

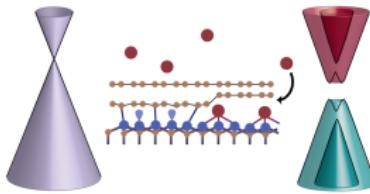
Angle-Resolved Photoemission Spectroscopy for crystalline (two-dimensional) material characterization

M2i Meeting Materials

Antonija Grubišić Čabo¹

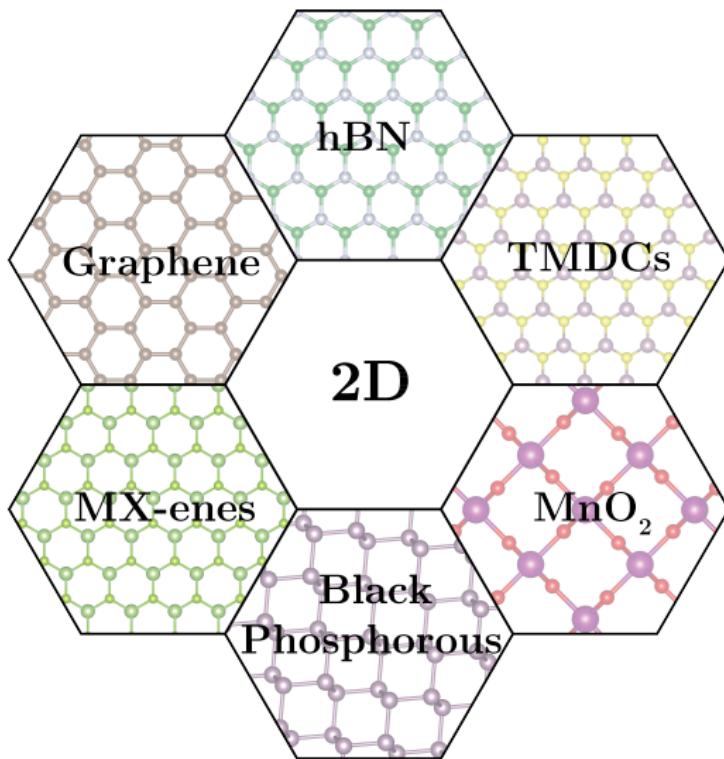
¹Zernike Institute for Advanced Materials, University of Groningen

13/12/2022



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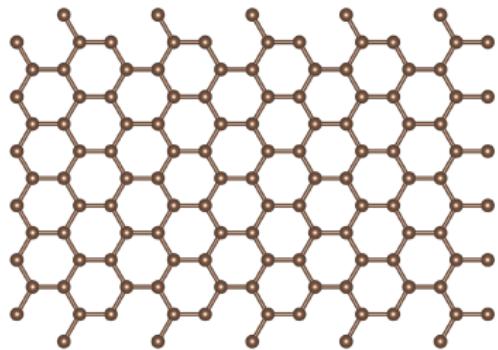
2D Materials



