Imaging and Understanding Quantum States in Semiconductors and 2D Materials

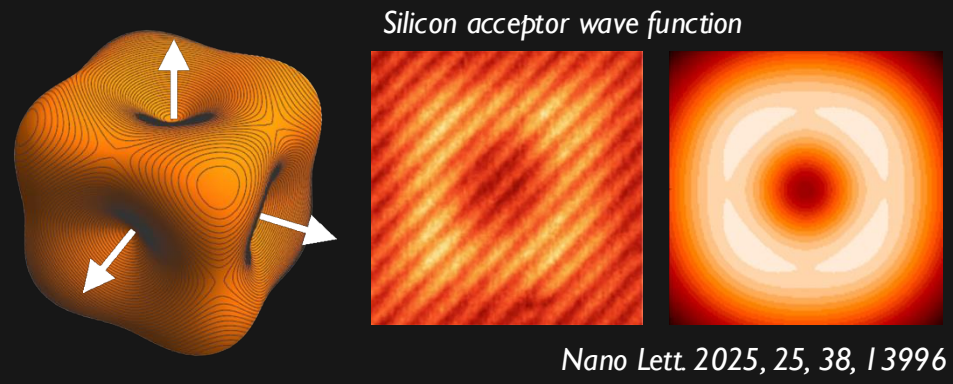
Steven R. Schofield

Professor of Physics

University College London

s.schofield@ucl.ac.uk

schofield-lab.github.io



Nano Lett. 2025, 25, 38, 13996

PhD studentships available, including: "Mapping the Quantum Landscape of 2D Materials, One Atom at a Time"

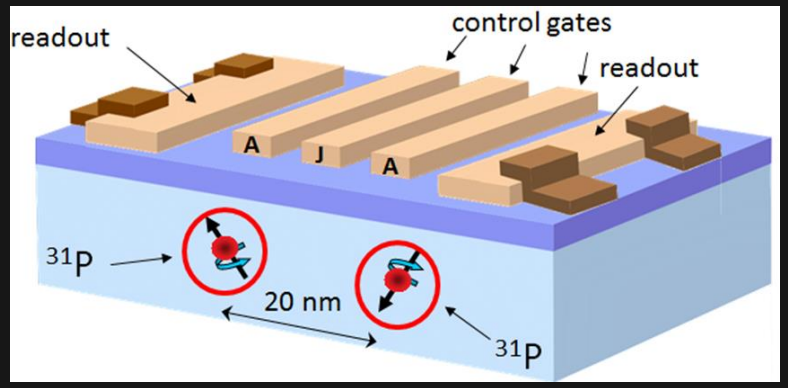
Deterministically positioned defects → scalable quantum technologies

- Single dopant atoms can be positioned deterministically in semiconductors using STM
- Enabling atomically-precise quantum devices
- Scaling to many dopants is essential for qubit arrays and quantum architectures

See also: Roadmap on atomic-scale semiconductor devices, Schofield et al., Nano Futures 9 012001 (2025)

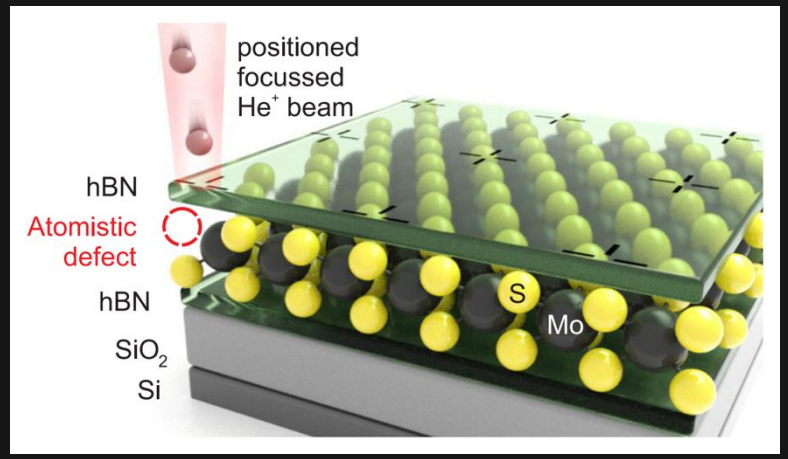
- Single atomic defects can also be created deterministically in 2D materials (e.g., MoS_2, hBN), enabling quantum emitters, photonic circuits, and single-atom devices

Single Dopant Atoms in Si as Qubits



Kane, Nature **393** 133 (1998)

Atomically Precise Positioning Defects in MoS_2



Nano Letters, 20, 4437 (2020)

Fabrication to Understanding: Exploring the Foundations of Atomic-Scale Devices

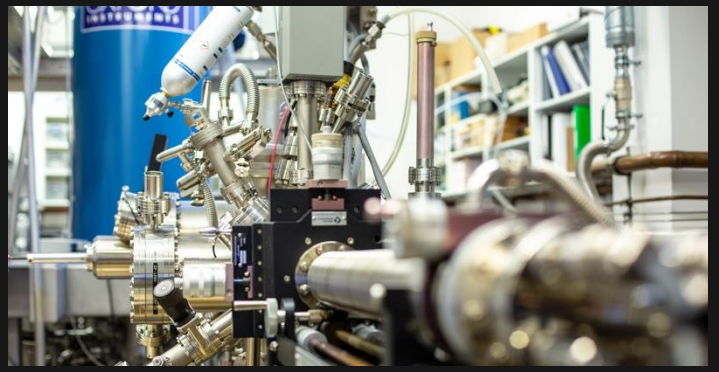
We study atomic-scale quantum phenomena, helping to build the scientific foundation for future atomic-scale device concepts:

- Surface chemistry and adsorption studied using STM
- Surface and sub-surface defect and dopant states probed using tunnelling spectroscopy
- Band and valley structure characterised with ARPES
- EUV-surface interactions to understand → atomic-scale patterning mechanisms
- Electronic structure and defect wave functions modelled computationally (in-house and with collaborators)

Constantinou et al., Nature Commun. 15, 694 (2024)

Tseng, et al., Science Advances 9, eadf5997 (2023)

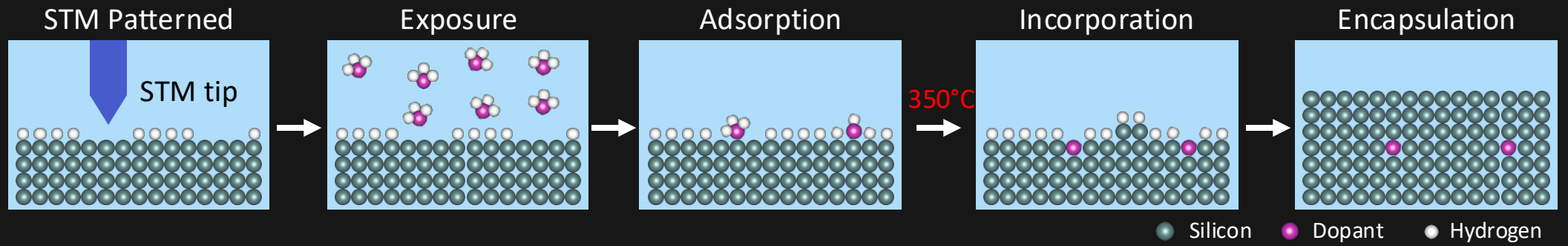
Cryogenic Scanning Tunnelling Microscopy



Synchrotron (ARPES, EUV Patterning)

High Performance Computing

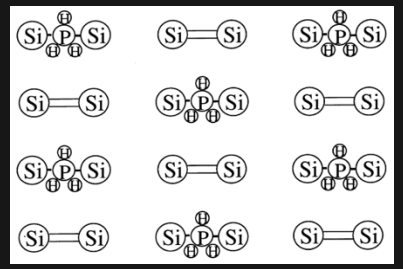
Fabrication strategy: atomic-scale dopant devices in semiconductors



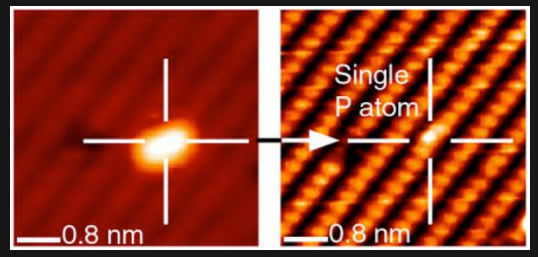
- Hydrogen terminated silicon patterned by STM
- Dopant precursors adsorb onto exposed silicon
- Annealing incorporates dopants; MBE overgrowth encapsulates them
- Single dopants first positioned in 2003
- Single-atom devices demonstrated (e.g., the single-atom transistor)

Atomic-scale dopant devices

Dopant placement concept

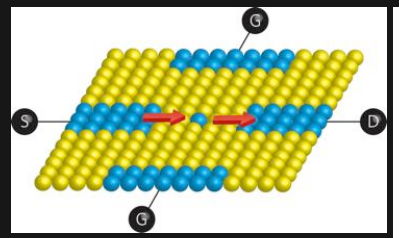


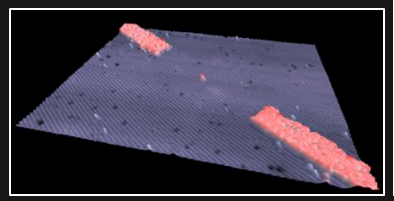
Tucker & Shen, Solid. State. Electron. 42 1061 (1998)

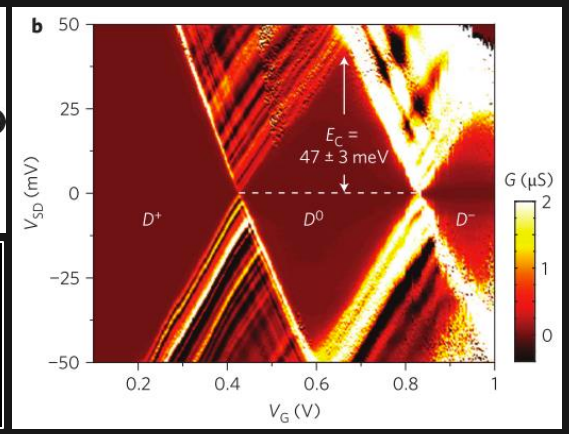


Schofield, et al., PRL 91, 136104 (2003)

Single-atom devices





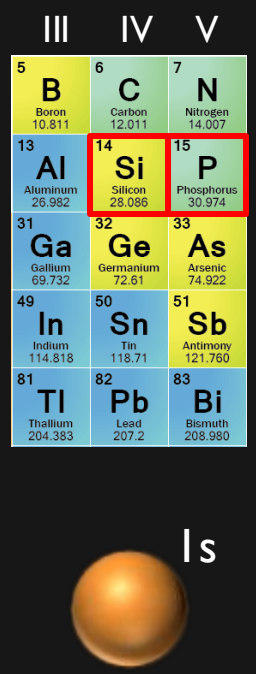


Fueschle et al., Nature Nano. (2012)

