University of Nottingham

UK China Malaysia

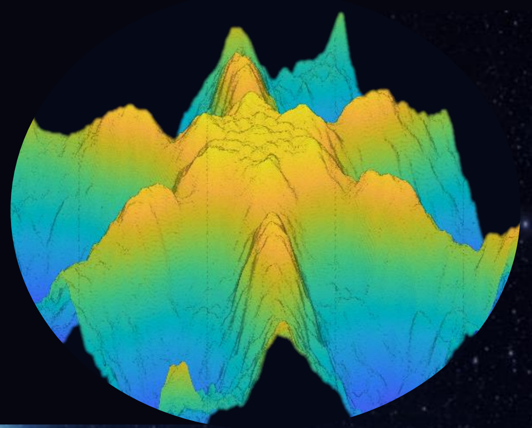
Layered Semiconductors with Inverted Mexican Hat Valence Band

A. Patanè

School of Physics and Astronomy, University of Nottingham, Nottingham, UK

Outline

- ❖ Semiconductors with Mexican hat valence band
- ❖ Ferroelectric semiconductors with Mexican hat valence band
- ❖ Challenges and Opportunities



UKRI

University of Nottingham

UK China Malaysia

Founded in 1881
4 campuses in the UK

45,500 students
7,000 staff

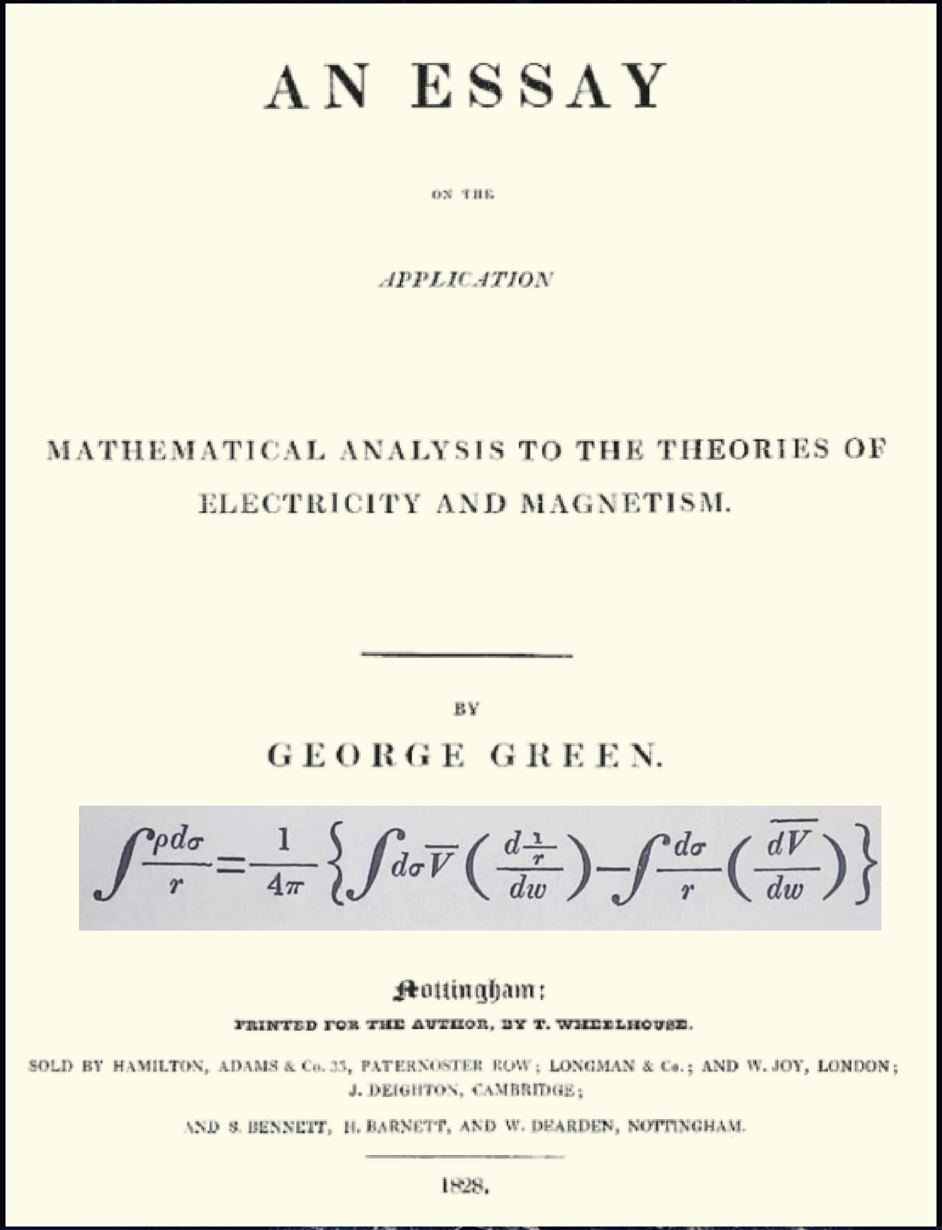
Nottingham Castle & Robin Hood
13th century

International campuses in Malaysia (1999) and China (2004)

University of Nottingham

UK China Malaysia

George Green 1793-1841



AN ESSAY

ON THE

APPLICATION

OF

MATHEMATICAL ANALYSIS TO THE THEORIES OF ELECTRICITY AND MAGNETISM.

BY

GEORGE GREEN.

$$\int \frac{\rho d\sigma}{r} = \frac{1}{4\pi}\left\{\int d\sigma \overline{V}\left(\frac{d\frac{1}{r}}{dw}\right) - \int \frac{d\sigma}{r}\left(\frac{d\overline{V}}{dw}\right)\right\}$$

Nottingham:

PRINTED FOR THE AUTHOR, BY T. WHEELHOUSE.

SOLD BY HAMILTON, ADAMS & Co. 33, PATERNOSTER ROW; LONGMAN & Co.; AND W. JOY, LONDON; J. DEIGHTON, CAMBRIDGE;

AND S. BENNETT, H. BARNETT, AND W. DEARDEN, NOTTINGHAM.

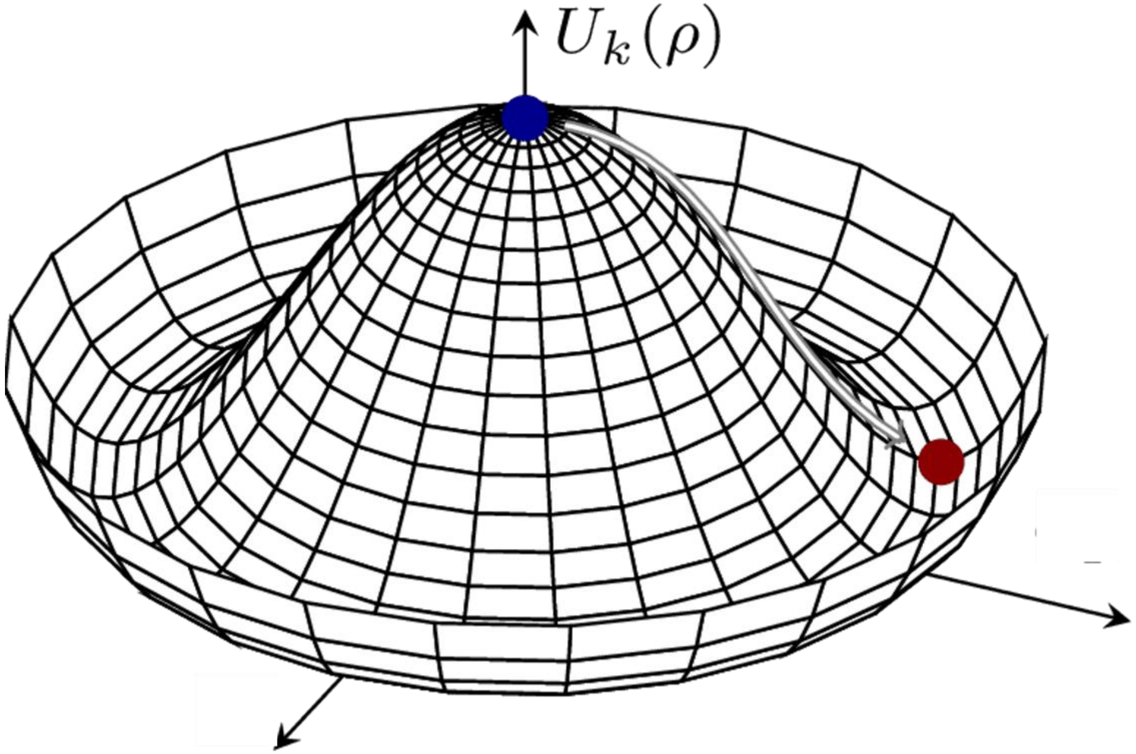
1828.

The 1828 essay introduced the concept of **potential** and **Green's function**, the foundation of electromagnetism and many discoveries across disciplines.

Mexican Hat-Shaped Bands

- **Van Hove singularity** in the density of states can induce strong *electron-electron interactions*, *ferromagnetic phases*, *superconducting pairing…*

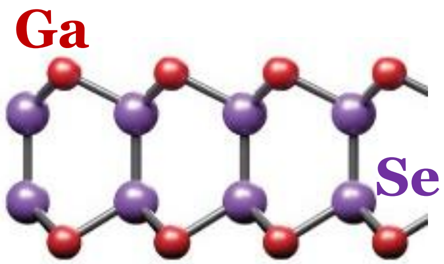
- **Negative** or **positive electron effective mass**, dependent on energy.

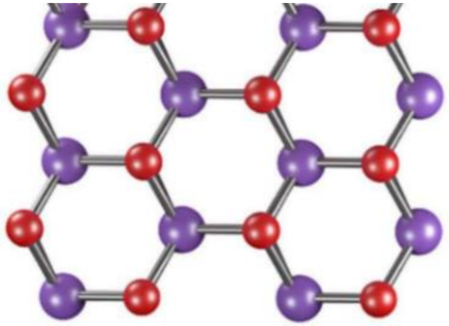


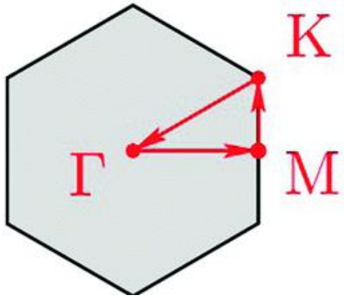
Hirsch et al. *Phys. Rev. Lett.* 56 (1986)
Stauber et al *Phys. Rev.* B 75 (2007)
Cappelluti et al. *Phys. Rev. Lett.* 98 (2007)

Inverted Mexican-Hat Valence Band

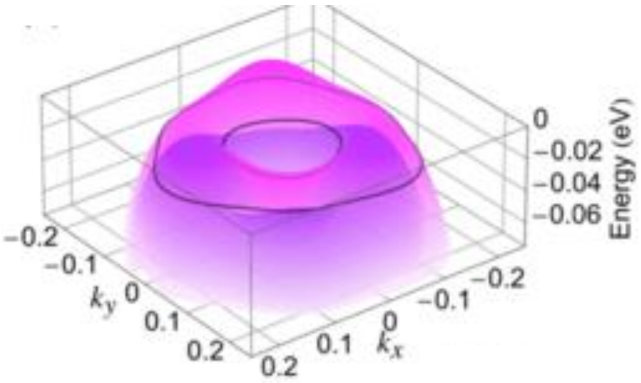
Monolayer GaSe: Tuneable Magnetism by Doping

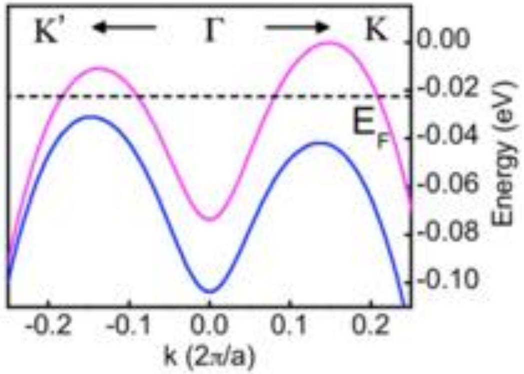




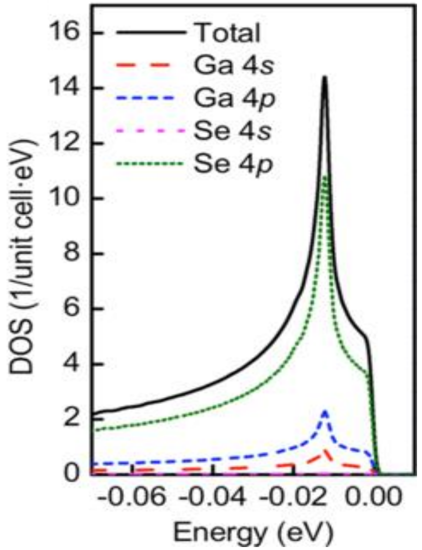


- Large average spin magnetic moment per carrier (up to ~1.0 μ_B)
- Itinerant magnetism from exchange splitting of electronic states near the top of the VB/van Hove singularity.