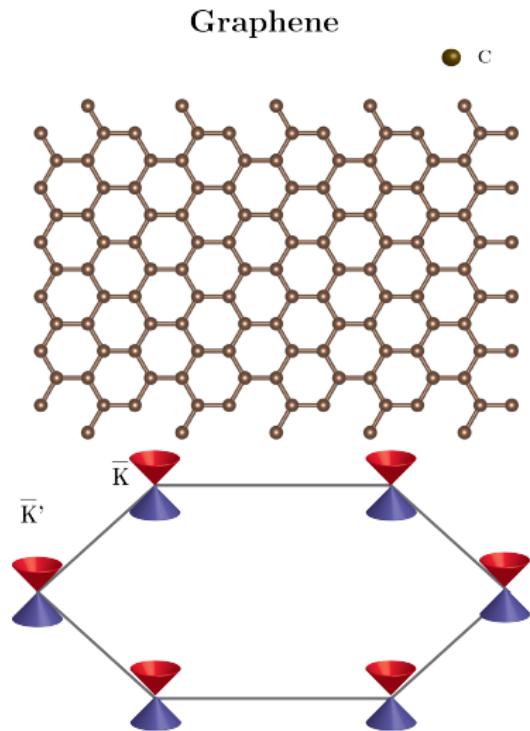
Graphene

Graphene

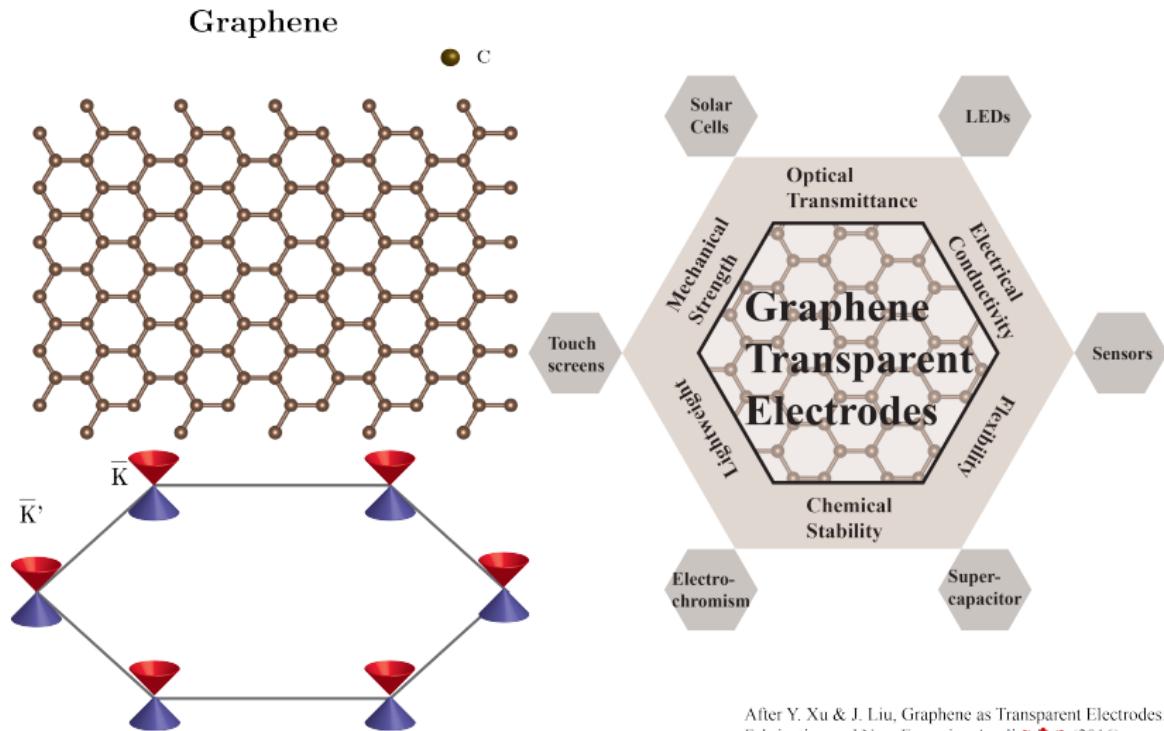
C



Graphene



Graphene applications

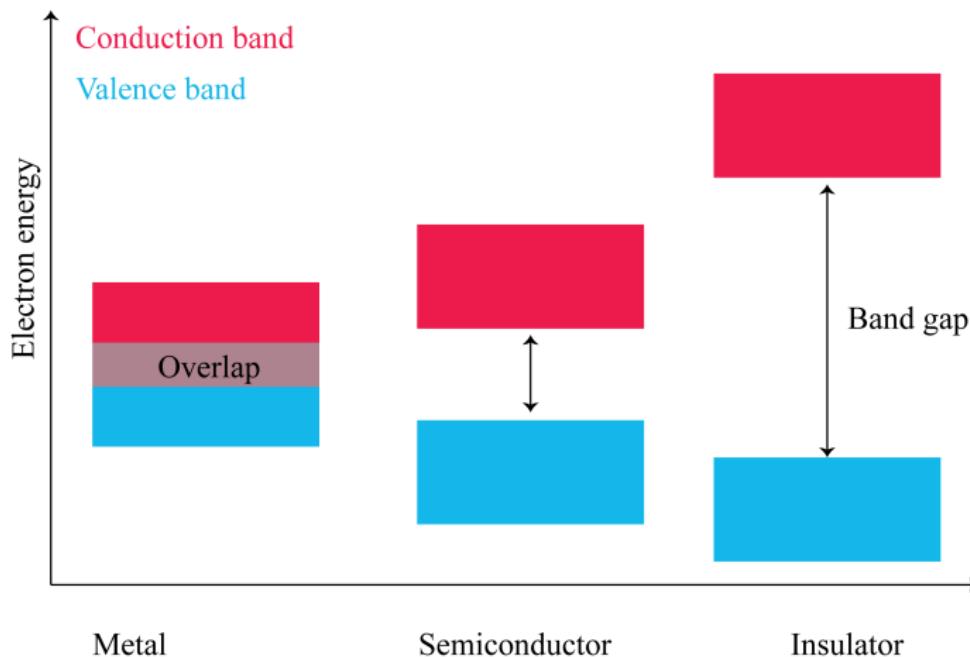


Dictionary

- Electronic bands - Allowed energy states for electrons
- Reciprocal (momentum or K-) space - Fourier Transform of real space electron wavefunctions
- Energy vs Momentum
- Parallel momentum is preserved - photon energy determines the "size" of energy and moment axis
- High symmetry points (Γ , K) - Defined on the Brillouin zone
- Brillouin zone - a unit cell of materials in the reciprocal space
