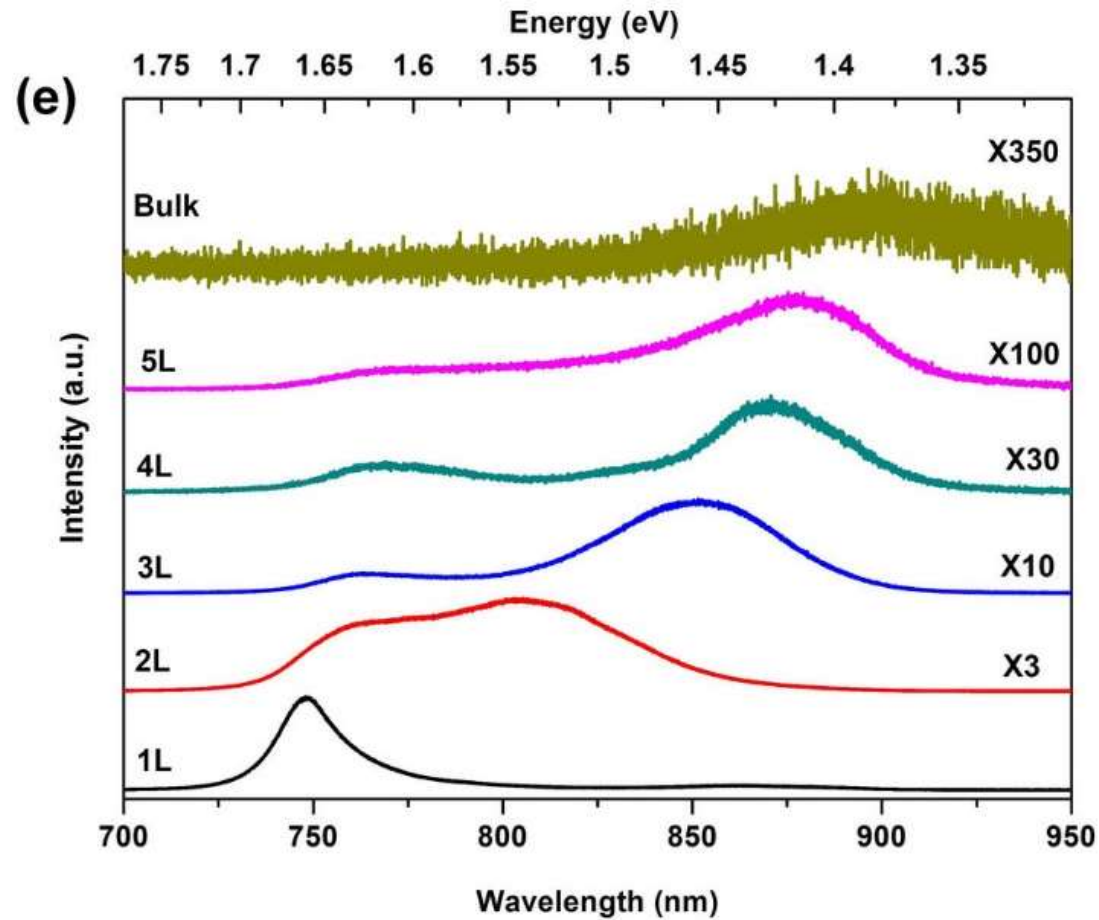
K.S. Novoselov, et al., *Two-dimensional atomic crystals*,
Proc. Natl Acad. Sci. USA, **102**, 10451–10453 (2005)
K.S. Novoselov and A.K. Geim,
The rise of graphene, *Nature Materials*, **6**, 183, (2007)

Van der Waals heterostructures – new possibilities

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		Semiconducting dichalcogenides: MoTe ₂ , WTe ₂ , ZrS ₂ , ZrSe ₂ and so on	Metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NiSe ₂ and so on	
				Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ and so on	
2D oxides	Micas, BSCCO	MoO ₃ , WO ₃	Perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀ and so on		Hydroxides: Ni(OH) ₂ , Eu(OH) ₂ and so on
	Layered Cu oxides	TiO ₂ , MnO ₂ , V ₂ O ₅ , TaO ₃ , RuO ₂ and so on			Others

A. K. Geim & I. V. Grigorieva, Nature 499, 419 (2013)

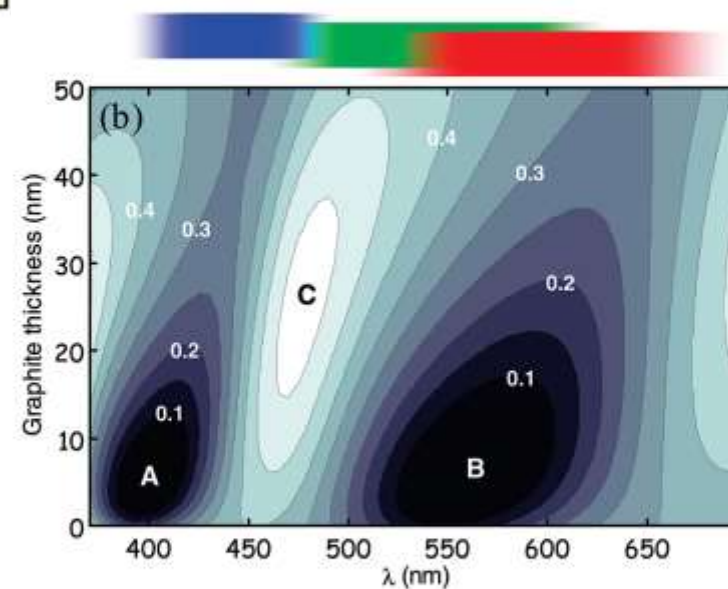
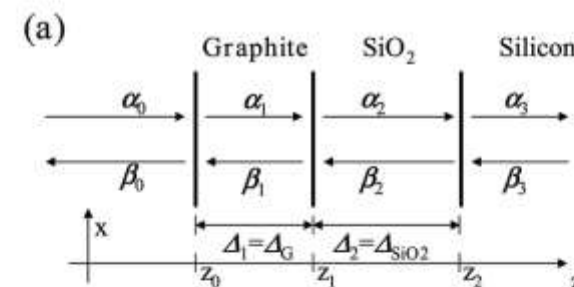
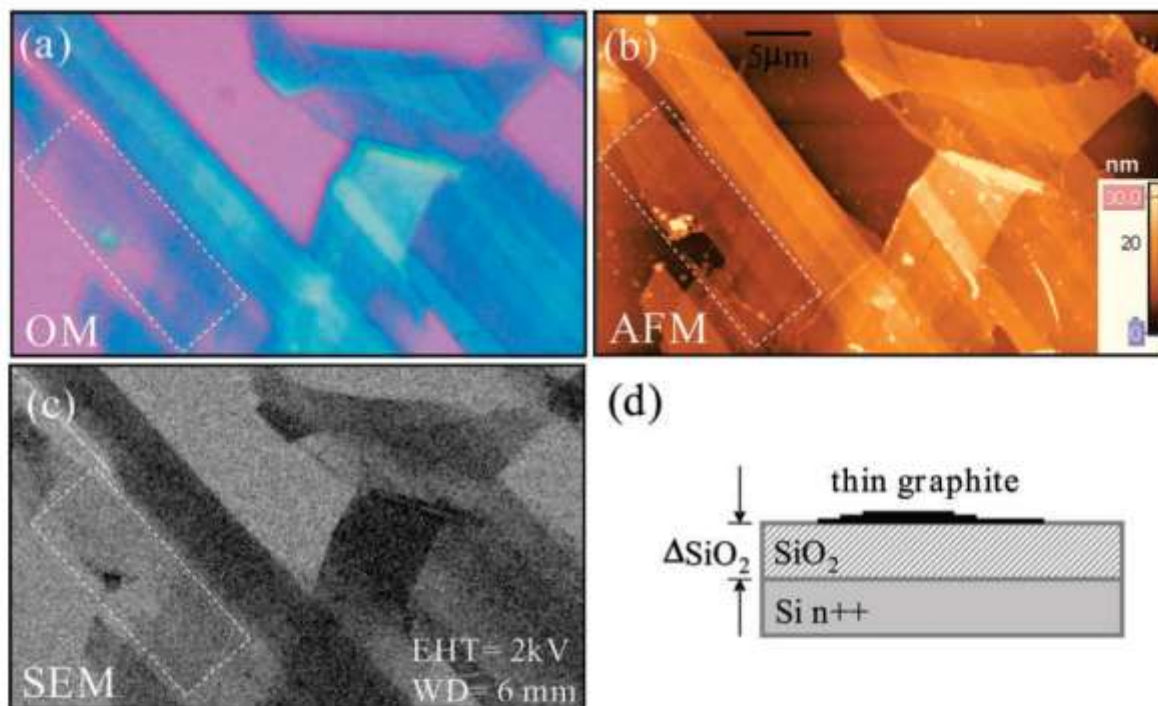
Unexpected behavior of the emission



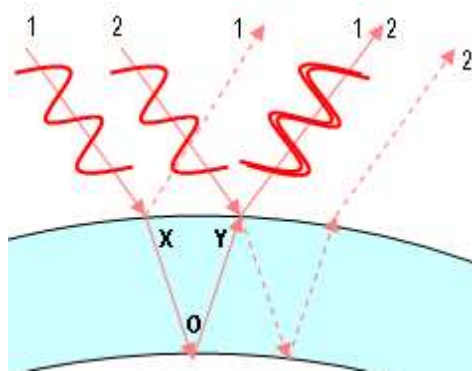
H. Terrones et al. Scientific Reports 4, 4215 (2014)

M. Amani et al. SCIENCE 350, 1065 (2015)

Interferences make 2D materials visible...

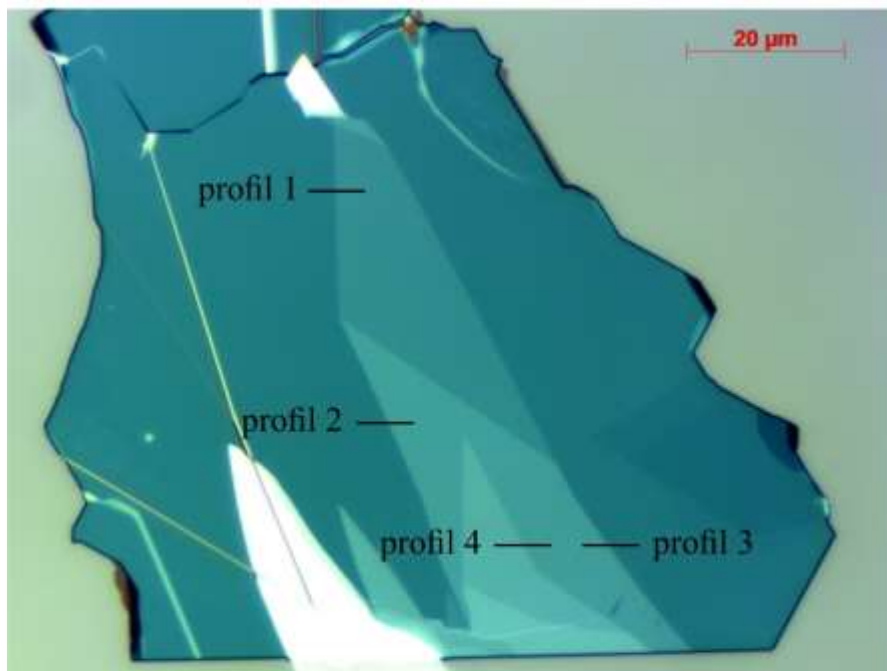


wikimedia.org

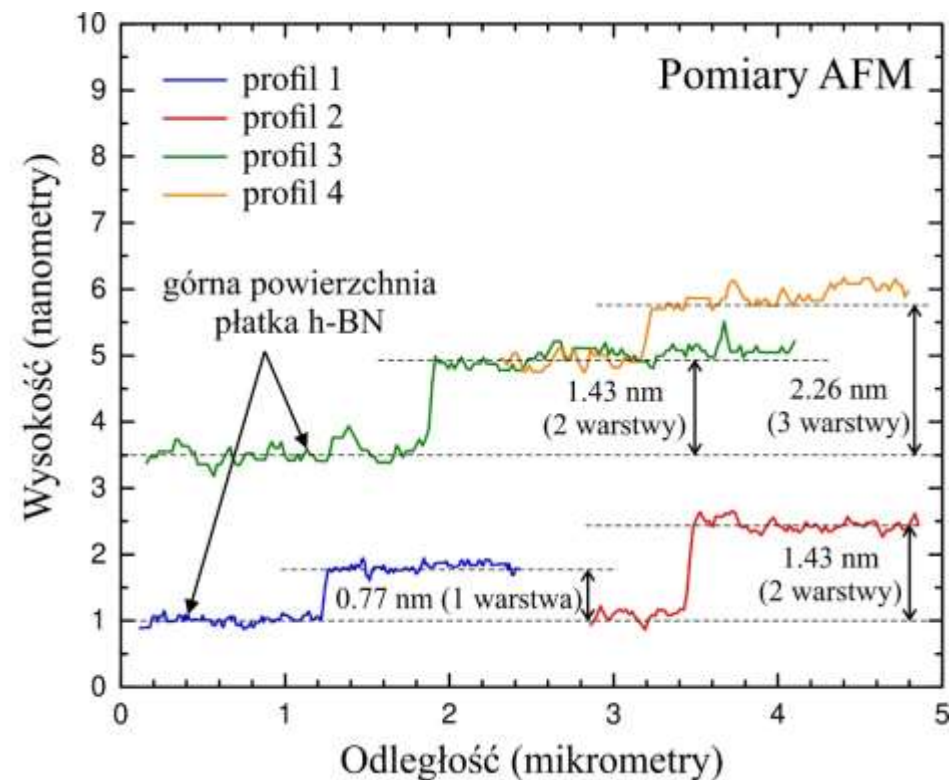
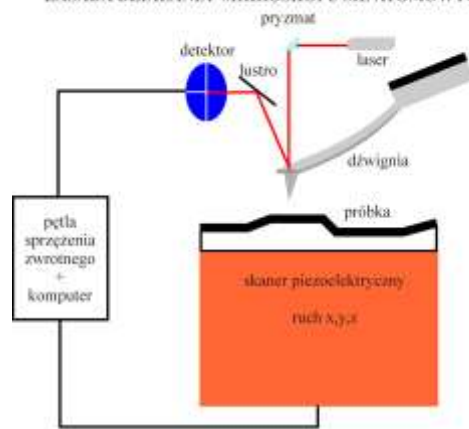


S. Roddaro et al. Nano Lett., 7, 2707 (2007)

Optical microscopy and Atomic Force Microscopy



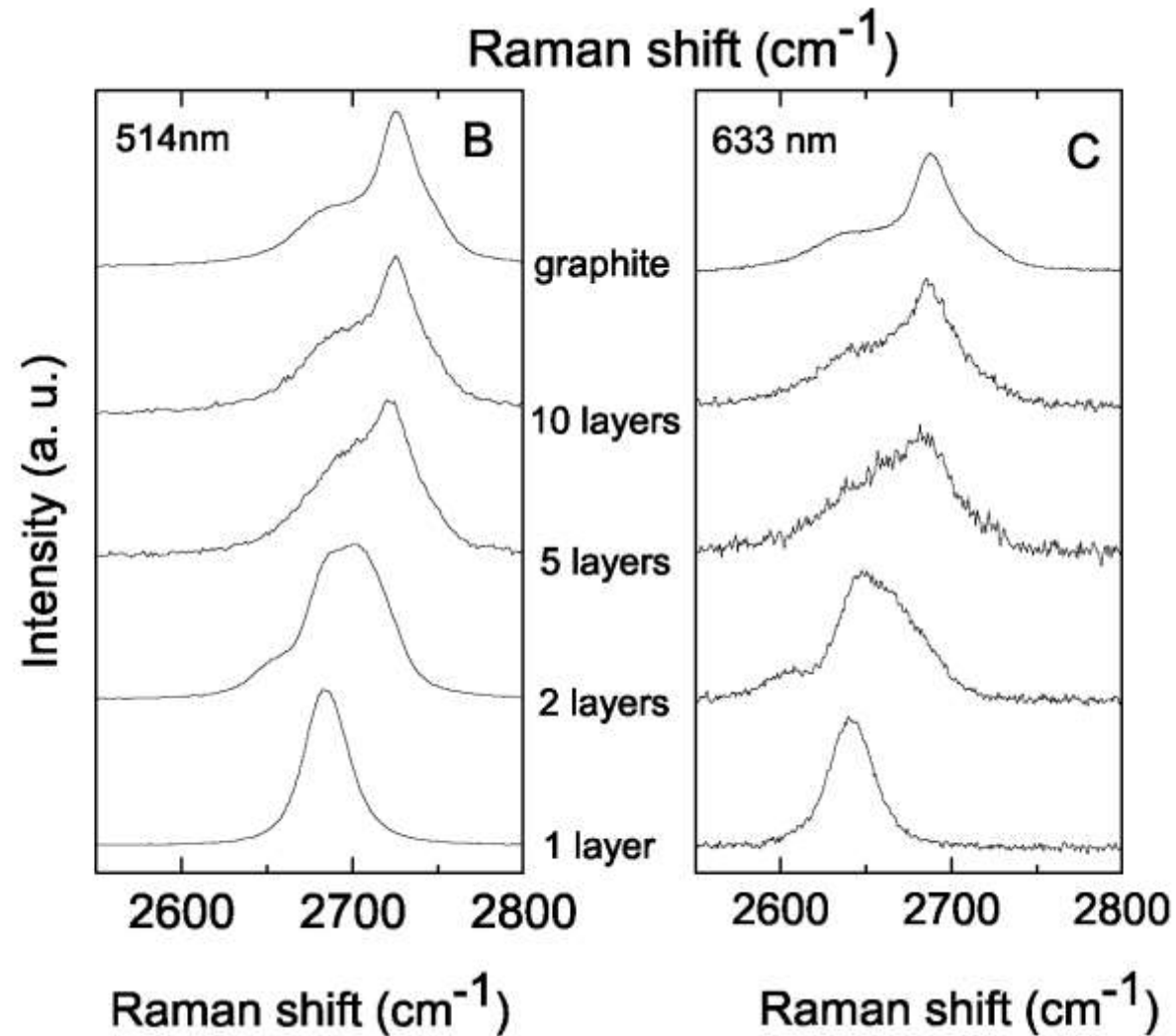
ZASADA DZIAŁANIA MIKROSKOPU SIŁ ATOMOWYCH



MoS₂ on h-BN

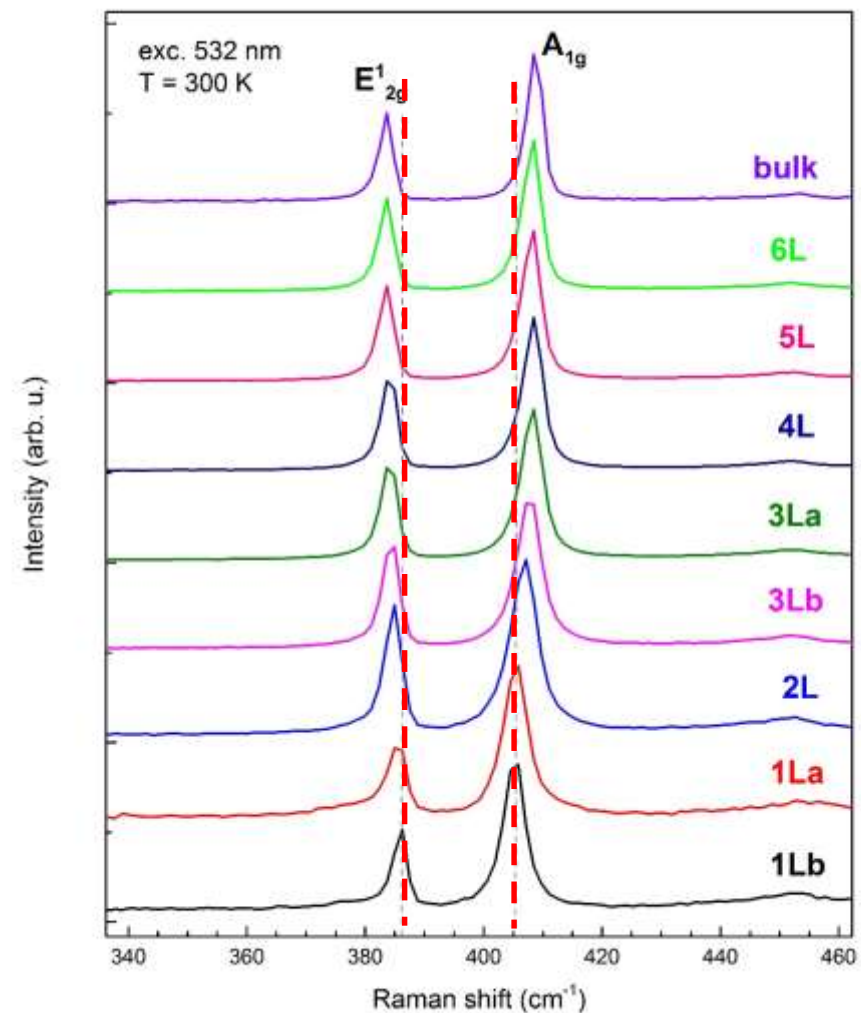
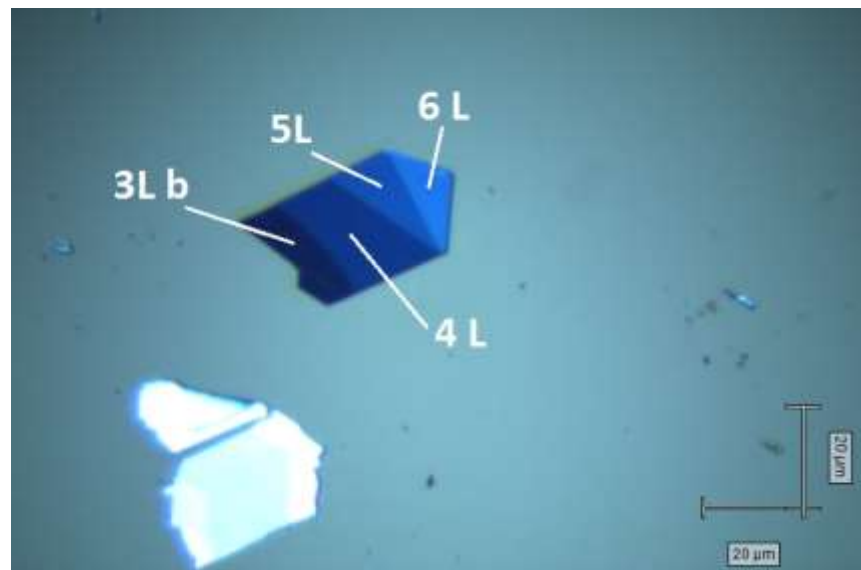
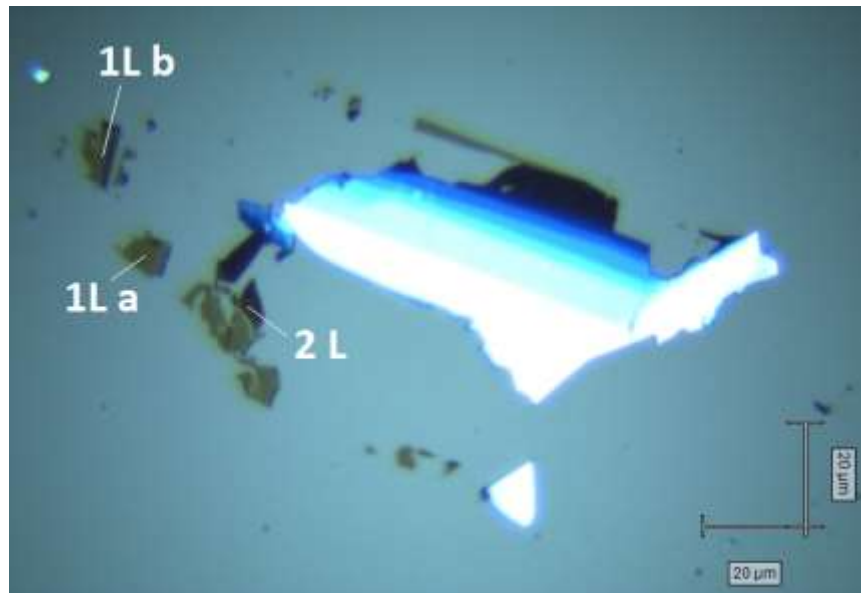
K. Nogajewski (2018)
Wydział Fizyki, NHMF Grenoble