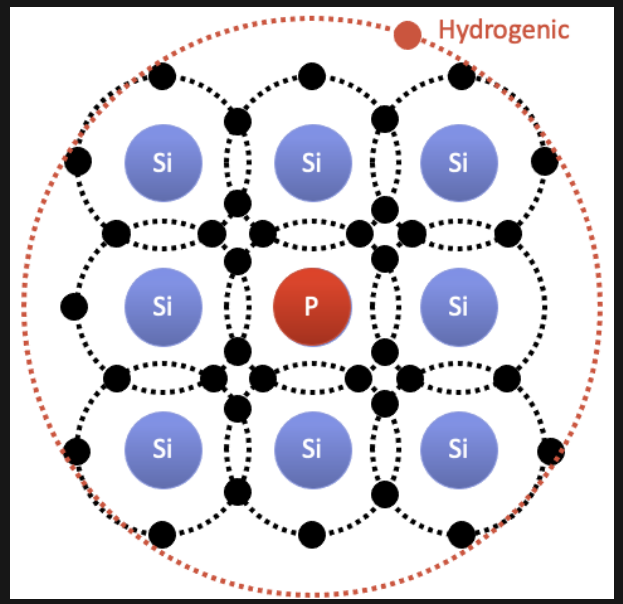
Group-V donors in Si behave like hydrogen: 1s, 2p,…

- Substitutional group-V atoms in silicon (P, As, Sb, Bi) donate one electron which can be bound in hydrogen-like defect states, 1s, 2p, …
- Valley–orbit coupling lifts the six-fold degeneracy
  → unique A_1 ground state
- Binding energy and Bohr radius depend systematically on the donor species

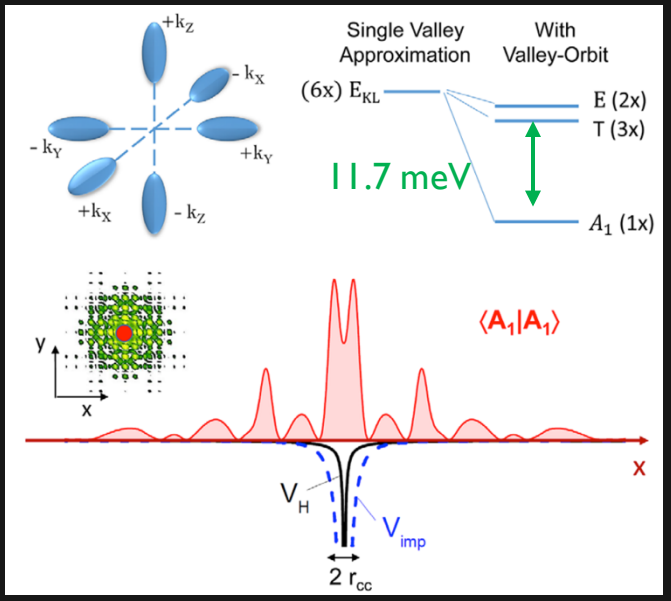
Donor Physics in Silicon



Donor schematic



Valley-Orbit Interference



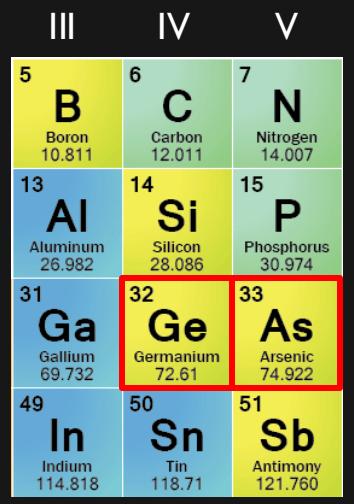
J. Phys. Condens. Matter **27**, (2015)

Bohr radius ~1 nm
Valley interference → oscillatory wave function
A_1 ground state, $E_B \approx 45$ meV (P in Si)

Germanium for Atomic-Scale Quantum Technologies

Why Germanium?

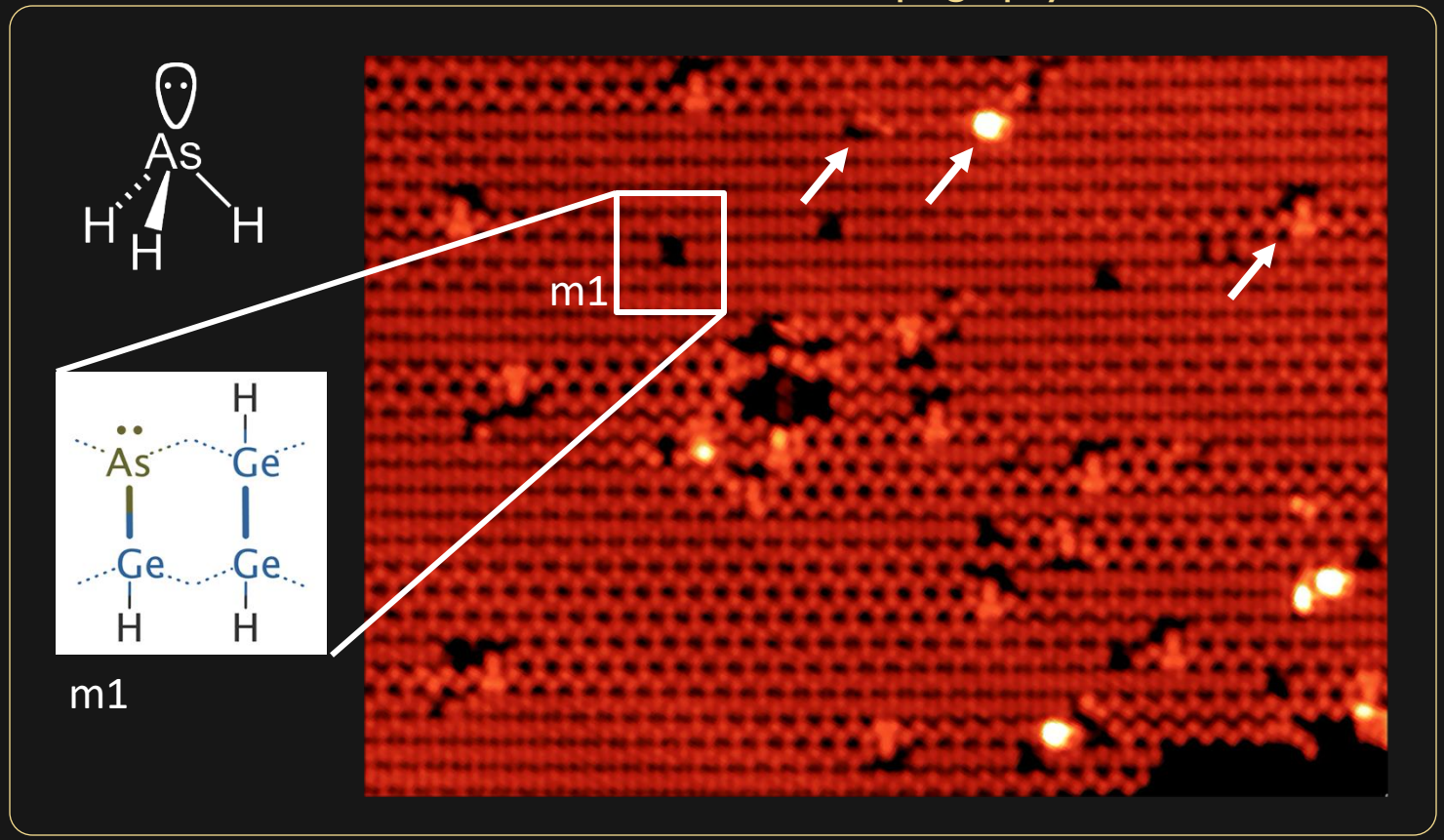
- Larger Bohr radius → wider qubit spacing
- Stronger Stark effect
- Reduced exchange oscillation sensitivity
- Long donor spin coherence times (~ms)
- Isotopically purified & industry compatible



Why Arsenic?

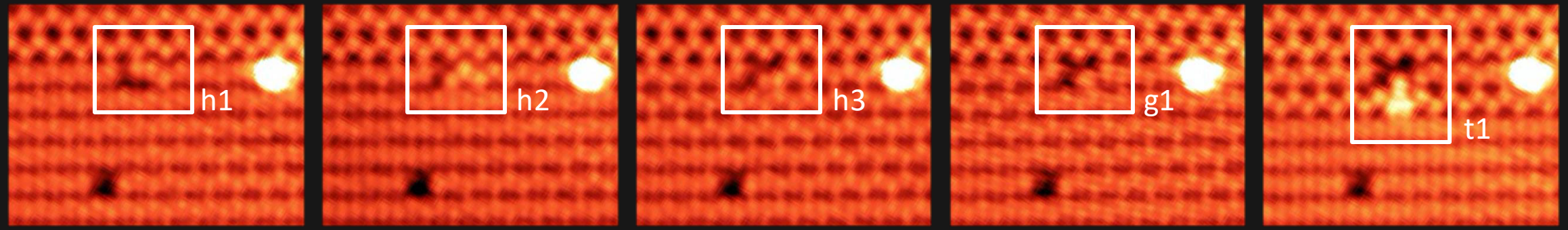
Arsine fully dissociates at room temperature on Ge(001), leading to As incorporation into the surface

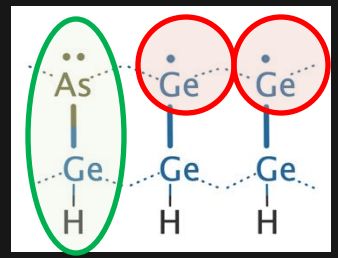
Atomic-resolution STM topography



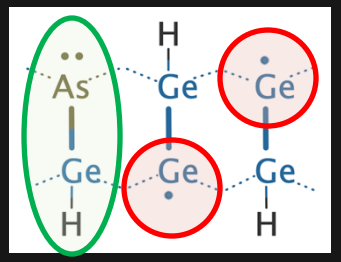
Dynamic behavior of features in STM data

Structures are assigned based on their calculated stability, their appearance, and observed transitions.