- Fermi level - highest energy state an electron can occupy
- Valence band and conduction band - bands closest to the Fermi level
- VB lies below, and CB lies above the Fermi level



Electronic structure - Simple picture

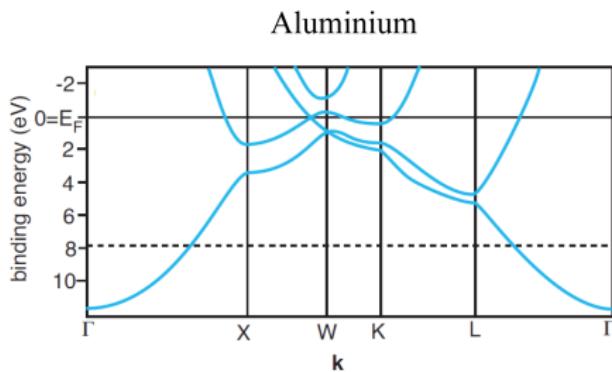
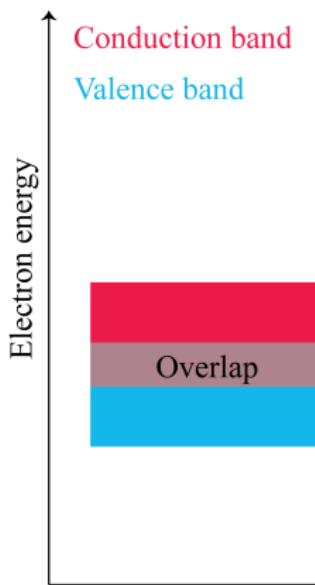


Metal

Semiconductor

Insulator

Electronic structure - metal



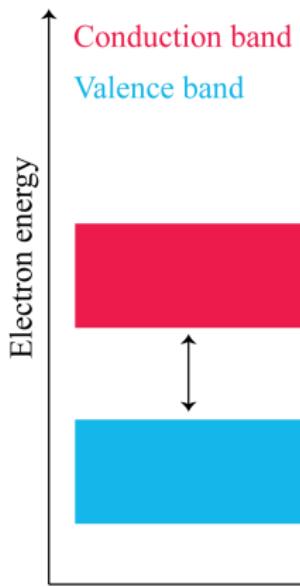
Metal

P. Hofmann, Surface Physics: An Introduction
After Physical Review B, 27, 727, 1983

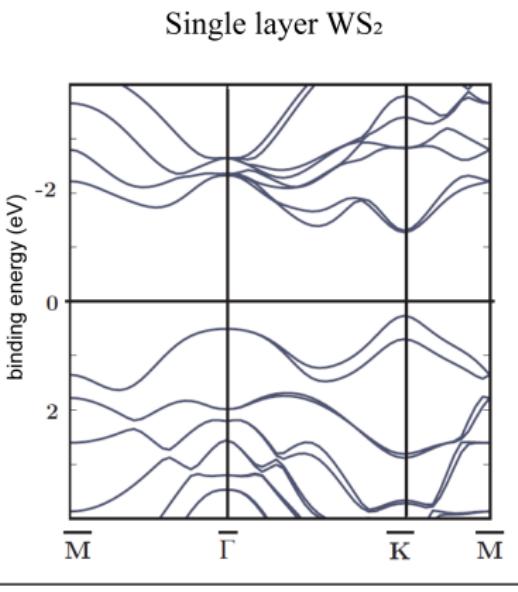


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Electronic structure - semiconductor