spin-up/-down states for p ~ $10^{14}/cm^2$

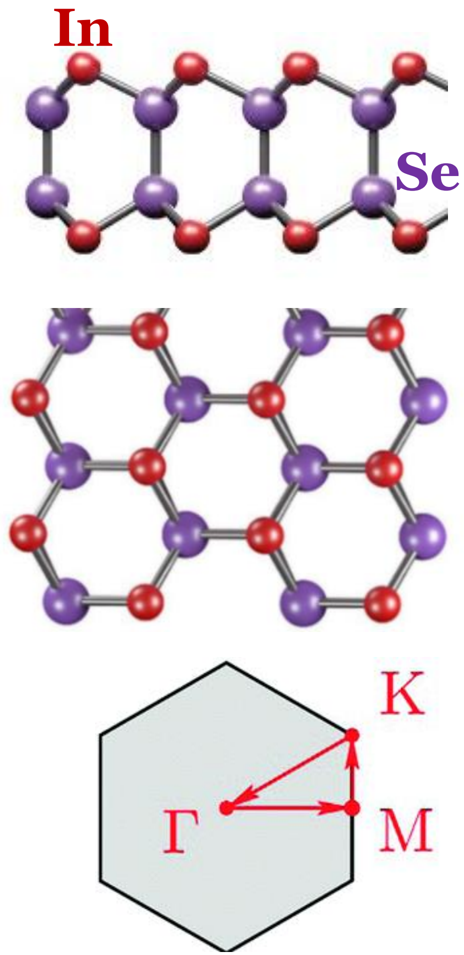


Van Hove singularity in DOS

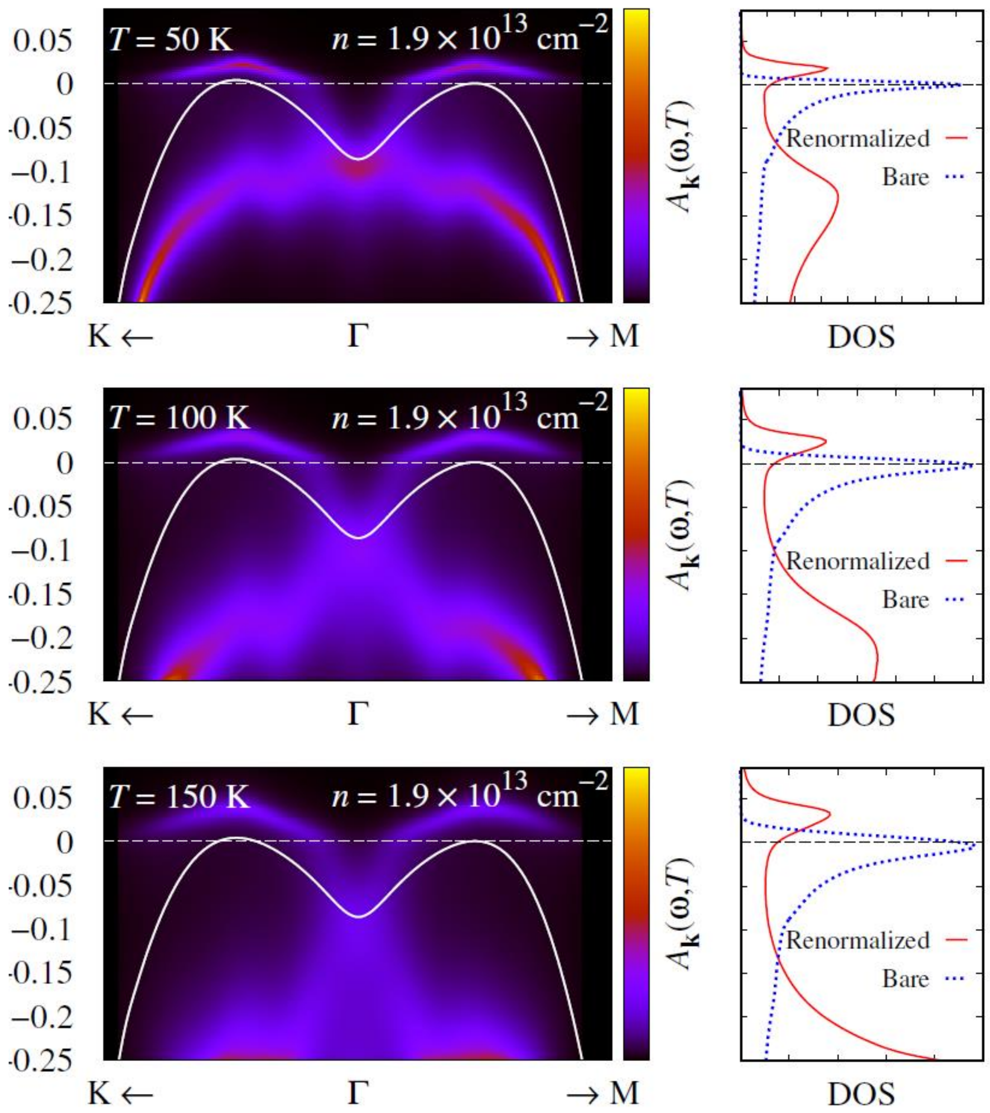
Cao et al. *Phys. Rev. Lett.* 114 (2015)

Inverted Mexican-Hat Valence Band

Monolayer InSe: Charge Instabilities by Doping



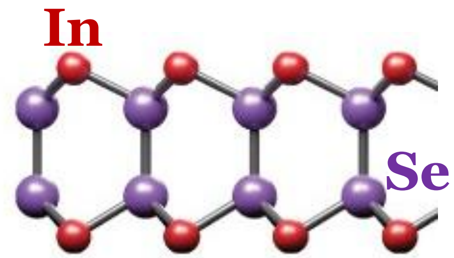
- ❖ Strong hole interaction with acoustic phonons
- ❖ Quasi-particle states near the Fermi surface
- ❖ Charge density waves and ferromagnetic order

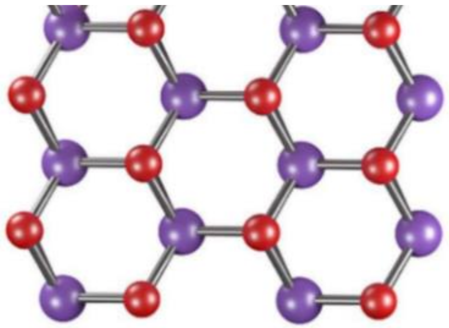


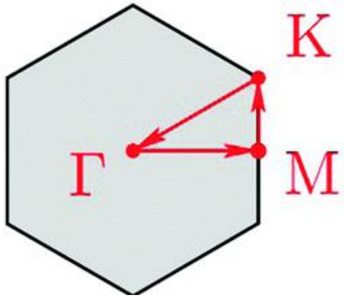
Lugovskoi et al. *Phys. Rev. Lett.* 2019
Stepanov et al. *npj Comp. Mat.* 2022

Tuneable Band Structure

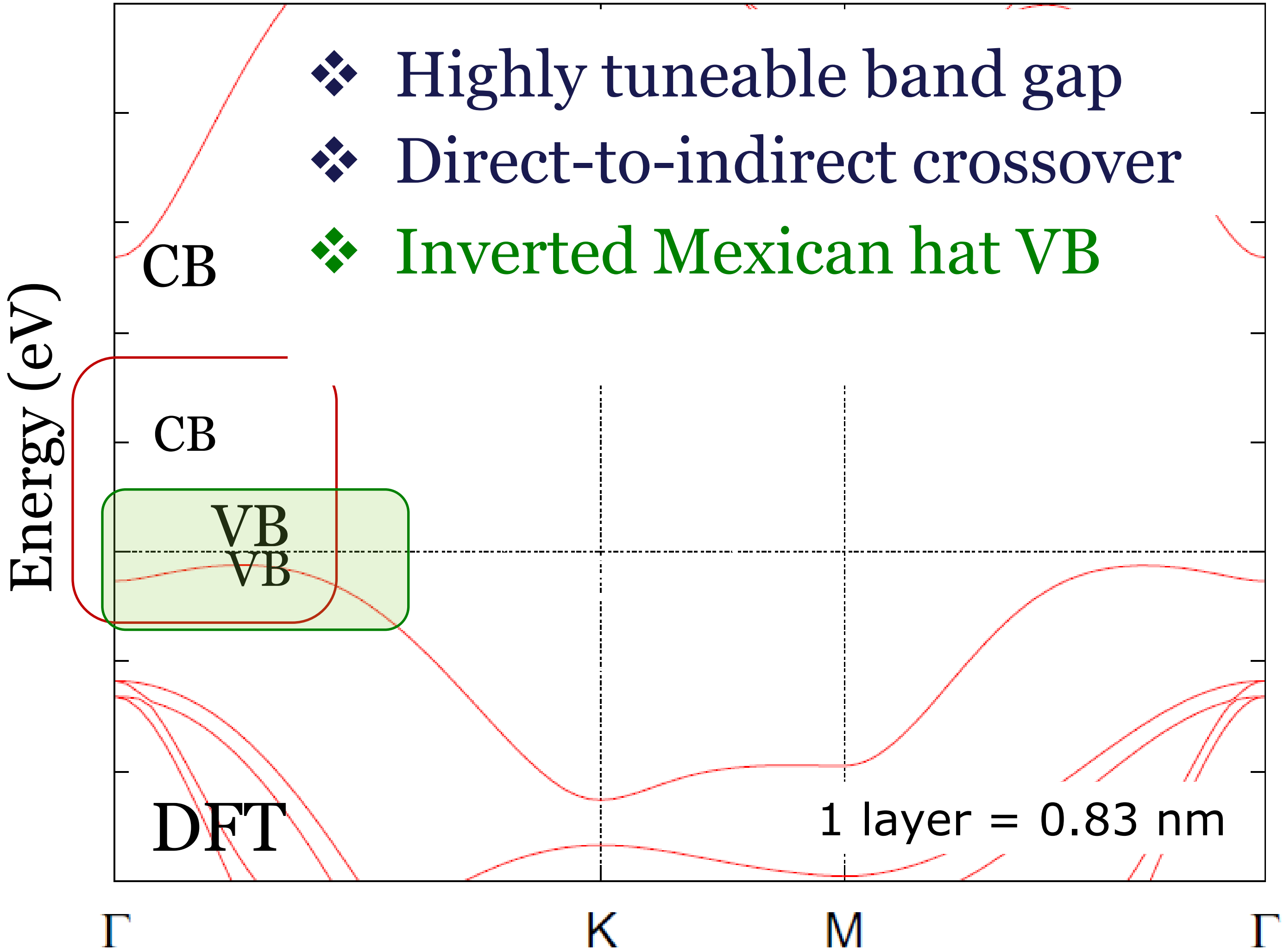
From Monolayer to Multiple-layer InSe



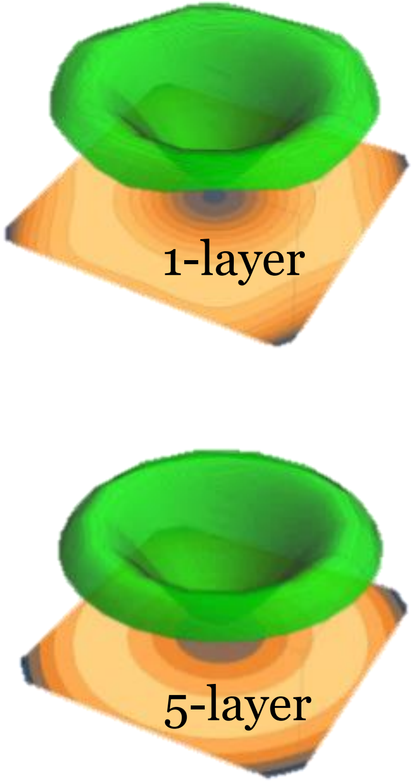




- ❖ Highly tuneable band gap
- ❖ Direct-to-indirect crossover
- ❖ Inverted Mexican hat VB



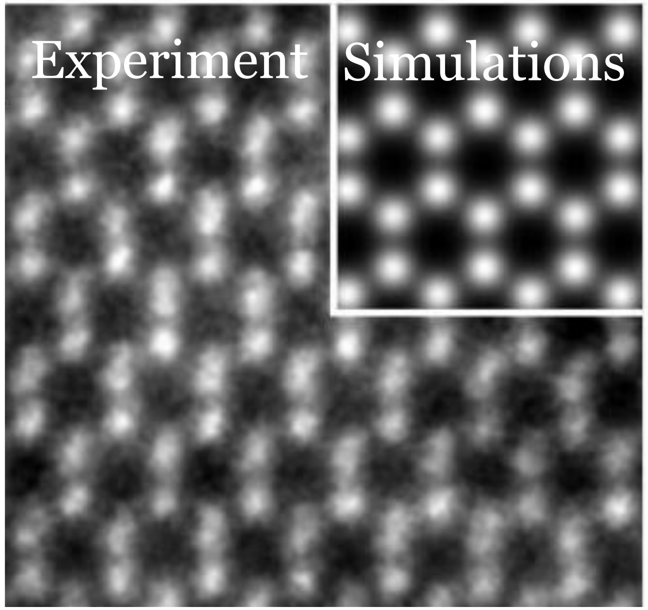
Inverted Mexican hat VB



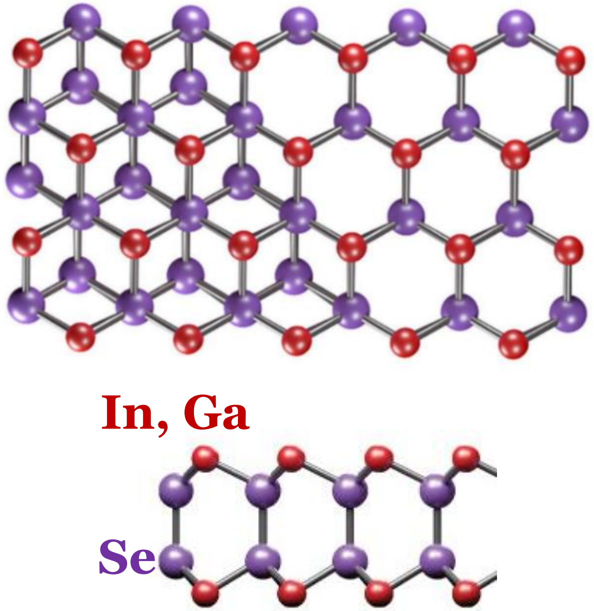
Mudd et al. *Sci. Rep.* 2016 Bandurin et al. *Nature Nano.* 2017 Sun et al. *Adv. Fun. Mat.* 2020