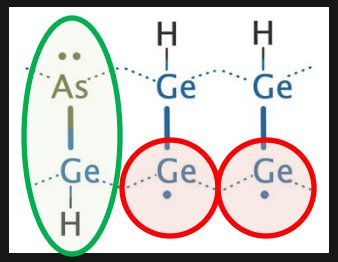




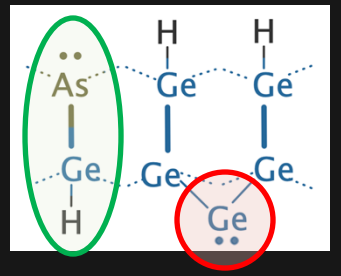
h1
(-2.8 eV)



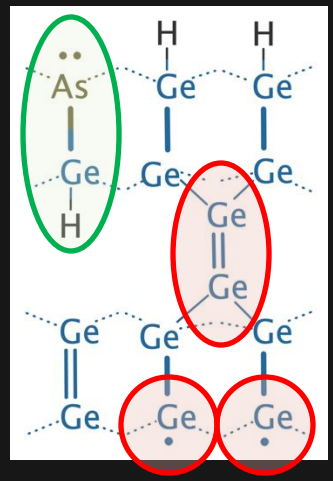
h2
(-2.8 eV)



h3
(-2.8 eV)



g1
(-2.9 eV)

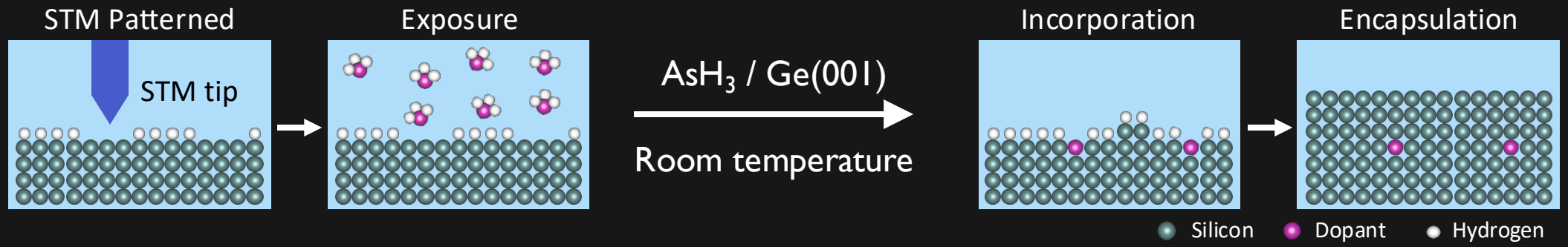


t1

Energies are from Gaussian 16 DFT calculations, B3LYP, 6-311G++(2df,2pd), see manuscript for details.

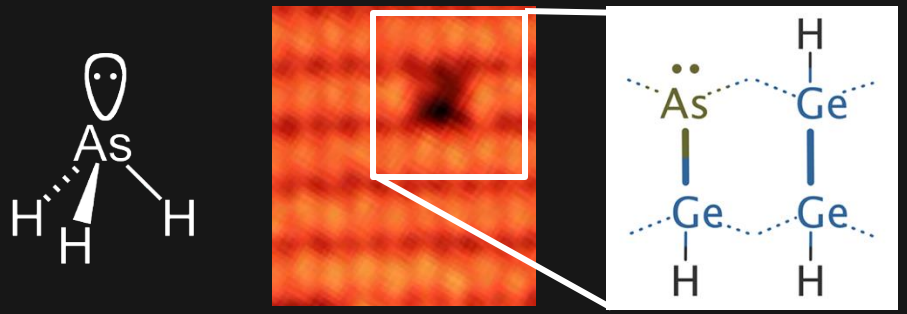
Hofmann, et al., Angewandte Chemie, 62, e202213982 (2023)

A New Surface-Chemistry Advantage for Germanium Quantum Technologies

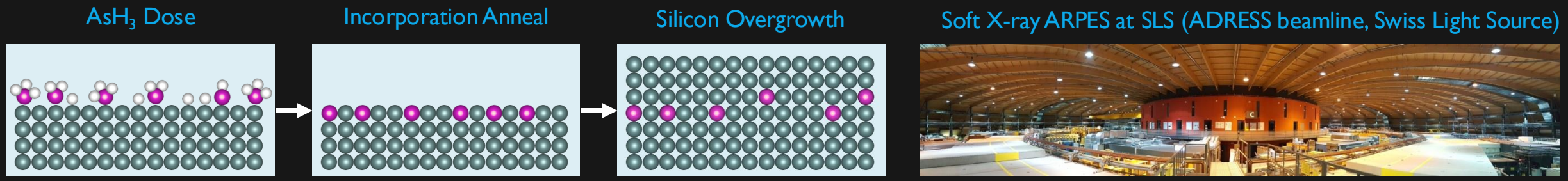


- Eliminating the incorporation anneal for arsenic in germanium compared to phosphorus in silicon removes a major obstacle to scaling deterministic donor arrays.
- This positions germanium as a compelling material platform for next-generation atomic-scale quantum technologies.
- Next steps: develop hydrogen-lithography methods to deterministically create the m1 incorporated structure.

Arsenic room temperature incorporation

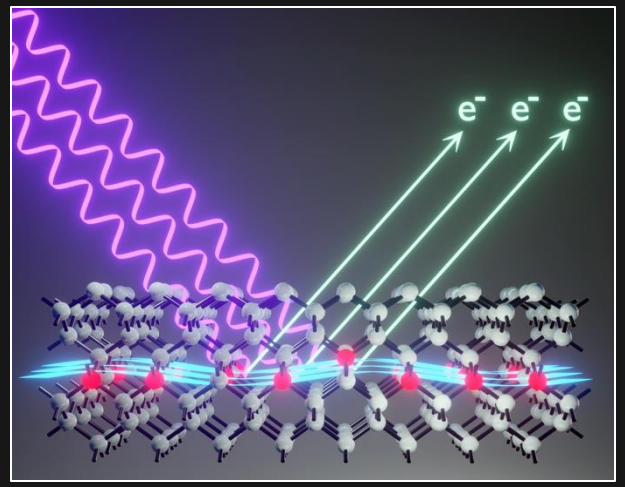


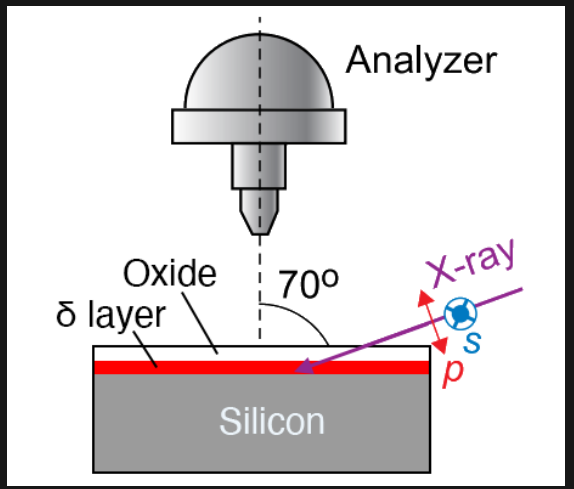
Electronic Structure of Atomic-Scale δ-Doped Layers Probed with SX-ARPES



- δ-layers are atomic planes of dopants confined in crystalline silicon.
- δ-layers provide a pathway to 2D electron liquids with high densities (10^{14} cm^{-2}).
- SX-ARPES directly accesses the buried δ-layer's quantized sub-band structure and a way to measure their out-of-plane electronic thinness.

- Angle-resolved photoelectron spectroscopy (ARPES)
- Soft x-rays (300–820 eV) gives subsurface sensitivity (electron escape depth $\lambda_e \approx 2$ nm).
- 12 K sample environment, 50–90 meV / 0.1° resolution. Spot size ~10 × 72 μm².

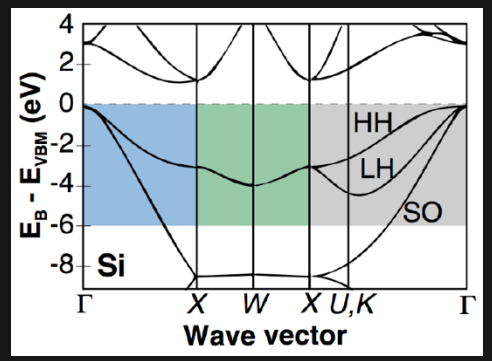




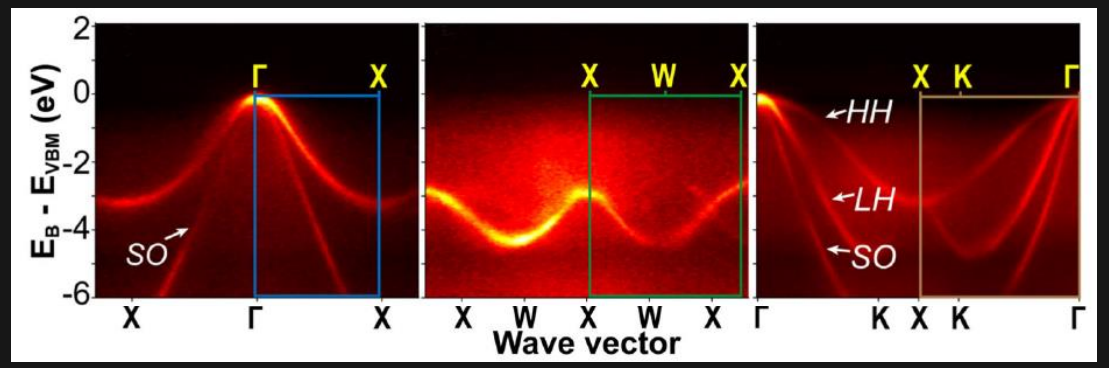
Resolving Quantum-Confined States in δ-Doped Silicon with SX-ARPES

- Valence bands are well resolved, including heavy hole (HH), light hole (LH), and split-off (SO) bands.

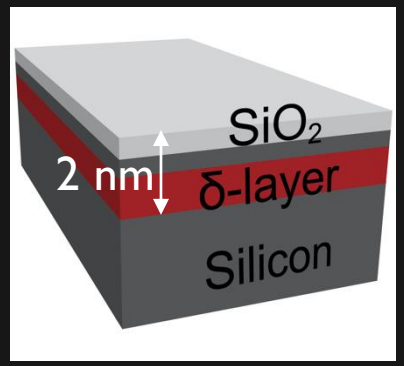
Si band structure



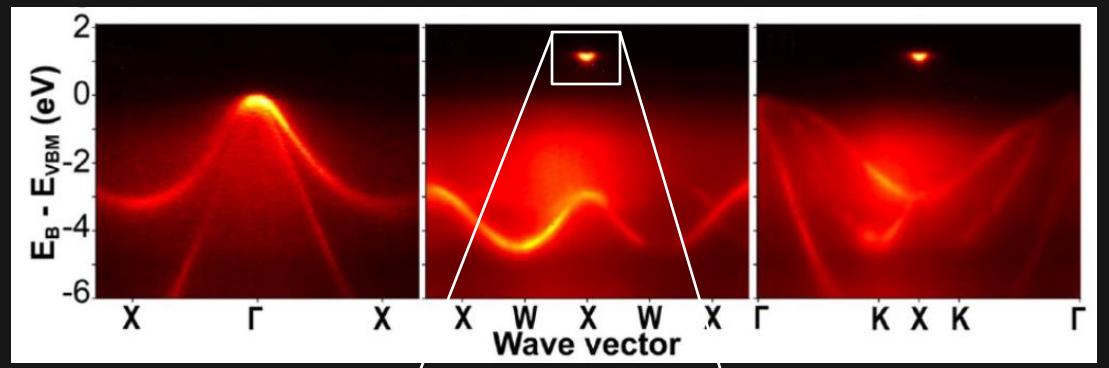
ARPES of bulk silicon



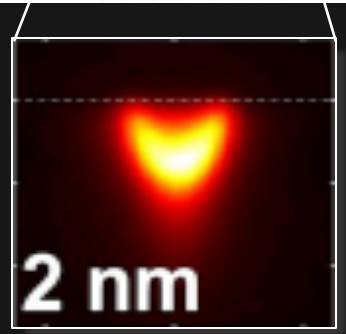
- Fabricated an arsenic δ-layer with 2 nm Si overgrowth.
- The δ-layer donor band pockets appear near the conduction-band minimum close to the X points in the spectra.
- Quantum confinement in the δ-layer produces discrete subbands at the CBM.