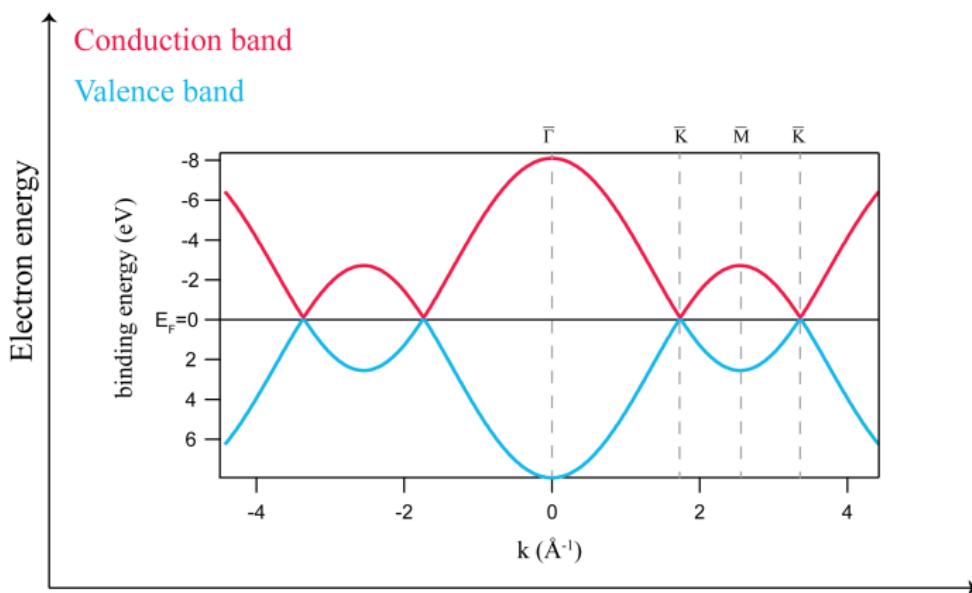


Semiconductor



After 2D Mater., 2:022001, 2015

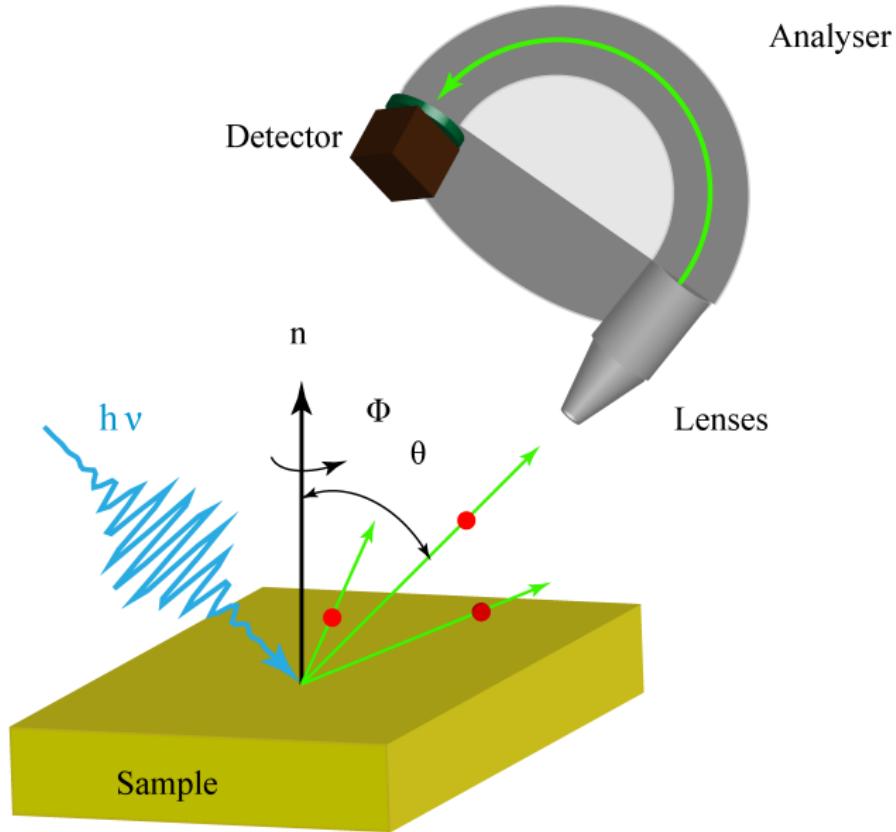
Electronic structure - Graphene is something new