From graphite to graphene



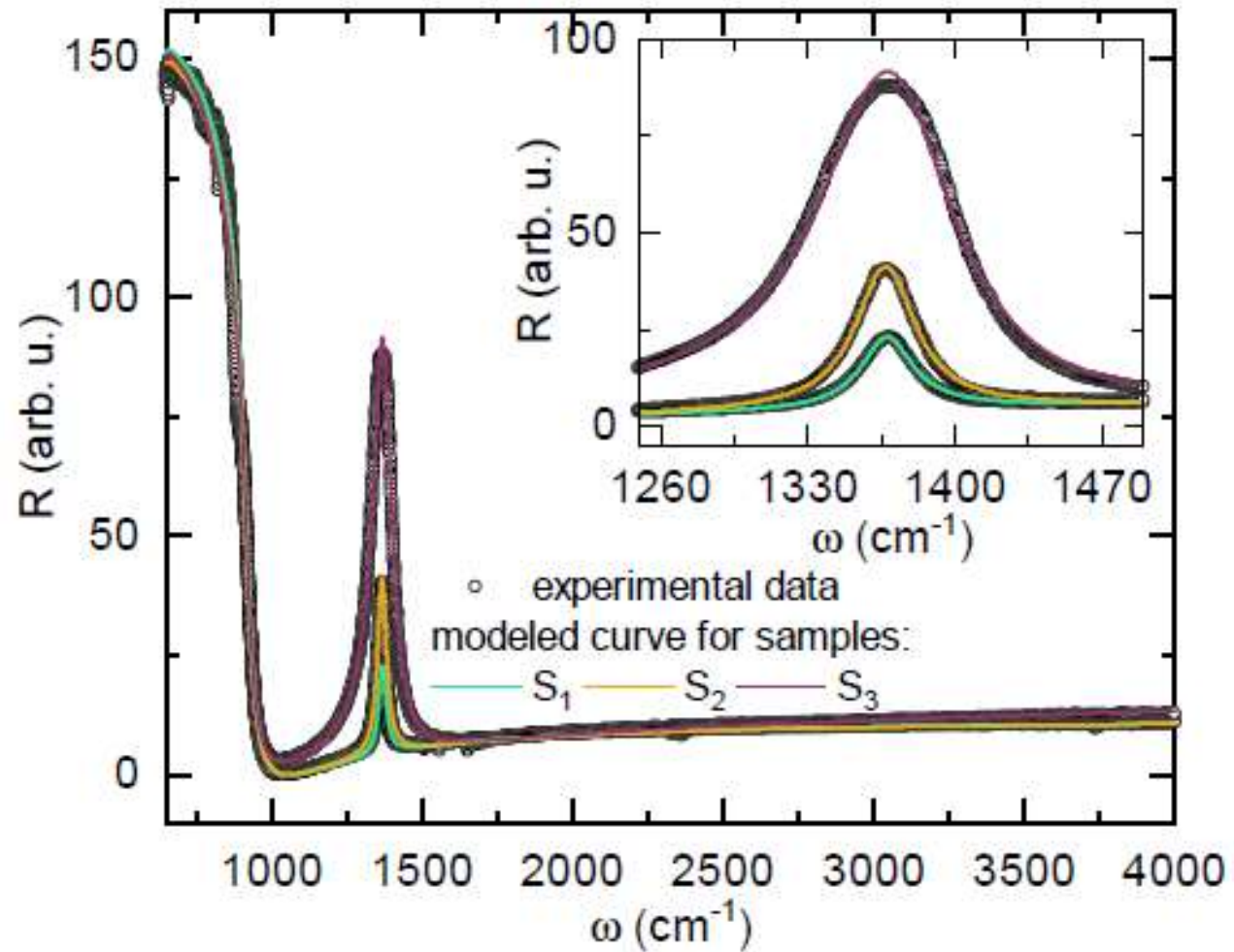
A.C. Ferrari et al. Phys. Rev. Lett. 97, 187401 (2006)

Number of layers – example: MoS_2



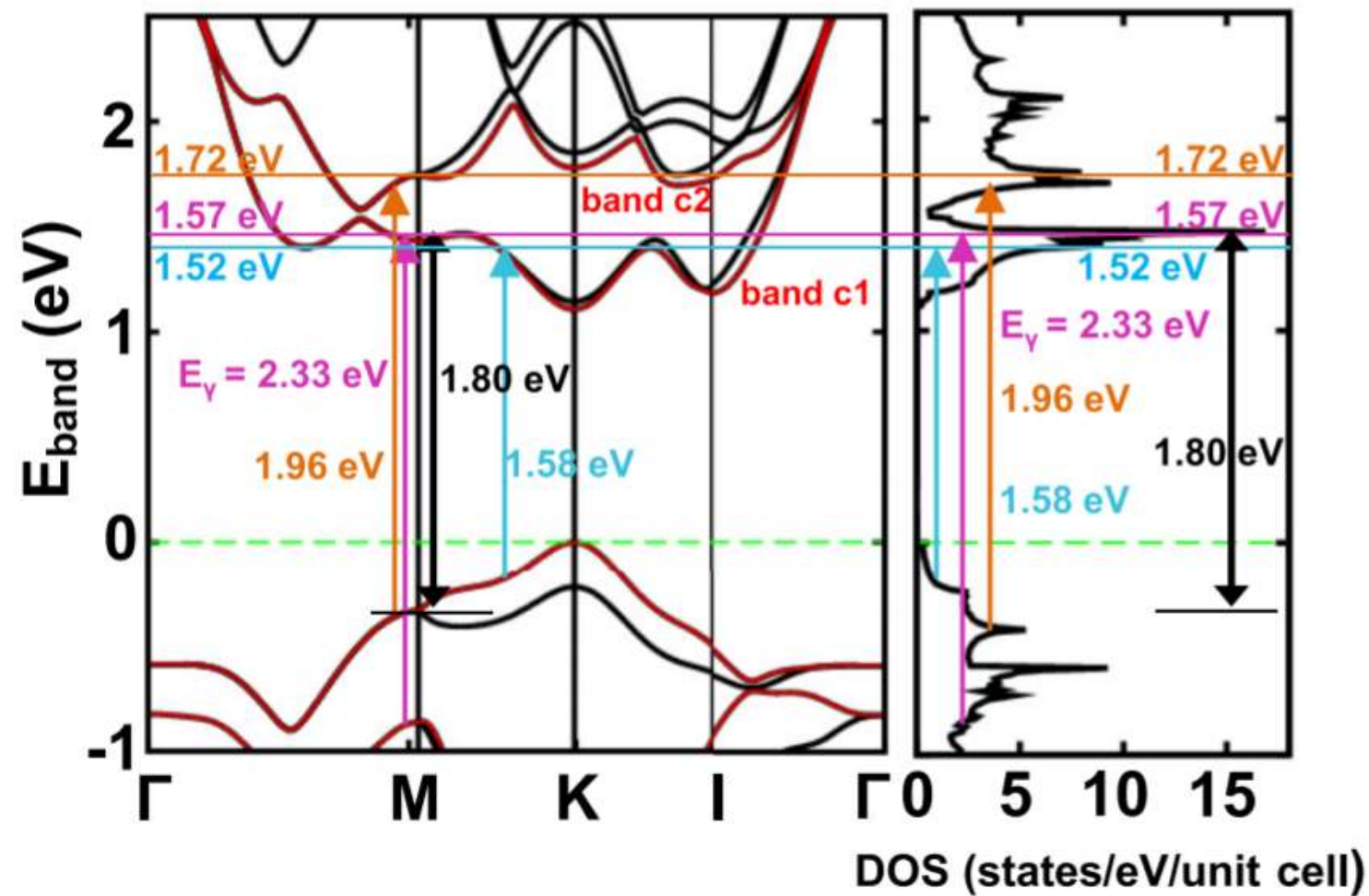
Ewa Łacińska (2017)
Wydział Fizyki UW

FTIR of BN layers



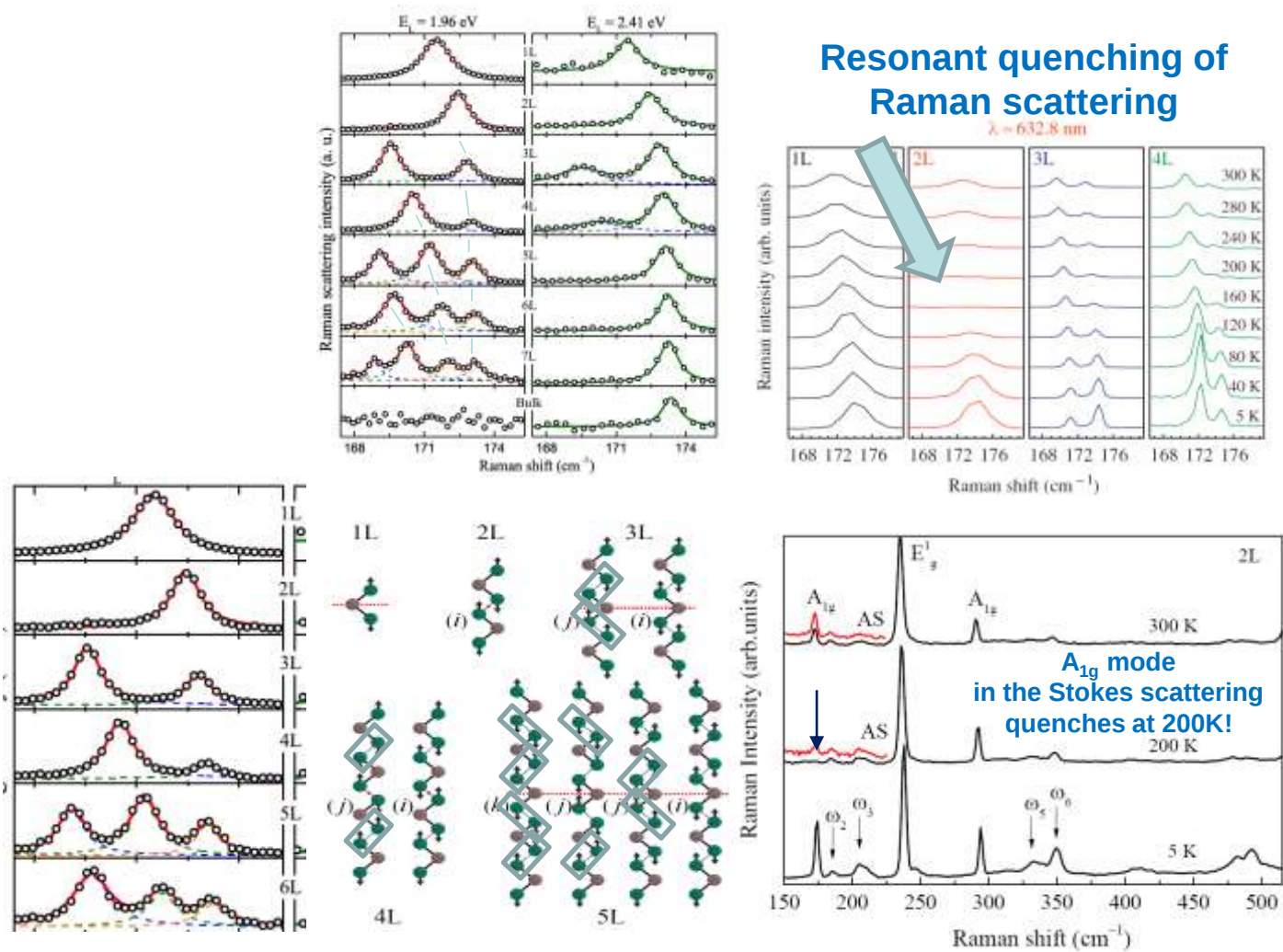
J. Iwanski et al (2022)

Raman Scattering of TMDC (examples)



Raman Scattering of TMDC (examples)

A_{1g}/A'_{1g} modes
in MoTe_2
Davydov splitting

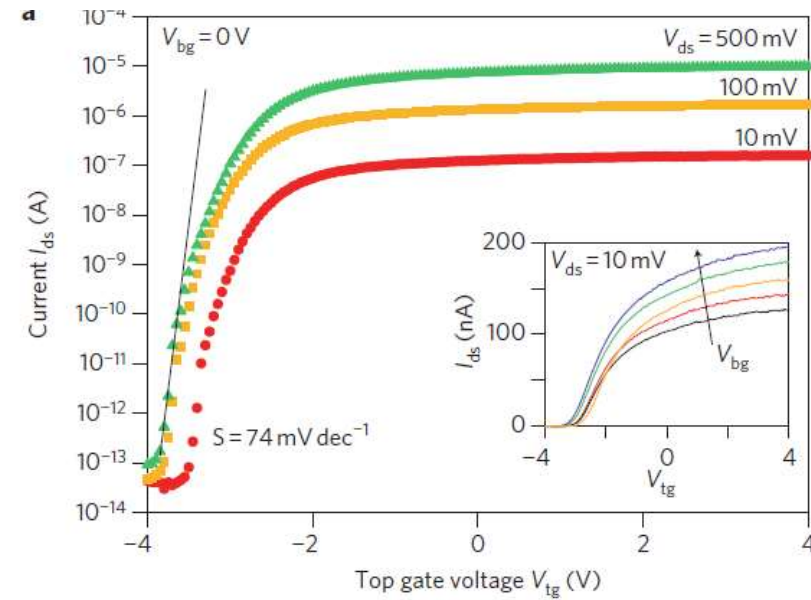
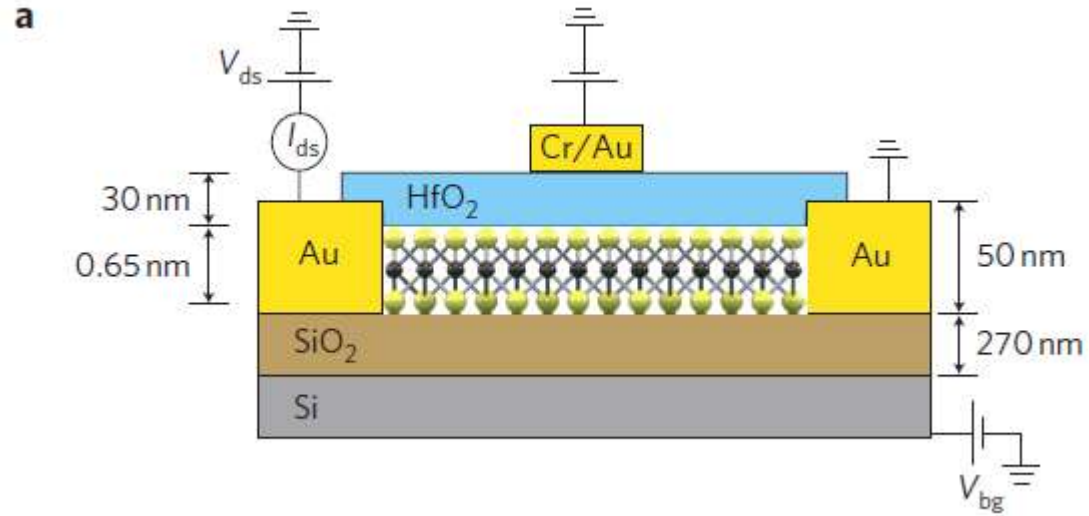
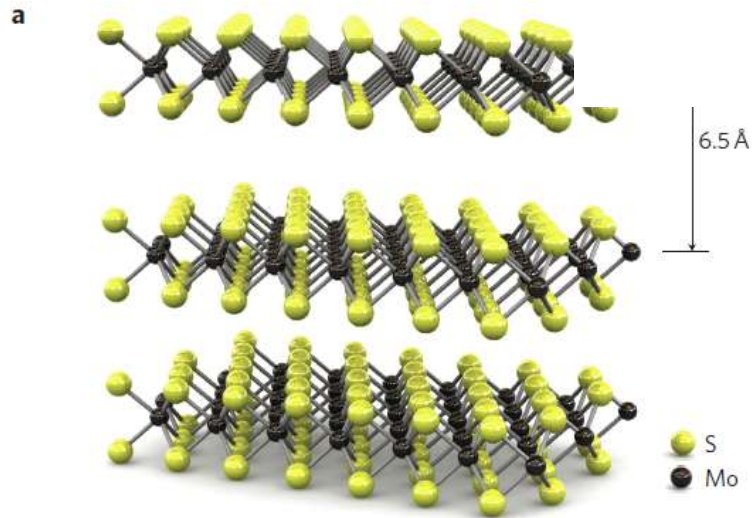


M.Grzeszczyk et al., *2D Materials* **3** 025010 (2016)

K. Gołasa et al, *Nanophotonics* **6**, 1281 (2017)

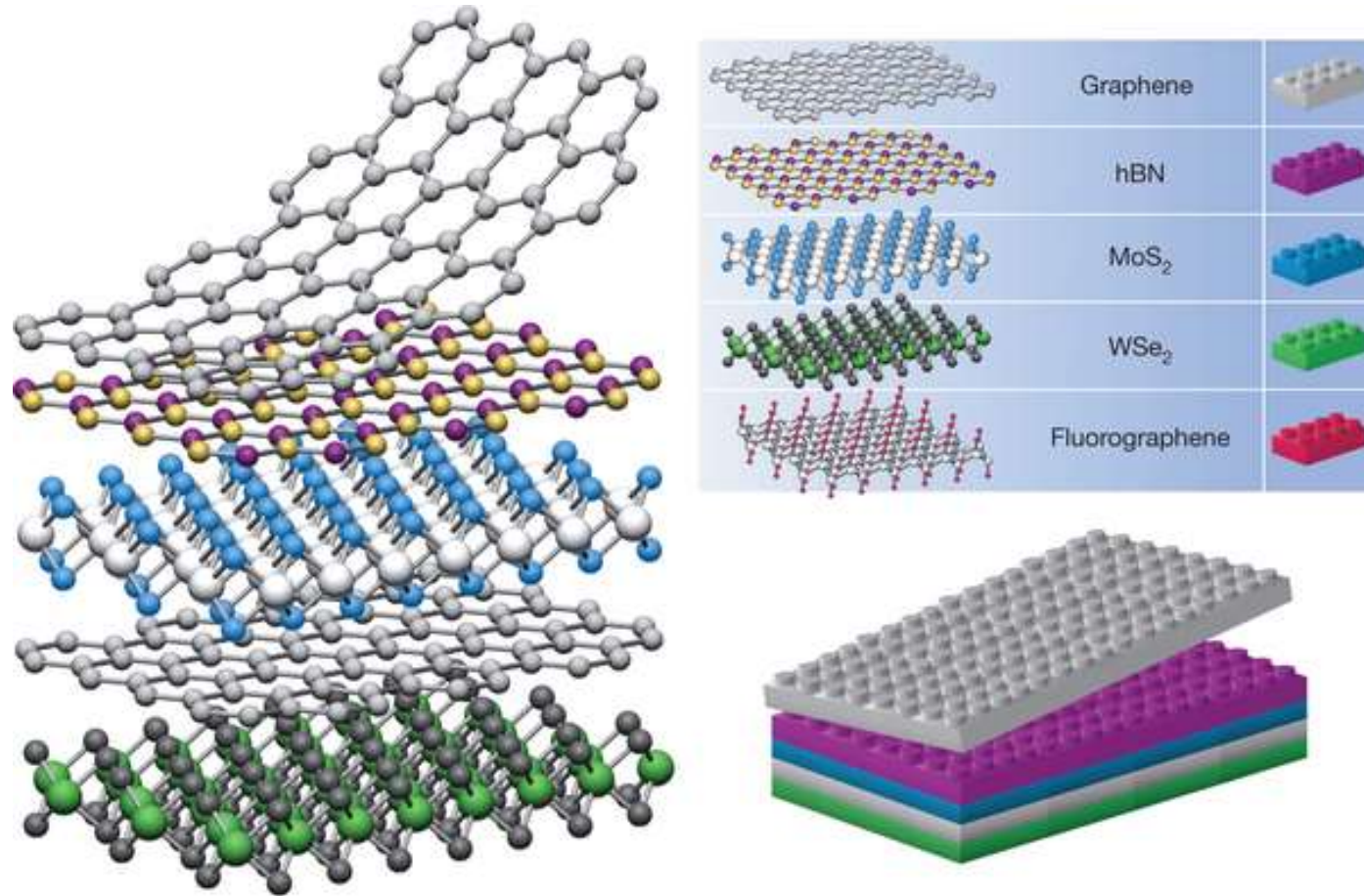
MoS₂ – silicon competitor?

Scotch tape method works!