ARPES of δ-doped silicon



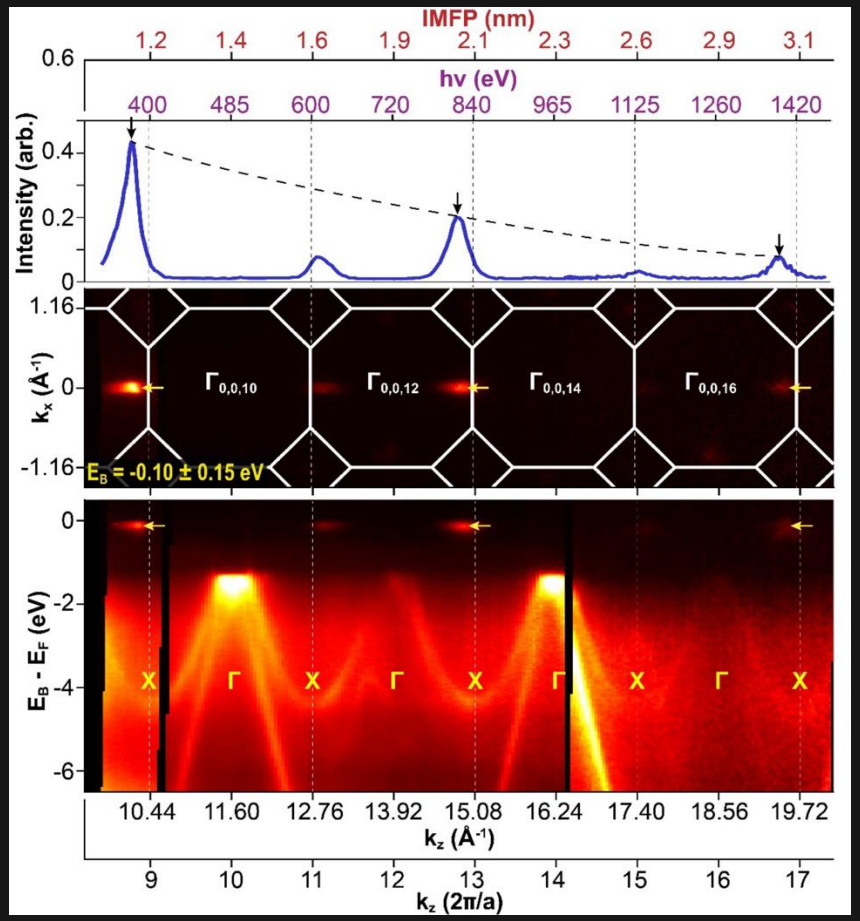
Constantinou et al., Advanced Science, 2302101 (2023)



Oscillating photoemission intensity in k_z for the δ layer state

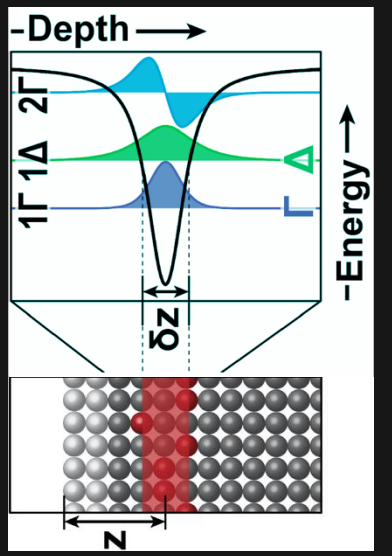
- δ-layer confinement produces a 1D envelope function in z, modulated by an oscillatory Bloch component.
- The interference between the envelope and Bloch components produces a photon-energy–dependent oscillation in k_z.
- The resonance width in k_z is inversely related to the envelope's spatial extent, providing a direct measure of the confinement length.

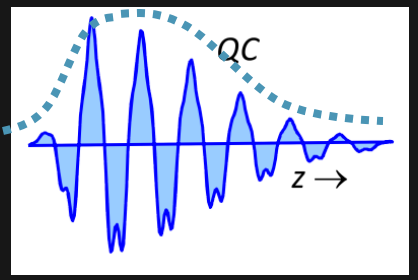
Oscillatory photoemission response in k_z



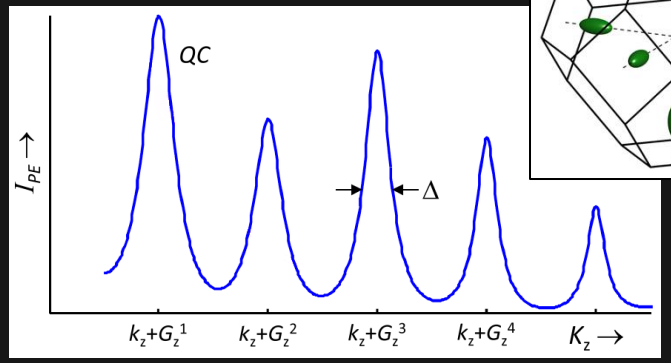
Constantinou et al., Advanced Science, 2302101 (2023)
Van Venrooij, et al., In preparation

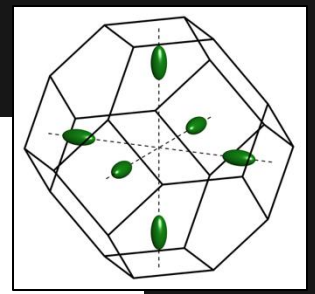
δ-layer potential and wave function





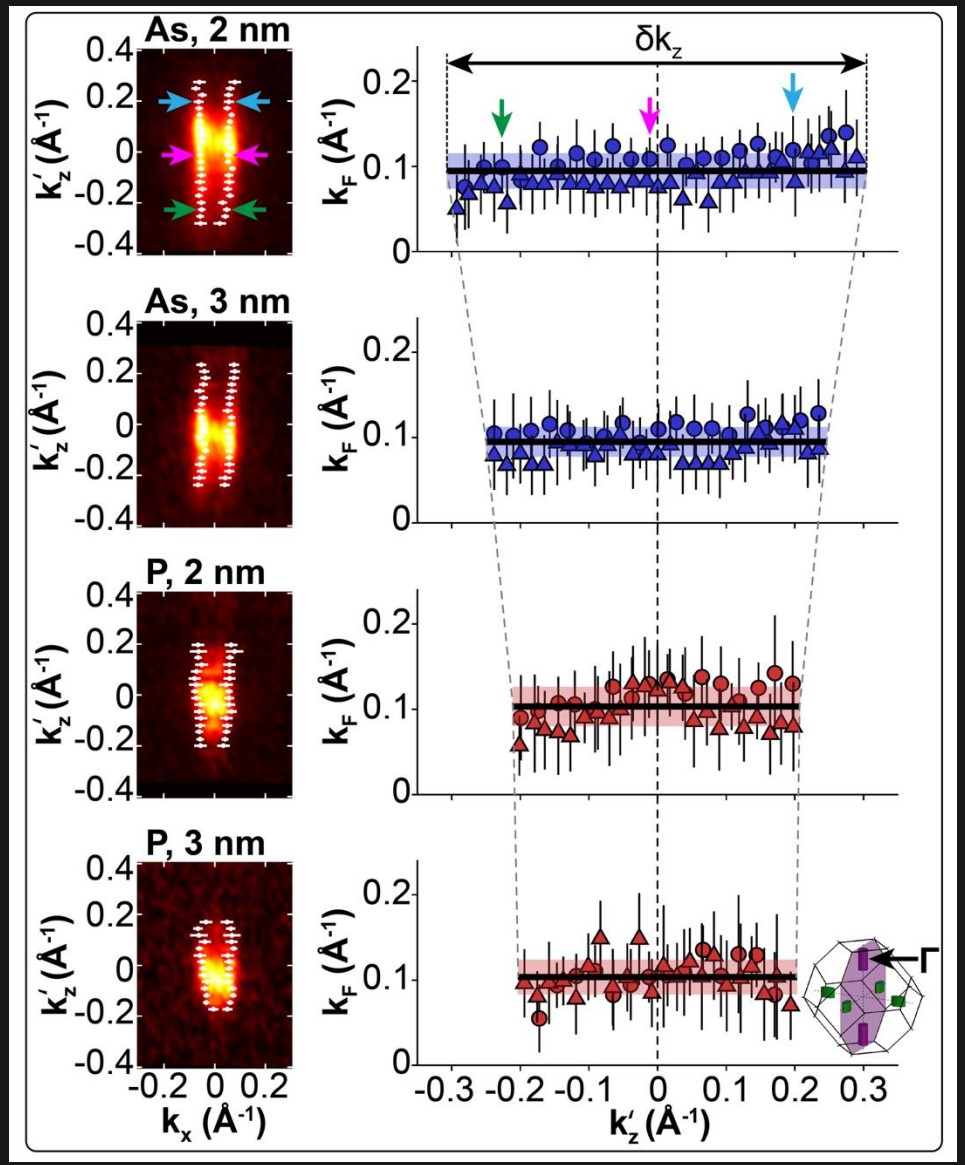
δ-layer Photoemission response and Brillouin Zone

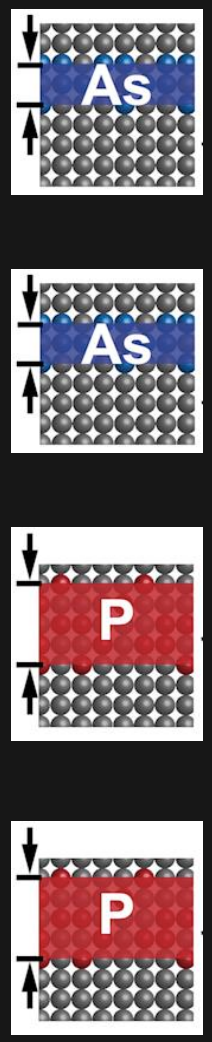




J. Electron Spectrosc. Relat. Phenom. 229, 100 (2018)

Arsenic δ-layers Have Stronger Confinement than Phosphorus





Growth thickness

2 nm

3 nm

2 nm

3 nm

- We fabricated P and As δ-layers with 2 nm and 3 nm Si overgrowth.
- The δ-layer width is extracted from the extent of the k_z valley in SX-ARPES.
- Arsenic δ-layers are more tightly confined than phosphorus δ-layers.
- The thinnest layer measured is 0.45 ± 0.04 nm – just over three atomic layers.