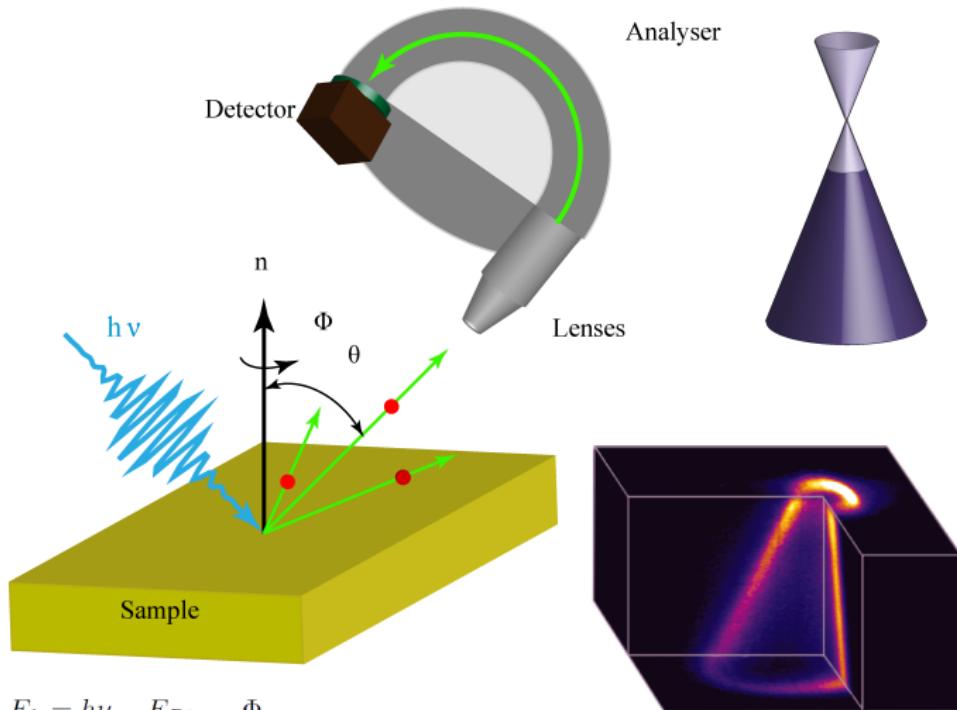
Graphene is a semimetal



ARPES - Angle-Resolved PhotoEmission Spectroscopy



Photoemission of Graphene

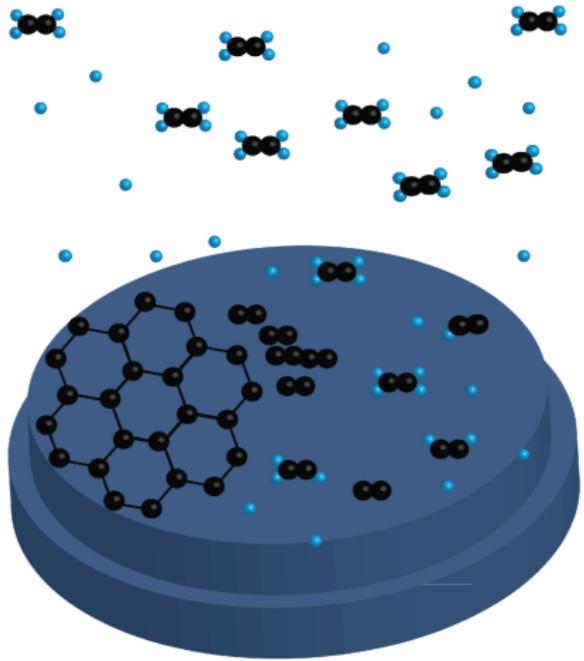


$$E_k = h\nu - E_{Bin} - \Phi$$

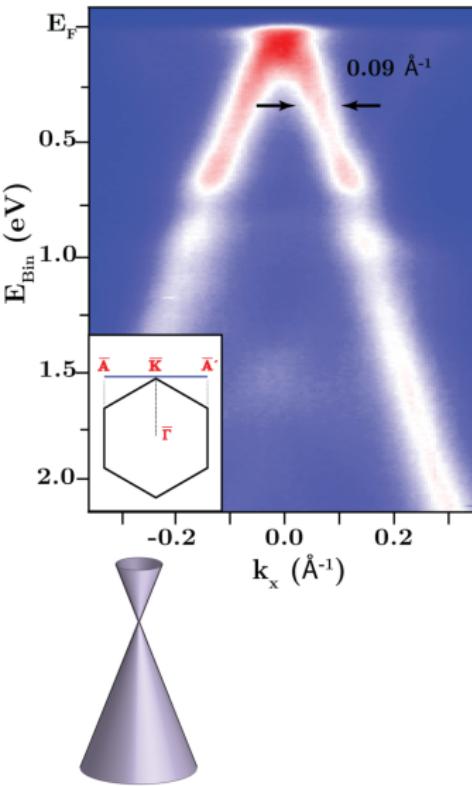
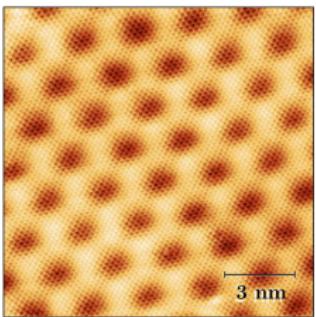
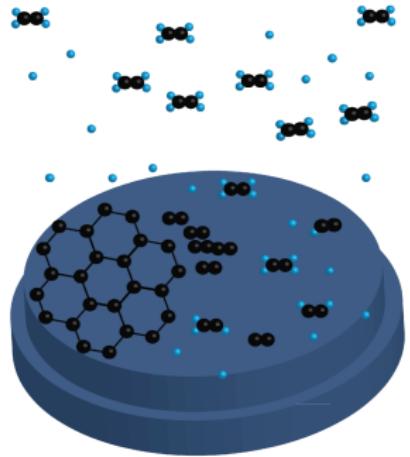
$$\mathbf{p}_{\parallel} = \hbar \mathbf{k}_{\parallel} = \sqrt{2mE_k} \sin \varphi (\cos \theta \hat{\mathbf{x}} + \sin \theta \hat{\mathbf{y}})$$

Graphene bandstructure

Adsorption - how to open a bandgap (for transistors)