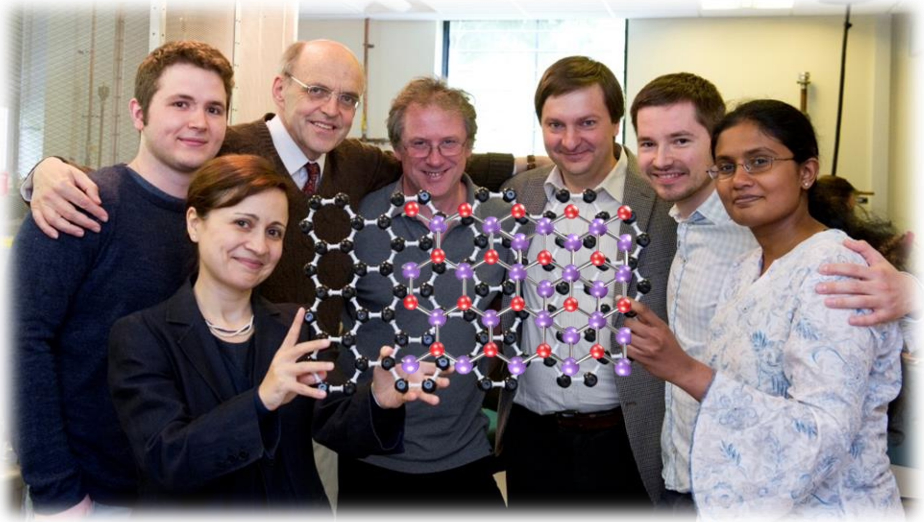
2D Semiconductors, 2SEM

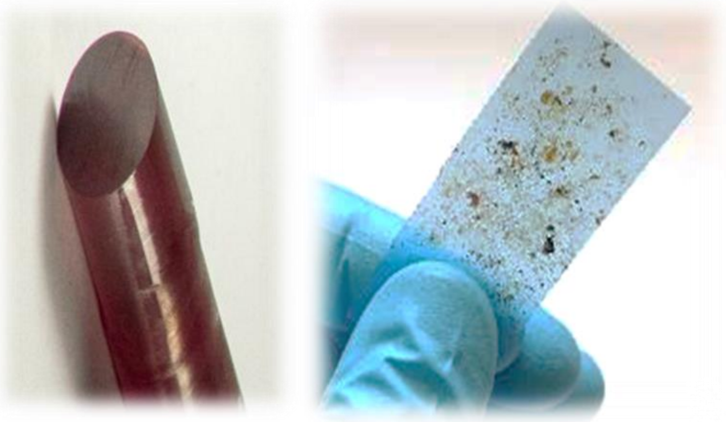
Metal III: Ga, In **Chalcogen VI**: Se

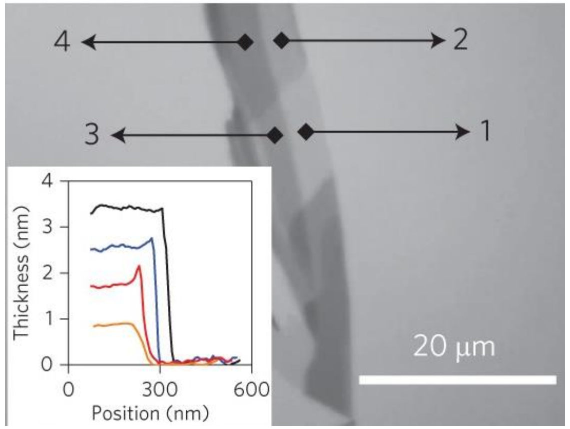


Hopkinson et al. *ACS Nano* 2019







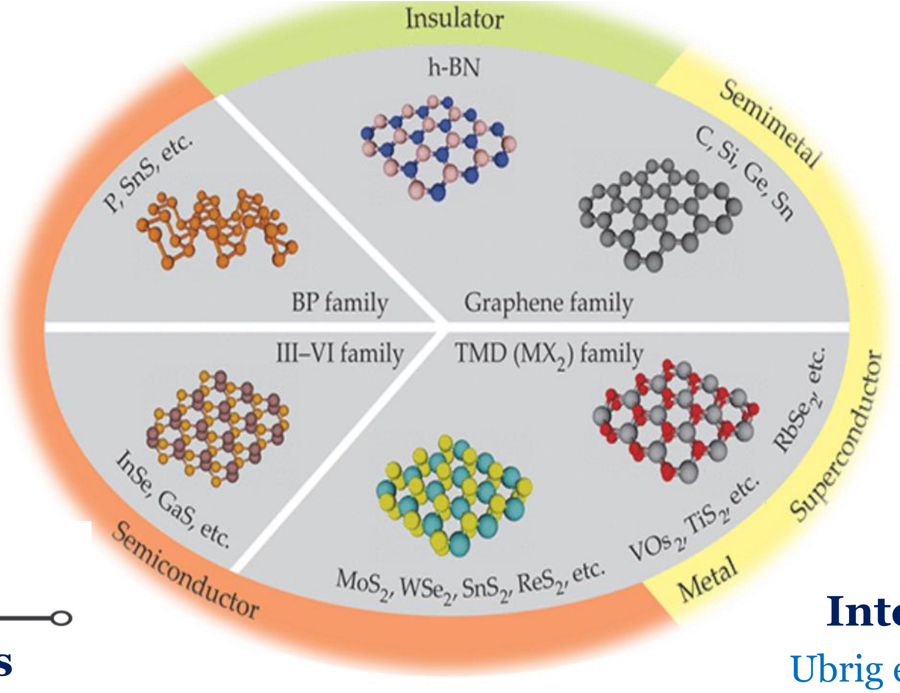


- High electron mobility (e.g. InSe)
- Tuneable band gap energy
- Optical anisotropy
- Ferroelectricity
- Elasticity

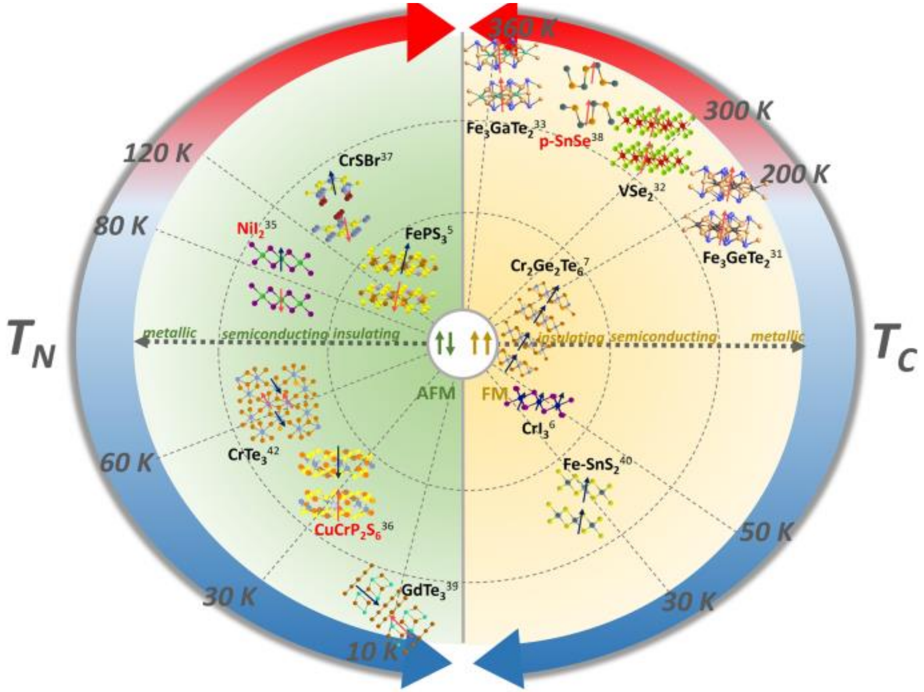
Mudd et al. *Adv. Mat.* 2013
Mudd et al. *Adv. Mat.* 2015
Bandurin et al. *Nature Nano.* 2017

2SEM Heterostructures

Ajayan et al *Phys. Today* 2016



Zhang et al. *npj Spintronics* 2024

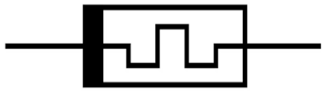


FETs

Bandurin et al.
Nature Nano. 2017

Interlayer Excitons

Ubrig et al. *Nature Mat.* 2020

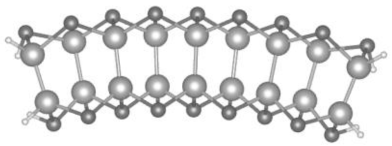


Ferroelectricity

Xie et al. *2D Mat.* 2021
Felton et al. *Nature Com.* 2025

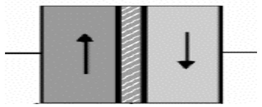
Quantum Hall Sensors

Kudrynskyi et al. *PRL* 2017



Flexible electronics

Blundo et al. *Nano Lett.* 2025
Barker et al. *npj Flex. El.* 2025



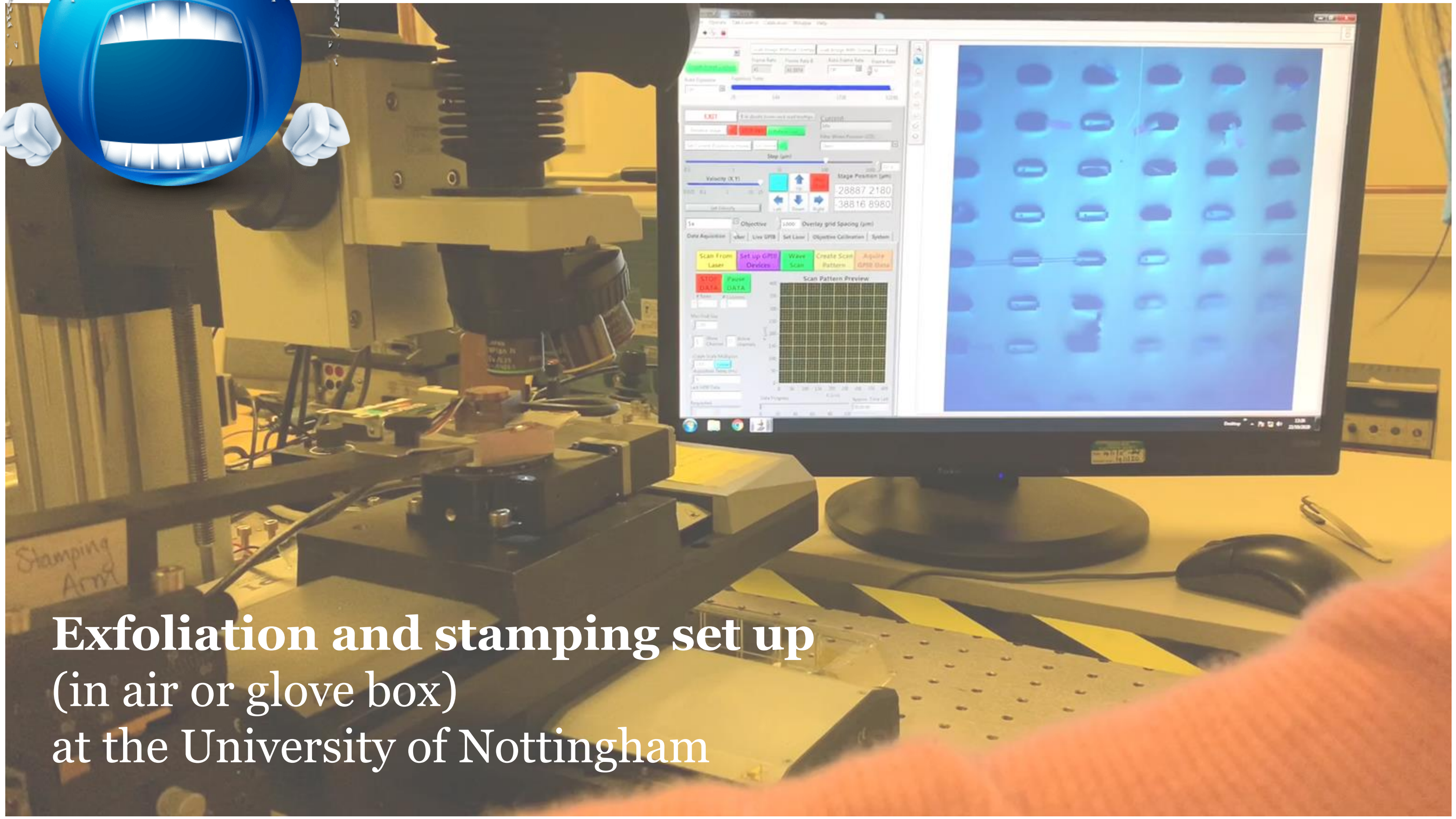
Spin valves

2D Magnetic/TMD/MC

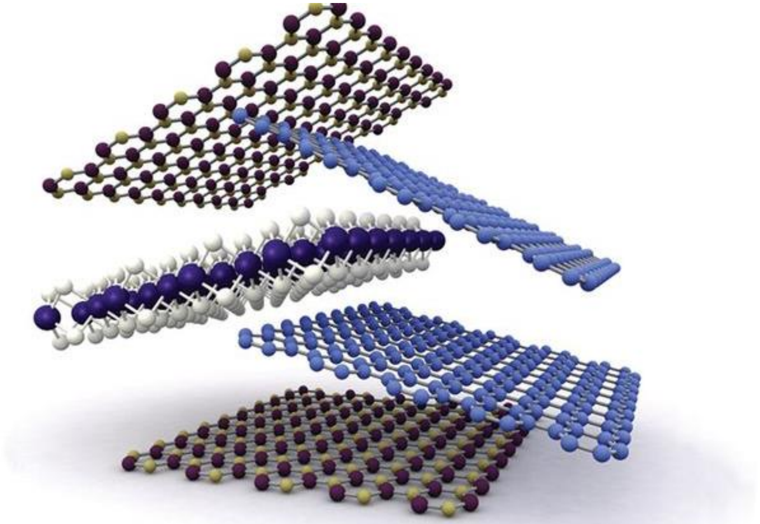
Zhu et al. *Adv. Mat.* 2021
Zhu et al. Nature Com. 2025

Making 2SEM

Mechanical exfoliation and stamping of 2SEM



Exfoliation and stamping set up
(in air or glove box)
at the University of Nottingham



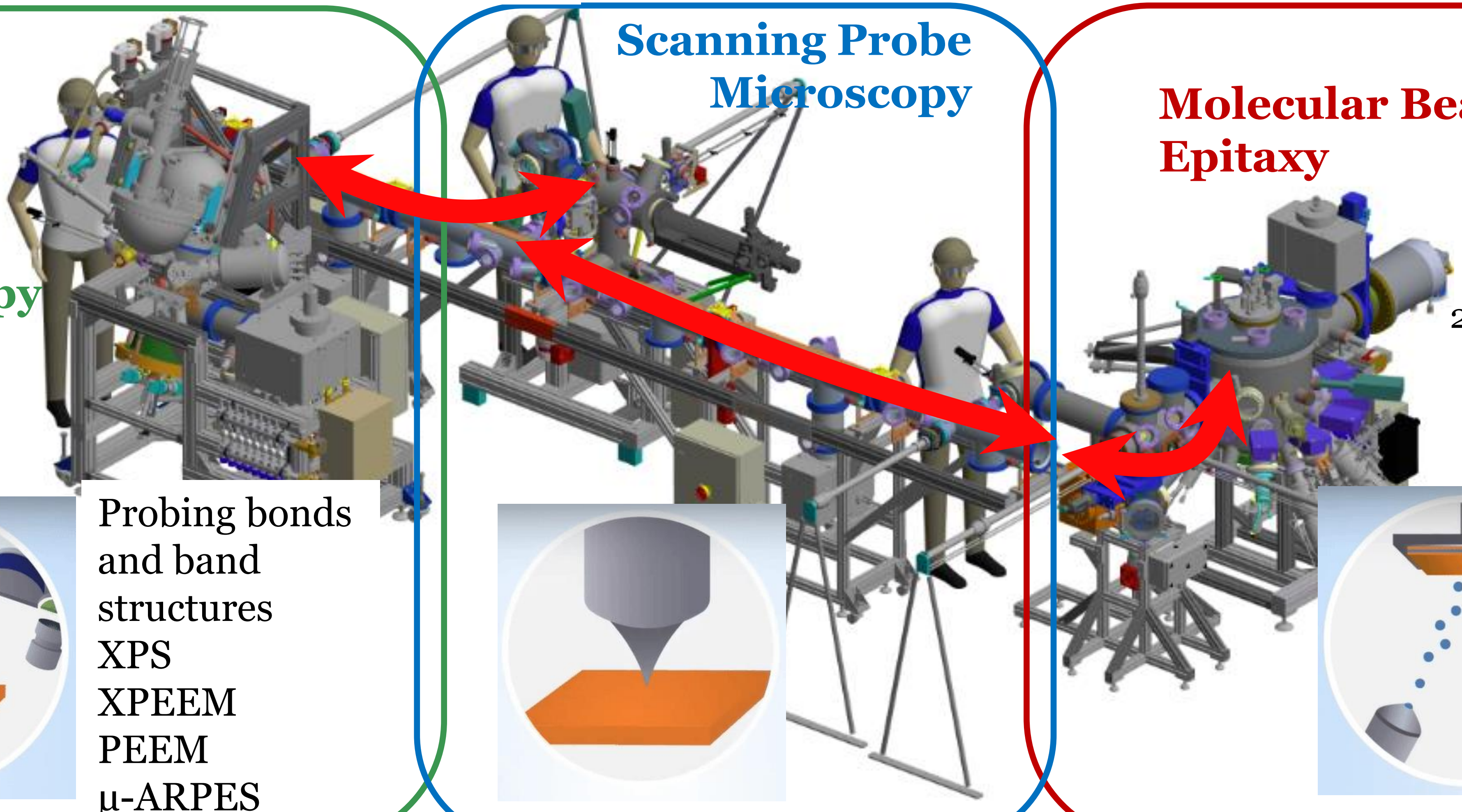
Novoselov et al. *Science* 2016

- ❖ No scalability
- ❖ Contamination
- ❖ Limited control of size, composition, doping…