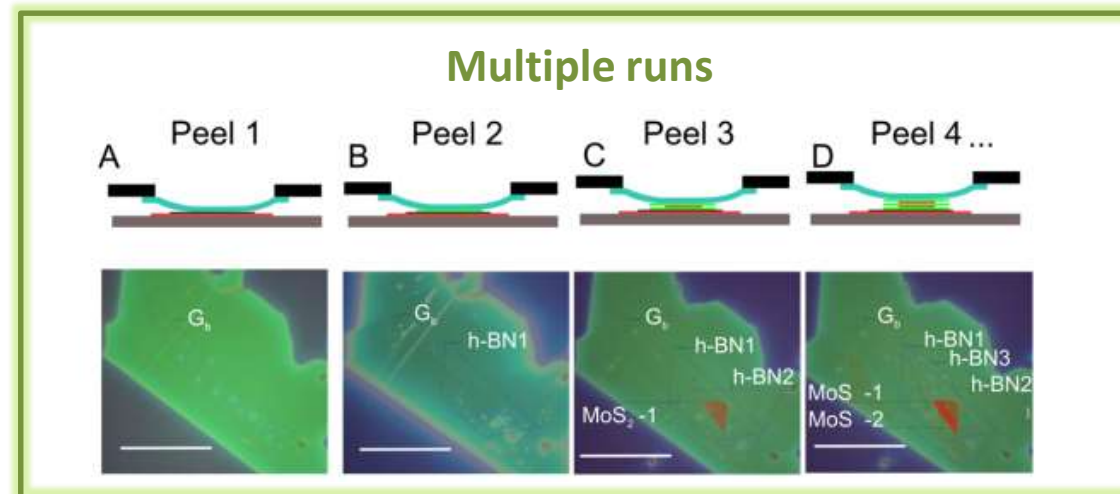
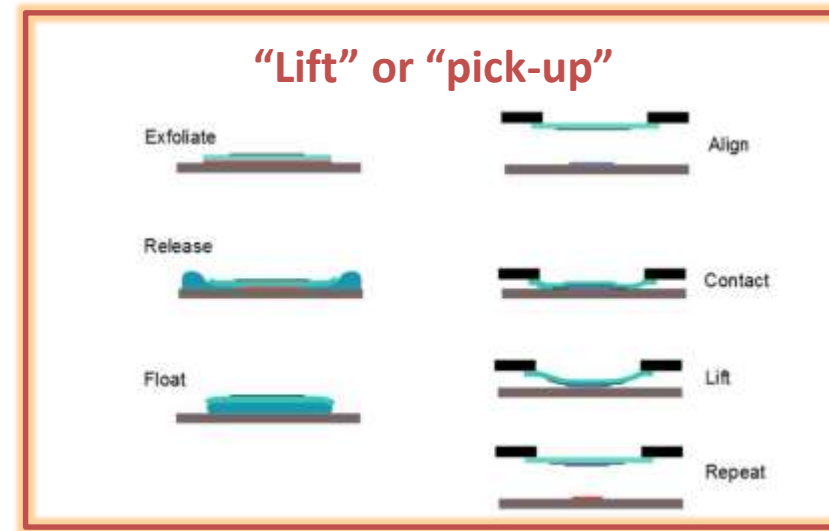
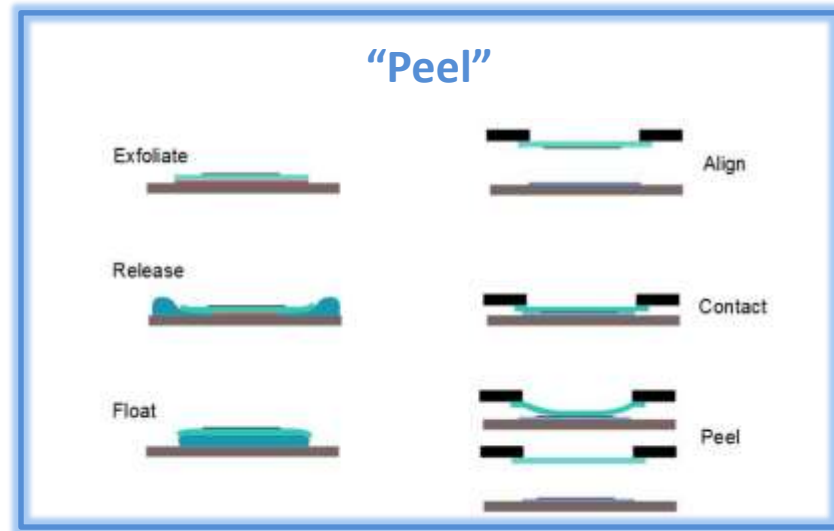
B. Radisavljevic et al., Nature nanotechnology (2011)

Nano-LEGO system

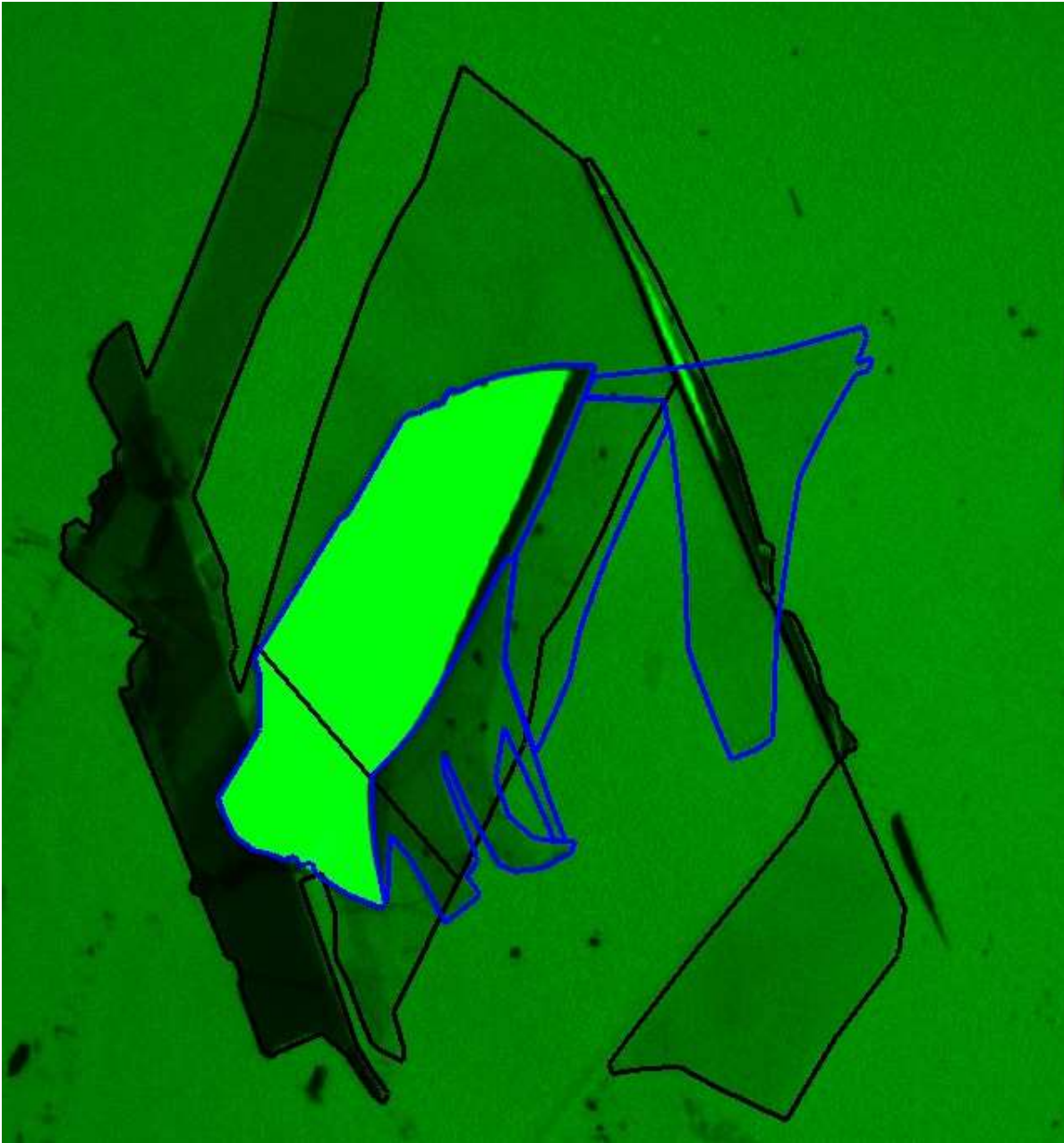


A. K. Geim & I. V. Grigorieva, Nature 499, 419 (2013)

Fabrication

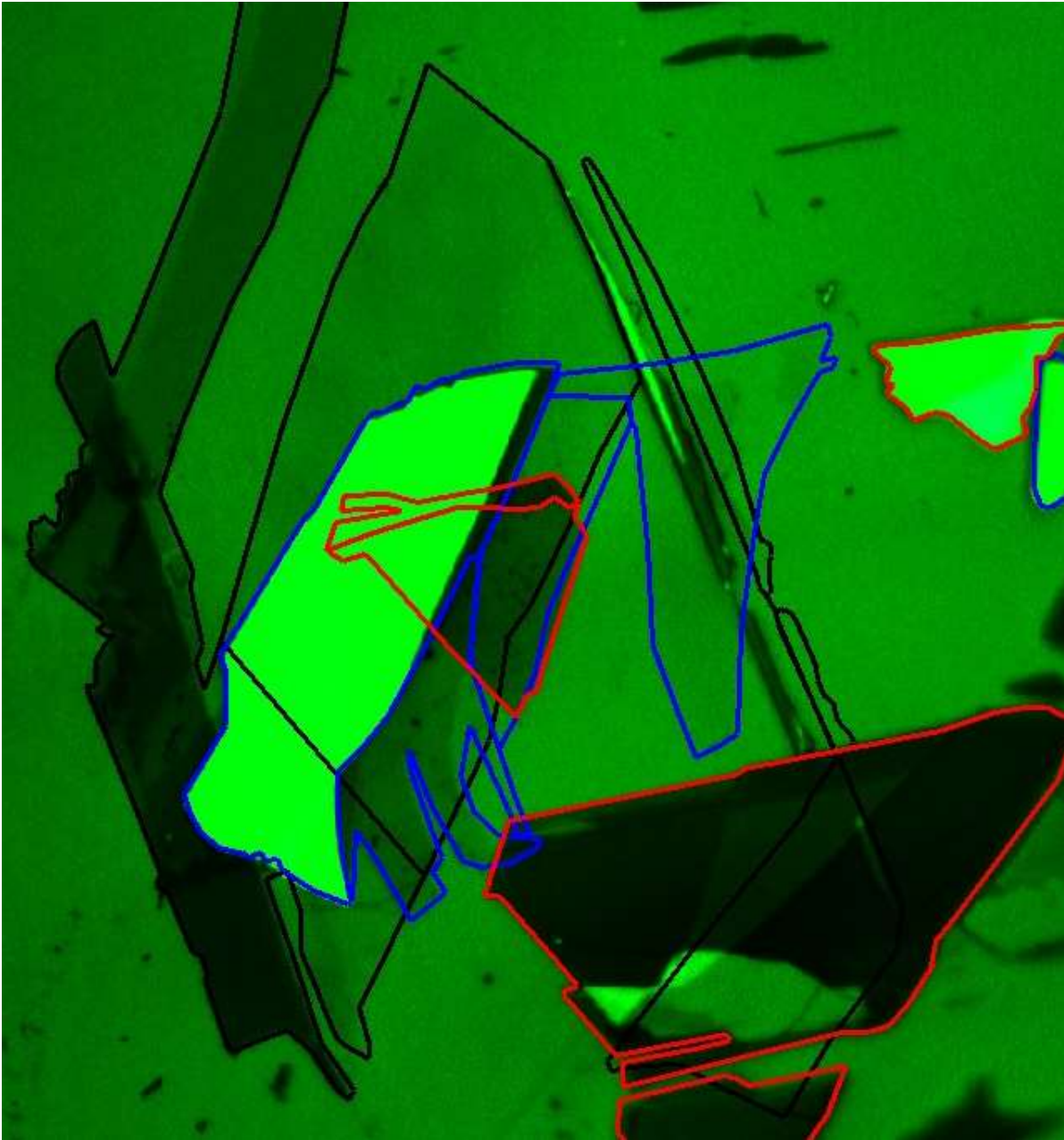


Transfer



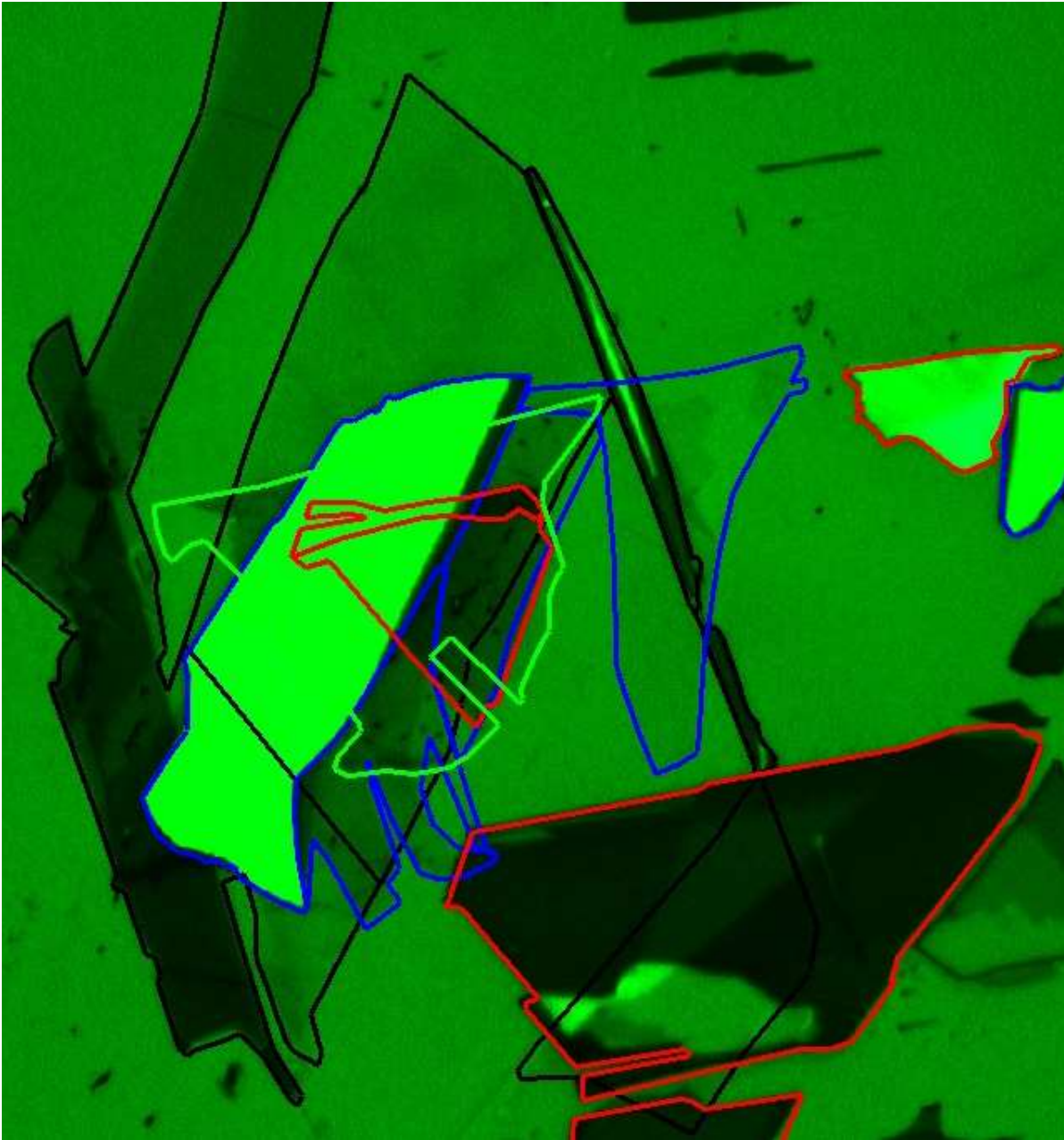
— Gr
— BN

Transfer



- Gr
- BN
- MoS₂

Transfer



- Gr
- BN
- MoS₂
- BN

Transfer



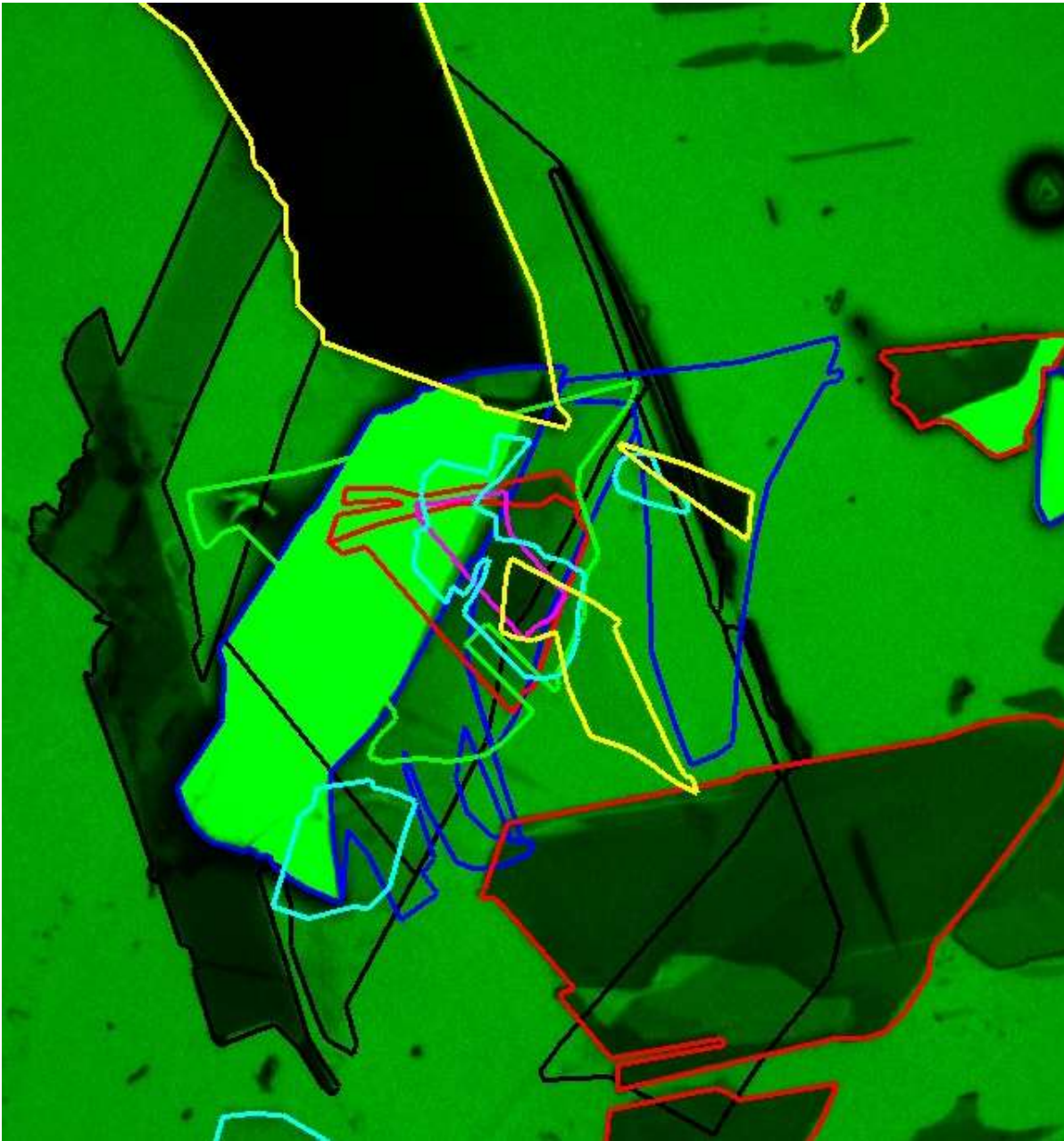
- Gr
- BN
- MoS₂
- BN
- WSe₂

Transfer



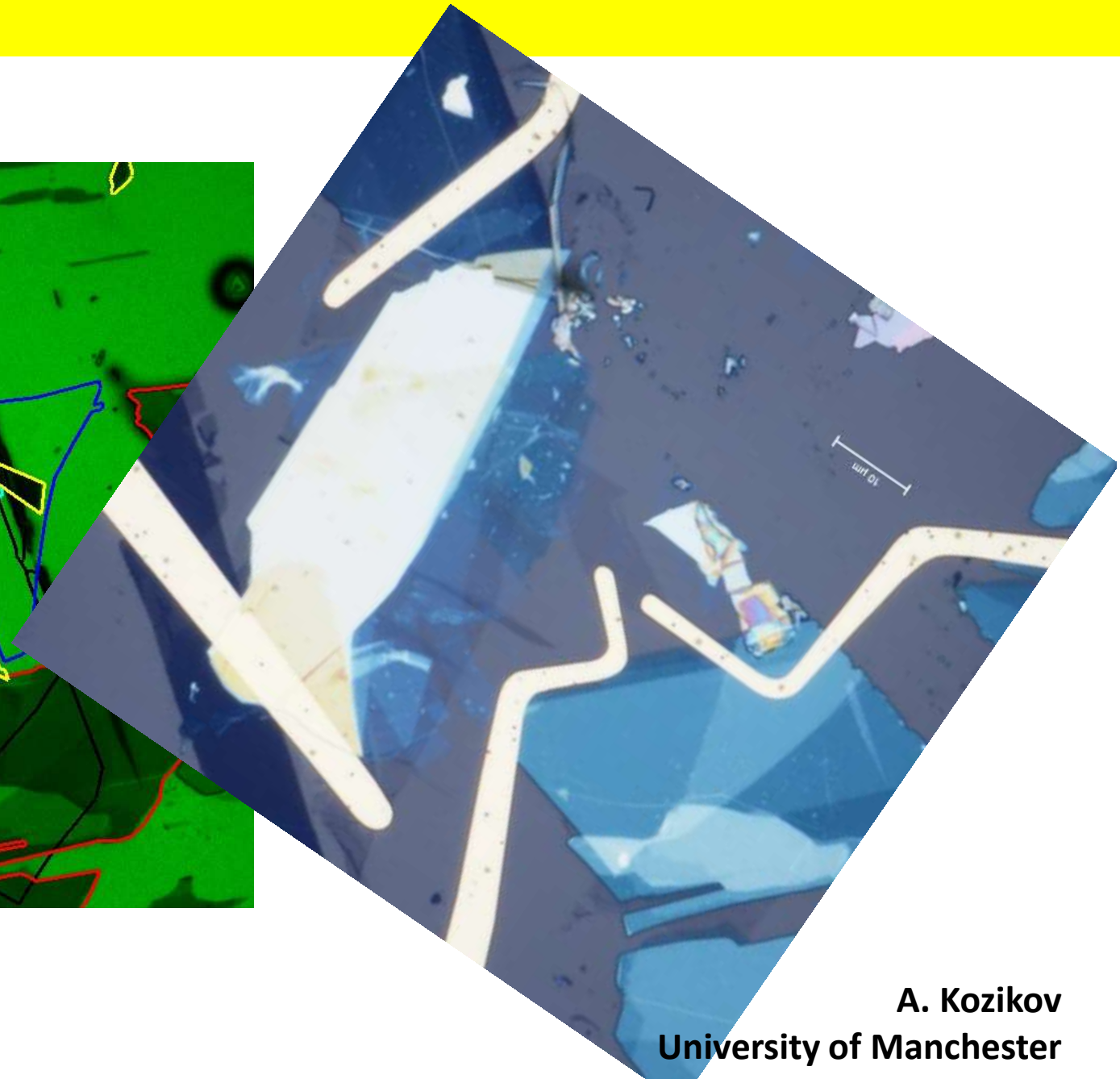
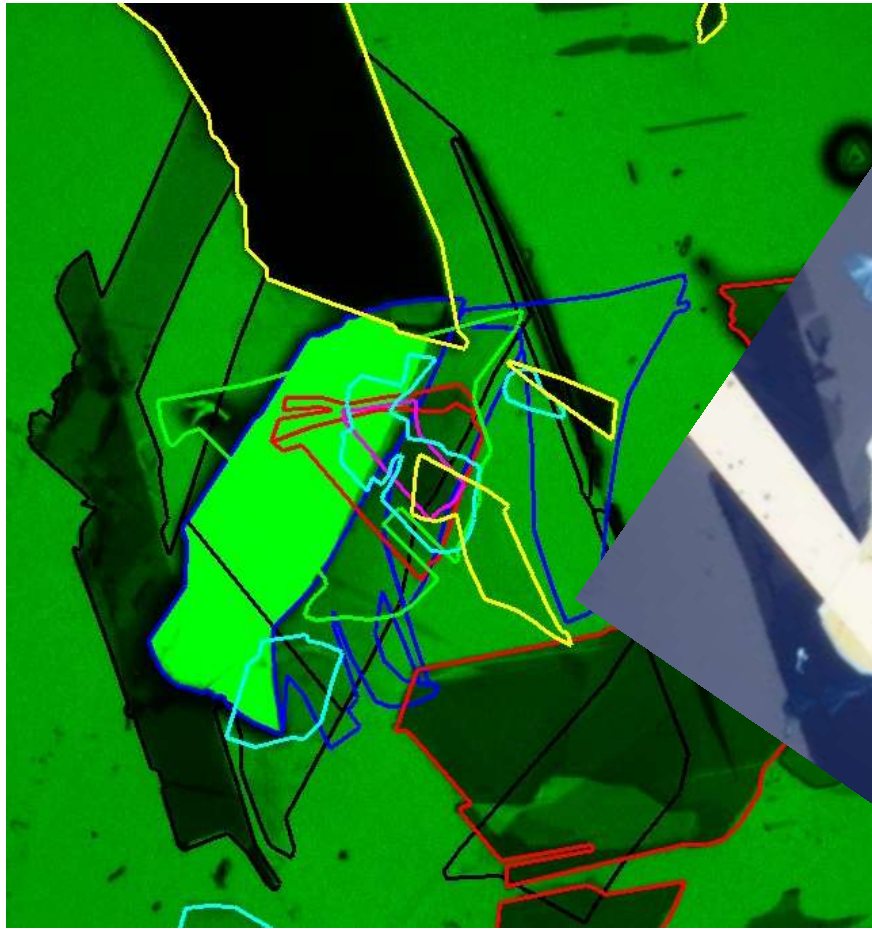
- Gr
- BN
- MoS₂
- BN
- WSe₂
- BN