Overgrowth depth (left) versus δ-layer thickness (right)

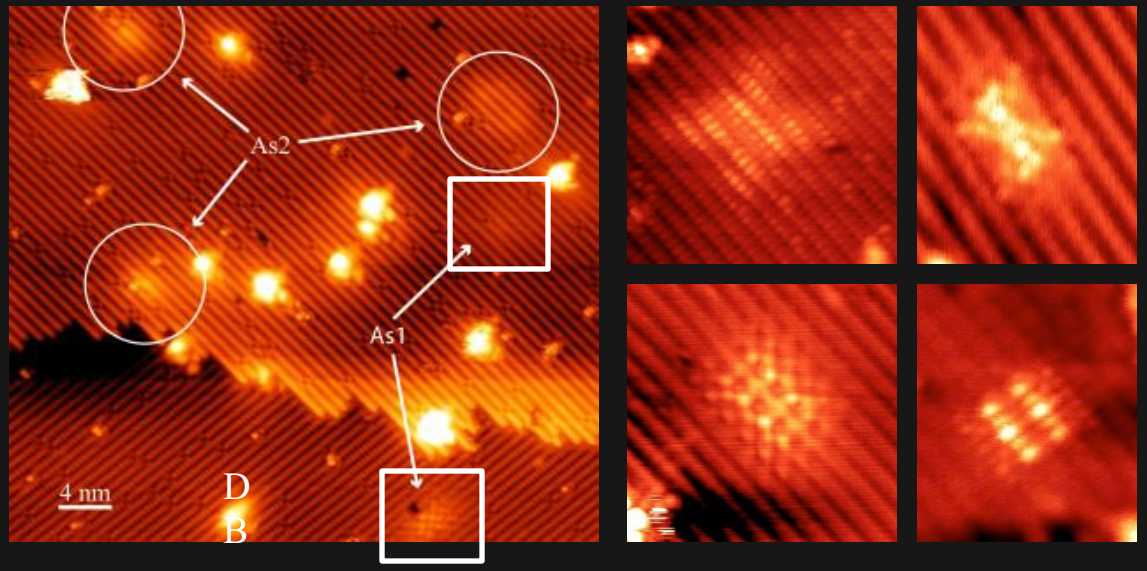
δ-layer species, depth	SX-ARPES (nm)
As, 2 nm	0.45 ± 0.04
As, 3 nm	0.62 ± 0.10
P, 2 nm	0.91 ± 0.21
P, 3 nm	1.03 ± 0.35

Constantinou et al., Advanced Science, 2302101 (2023)

Imaging Donor Wave Functions with STM: Arsenic in Silicon

- Degenerately doped Si(001):As samples reveal subsurface donor wave functions with STM
- Samples must be prepared using a low thermal budget to preserve donors near the surface
- STM resolves both the 1s envelope and the Bloch-wave interference patterns of the donor states

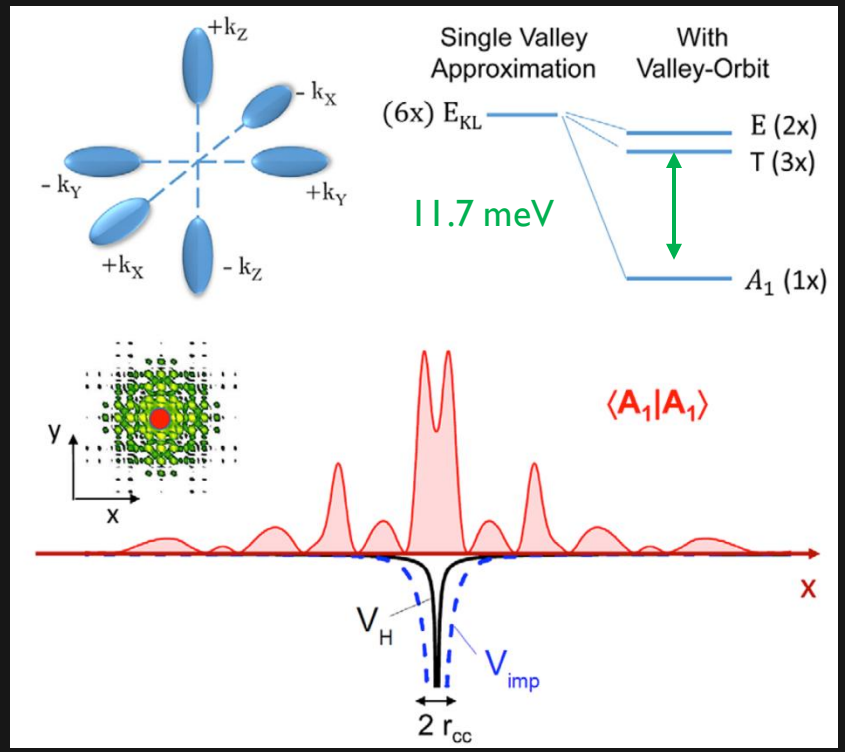
STM Images of Arsenic Donors near H-terminated Si(001) (77 K)



J. Phys.: Condens. Matter 26, 012001 (2014)

The oscillatory features arise from interference between the six silicon conduction-band valleys (valley–orbit interference)

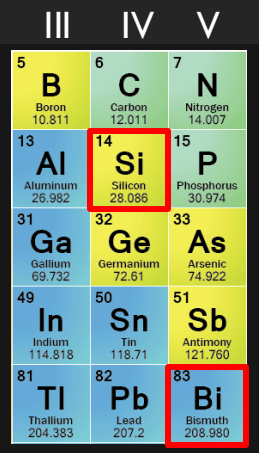
Valley-Orbit Interference



J. Phys. Condens. Matter **27**, (2015)

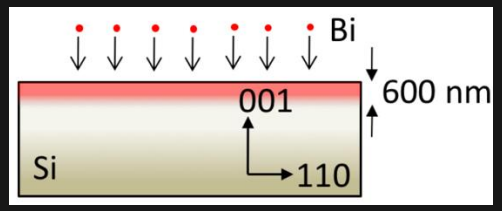
Implanting Si(001) with bismuth

- Si(001) wafers implanted with bismuth to create high density of bismuth 20 – 600 nm below the surface.
- Samples were flash-annealed to 1050 °C in UHV and H-terminated for STM.
- STM reveals long-ranged features consistent with hydrogenic defects states

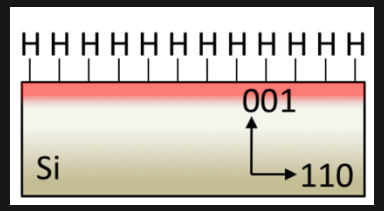


Sample fabrication: bismuth implantation

Ion implantation

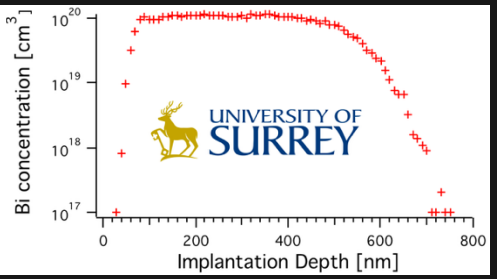


H-terminated

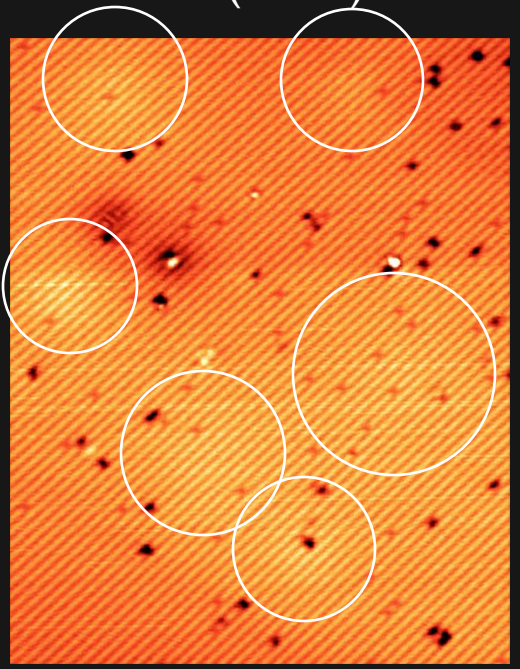


Bi ion implantation doses and profile (SRIM)

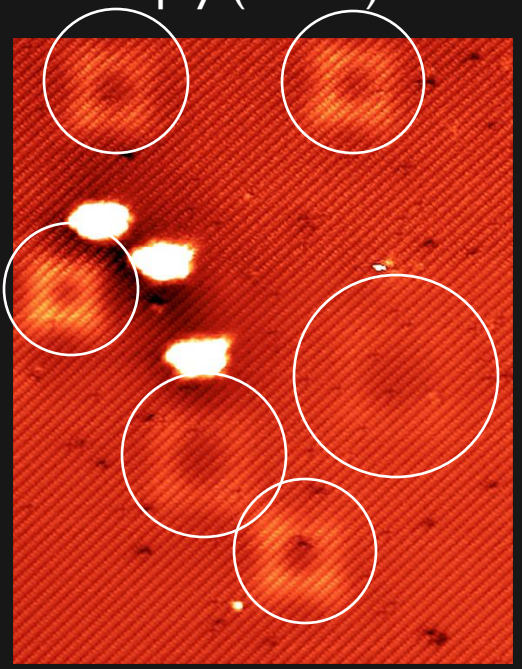
Energy [MV]	Dose [cm^{-2}]
2	1.9×10^{15}
1.35	1.2×10^{15}
0.85	0.9×10^{15}
0.5	0.64×10^{15}
0.25	0.41×10^{15}



Filled (-1.2 V)



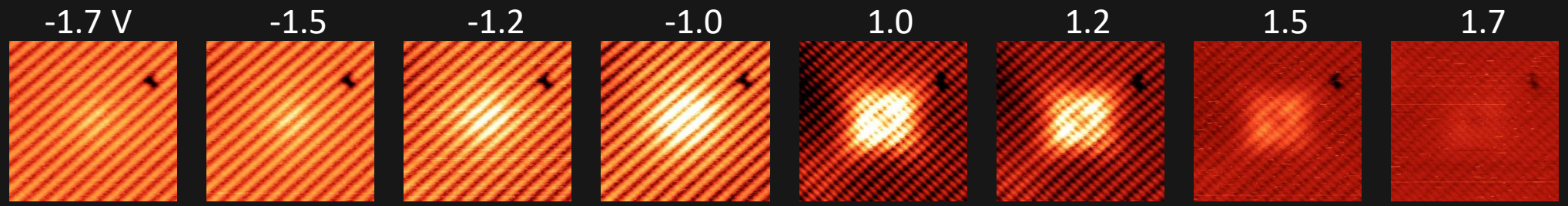
Empty (+1.2 V)