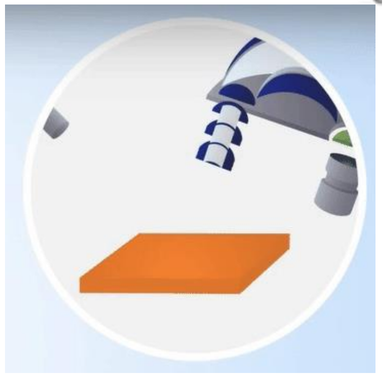
Epitaxial 2SEM

EPI2SEM: EPItaxial growth and In-situ analysis of **2SEM**

2SEM: 2D semiconductors   3-chamber cluster in ultra high vacuum



Electron Spectroscopy for Chemical Analysis

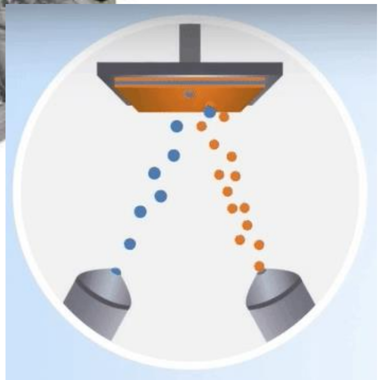


Probing bonds and band structures
XPS
XPEEM
PEEM
μ-ARPES

Scanning Probe Microscopy

Molecular Beam Epitaxy

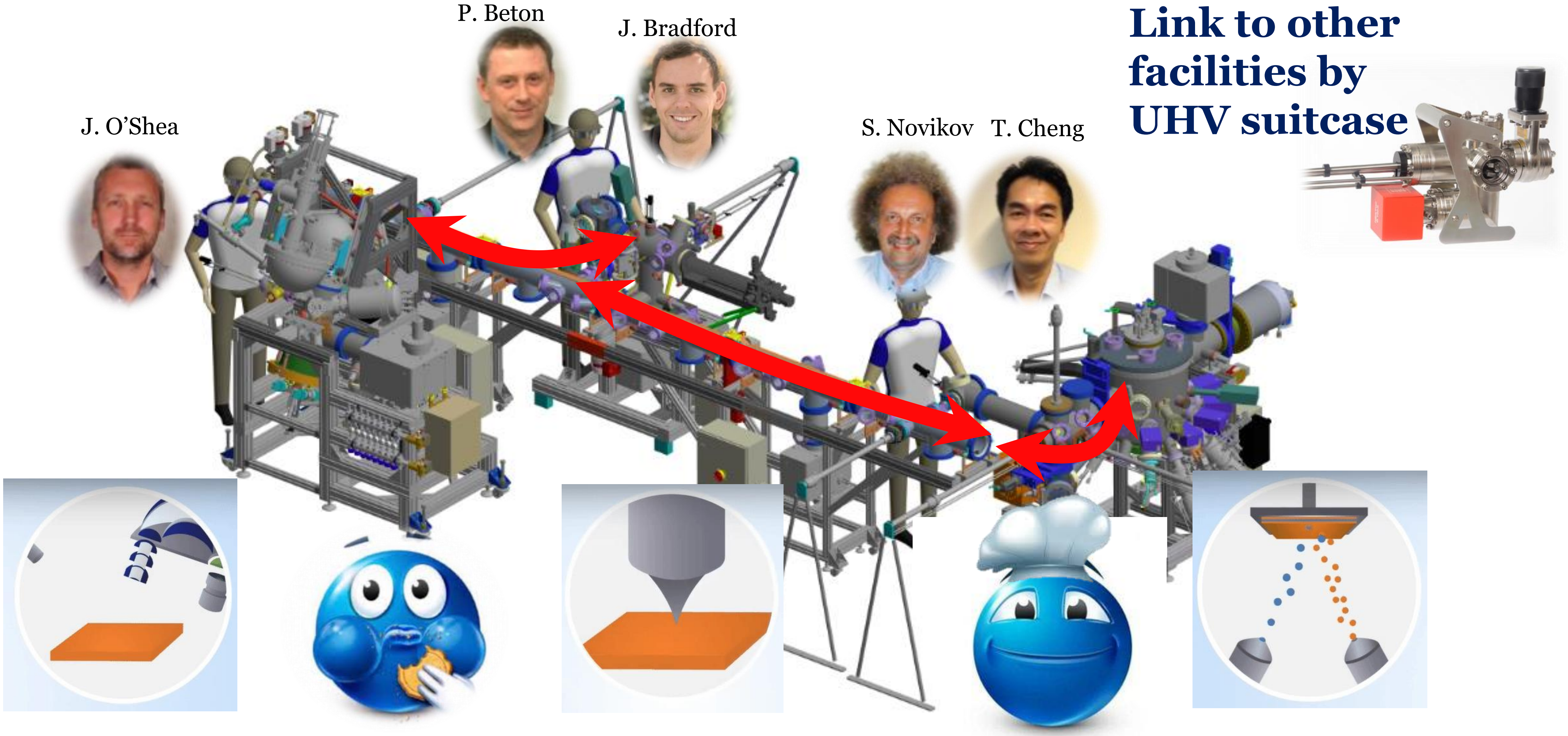
Epitaxy in UHV (up to 3”wafers) for growth of 2SEM with atomic resolution
Focus on In, Se, Ga…



£3.2 m UKRI Strategic Equipment Award 2020-24 (with Scienta Omicron/MBE Komponenten)

EPI2SEM: “Cooking and Tasting”

Link to other facilities by UHV suitcase



£3m UKRI Strategic Equipment Award 2020-24 (with Scienta Omicron/MBE Komponenten)

2021-22 Installation of EPI2SEM

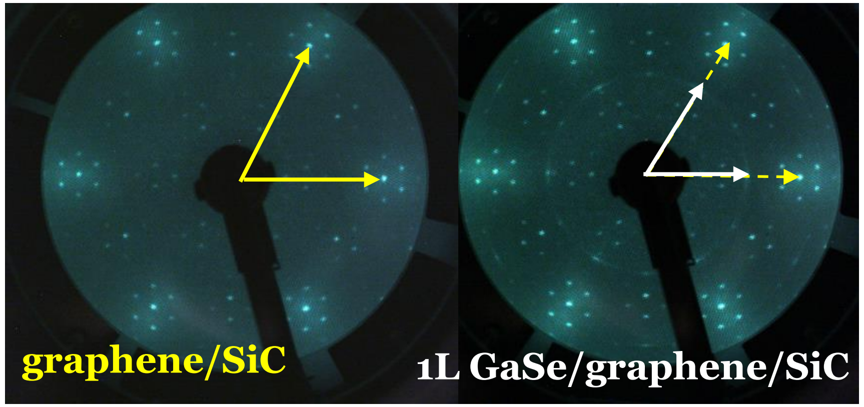
https://www.youtube.com/watch?v=mtXWhMOs9D4

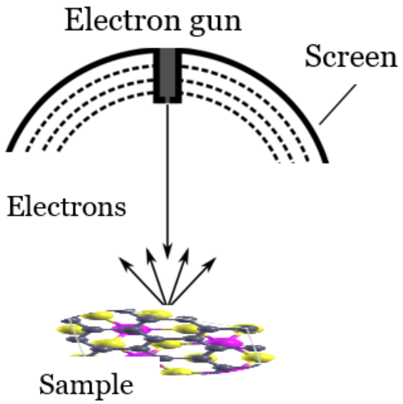
https://www.youtube.com/watch?v=GHCxEDMh3R0

2D GaSe on Graphene

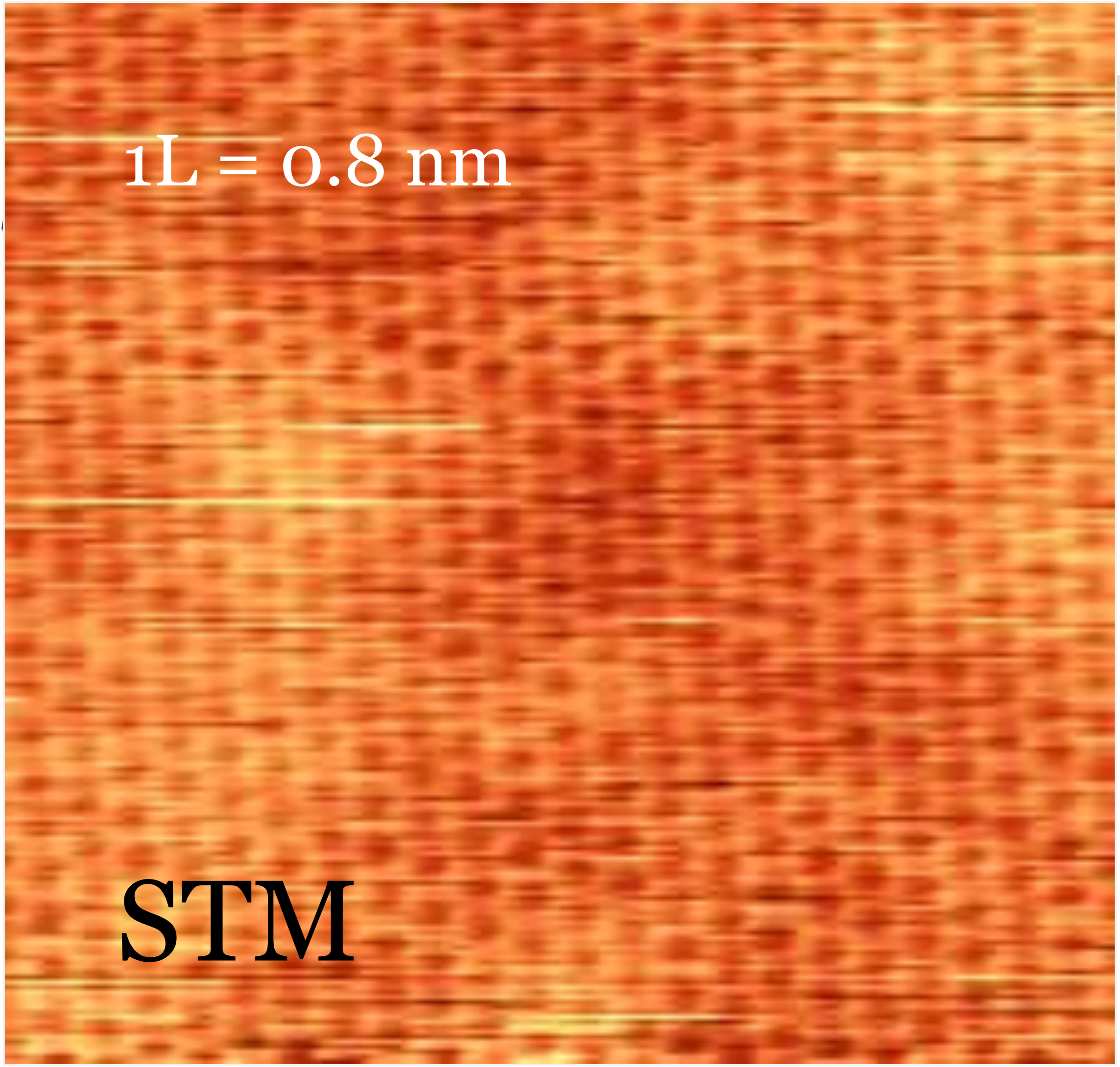
Epitaxy of 2D GaSe on epitaxial graphene

Low-energy electron diffraction (LEED)





Crystallinity and
in-plane alignment of
1 layer (1L = 0.8 nm) GaSe
with graphene



Bradford et al. *Small* 2024

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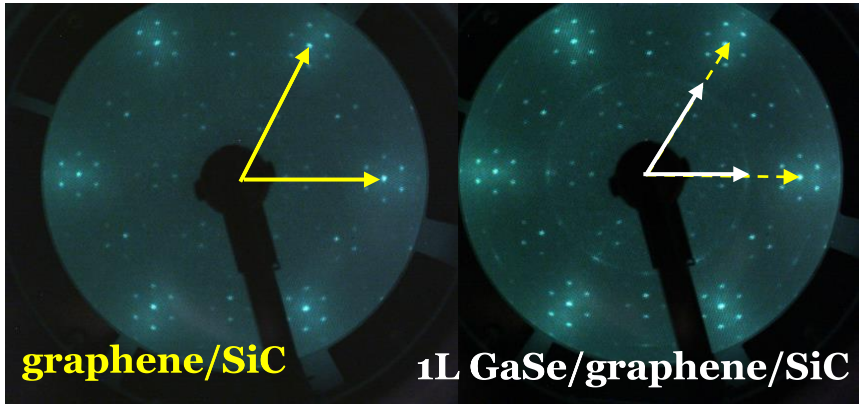
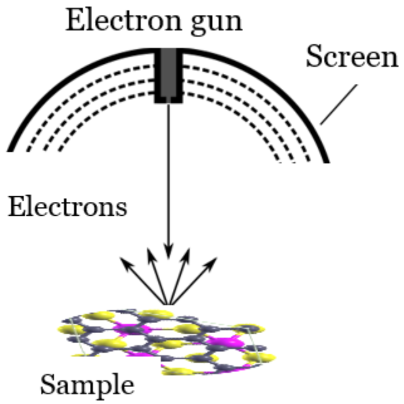
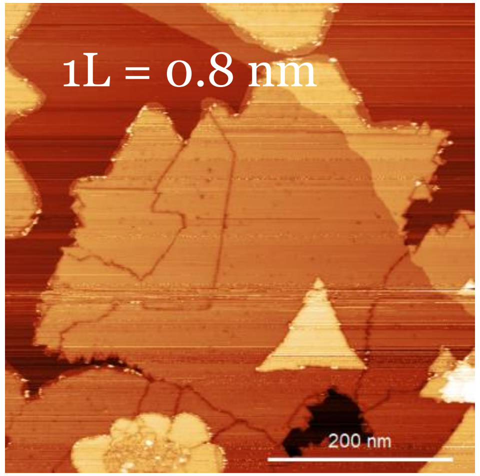
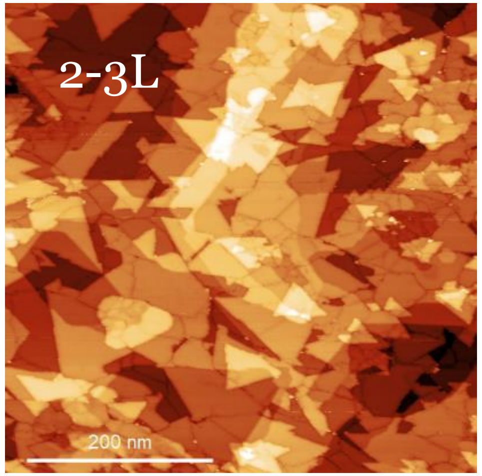
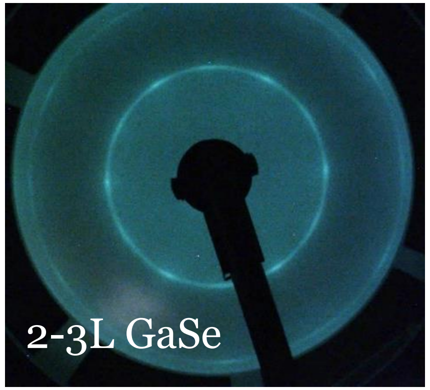
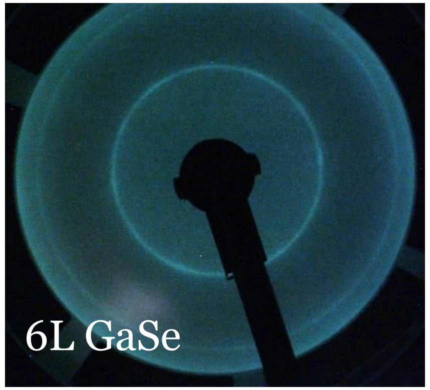