Transfer



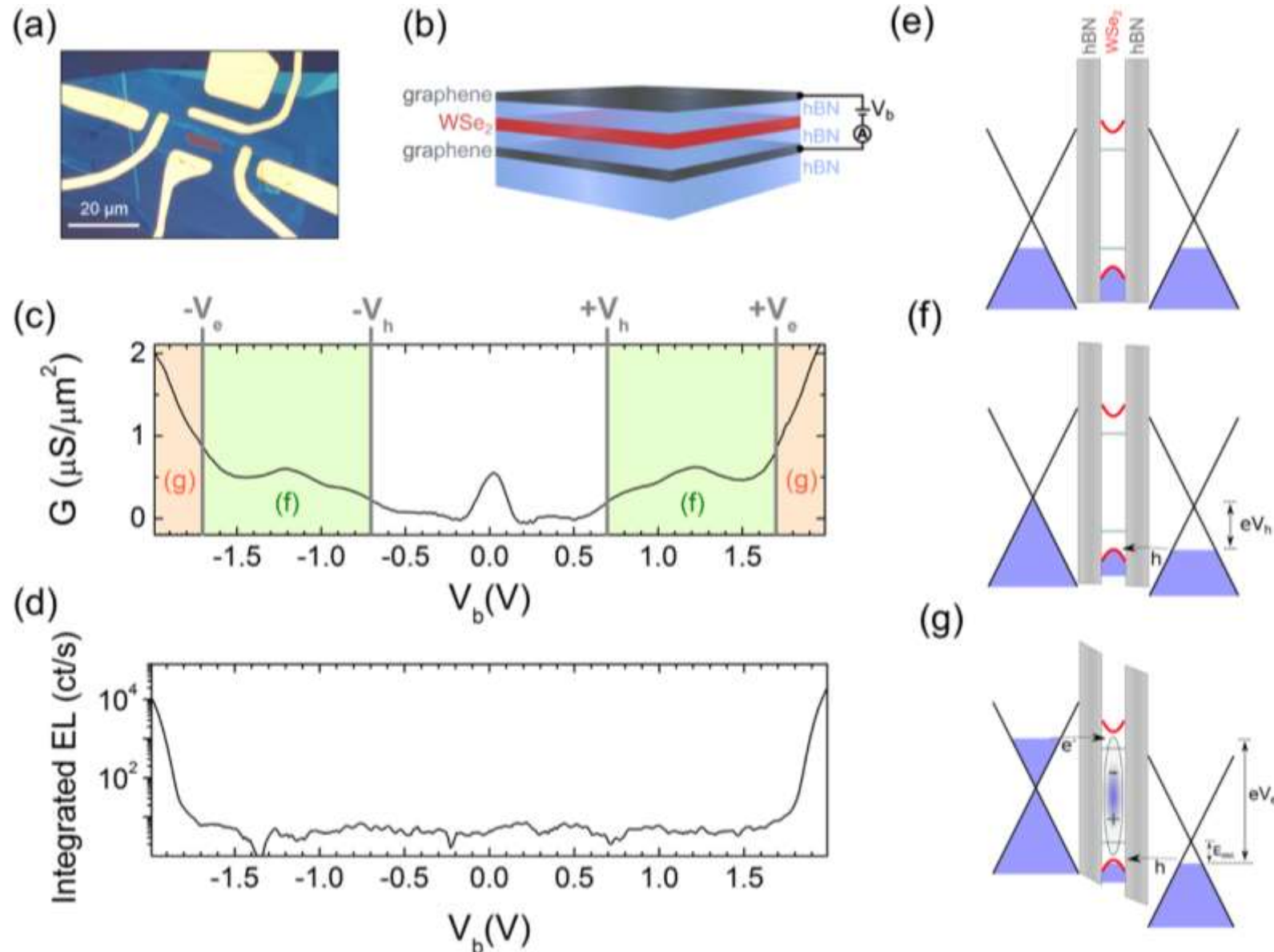
- Gr
- BN
- MoS₂
- BN
- WSe₂
- BN
- Gr

Transfer

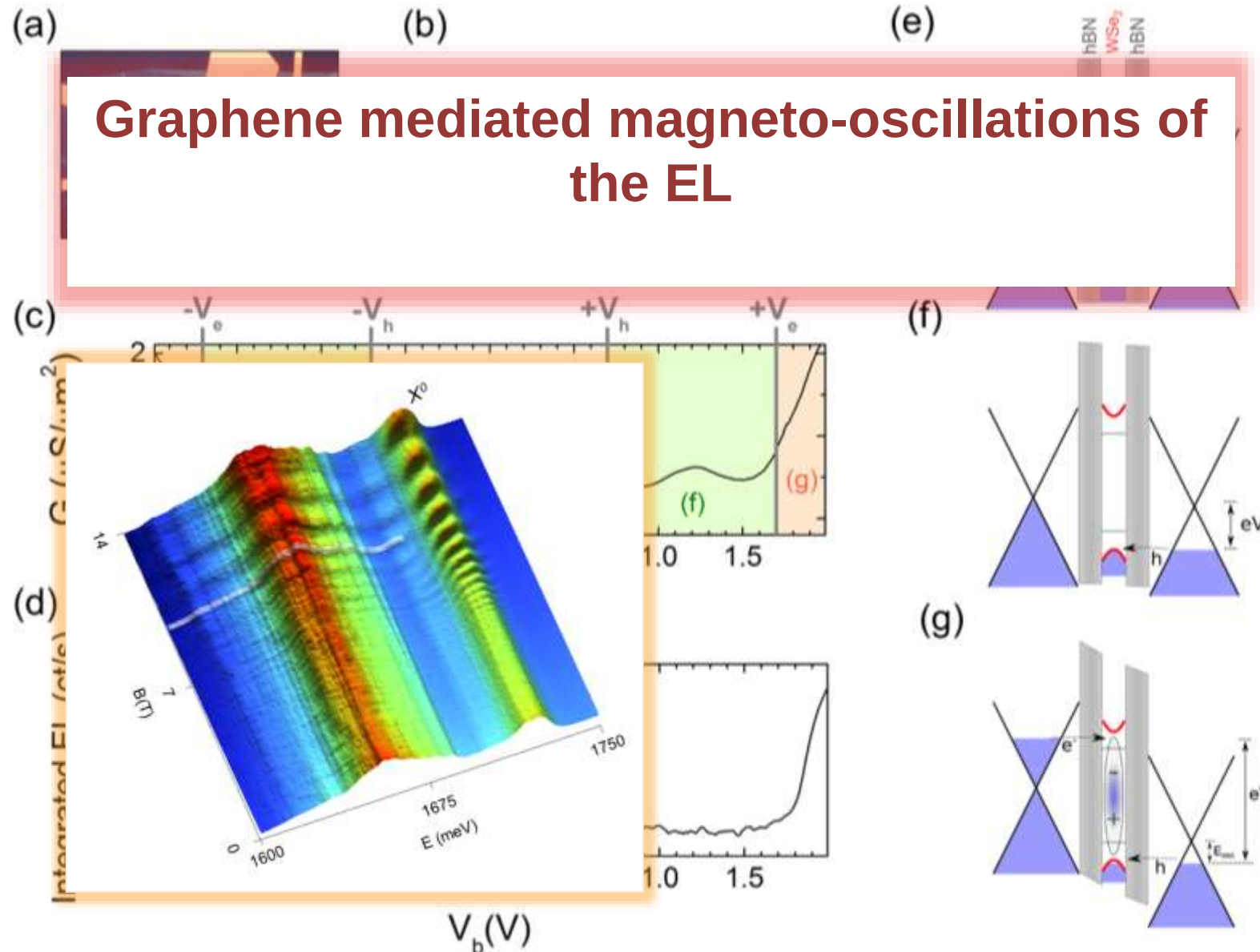


A. Kozikov
University of Manchester

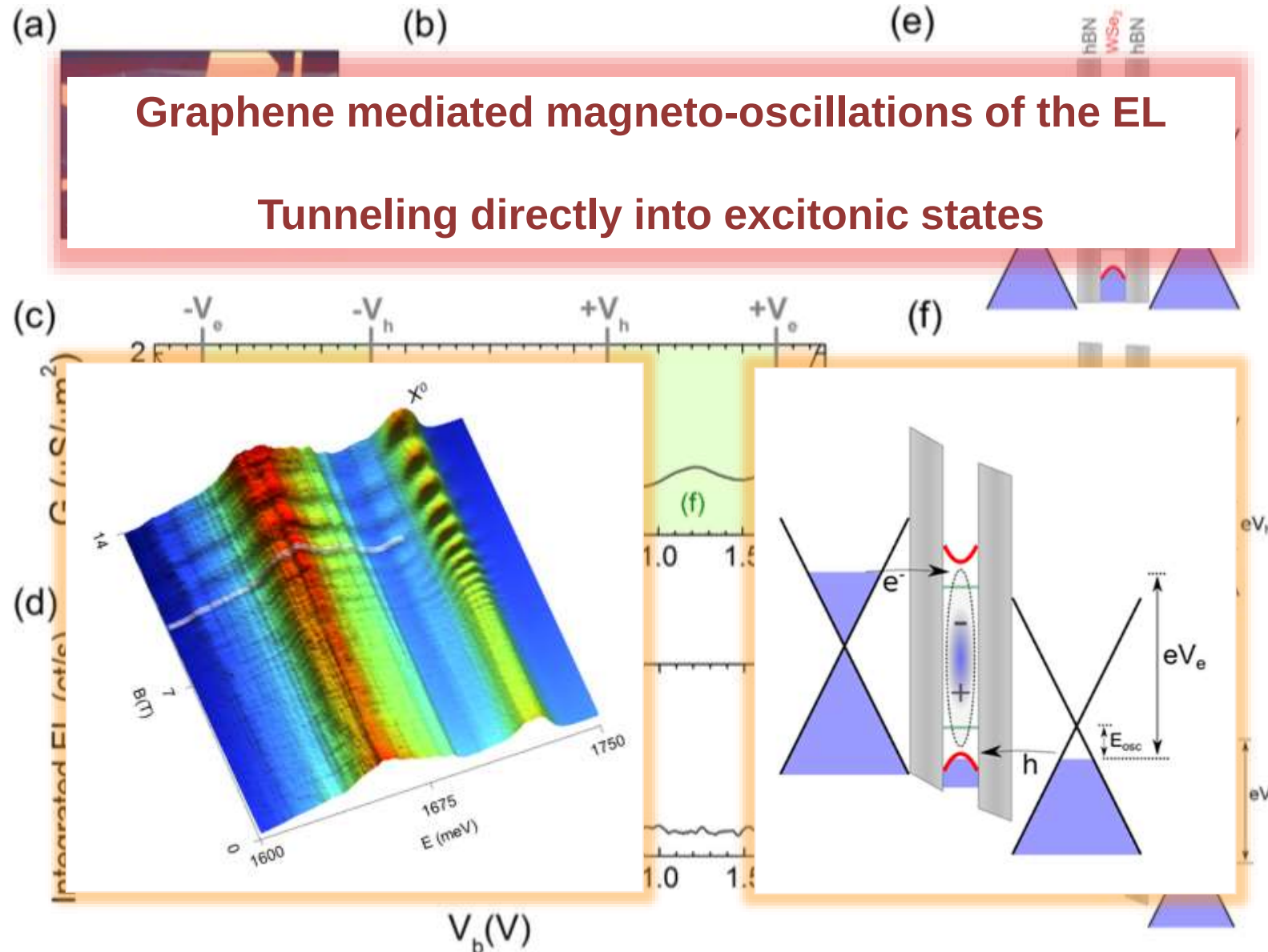
Structures with a single TMDC



Structures with a single TMDC



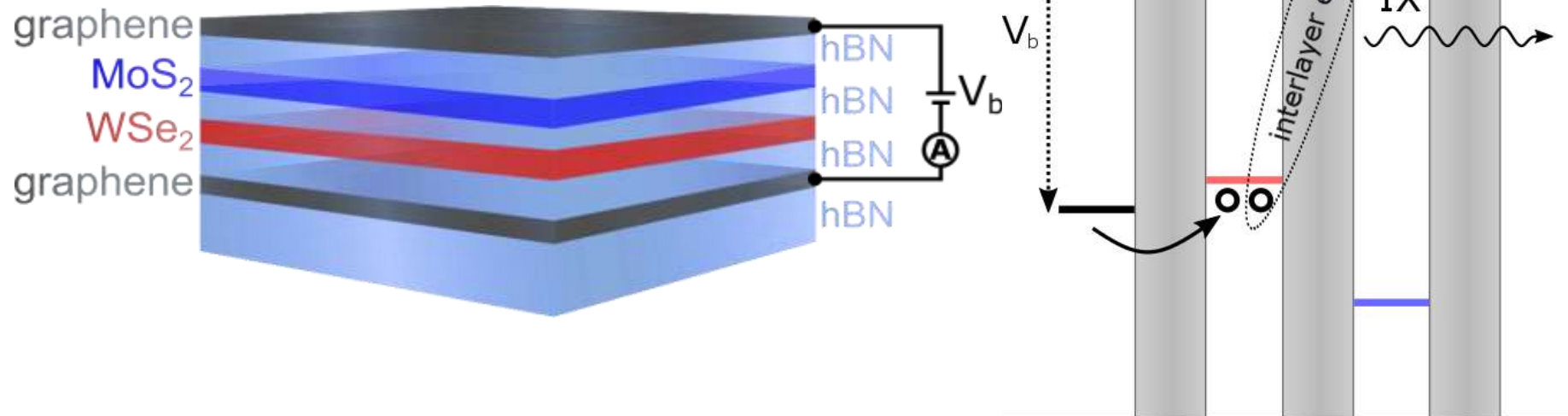
Structures with a single TMDC



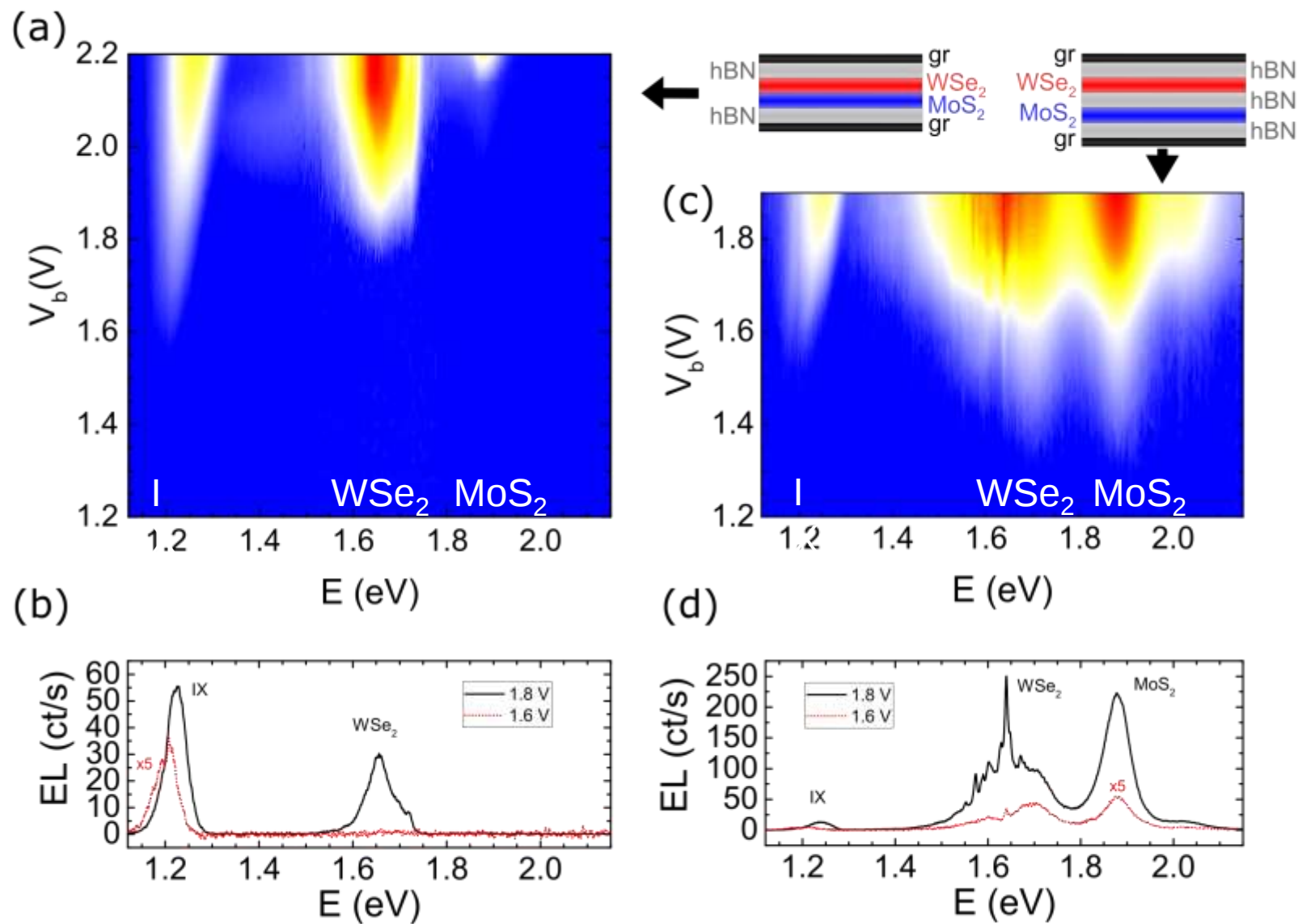
Two TMDCs in a vdW heterostructure

Increase in complexity:

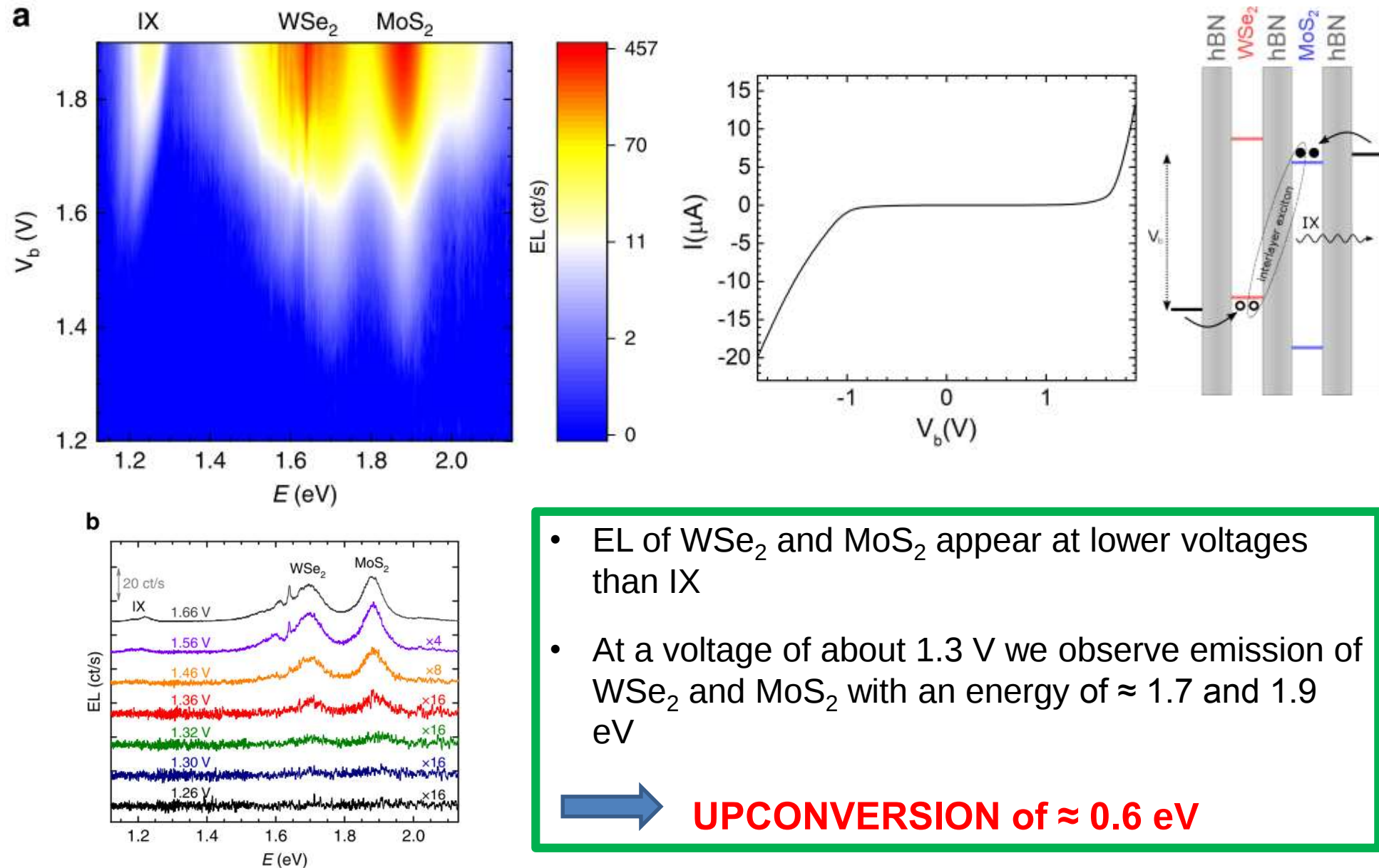
- Adding a 2nd TMDC monolayer
- Indirect (interlayer) excitons!