Appearance: bias dependence

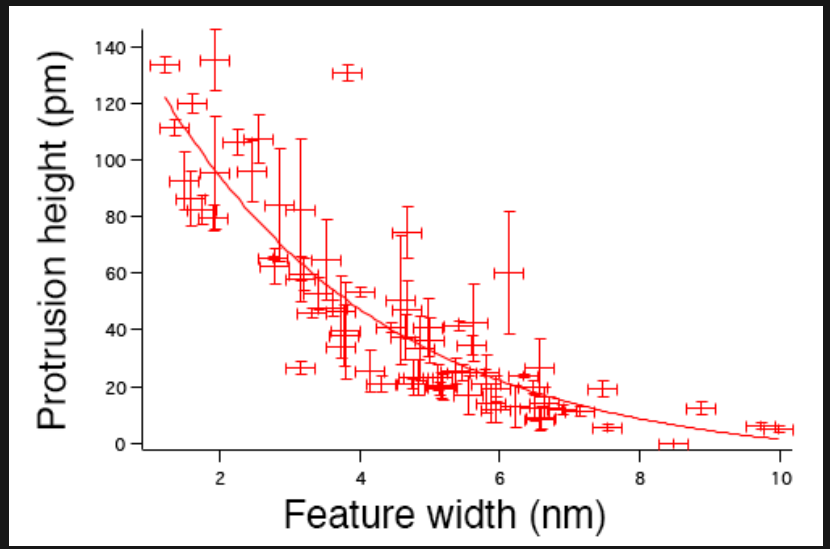
Filled-state (negative sample bias)

Empty-state (positive sample bias)

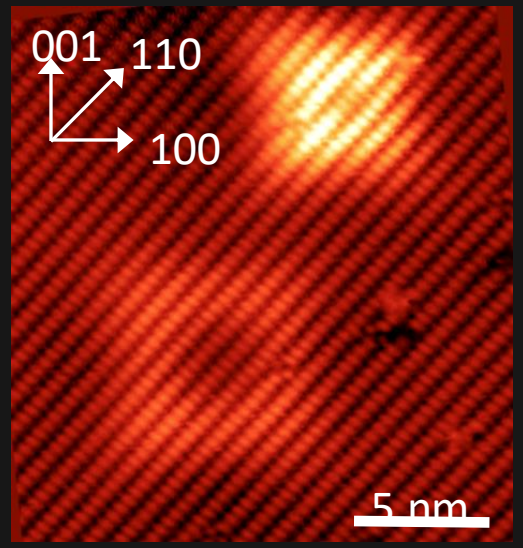


- In filled-state images the features appear as isotropic protrusions, whereas in empty-state images they develop a characteristic square anisotropy.
- They do not vary bias (other than in intensity) ruling out origins like quasiparticle interference
- We observe a range of correlated feature widths and intensities, consistent with defects at different depths within the substrate

Feature height versus depth



Empty-state image



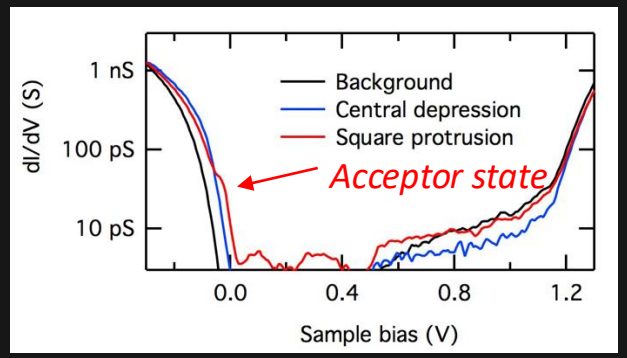
+0.9 V / 100 pA

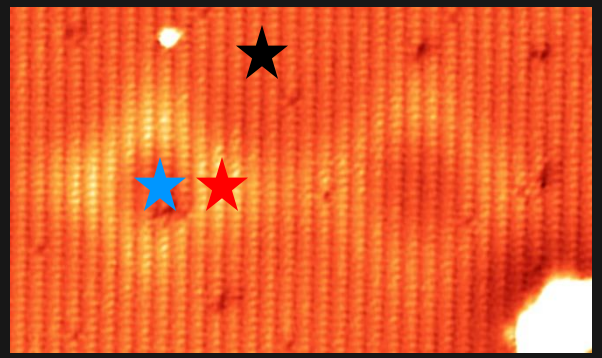
Identifying Acceptor States in Bi-Implanted Silicon

- Surface becomes p-type after Bi implantation.
- STM features lack the characteristic valley-orbit interference expected for donor states.
- Together, these observations show the states are
- Effective-mass and tight-binding calculations (Flatté group) independently confirm the features are acceptors, not donors.

Nano Lett. 2025, 25, 38, 13996

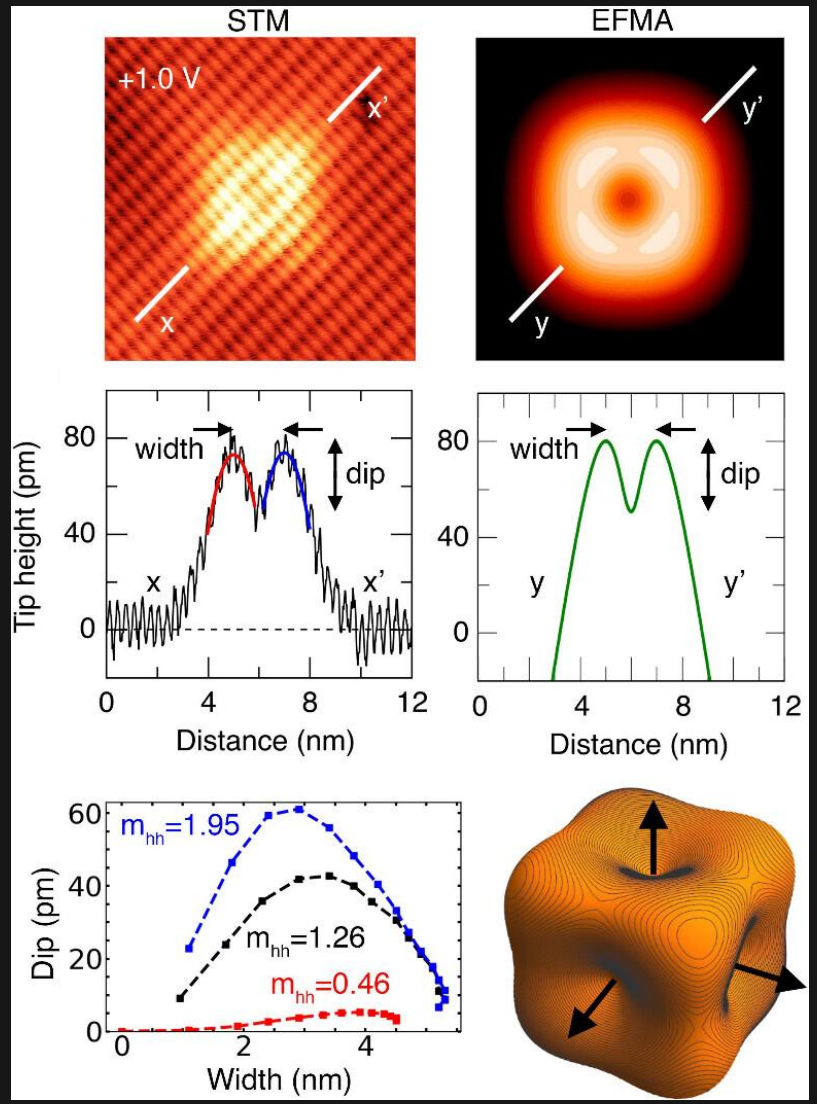
Tunnelling Spectroscopy (dI/dV)





Bismuth implantation produced acceptor-like states rather than donors.

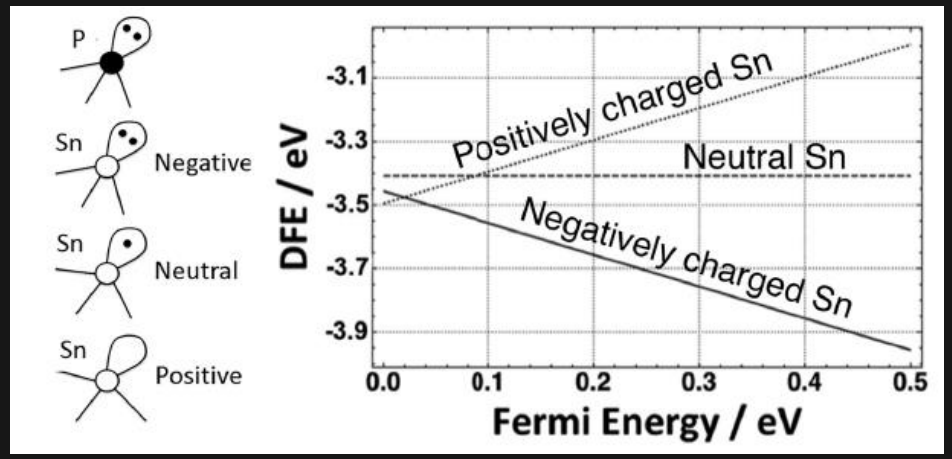
Acceptor wave-function modelling matches the experimental STM data



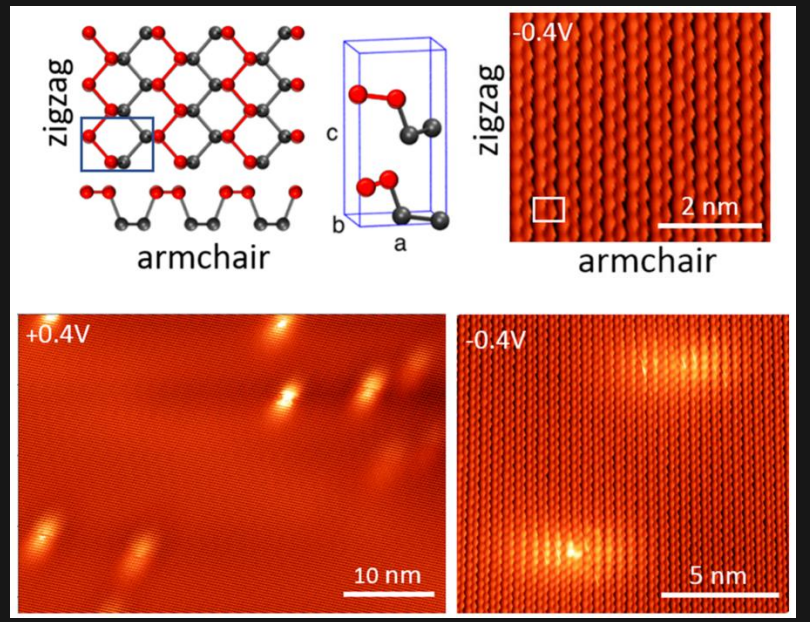
Electronic Defects in Black Phosphorus Revealed by STM

- Nominally pure black phosphorus behaves as a p-type semiconductor.
- This points to a ubiquitous presence of intrinsic defects.
- Using STM, STS, XPS, DFT, and tight-binding, we identify substitutional Sn impurities.
- These defects are negatively charged over a wide Fermi-level range, producing hydrogenic in-gap states.