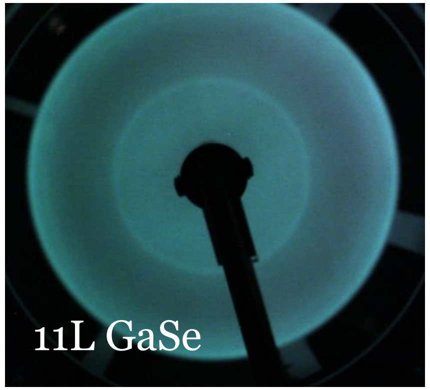












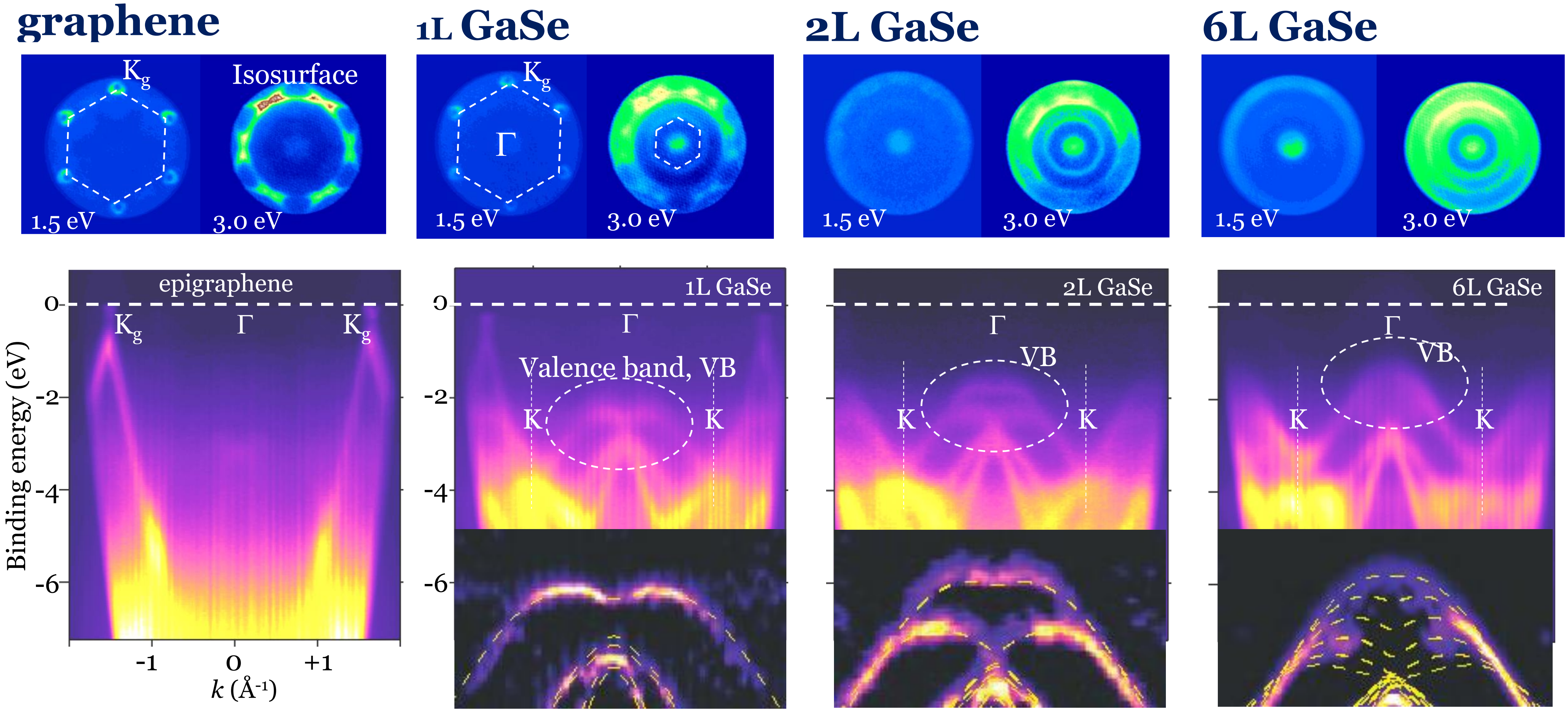
Orientation-disorder in thick layers

In-plane alignment not detected in thicker (> 3L) GaSe due to the small penetration depth of the electron beam and grains with smaller (100 nm) lateral dimensions.

Bradford et al. *Small* 2024

GaSe: Band Structure and Symmetry

Angle Resolved Photoemission Spectroscopy, ARPES



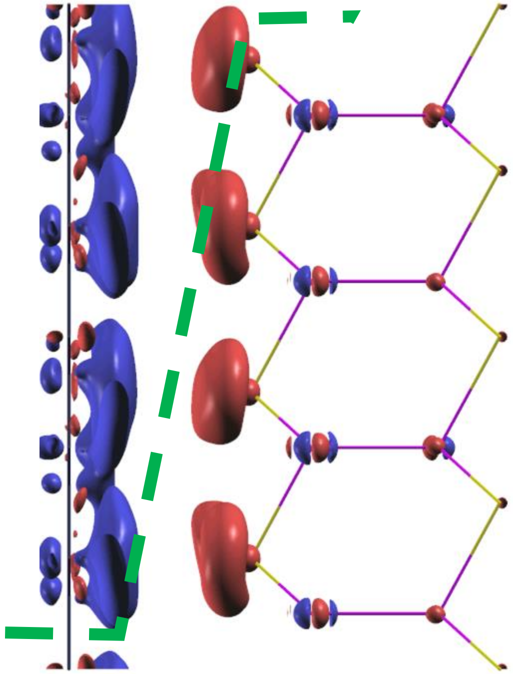
Mexican Hat VB

Mexican Hat VB

Parabolic VB

Interfacial Charge Dipole

Charge Dipole

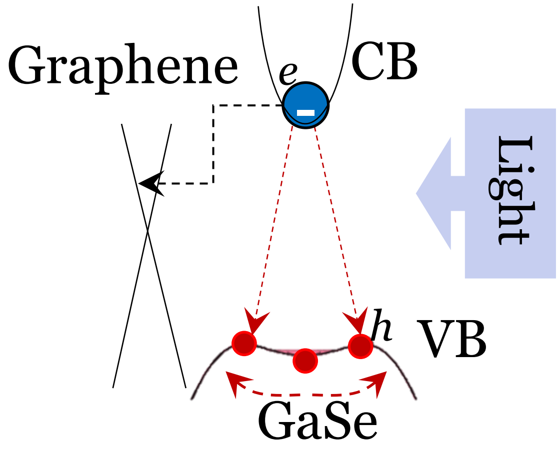


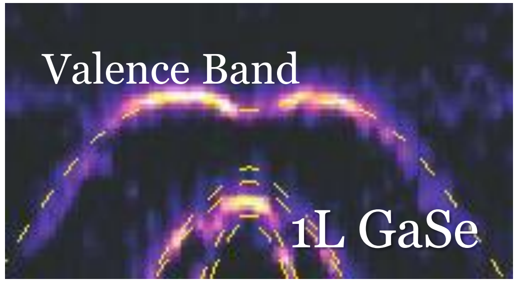
Graphene GaSe

Blue = fewer electrons | Red = more electrons

Built in potential
$\Delta\phi = 0.25$ eV
Modelled by DFT
Measured by UPS

Effects of Light on graphene

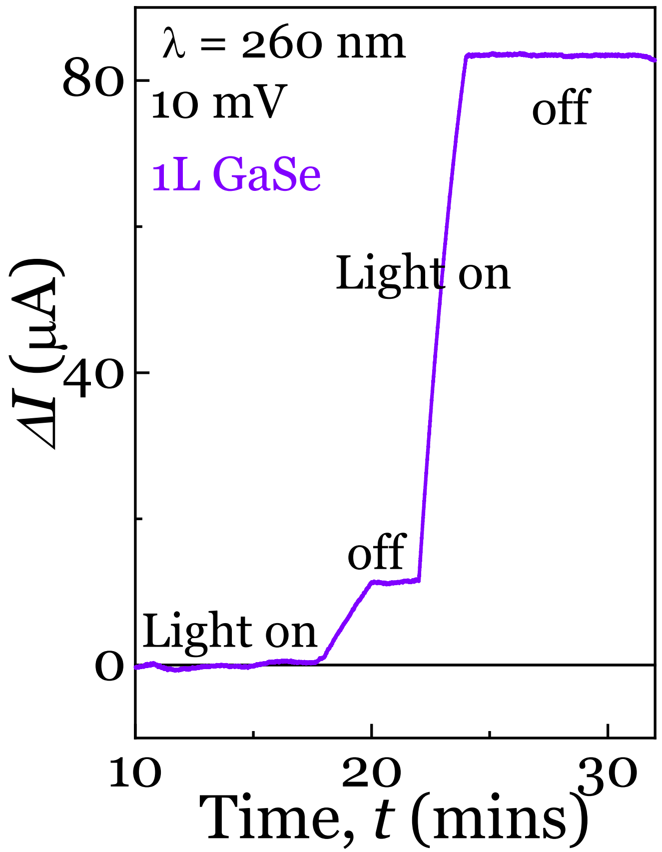




- ❖ e-h created in GaSe
- ❖ Electrons transfer to graphene
- ❖ Holes localized in GaSe

Photo-memory

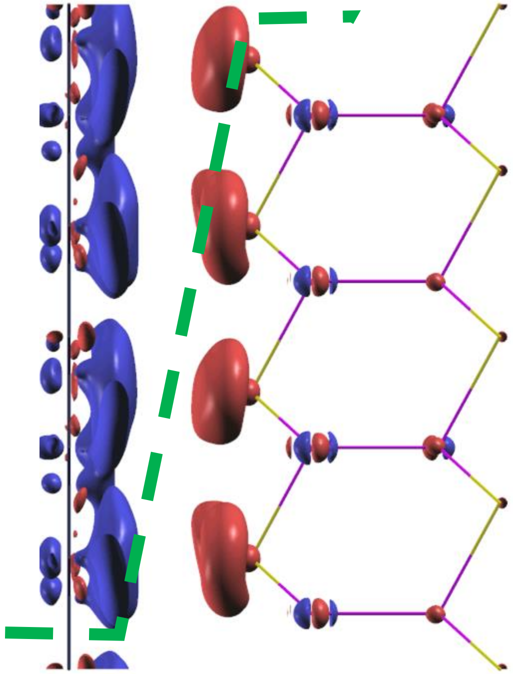
Persistent photocurrent in graphene



Bradford et al. *Small* 2024

Interfacial Charge Dipole

Charge Dipole



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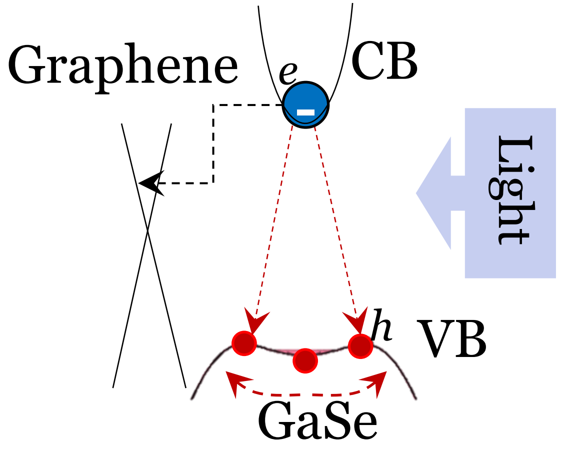

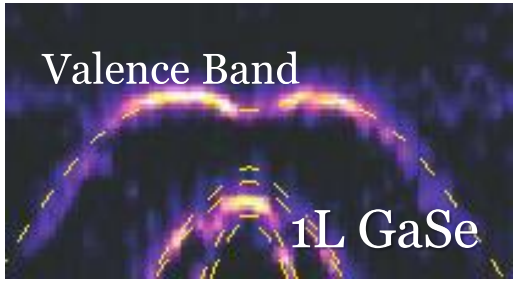

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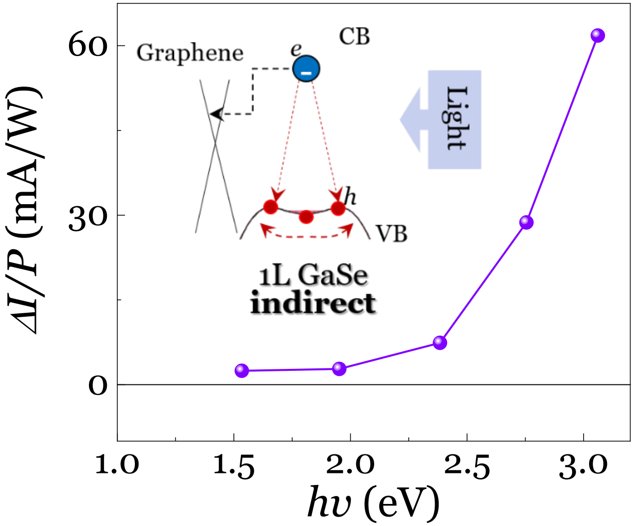
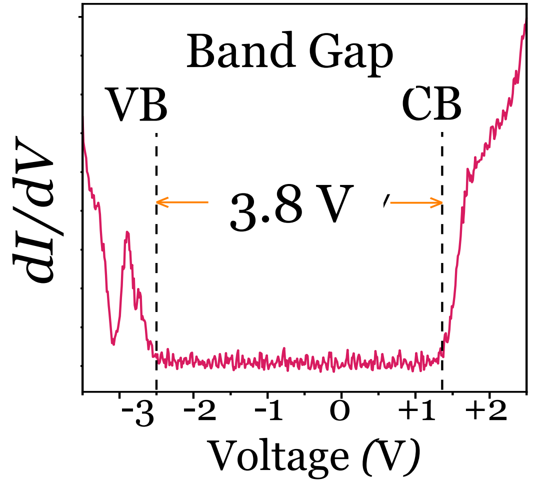
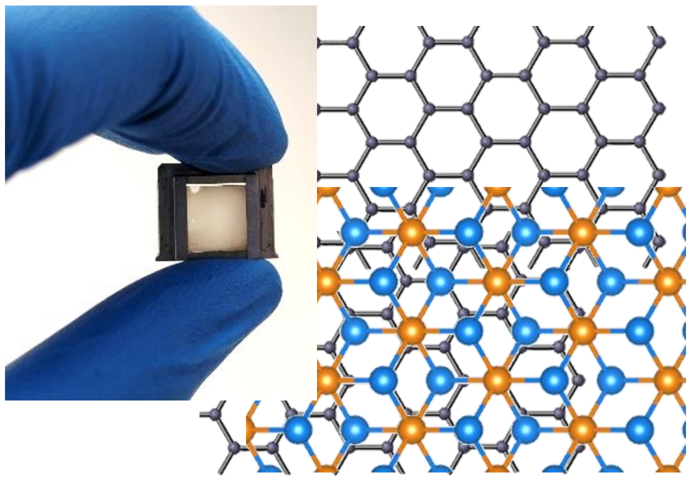