Electroluminescence

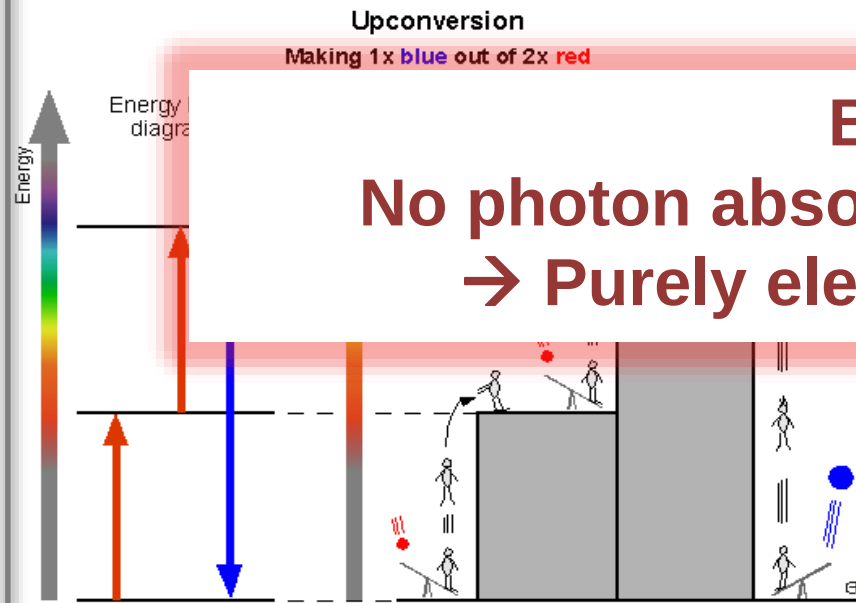


Electroluminescence



Upconversion (optical excitation)

Photon upconversion (e.g. ions)



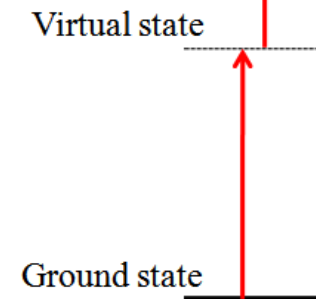
https://guedel.dcb.unibe.ch/research/hug_upc.htm

m

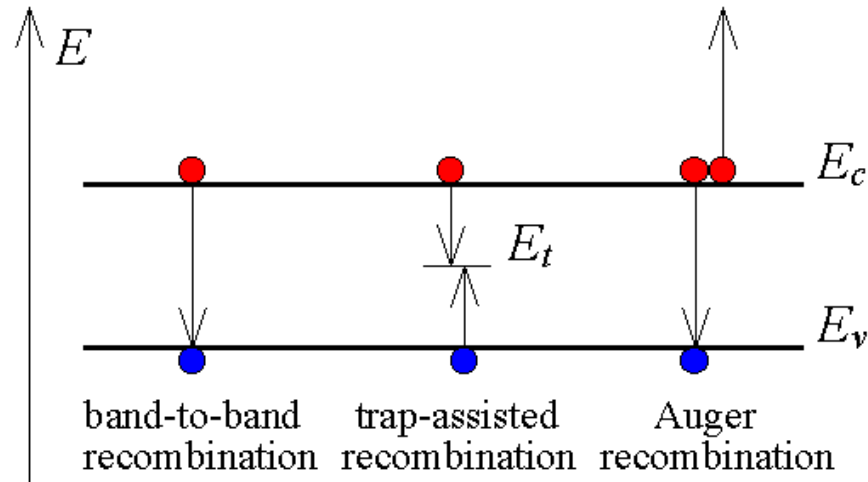
Nonlinear optical processes (second harmonic generation, two photon absorption)

BUT:

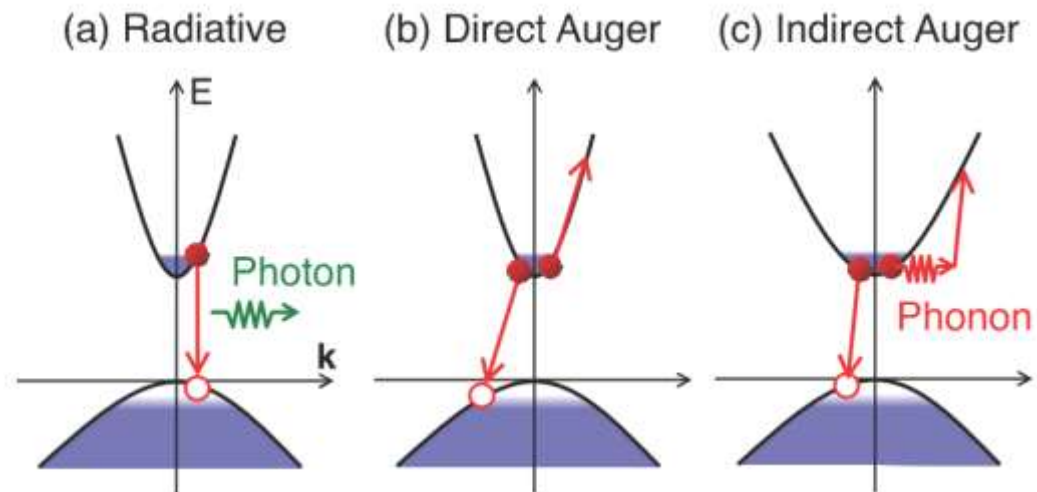
**No photon absorption in our case!
→ Purely electrical injection**



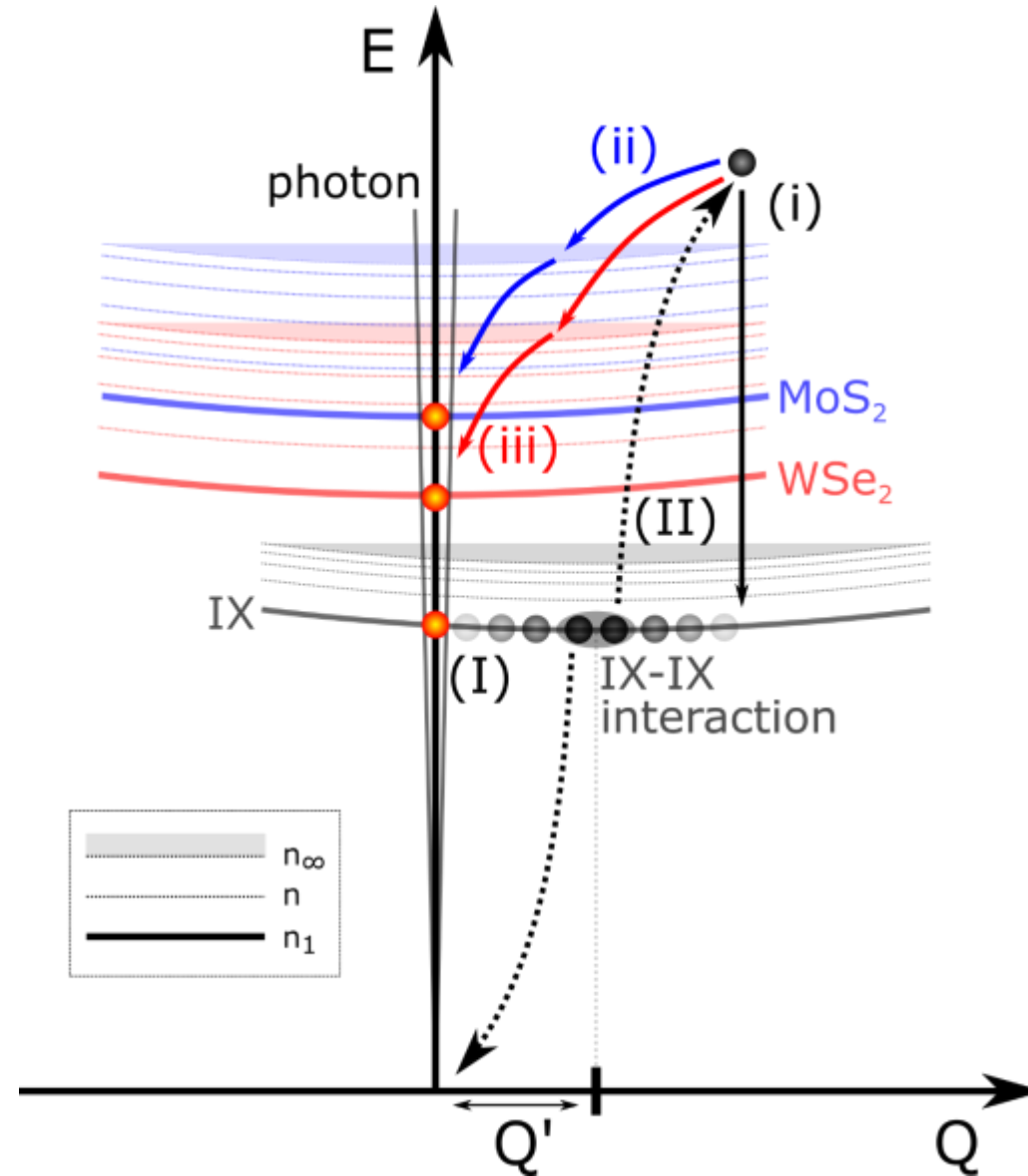
Auger effect



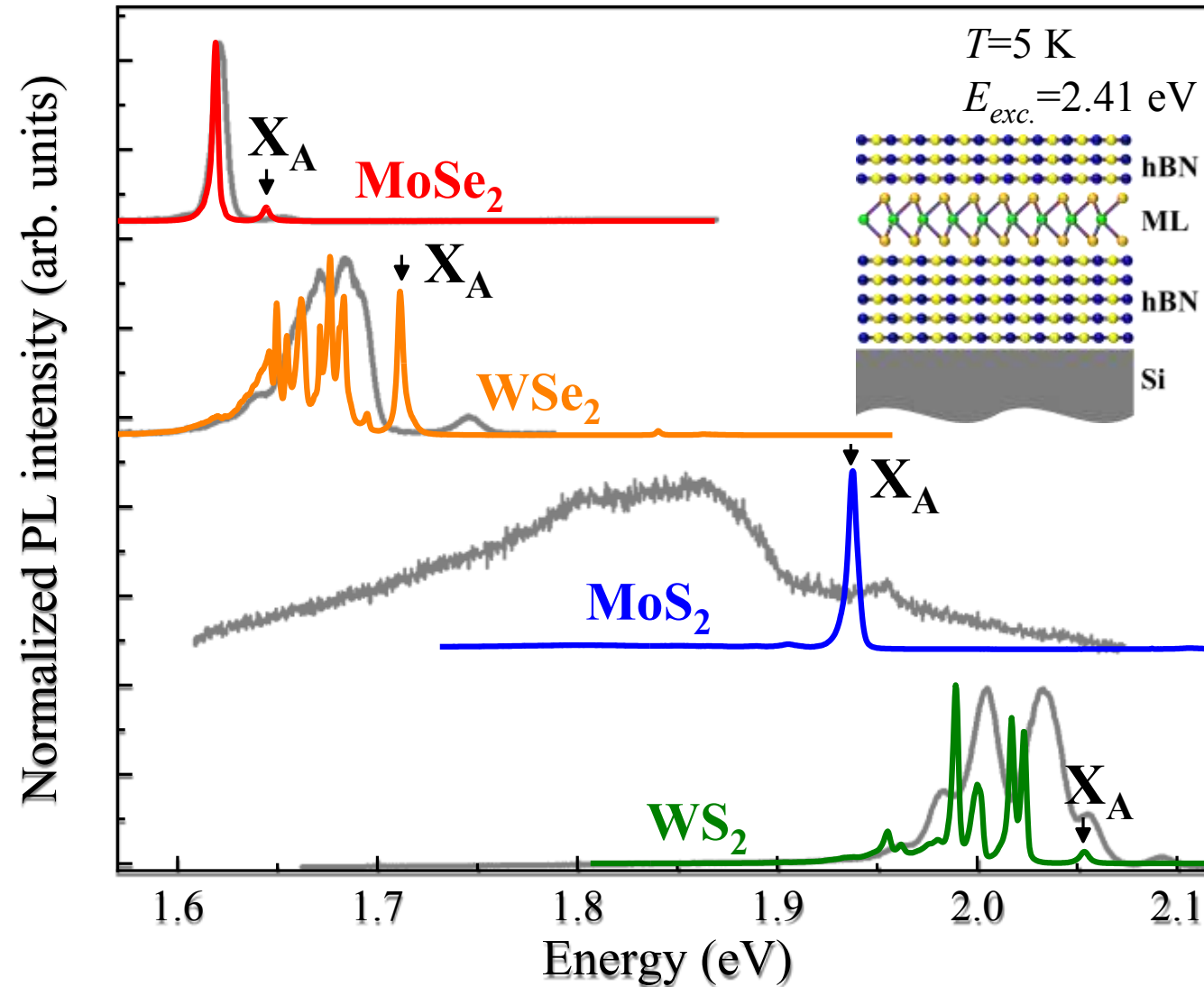
https://ecee.colorado.edu/~bart/book/book/chapter2/ch2_8.htm



Excitonic Auger Upconversion?

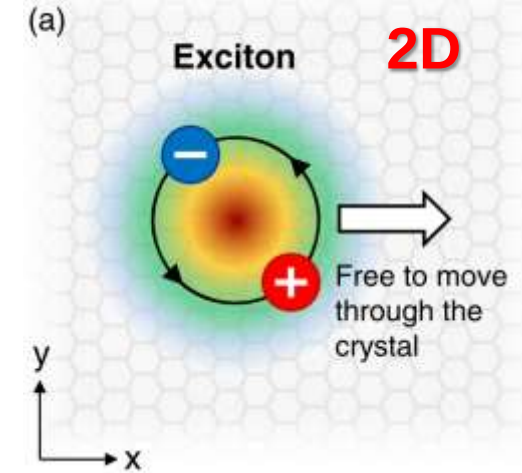
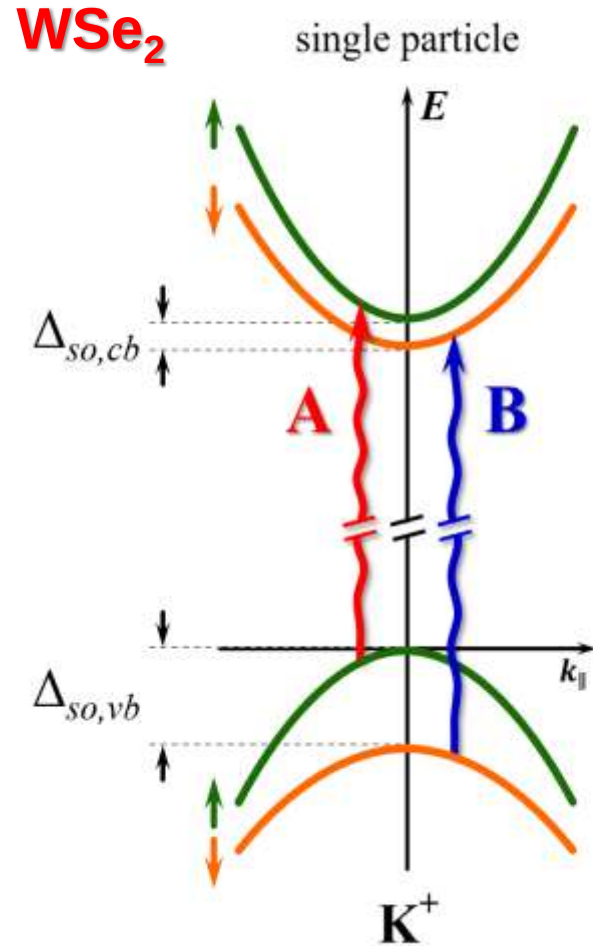


h-BN protective layers



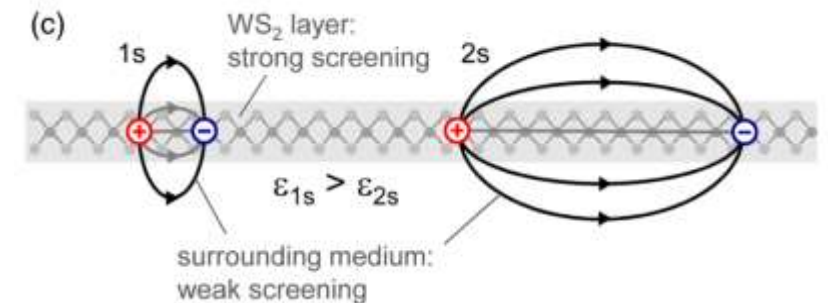
M. R. Molas et al..PRL 123, 136801 (2019).

Excitonic ladder in S-TMD monolayers



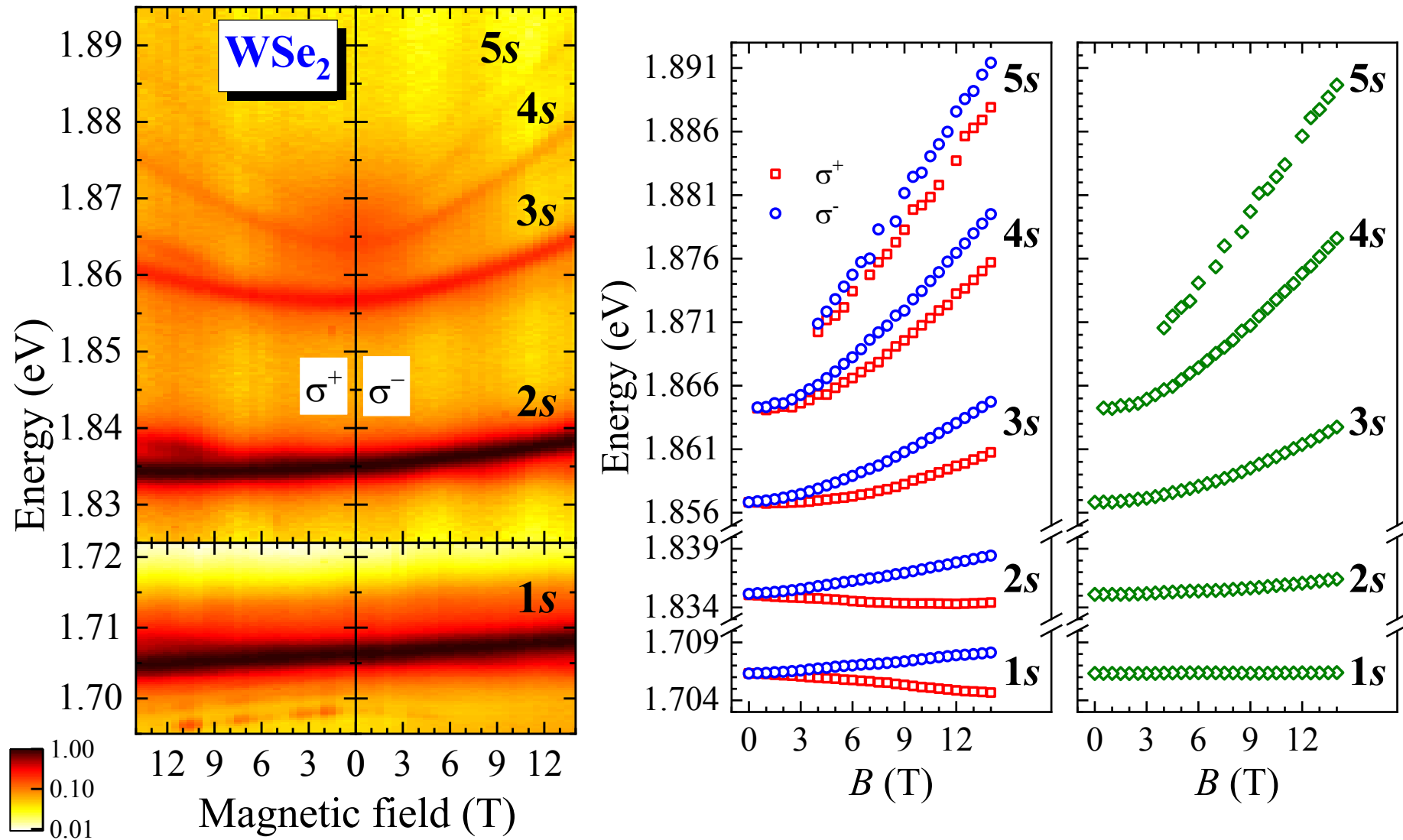
G. Wang et al., *Rev. Mod. Phys.* 90, 021001 (2018)

~~$$E_n = E_g + \frac{R^*}{(n - 1/2)^2}$$~~



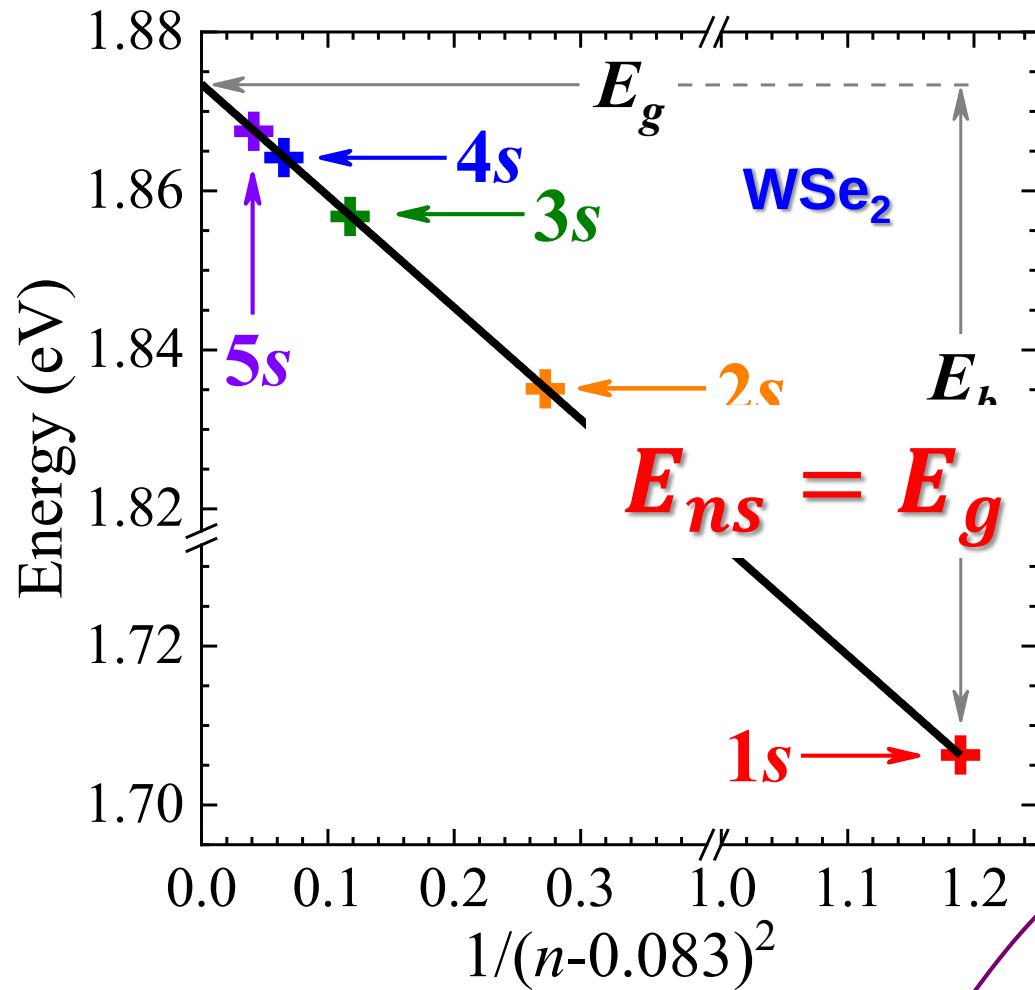
A. Chernikov et al., *Phys. Rev. Lett.* 113, 076802 (2014)

Example - energy spectrum of two-dimensional excitons WSe_2



M. R. Molas et al., Phys. Rev. Lett. 123, 136801 (2019)

Energy spectrum of two-dimensional excitons in a nonuniform dielectric medium



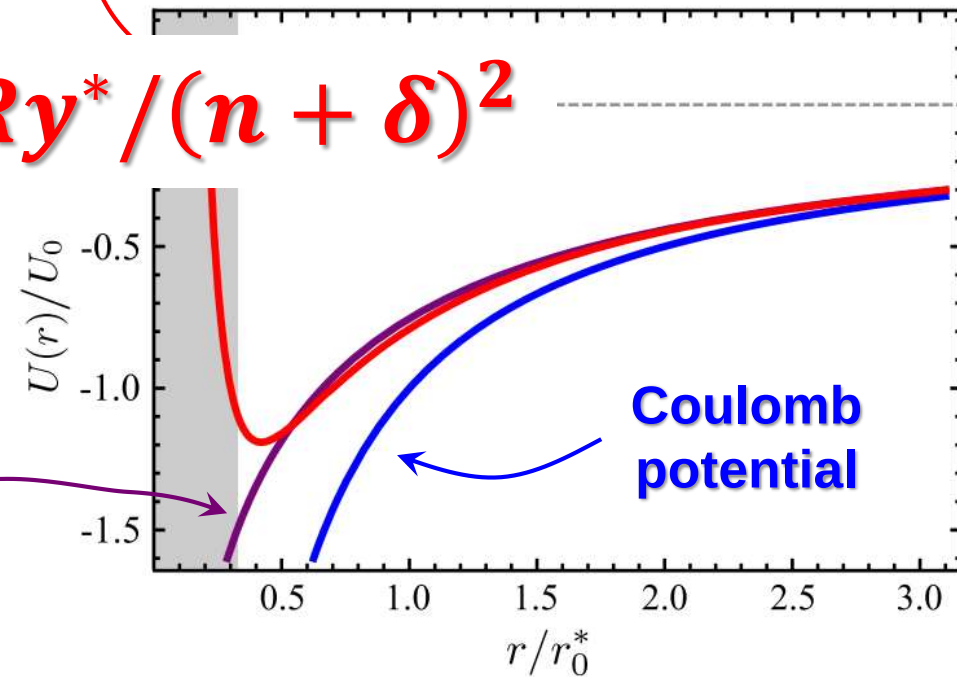
$$E_{ns} = E_g - Ry^* / (n + \delta)^2$$