DFT defect charge stability

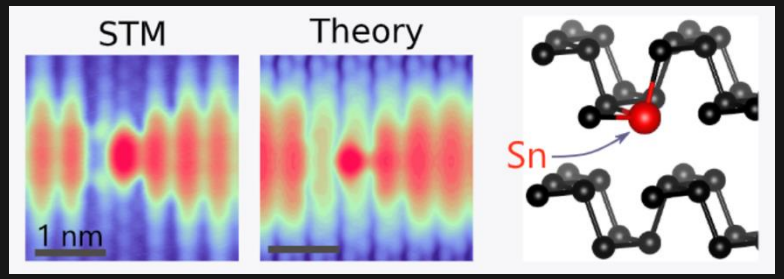


STM of Black Phosphorus



Wentink, et al., J. Phys. Chem. C, 125, 22883, 2021

Substitutional Sn defect: STM vs theory



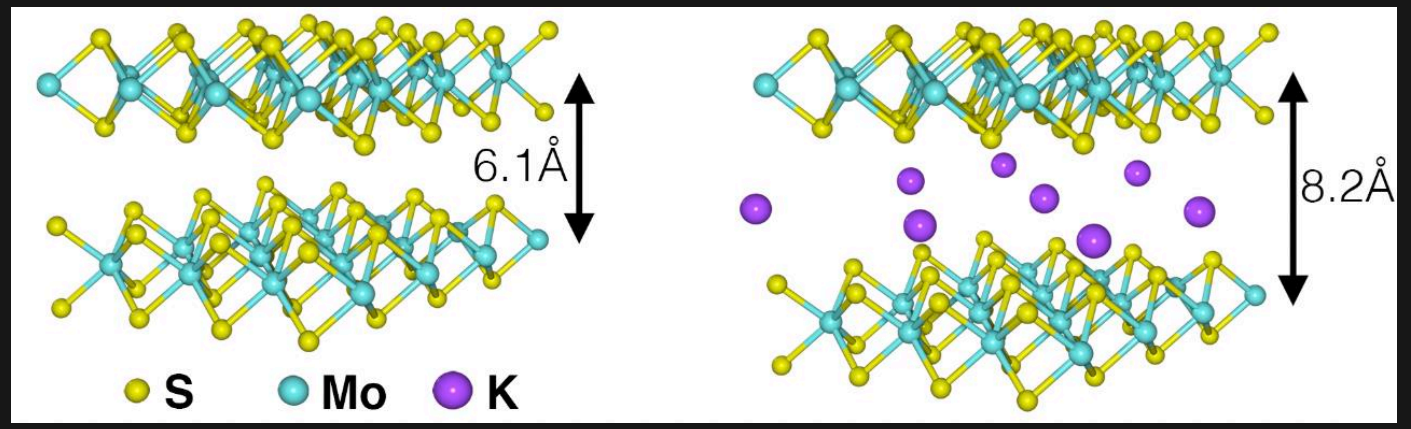
Harsh, et al., J. Phys. Chem. Let.. 13, 6276, 2022

Black phosphorus is inherently defect-rich, and substitutional Sn donors dominate its electronic character.

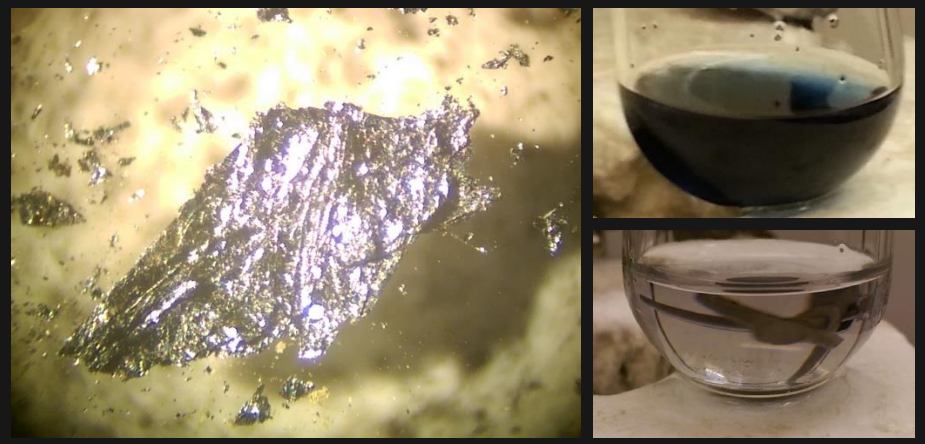
Electron doping via potassium intercalation: $K_{0.4}MoS_2$

- Intercalate potassium ions into the Van der Waals gaps using liquid ammonia.
- Intercalation completes at stoichiometry $K_{0.4}MoS_2$ after ~24 hours.
- Extremely high doping density: 4 x 10^{14} cm^2
- XRD confirms the expected 35% increase in layer separation (2.2±0.1 Å).

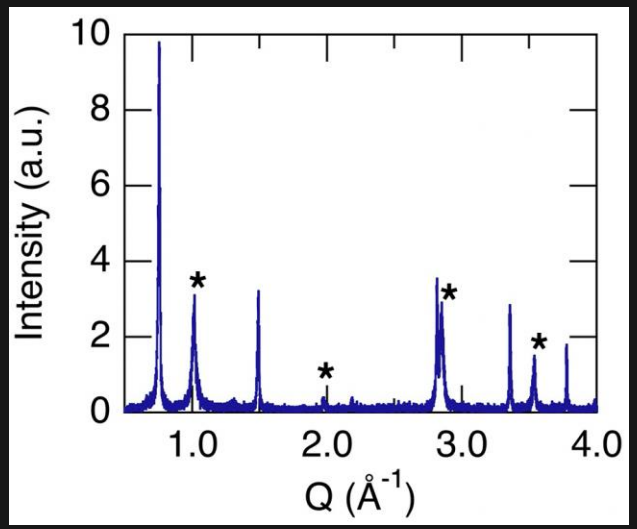
K intercalation in the VDW gaps



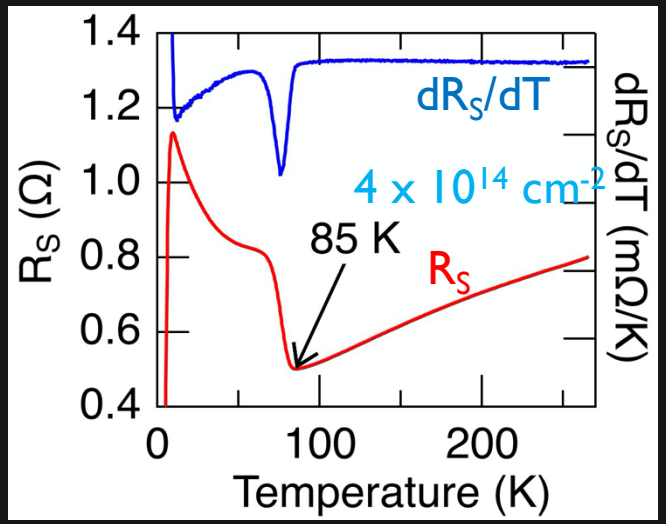
Intercalation of K using liquid ammonia



X-ray diffraction



Resistivity with temperature

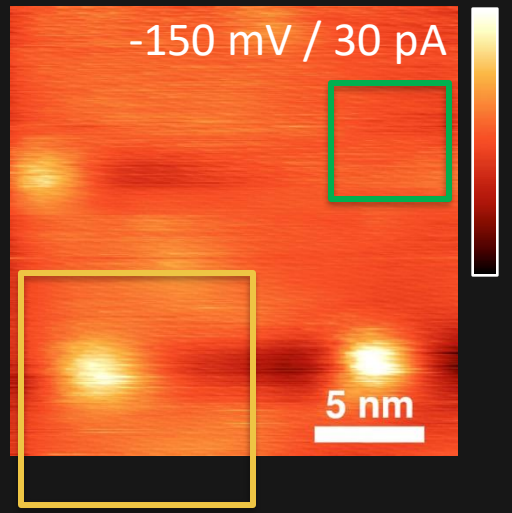


Bin Subhan, et al., Nano Lett., 21, 5516, 2021

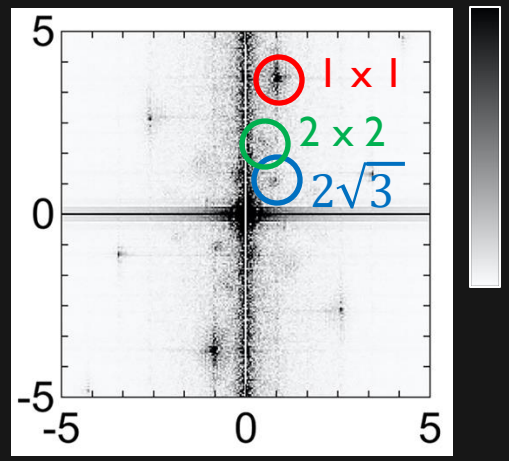
$K_{0.4}MoS_2$: additional periodicity at defect sites

- We observe a (2×2) modulation across the material, consistent with a CDW predicted by DFT.
- Closer inspection of the defect sites reveals a $(2\sqrt{3} \times 2\sqrt{3})R30°$ periodicity at these sites.

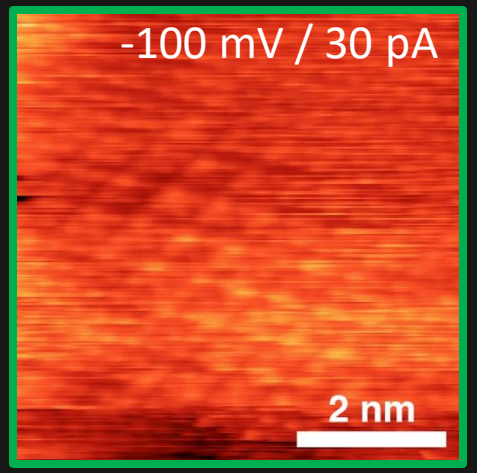
STM



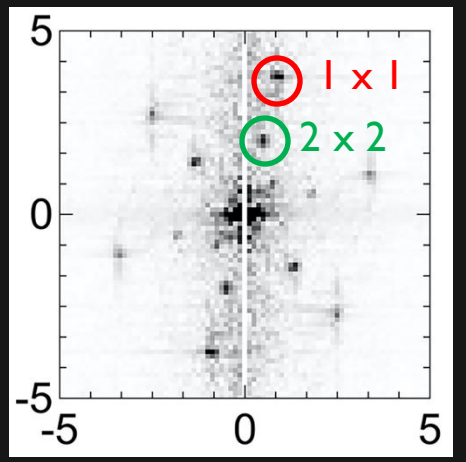
STM FFT



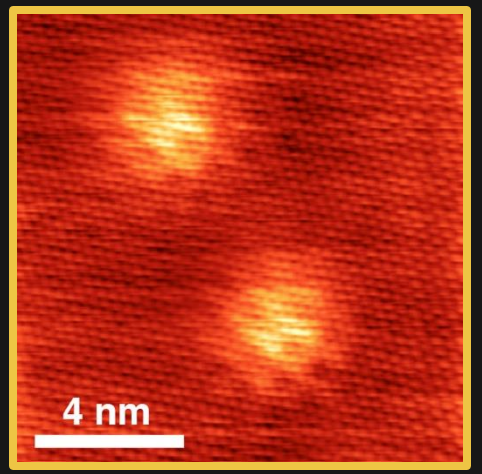
STM topography

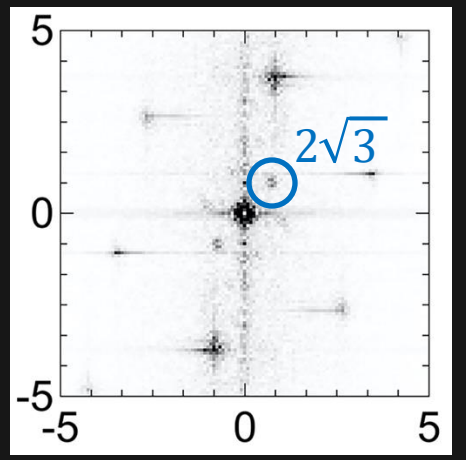


STM FFT



Measured wavevector (nm^{-1})	Real space lattice
3.6 ± 0.05	1×1
1.9 ± 0.1	2×2
1.1 ± 0.1	$(2\sqrt{3} \times 2\sqrt{3})R30°$