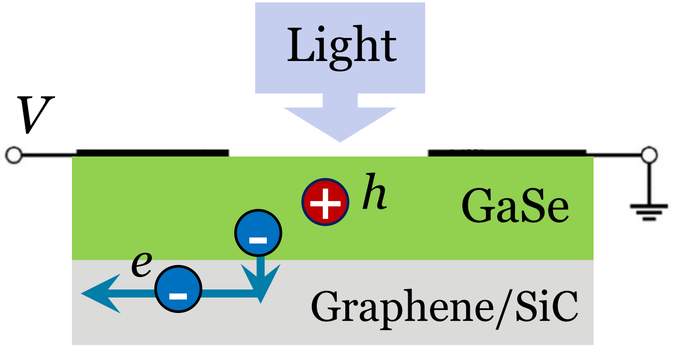


Bradford et al. *Small* 2024

VIS-UV Photonics

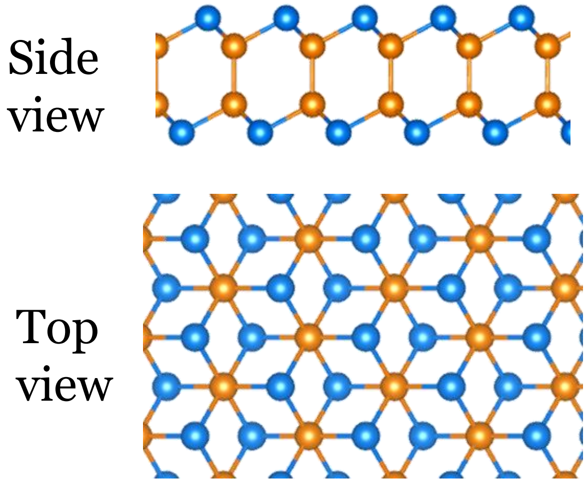
GaSe/graphene/SiC

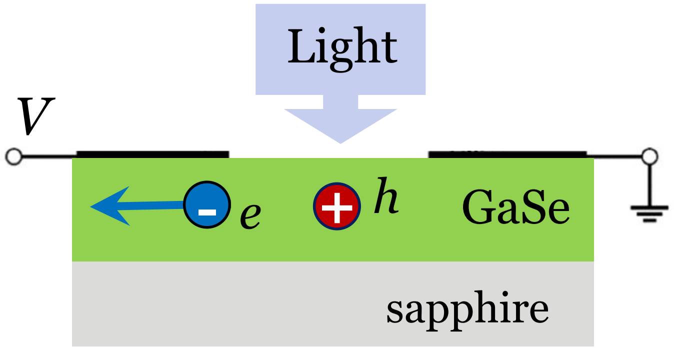




GaSe: Optical channel
Graphene: Transport channel
Bradford et al. *Small* 2024

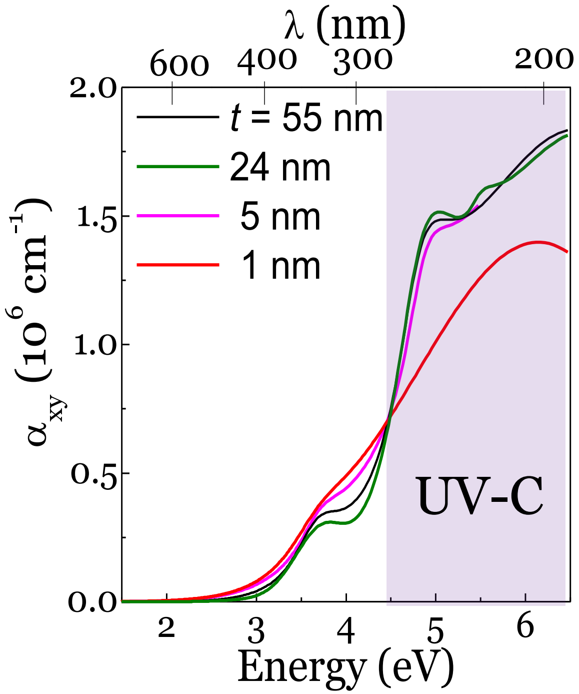
GaSe/sapphire

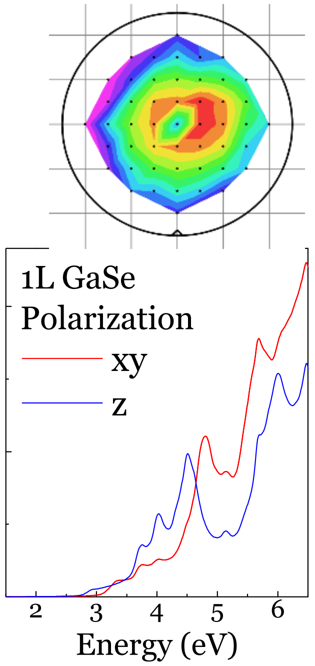


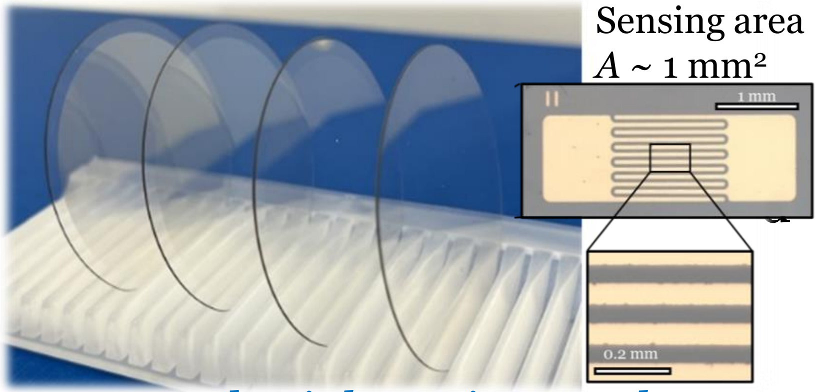


GaSe: Optical & Transport channel
Shiffa et al. *Small* 2024

Ellipsometry: Absorption





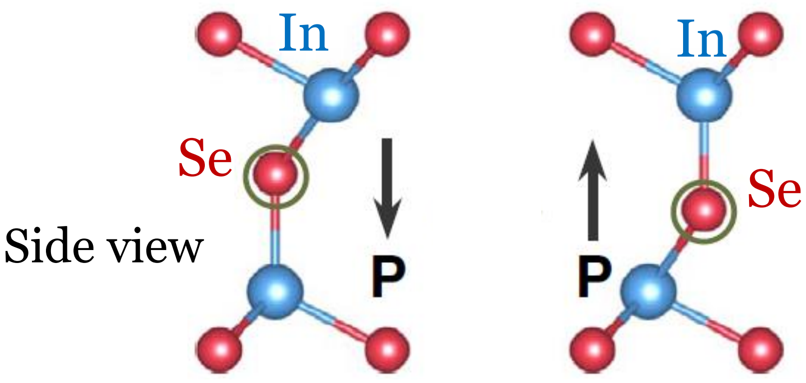


Dewes et al. *Light: Sci. & Appl.* 2025

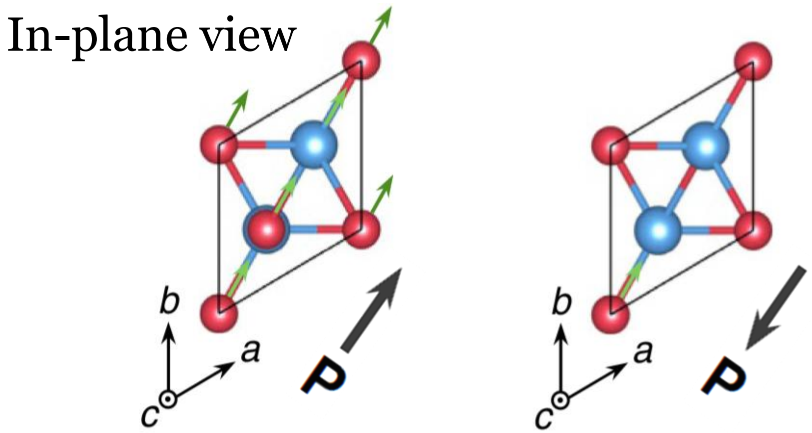
Ferroelectric In_2Se_3

Spontaneous electric polarization P in non-centrosymmetric In_2Se_3

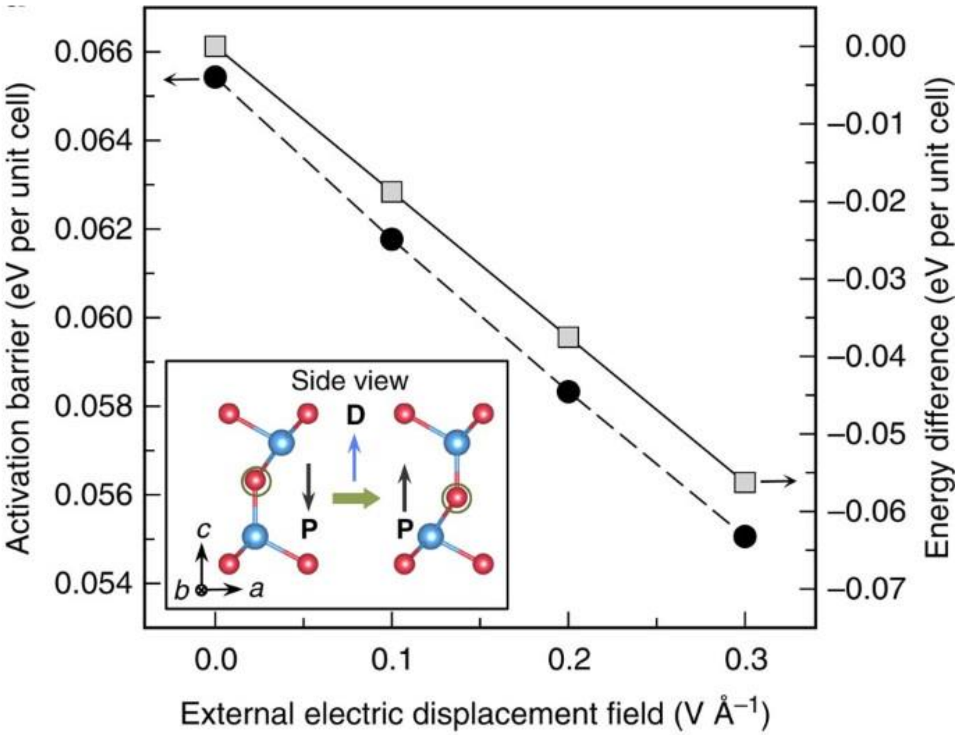
Out-of-plane P



In-plane P



- ❖ The electric field lifts the degeneracy of the two polarized states, thus reversing P.
- ❖ Room temperature polarization with energy difference between polarized states increasing with electric field.