Keldysh potential
solvable numerically ☹

Kratzer potential

$$U_{\text{ext}}(r) = -\frac{e^2}{r_0} \left(\frac{r_0^*}{r} - \frac{g^2 r_0^{*2}}{r^2} \right)$$

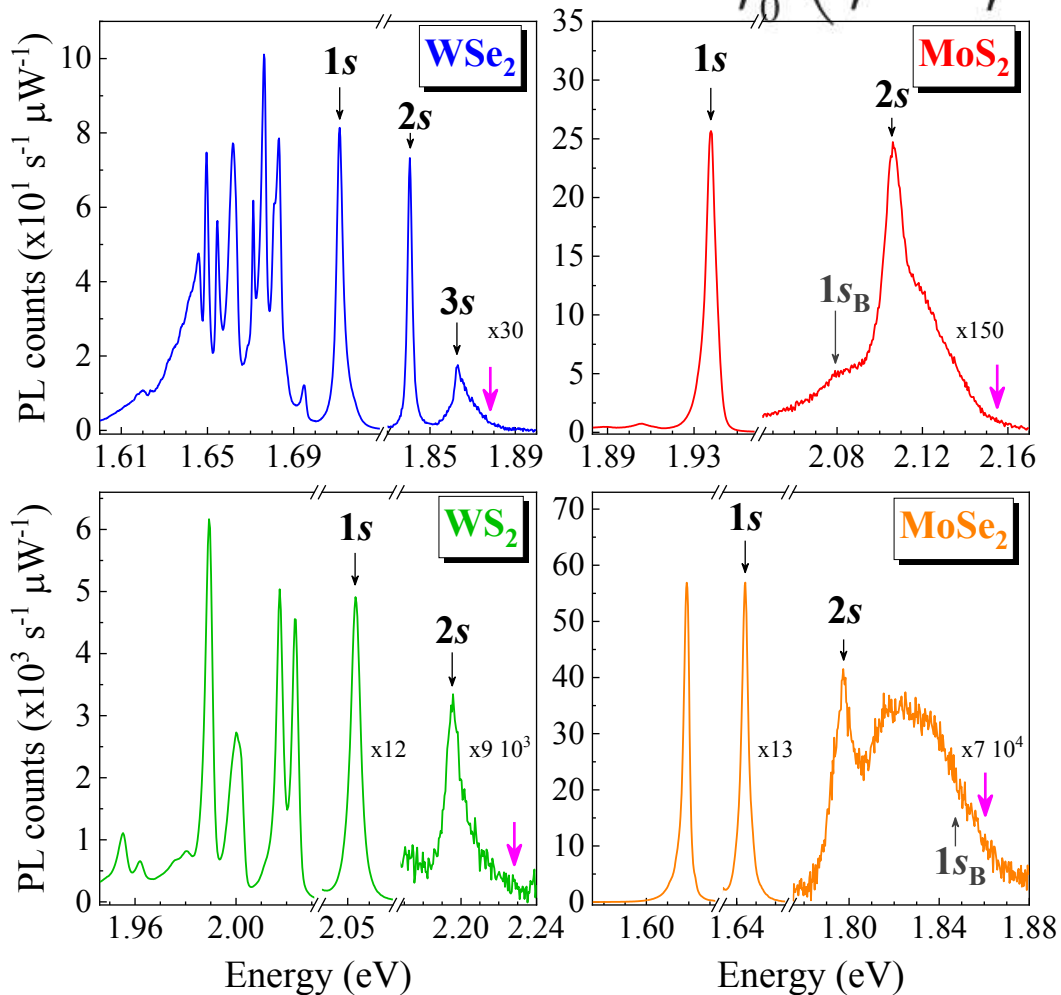
solvable analytically ☺



Energy spectrum of two-dimensional excitons in a nonuniform dielectric medium

Kratzer potential $U_{\text{ext}}(r) = -\frac{e^2}{r_0} \left(\frac{r_0^*}{r} - \frac{g^2 r_0^{*2}}{r^2} \right)$

$E_{ns} = E_g - Ry^*/(n + \delta)^2$

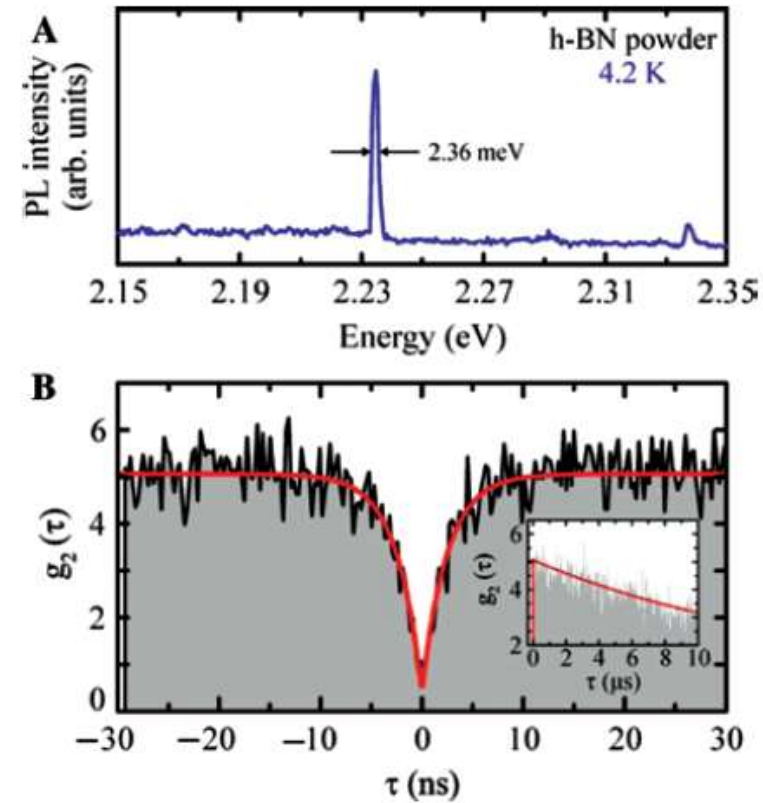
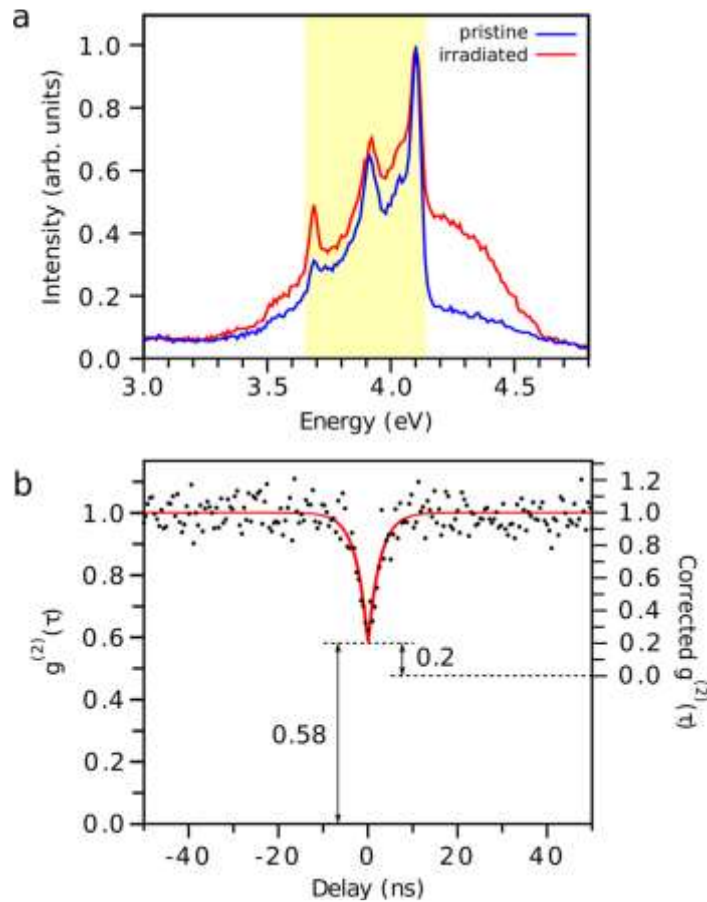


ML	<i>E_b</i> [1]
MoS ₂	217 meV
MoSe ₂	216 meV
WS ₂	174 meV
WSe ₂	167 meV

[1] Kratzer potential
M. R. Molas et al., Phys. Rev. Lett. 123, 136801 (2019)

[2] Keldysh potential
M. Goryca et al., Nature Comm. 10, 4172 (2019)

Point defects in h-BN - single photon emitters

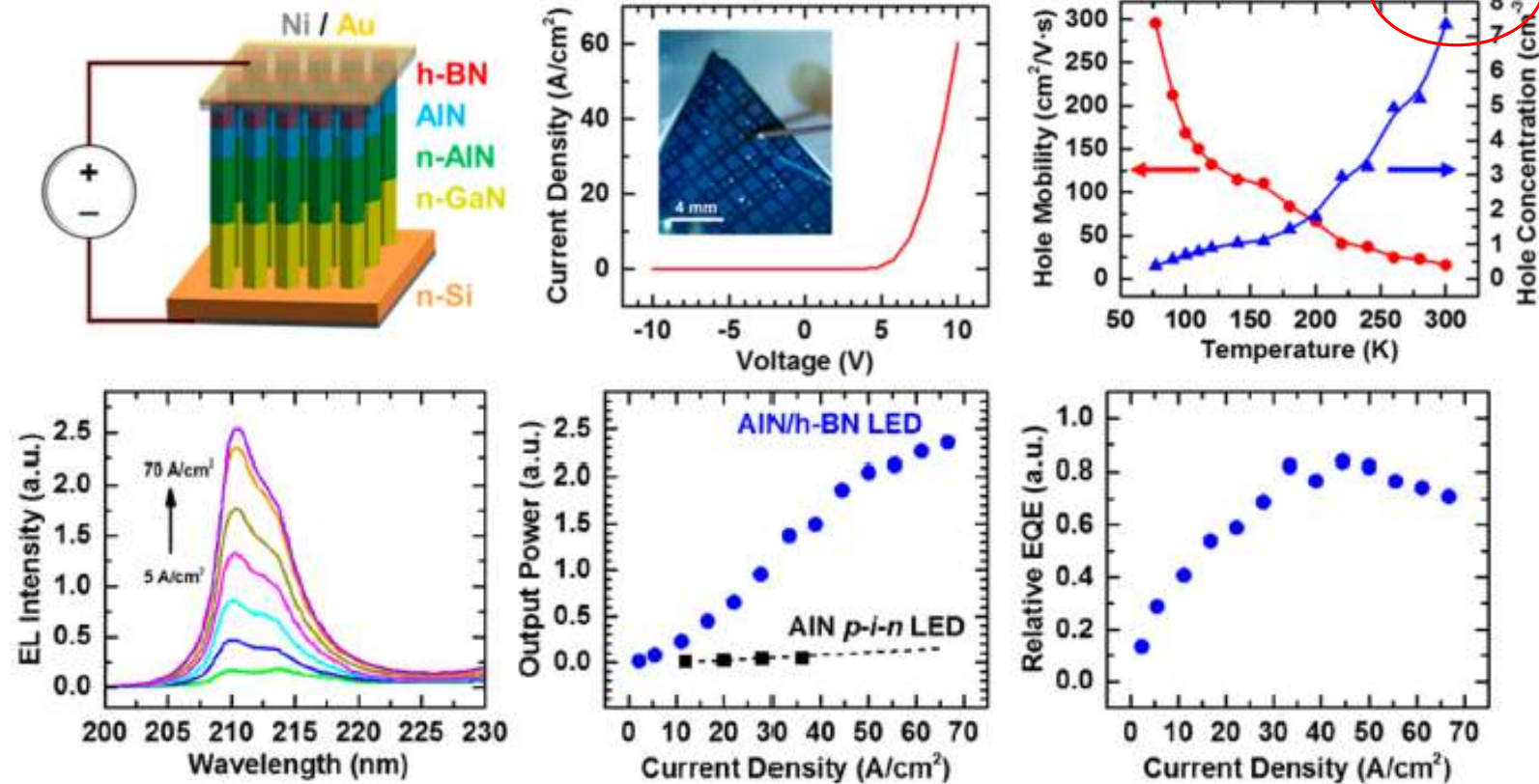


M. Koperski et al. ,Nanophotonics 6(6), 1289–1308 (2017)

R. Bourrellier et. al, Nano Lett. 2016, 16, 4317–4321

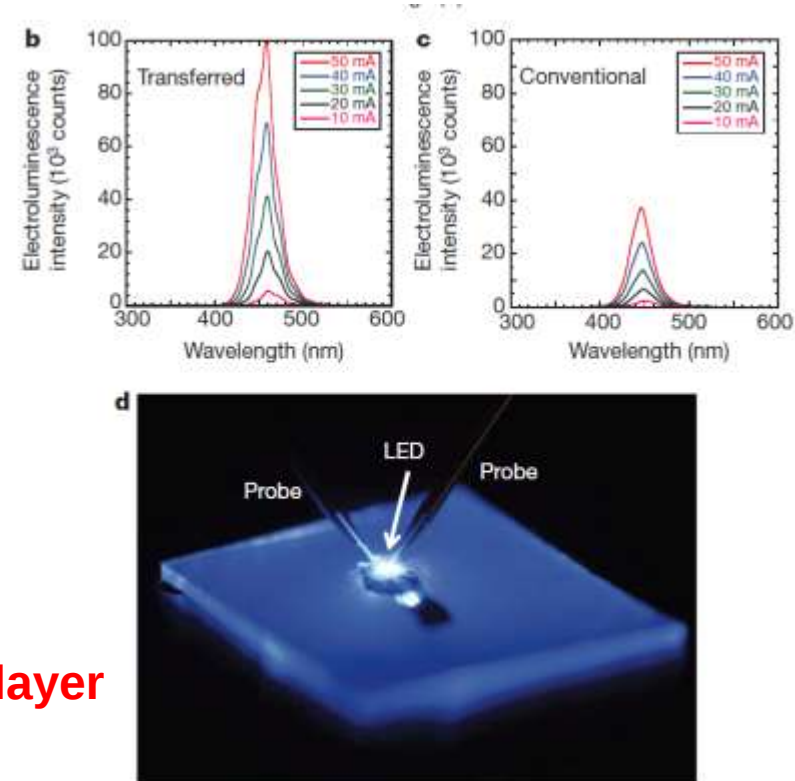
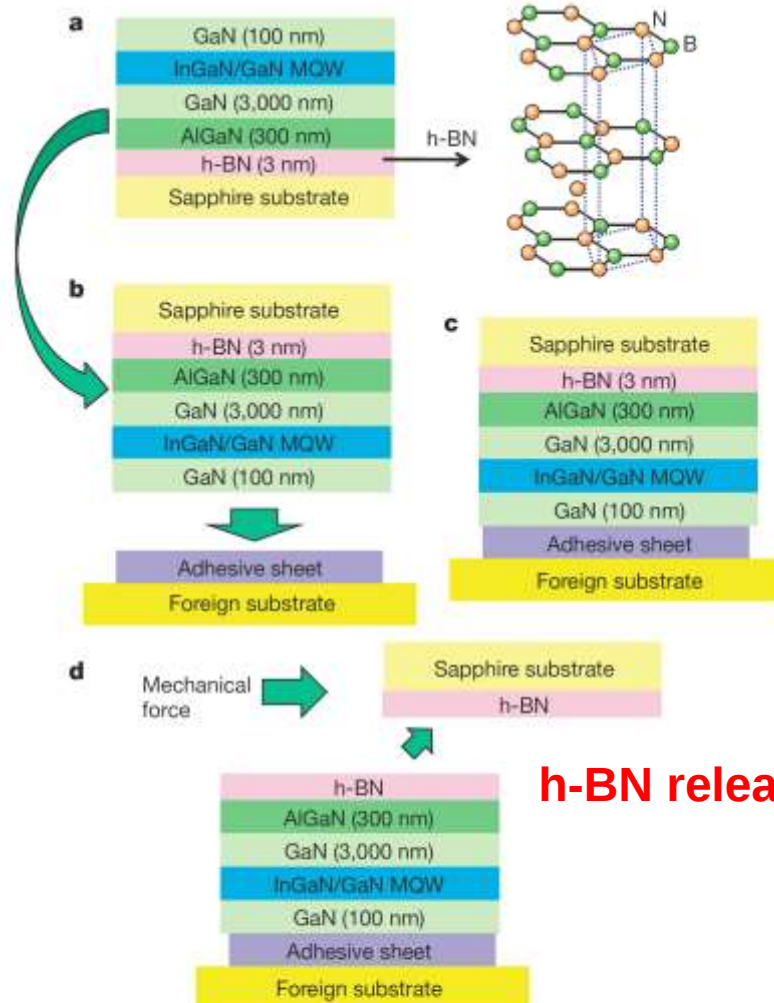
h-BN as p-type transparent material

$P \sim 10^{20} \text{ cm}^{-3}$



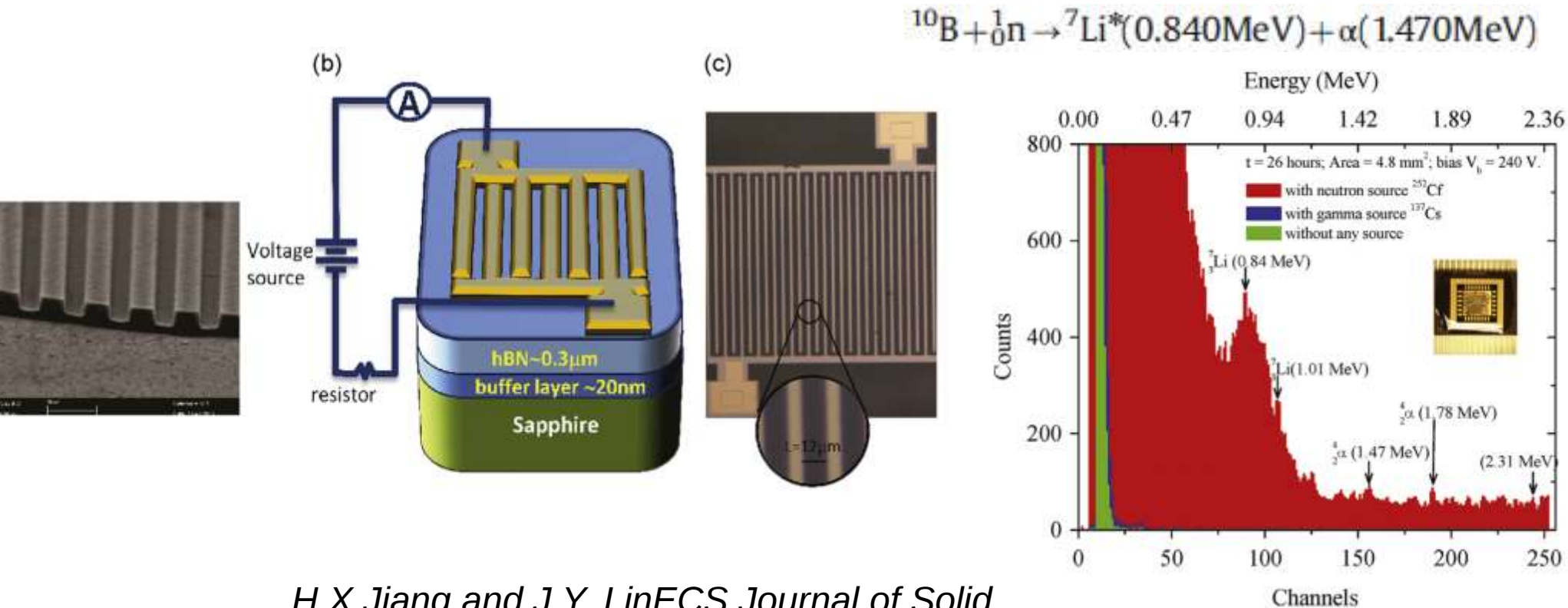
D. A. Laleyan et al. Nano Lett. 17, 3738 (2017)

Mechanical transfer of nitride-based devices



Y. Kobayashi et al. NATURE 484, 223 (2012)

BN- based neutron detectors



H.X.Jiang and J.Y. Lin ECS Journal of Solid State Science and Technology, **6** (2) Q3012-Q3021 (2017)

T.C. Doan et al. Nucl. Instr. Meth. Phys. Research A 748, 84 (2014)

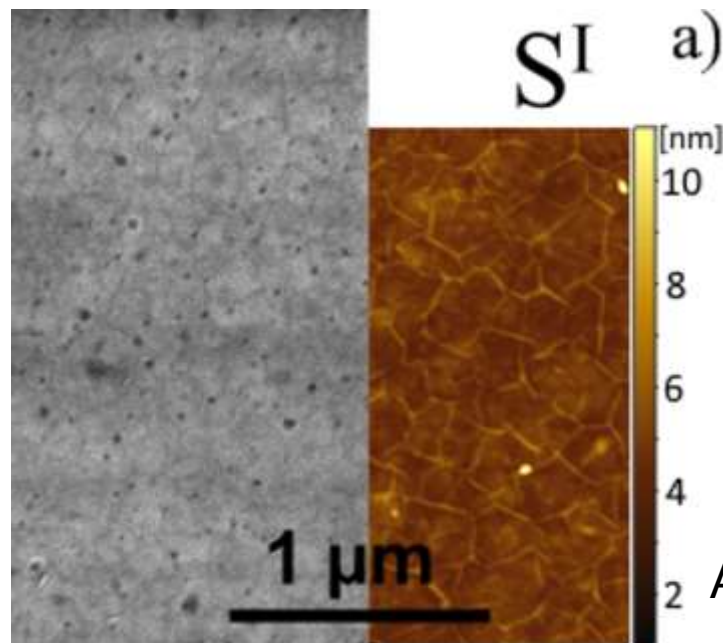
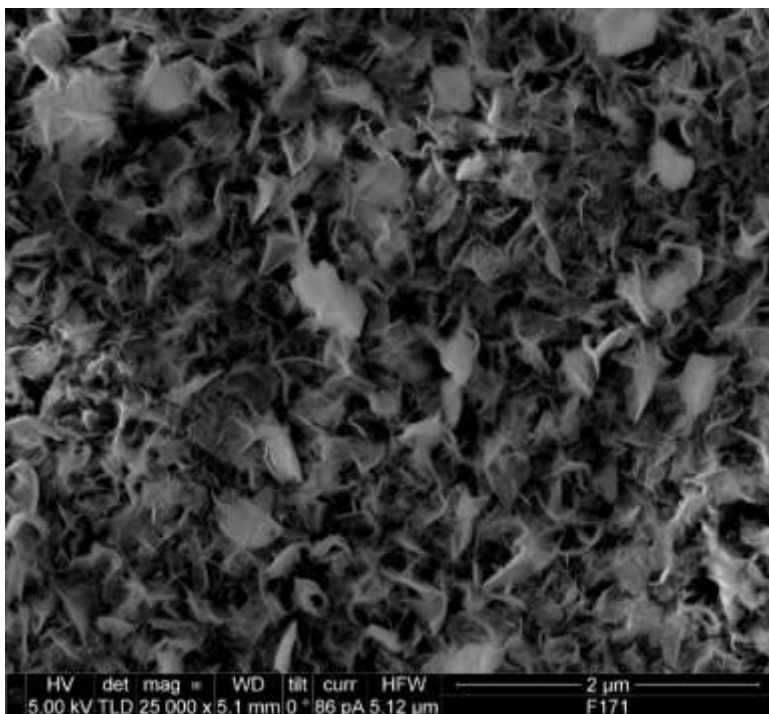
New MOVPE system



Established by Krzysztof Pakuła

Aleksandra Dąbrowska, Katarzyna Ludwiczak
fot. J.Iwański, J. Binder

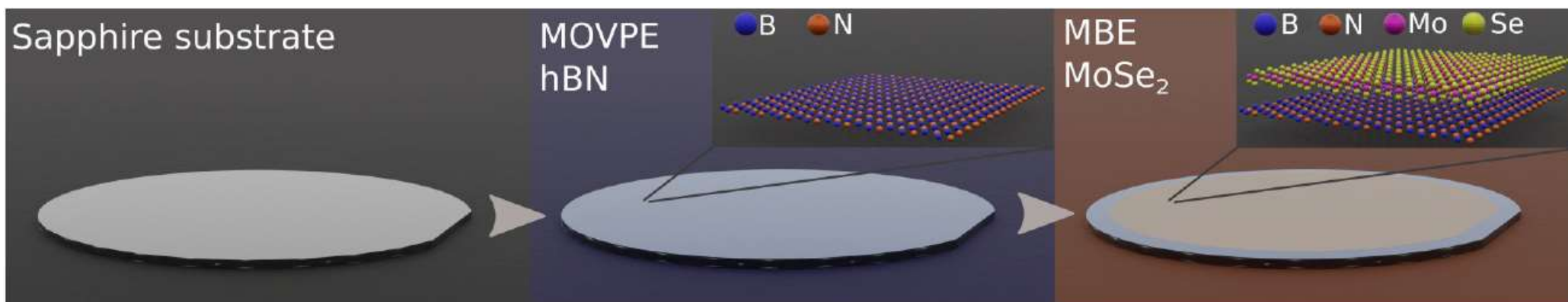
From flakes to high quality hBN layers...