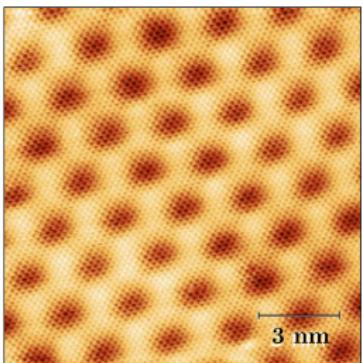


Graphene/Ir

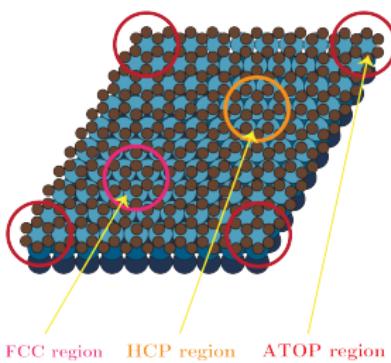


Hydrogenation of Graphene/Ir

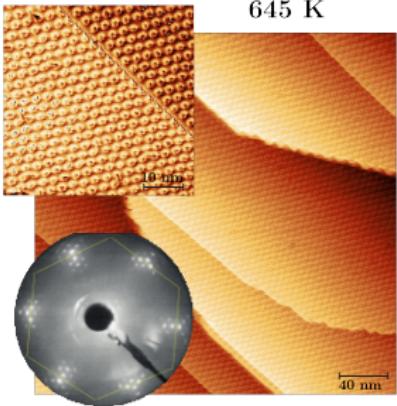
Clean



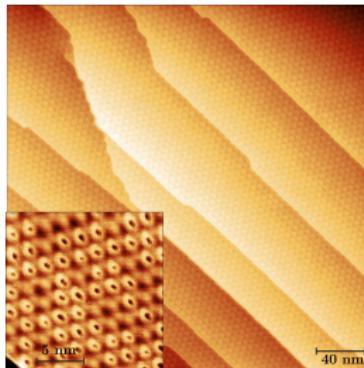
Moiré pattern



645 K

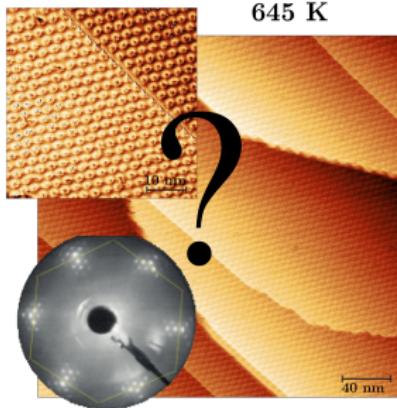
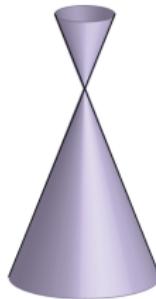