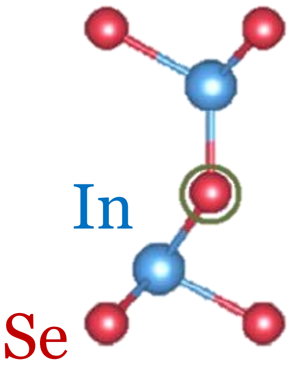


Ding et al. *Nature Com.* 2017

Ferroeletric 2H-α-In_2Se_3: Band Structure

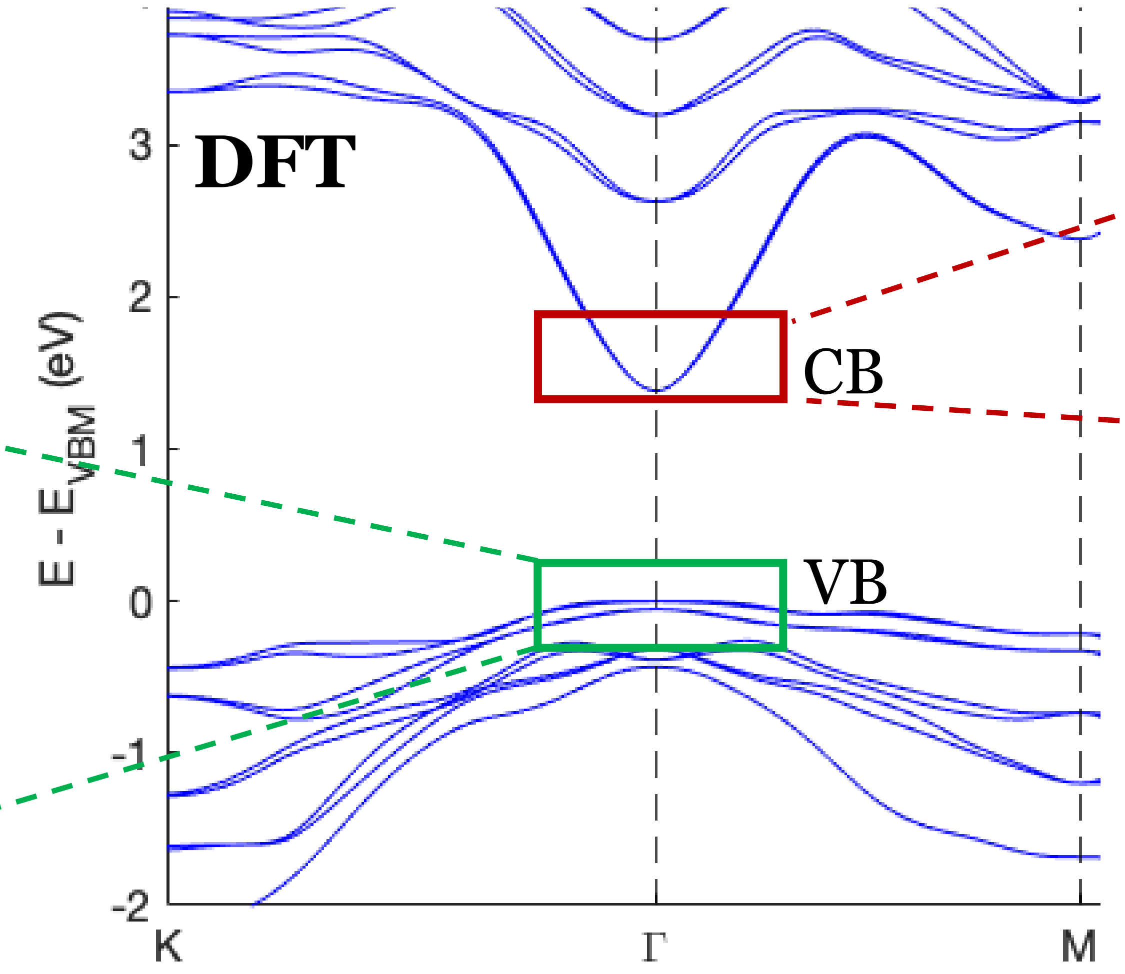
α-In_2Se_3

van der Waals layer

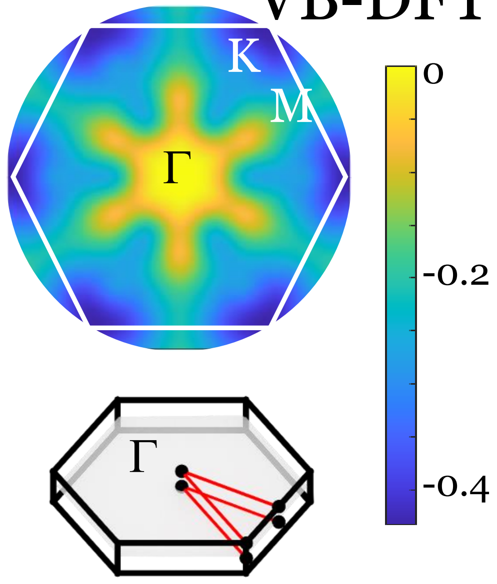


Inverted Mexican-Hat Valence Band, VB

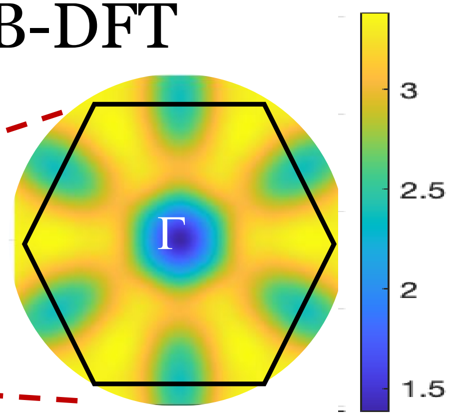
Energy *vs* Momentum



VB-DFT



CB-DFT

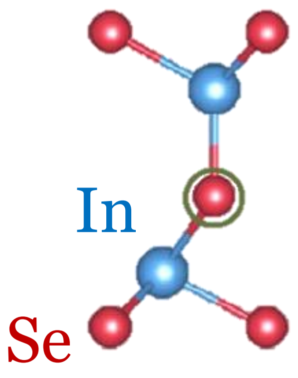


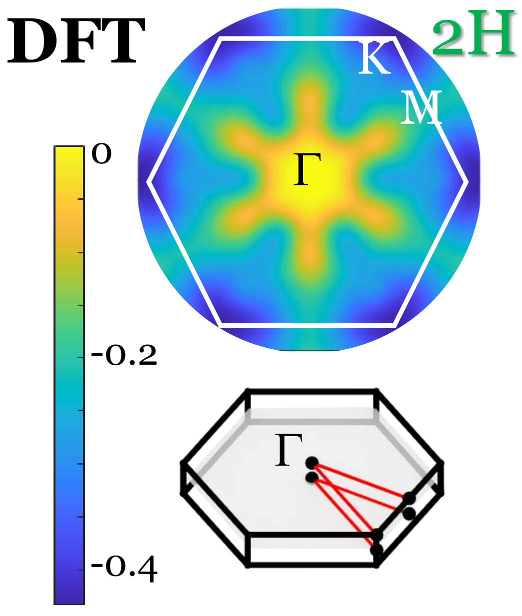
CB minimum at Γ
Light electron
(~ 0.1 m_e)