New possibilities!

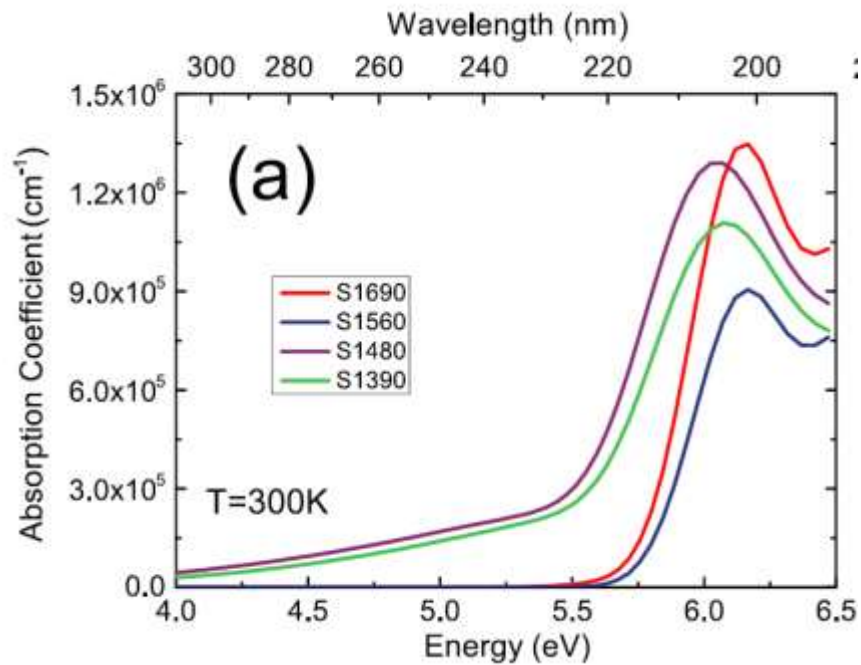
MBE MoSe₂ / BN MOCVD

A. Dąbrowska et al. 2D Materials (2020)



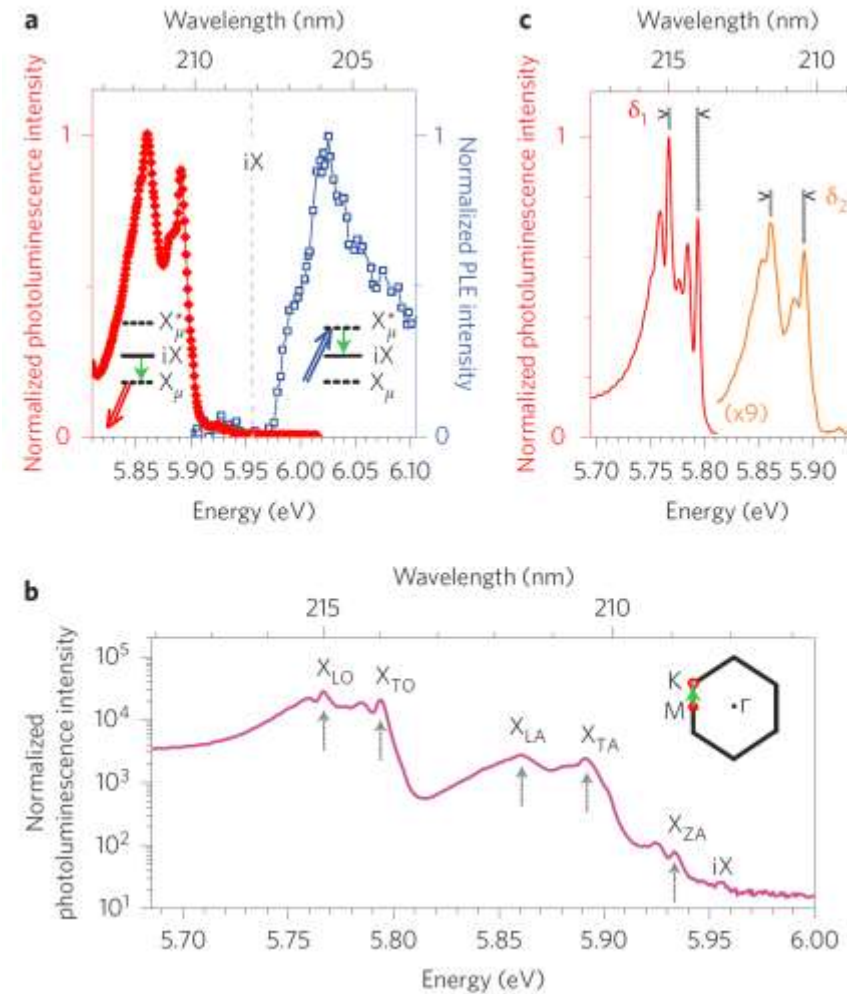
K. Ludwiczak et al. ACS Appl. Mater. Interfaces 13, 47904 (2021).

Direct or indirect bangap?



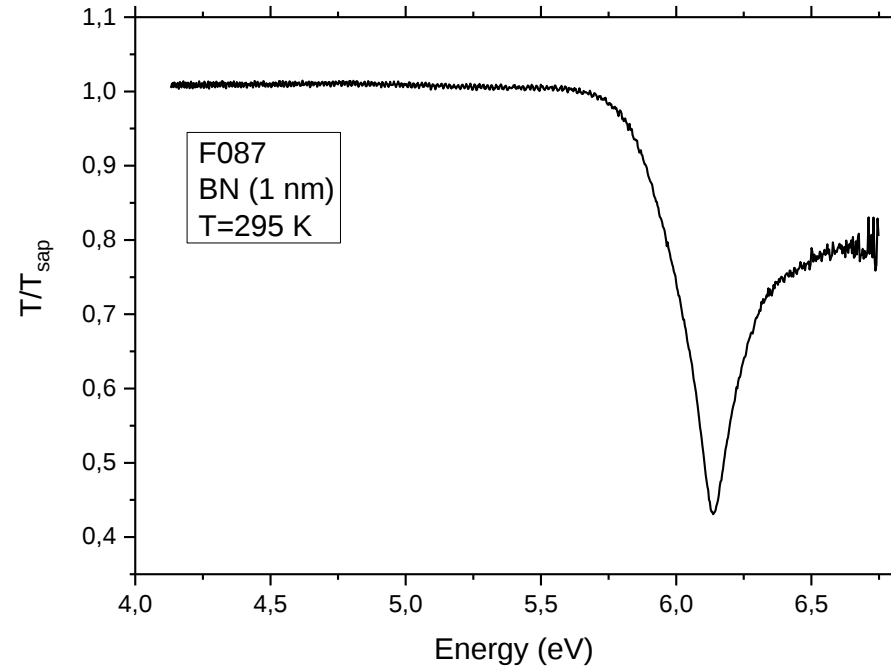
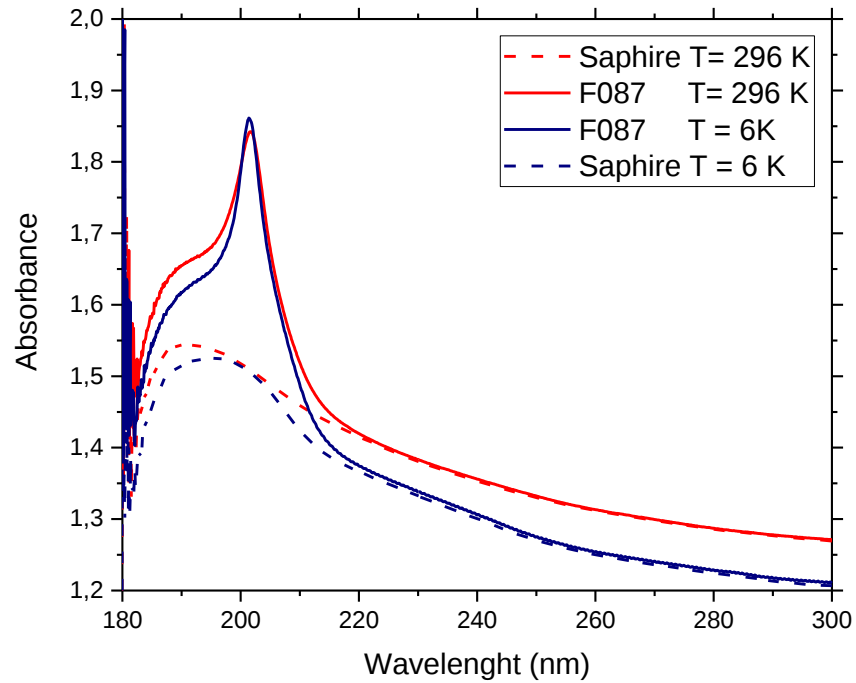
T. Q. P. Vuong et al. 2D Mater. 4
021023 (2017)

G. Cassabois, P. Valvin and B. Gil, Nature Photonics 10, 262 (2016)



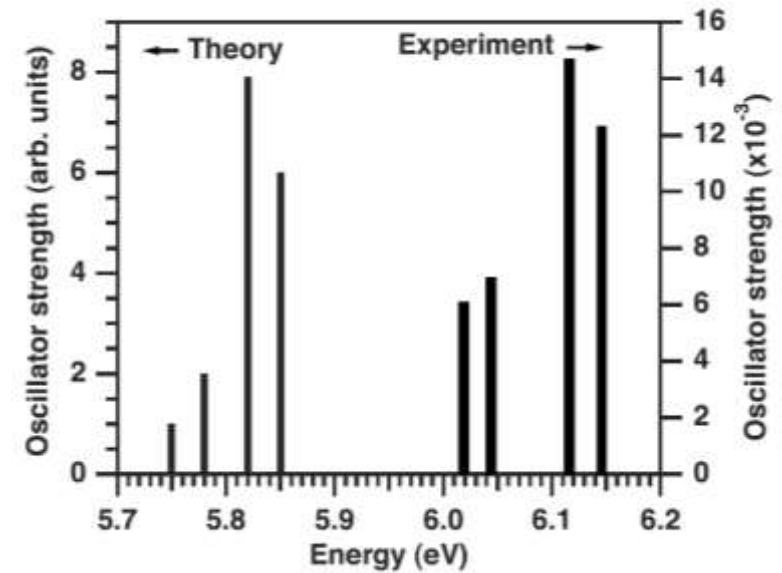
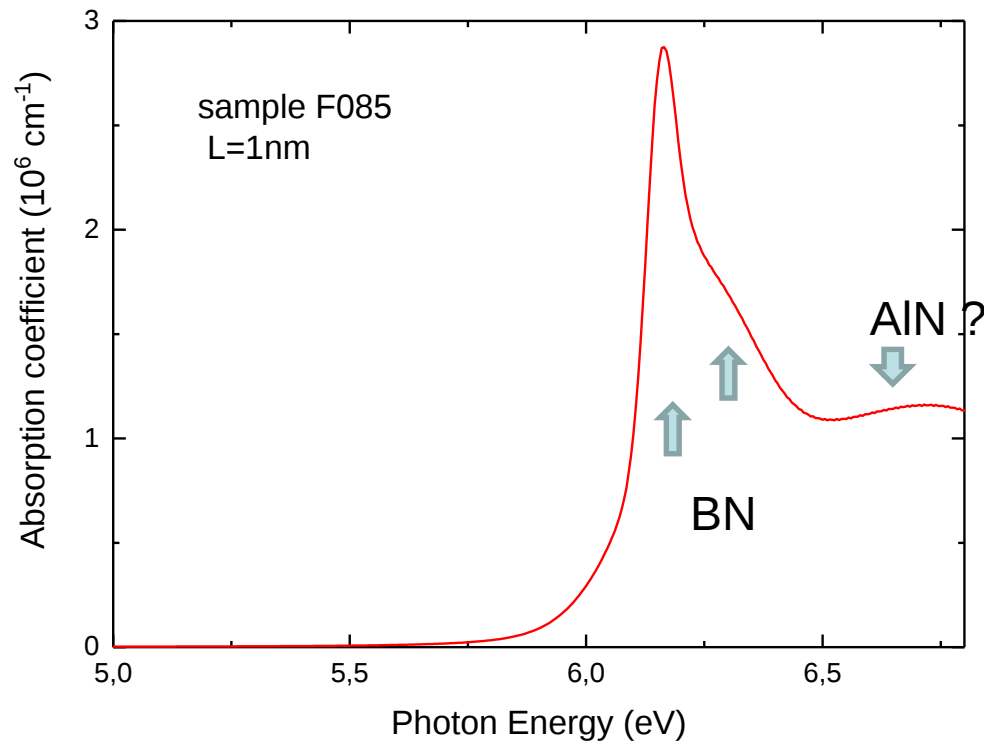
Optical absorption

1nm thick BN layer (~4 ML)!!!



Cary 5000 UV-Vis-NIR

Excitonic structure of h-BN – experiment vs. theory



B. Arnault et al. PRL **96**, 026402 (2006)

Direct-indirect transition in AlGaAs

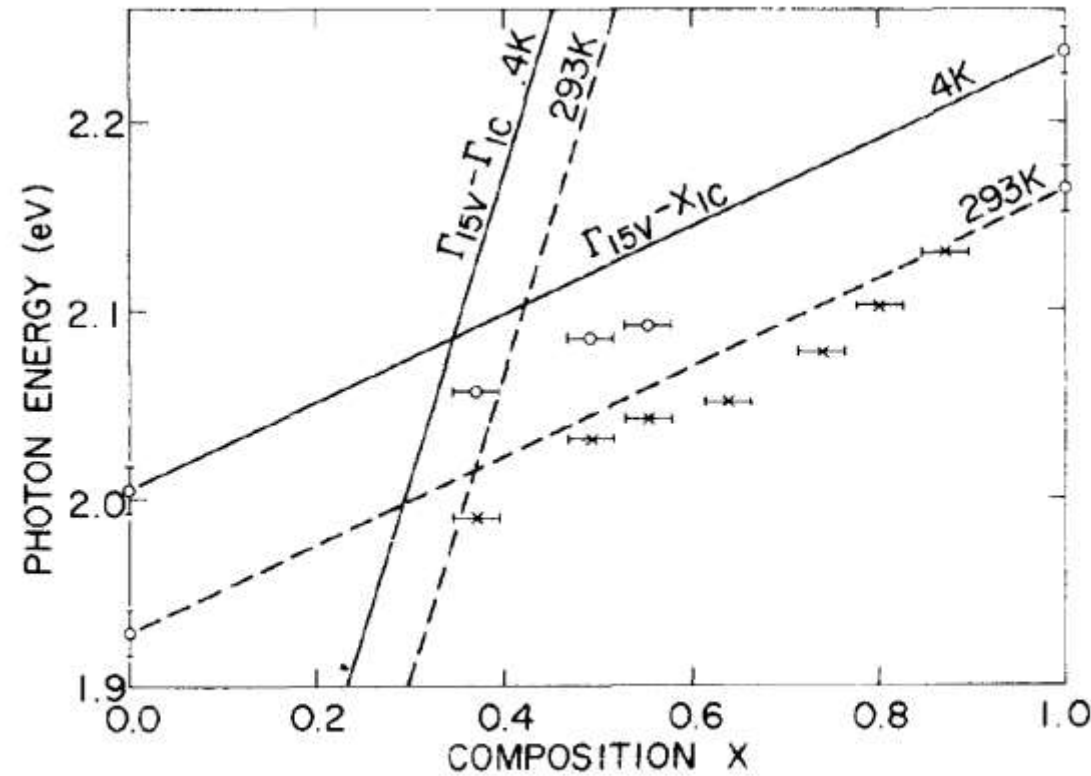
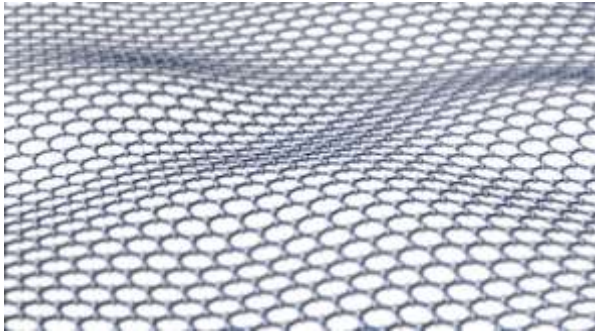


FIG. 9. Synopsis of luminescence peak positions for indirect-gap material at 4 K. (○) represents the bound-exciton peak and (x) the DA-pair peak position. The position of the DA-pair

B. Monemar et. al J. Appl. Phys. 47, 2604 (1976)

Graphene and other 2D materials – proximity effects ?

Graphene



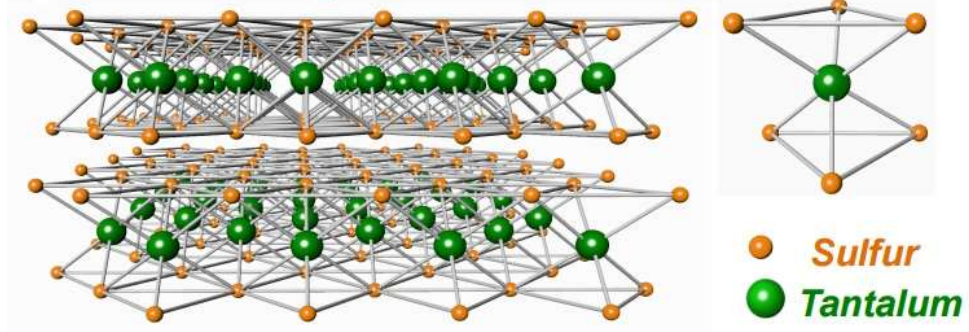
- High carriers mobility

➤ 2D hybrid structures

➤ Is it possible to observe enhancement of spin-orbit coupling in graphene/1T-TaS₂ hybrid structures?

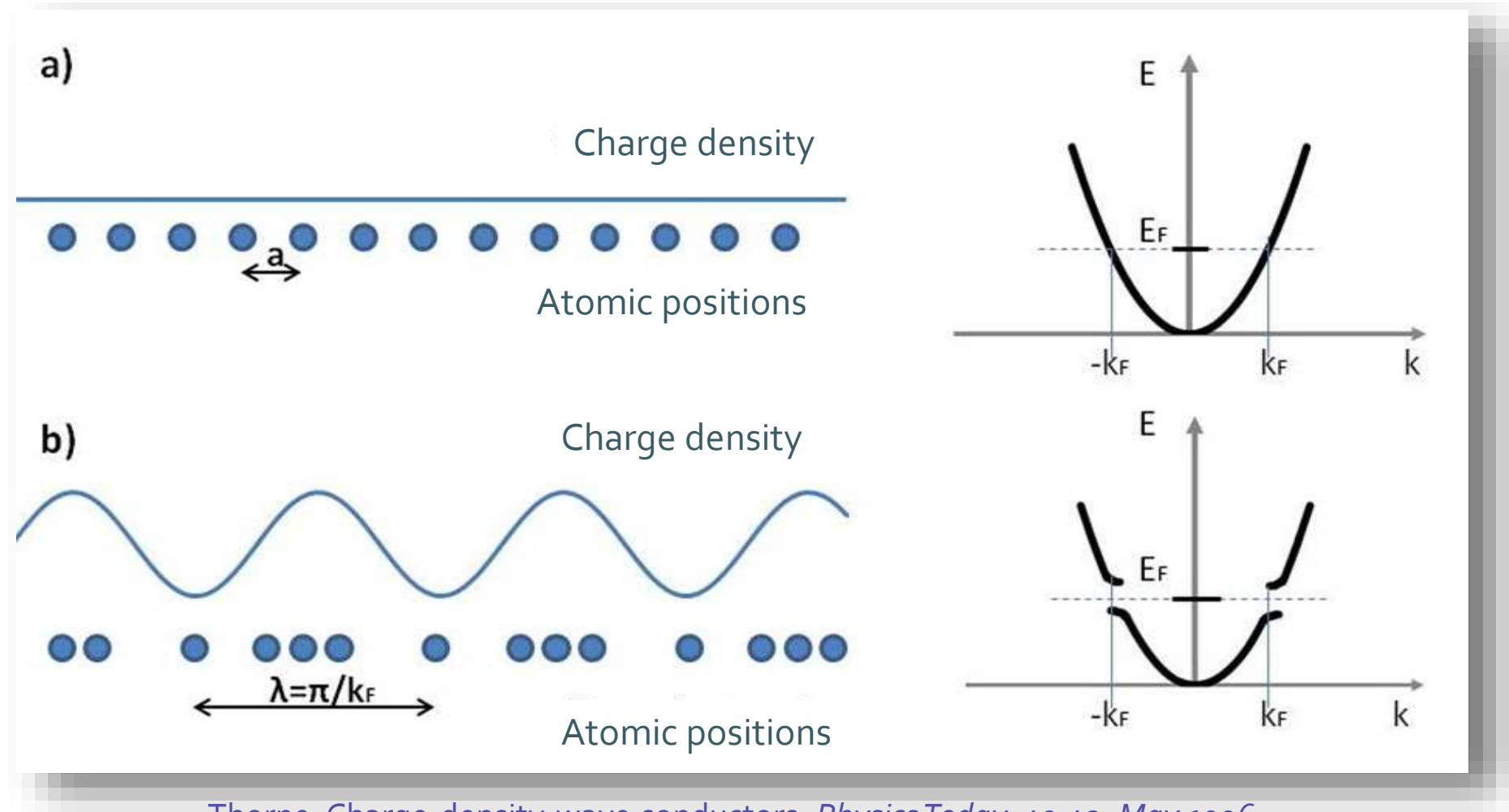
+

TaS₂ = ?