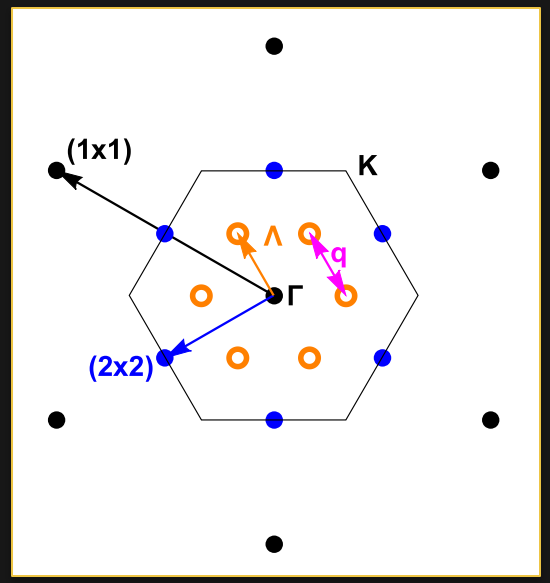




Bin Subhan, et al., Nano Lett., 21, 5516, 2021

Origin of the charge density waves

- The conduction band minimum lies midway along the Γ-K direction for bulk MoS_2.
- For monolayer undoped material the CBM is at the K point.
- Doping changes the balance again toward the bulk CBM.
- Defects are also known to increase inter-layer coupling.
- Fermi-surface nesting (FSN) at the bulk CBM has the correct wavelength for the observed $2\sqrt{3}$ modulation.

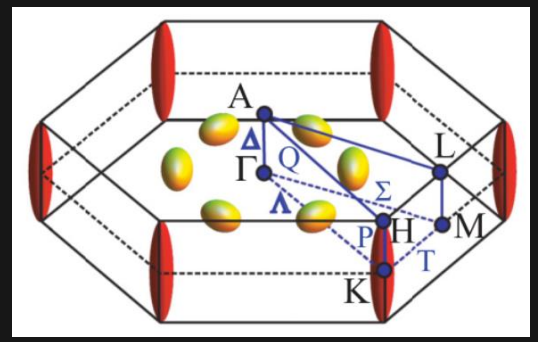


Measured wavevector (nm^{-1})	Real space lattice
1.1 ± 0.1	$(2\sqrt{3} \times 2\sqrt{3})R30°$

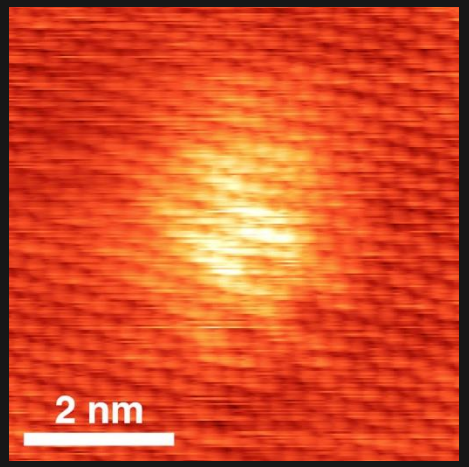
$$|\mathbf{\Gamma K}| = \frac{4\pi}{3a} = 13.26 \text{ rad nm}^{-1} = 2.11 \text{ nm}^{-1}$$

$$|\mathbf{\Gamma \Lambda}| \sim \frac{|\mathbf{\Gamma K}|}{2} = \frac{2\pi}{3a} = 6.63 \text{ rad nm}^{-1} = 1.05 \text{ nm}^{-1}$$

Fermi surface



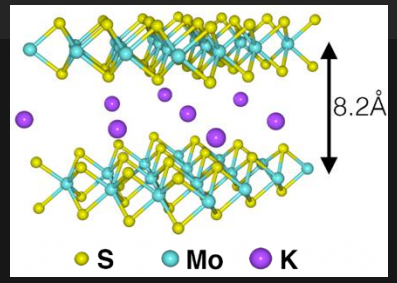
Peelaers et al. PRB 86, 241401(R) (2012)

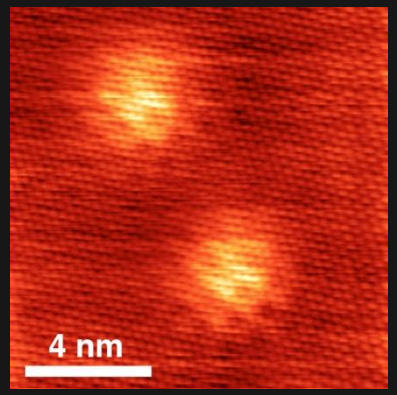


Bin Subhan, et al., Nano Lett., 21, 5516, 2021

Summary

- We study the atomic-scale physics of semiconductors and 2D materials, focusing primarily on dopants and defects
- Using a complementary toolset we probe, image, and manipulate electronic states with single-atom resolution
  - STM/STS, SX-ARPES, XPS, and DFT/effective mass/tight-binding
- These methods enable us to fabricate and characterise δ-doped layers, directly image donor and acceptor wave functions, and identify intrinsic defects in materials such as black phosphorus and MoS_2
- Overall, this research provides microscopic understanding essential for atomic-scale quantum devices and defect-engineered technologies.

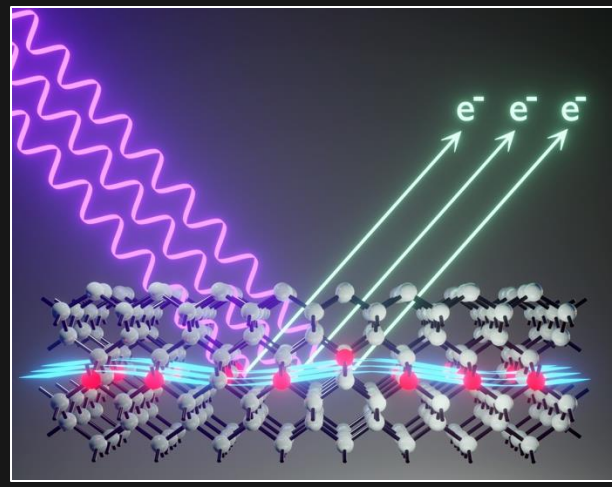




Nano Lett., 21, 5516, 2021

Nano Lett. 2025, 25, 38, 13996

PhD studentships available, including: "Mapping the Quantum Landscape of 2D Materials, One Atom at a Time"



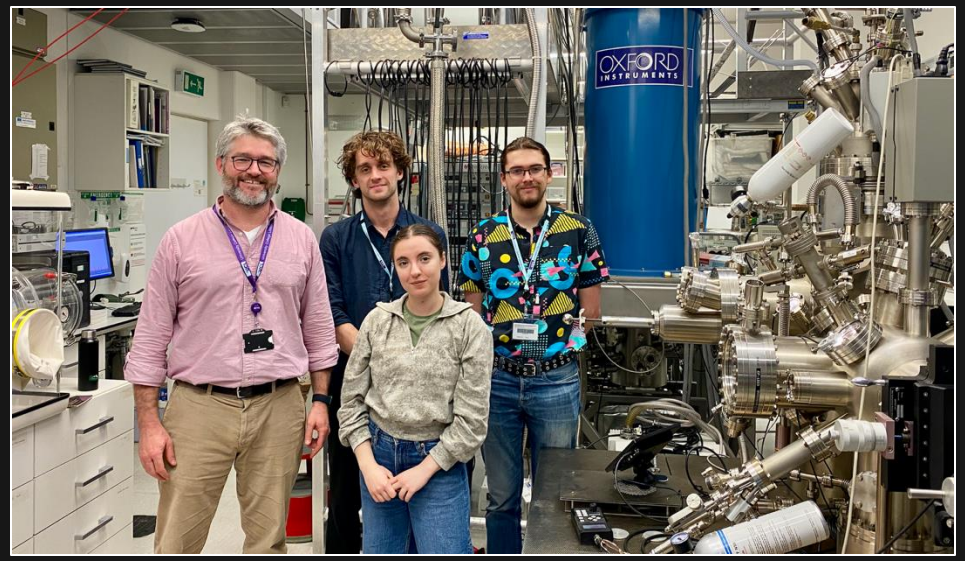
Constantinou, Advanced Science 10, 2302101 (2023)

Acknowledgements

Students and postdocs who did most of the work:

- Emily Hofmann: Ge(001):AsH_3
- Procopi Constantinou: SX-ARPES Si δ-layers
- Kitiphat Sinthiptharakoon: As donors in Si
- Manuel Siegl, Holly Hedgeland, Julian Zannon: Acceptor states
- Mark Wentink: Black Phosphorus
- Kashim Subhan and Asif Suleman: $K_{0.4}MoS_2$

Current group members

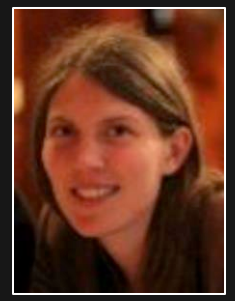



Emily Hofmann

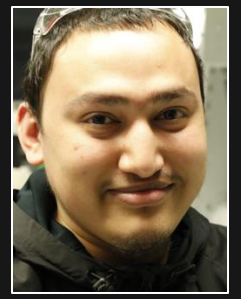

Procopios Constantinou


Kitiphat Sinthiptharakoon


Manuel Siegl


Holly Hedgeland


Mark Wentink


Kashim Subhan


Asif Suleman


Julian Zannon (Eindhoven)

Collaborators:

- Michael Flatté (Iowa/Eindhoven)
- Taylor Stock, Neil Curson, Chris Howard, David Bowler, Andrew Fisher, Alex Shluger (UCL)
- Vladimir Strokov, Gabriel Aeppli (PSI)

EPSRC
Pioneering research and skills