Felton et al.
Nature Com. 2025

Ferroelectric In_2Se_3: Band structure

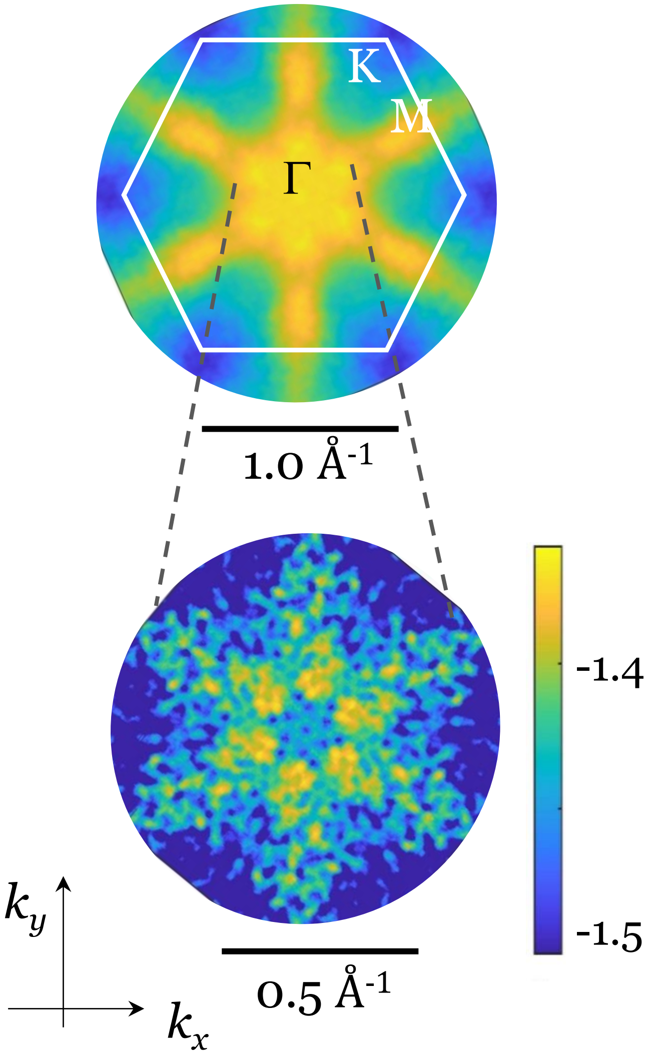
α-In_2Se_3

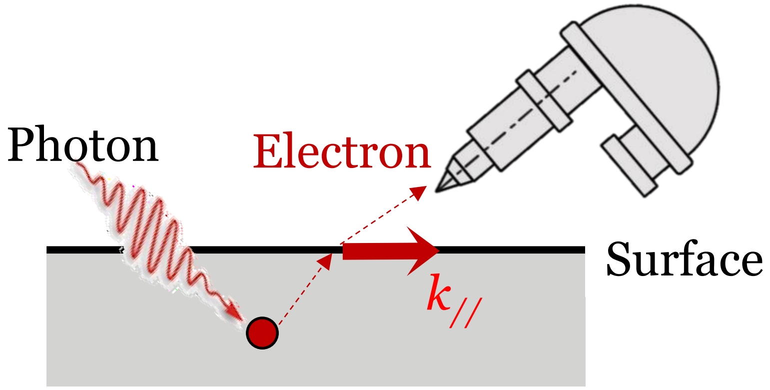


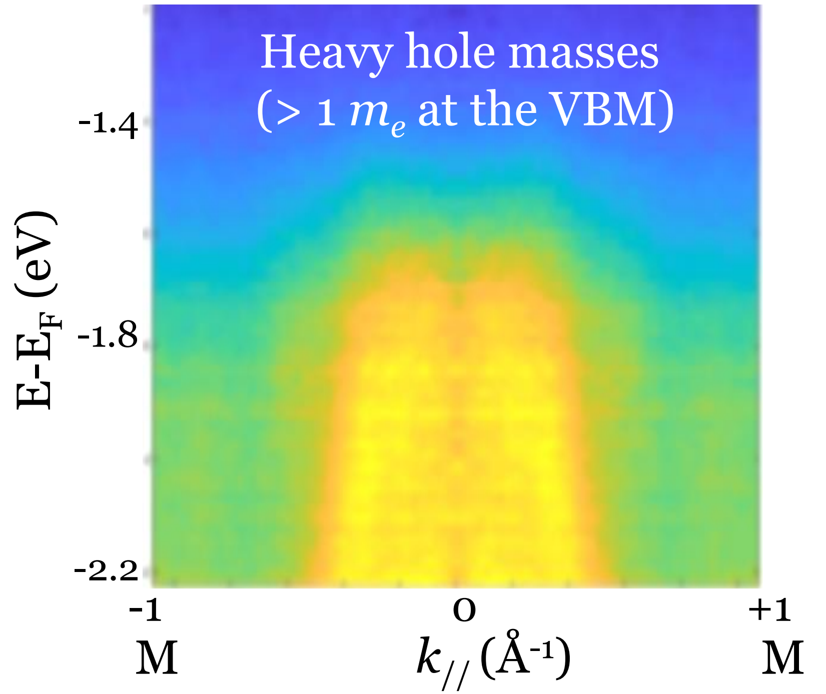


NanoARPES

6 VB maxima along ΓM
6 saddle points along ΓK

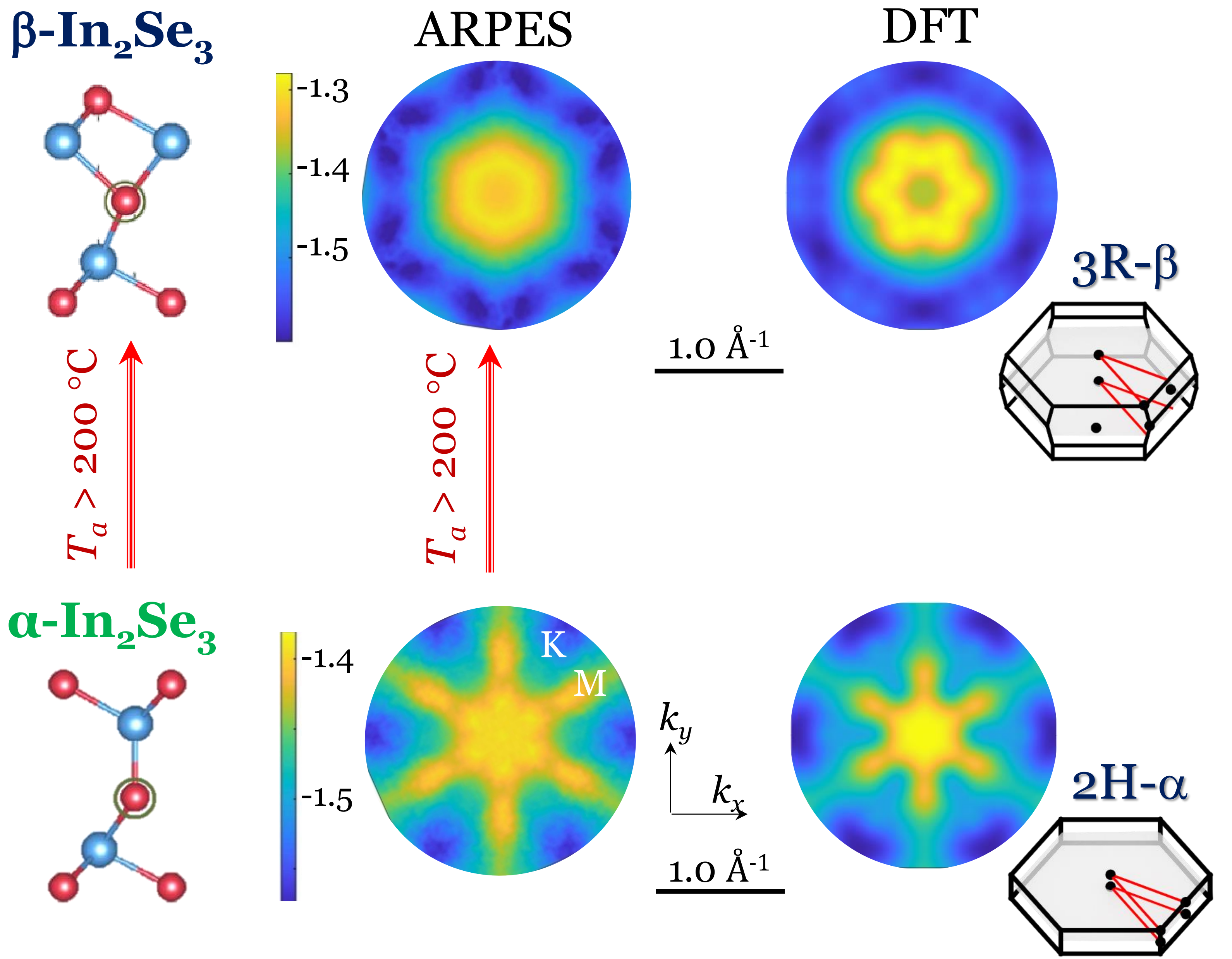




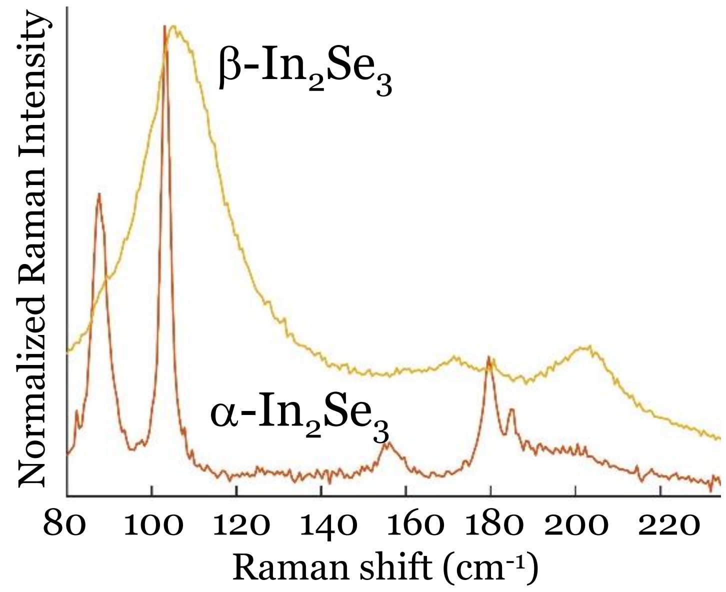


Felton et al. *Nature Com.* 2025

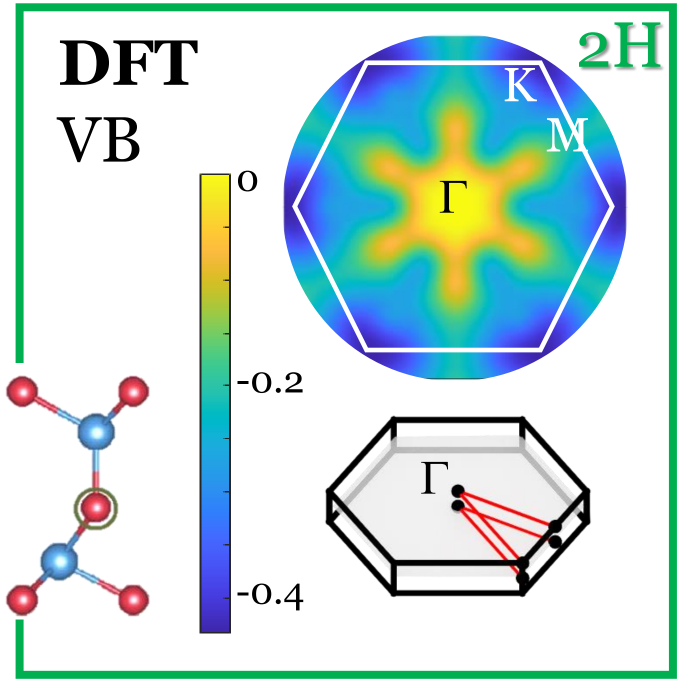
α-to-β Phase Transition

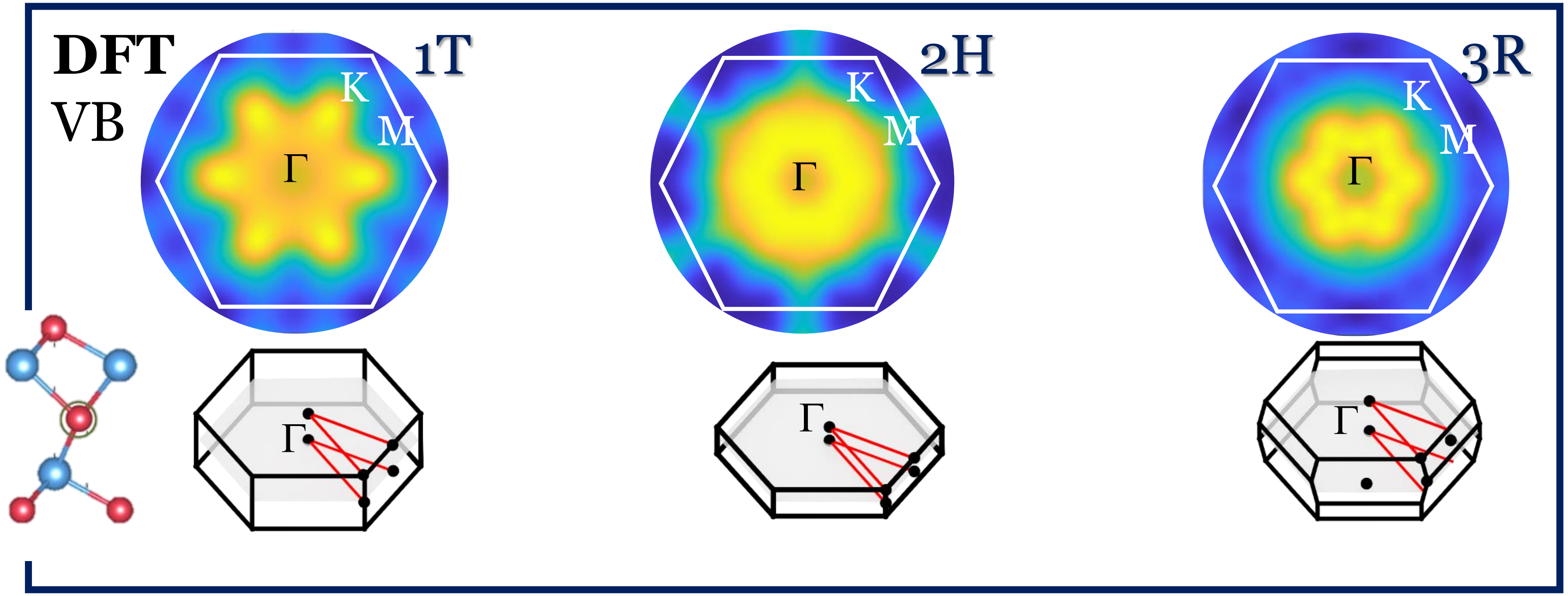


- The β-phase is realized via a structural phase transition at T_a > 200 °C in UHV
- Raman spectroscopy to probe transition from β-phase to α-phase



Zoo of "Mexican Hat" VB





Felton et al. *Nature Com.* 2025

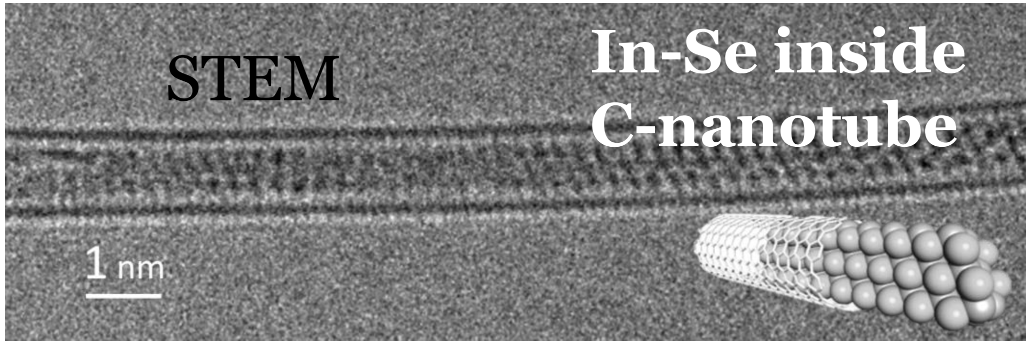
Opportunities: Muliferroic 2SEM

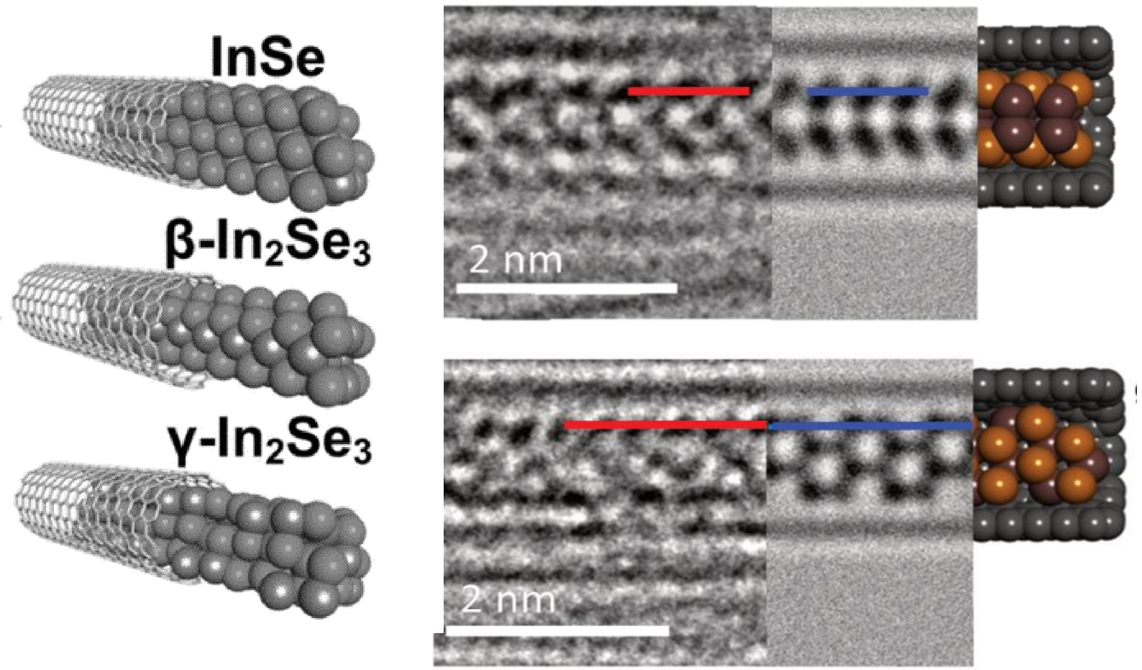
Hole doping can induce robust ferromagnetism in α-In_2Se_3 due to its flat Mexican-hat-shape VB with van Hove singularities. Hole doping can lead to time-reversal symmetry breaking with ferromagnetism and ferroelectricity within a wide range of doping concentrations.

Wang et al. *Adv Elec. Mat.* 2024

From 2D to 1D systems

Encapsulation of 2SEM within C and BN-nanotubes

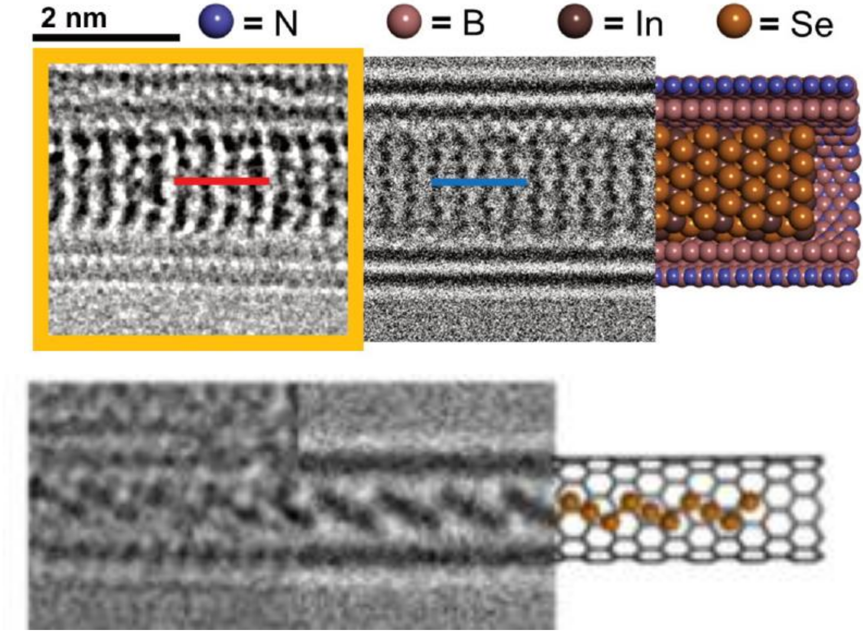




Cull et al. *ACS Nano* 2023

A wide range of polymorphs and nanostructures

In-Se/Se inside a BN-nanotube

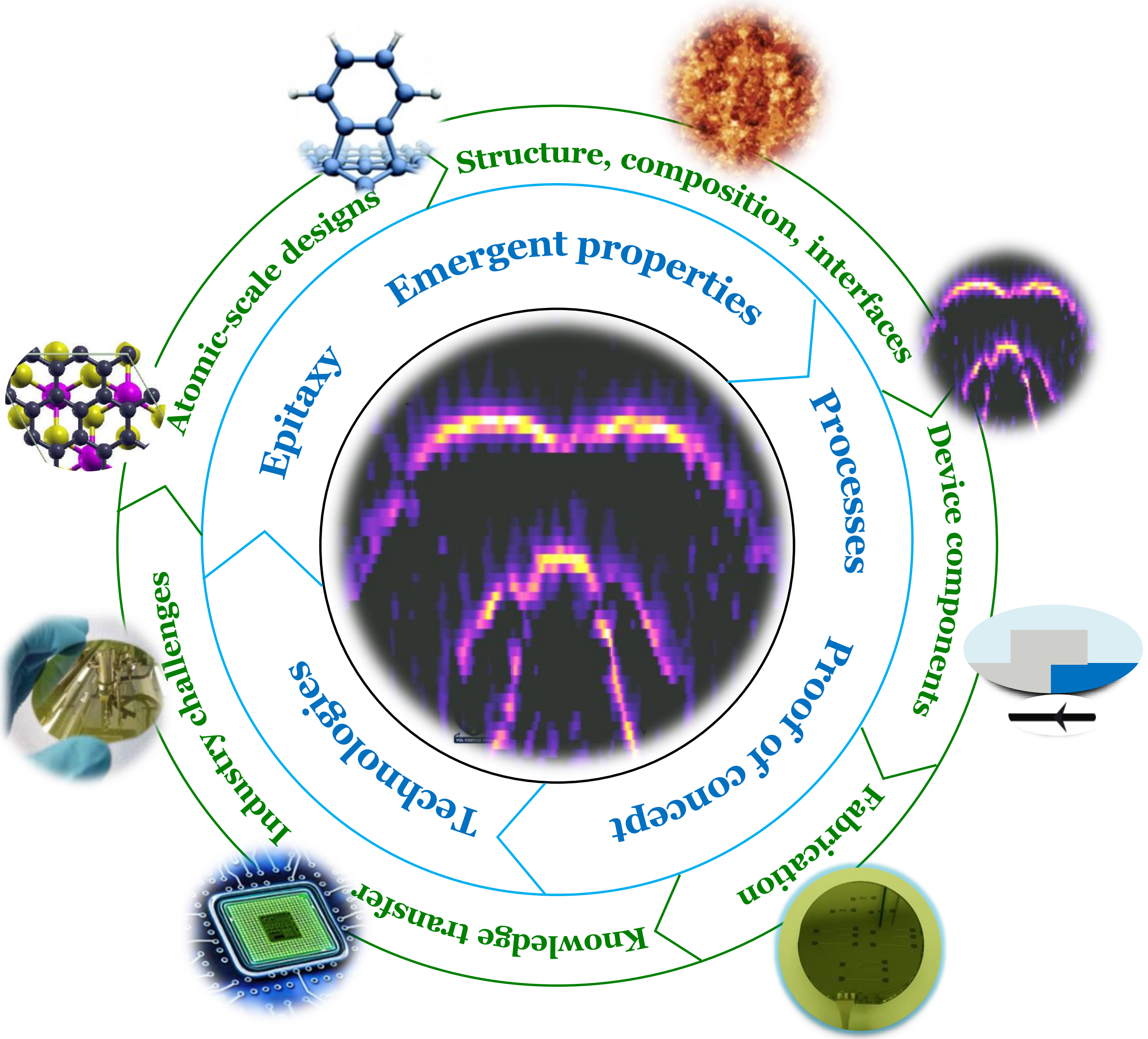


Cull et al. *Adv. Mat.* 2025

UK Research Programme: NEED2D

EPSRC Programme Grant 2025-30, £6.3M

- ❖ Queen Mary University of London, University of Glasgow and University of Nottingham will develop 2SEM for prototype low-energy consumption electronic devices that will reduce electricity demand from data centres/high-performance computing
- ❖ 2SEM produced at wafer-scale
- ❖ > 20 partners in academia/industry (Paragraf)



University of Nottingham
UK China Malaysia

Acknowledgement

Research Fellows/PhDs

J Bradford, Z Kudrynskyi, N Balakrishnan, M Bhuiyan, J Greener,
D Mazumder, G Mudd, S Xie, A Dey,
J Felton, W Yan, M Shiffa,
N Cottam, B Dewes, K Rahman…

Staff

S Novikov, T Cheng,
PH Beton, CJ Mellor, J O'Shea,
L Eaves, O Makarovsky…

…

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