- High spin-orbit coupling
(spin-orbit splitting 100 meV)

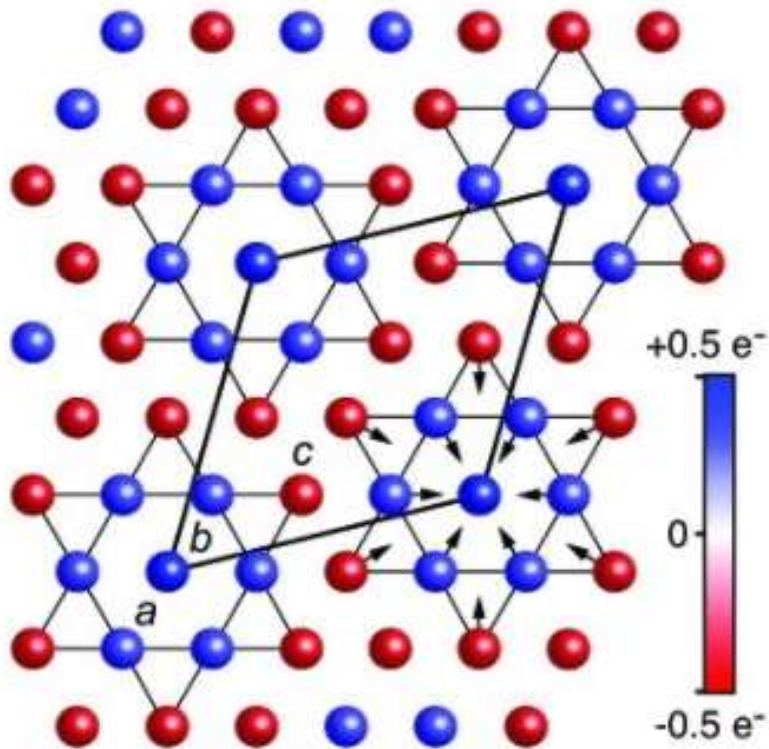
Charge density waves



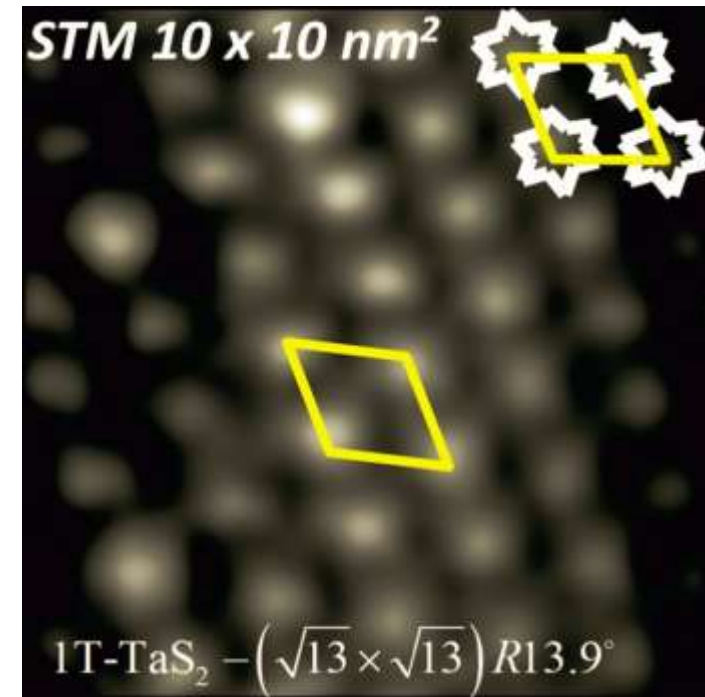
Thorne. Charge-density-wave conductors. *Physics Today*, 49:42, May 1996.

Charge density wave (CDW)

- Electron density standing wave due to strong coupling of charge carriers to atomic lattice
- Accompanied by periodic lattice distortion (PLD)
- Can be measured using scanning tunneling microscopy (STM)



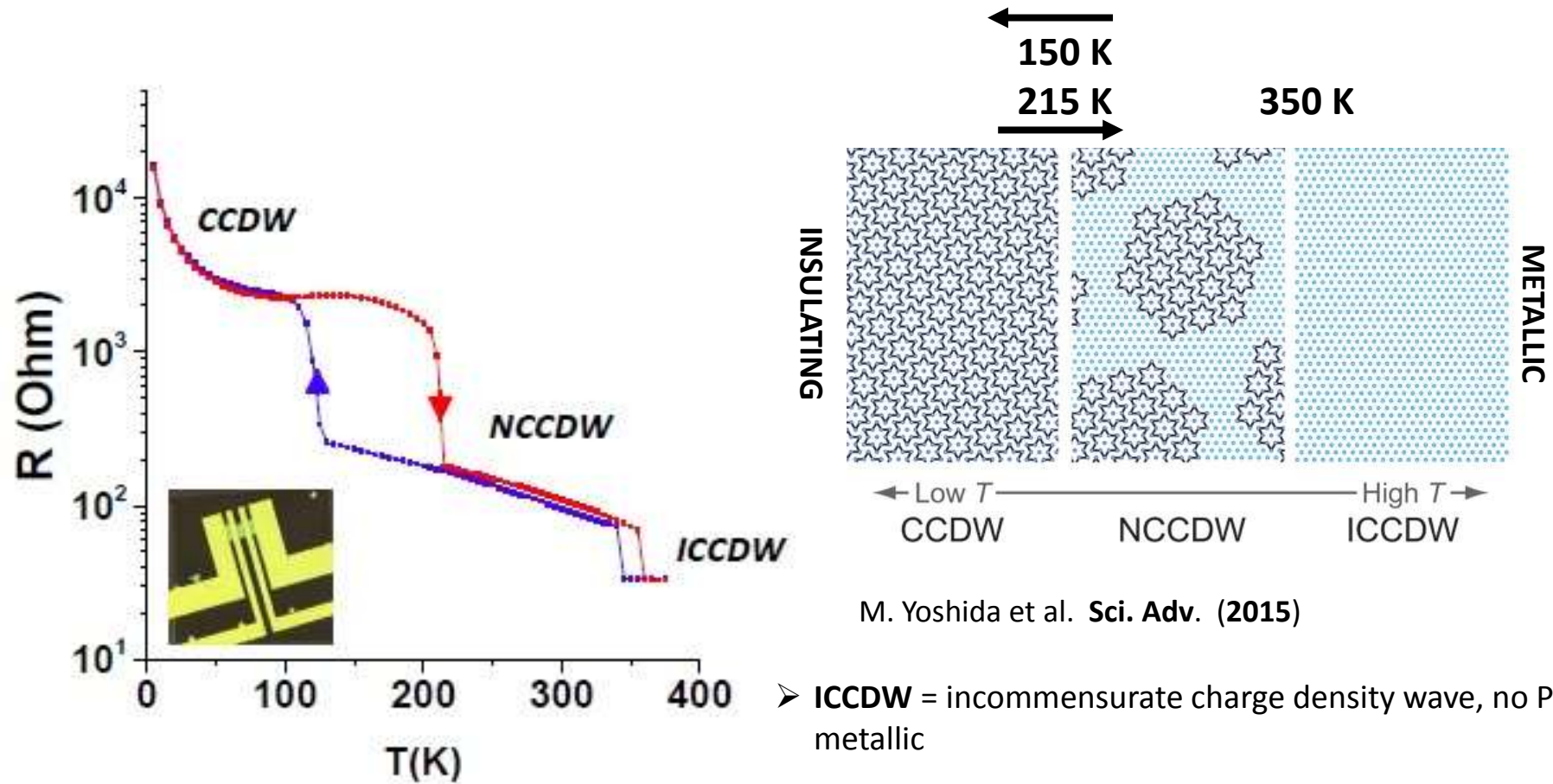
Phys. Rev. Lett. **105**, 187401 (2010)



I. Lutsyk et. al, Phys. Rev. B **98**, 195425 (2018)

- PLD: superlattice of „stars” (13 Ta atoms + 26 S atoms)
- Charge carriers localised at stars centre -
> system is insulating in CCDW phase

1T-TaS₂: phase diagram

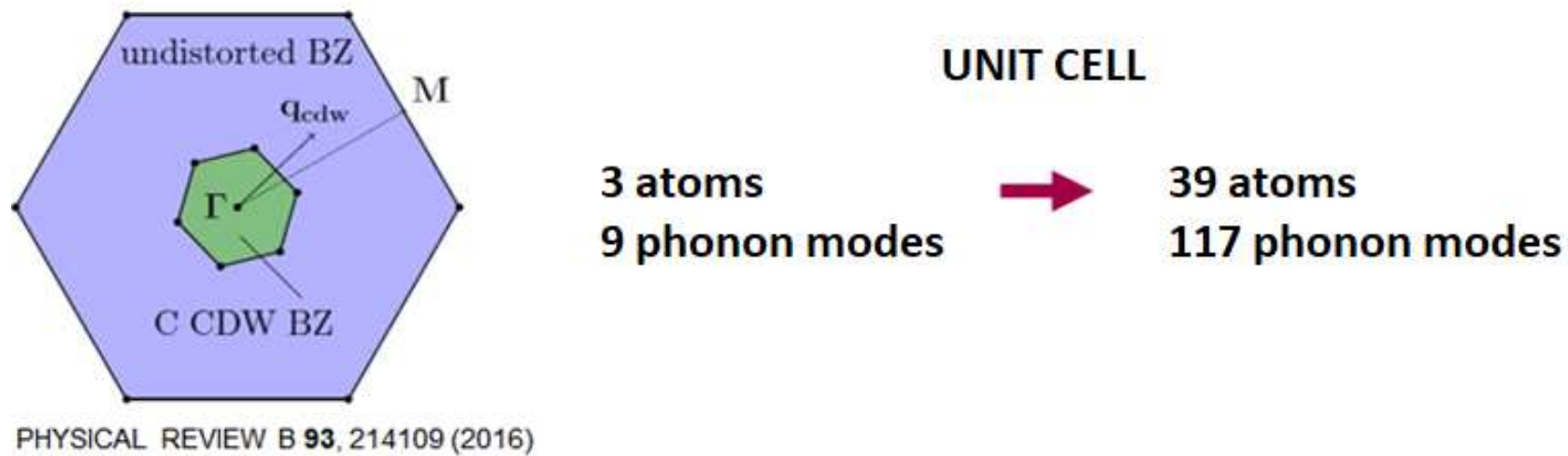


M. Yoshida et al. *Sci. Adv.* (2015)

Adina Luican-Mayer, Jeffrey R. Guest,
and Saw Wai Hla,
[arXiv:1506.04102v1](https://arxiv.org/abs/1506.04102v1)

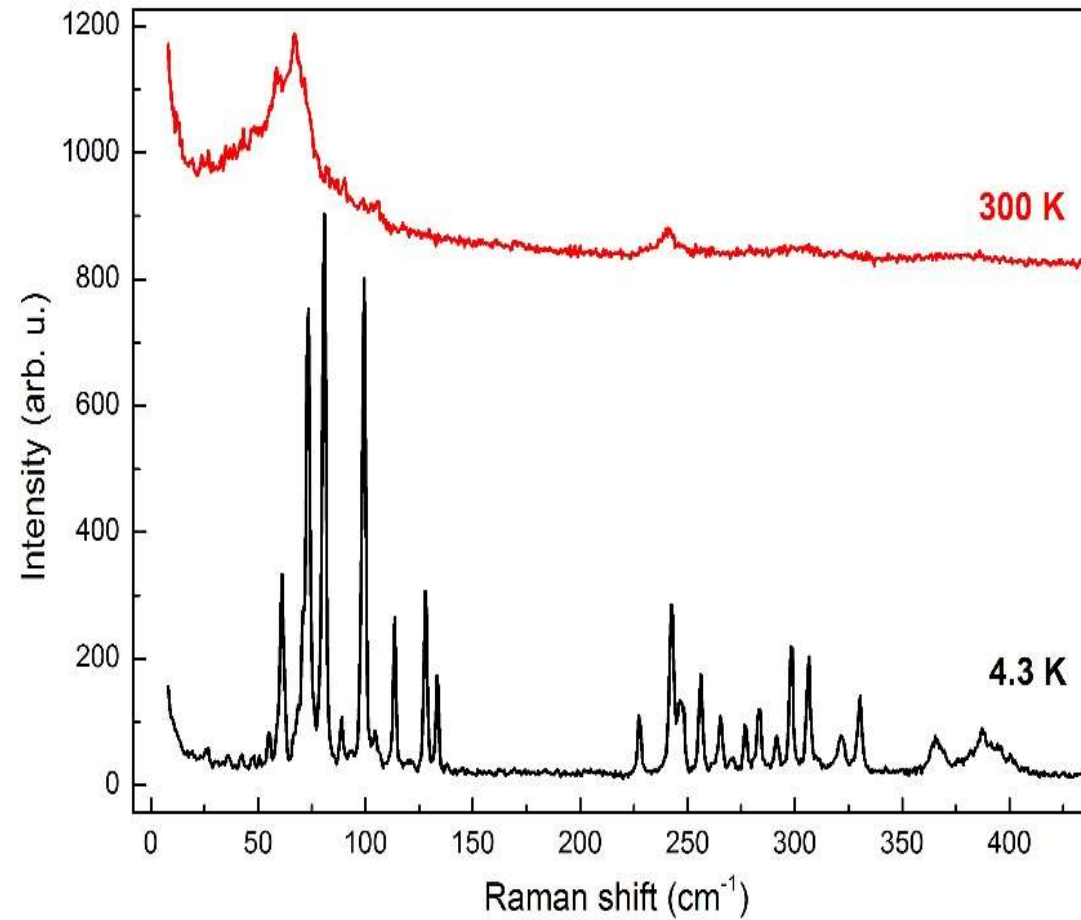
- **ICCDW** = incommensurate charge density wave, no PLD, metallic
- **NCCDW** = nearly commensurate CDW, domains of PLD stars
- **CCDW** = commensurate CDW, PLD, insulating

Raman scattering from TaS₂



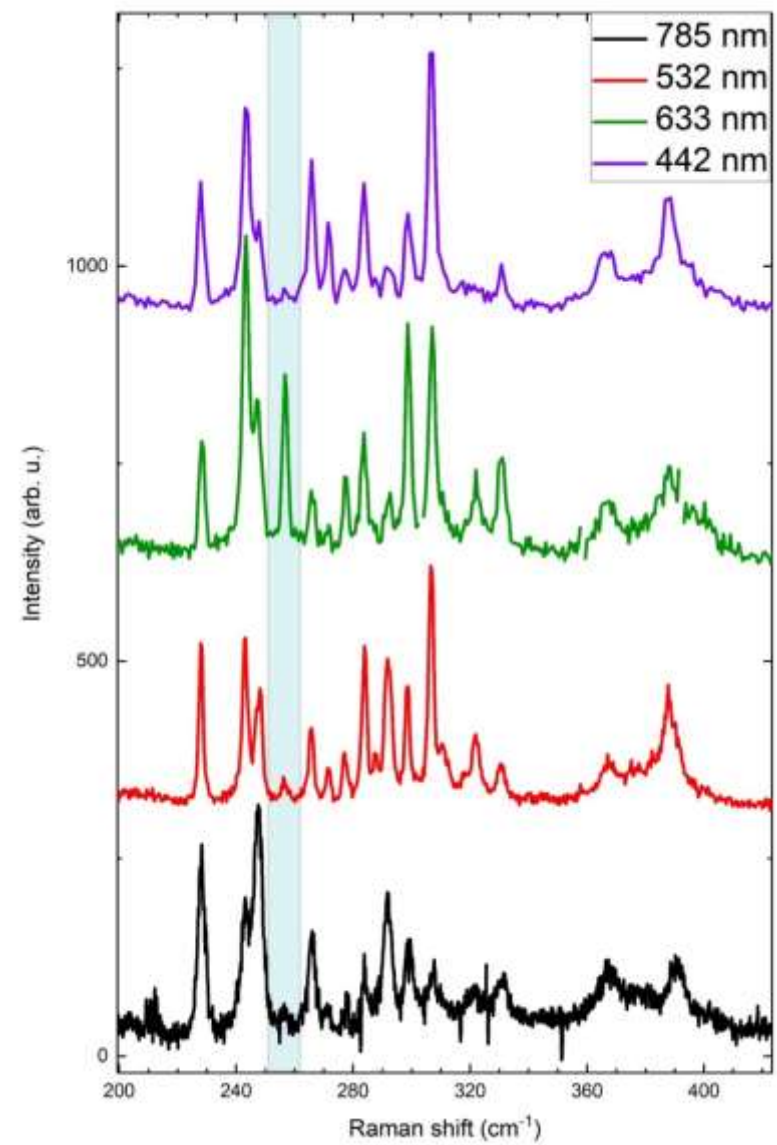
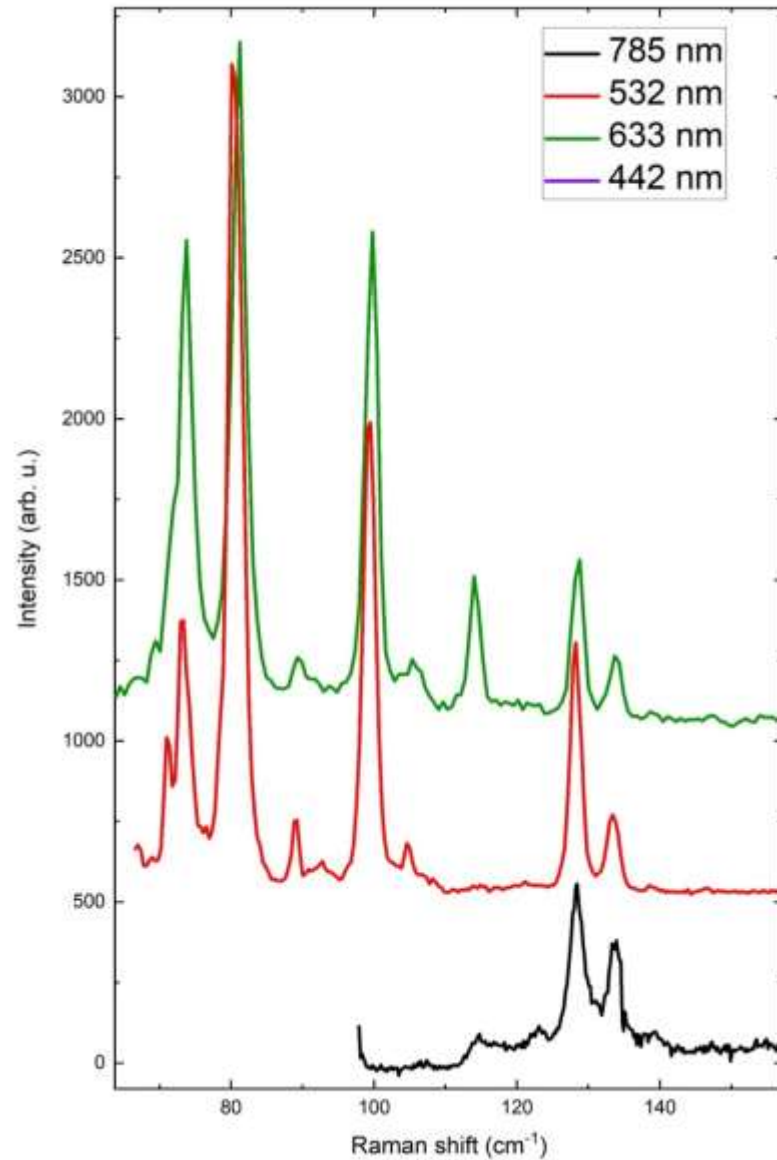
The first undistorted Brillouin zone 1T-TaS₂ (blue) and the first Brillouin zone in the CCDW phase (green).

Raman scattering from TaS₂



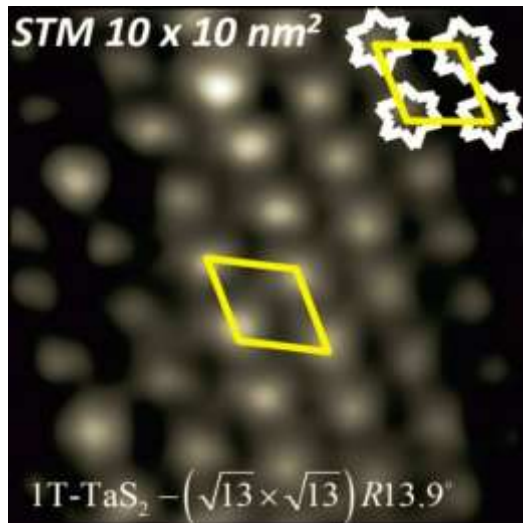
exc. 532 nm

Resonant effect

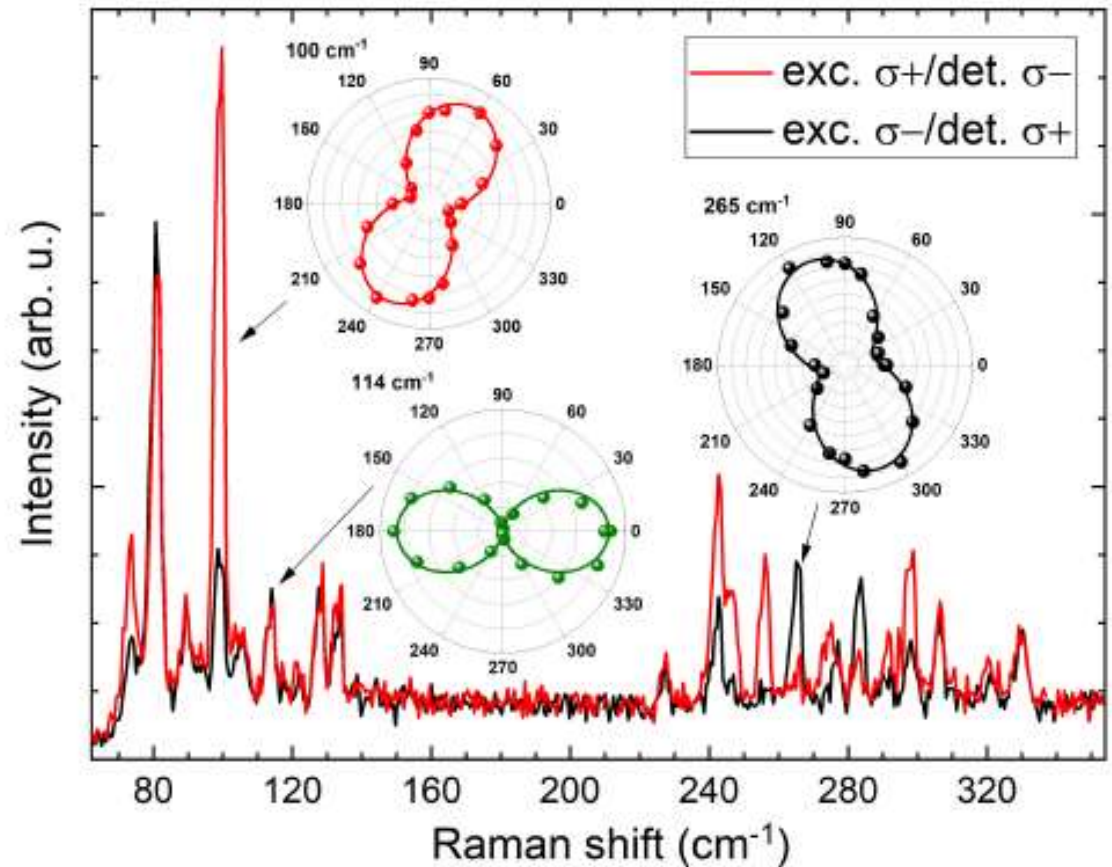


Raman Optical Activity of 1T-TaS₂

Charge density wave (CDW)



I. Lutsyk et. al, Phys. Rev. B **98**, 195425 (2018)



E. M. Lacinska, M. Furman, J. Binder, I. Lutsyk, P. J. Kowalczyk, R. Stepniewski, and A. Wysmolek, Nano Letters 2022, 22, 7, 2835-2842 (2022)

Thank you for your attention!