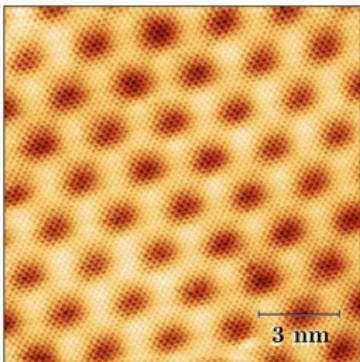


700 K



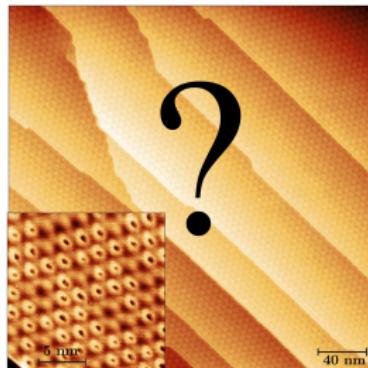
How does it affect the electronic structure?

Clean

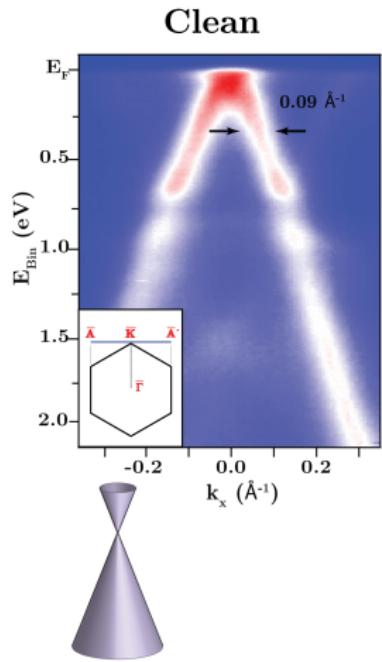


645 K

700 K



Gr/Ir electronic structure

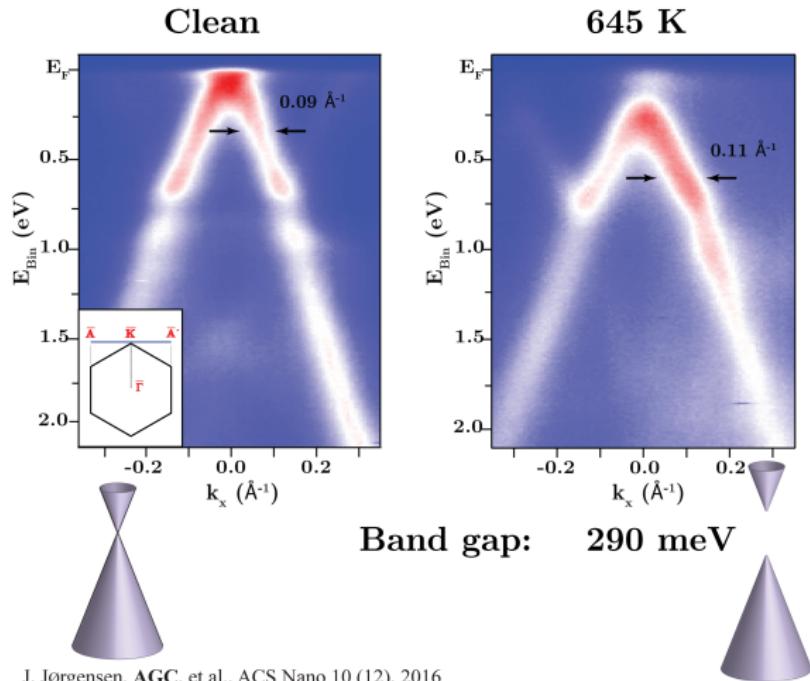


J. Jørgensen, AGC, et al., ACS Nano 10 (12), 2016



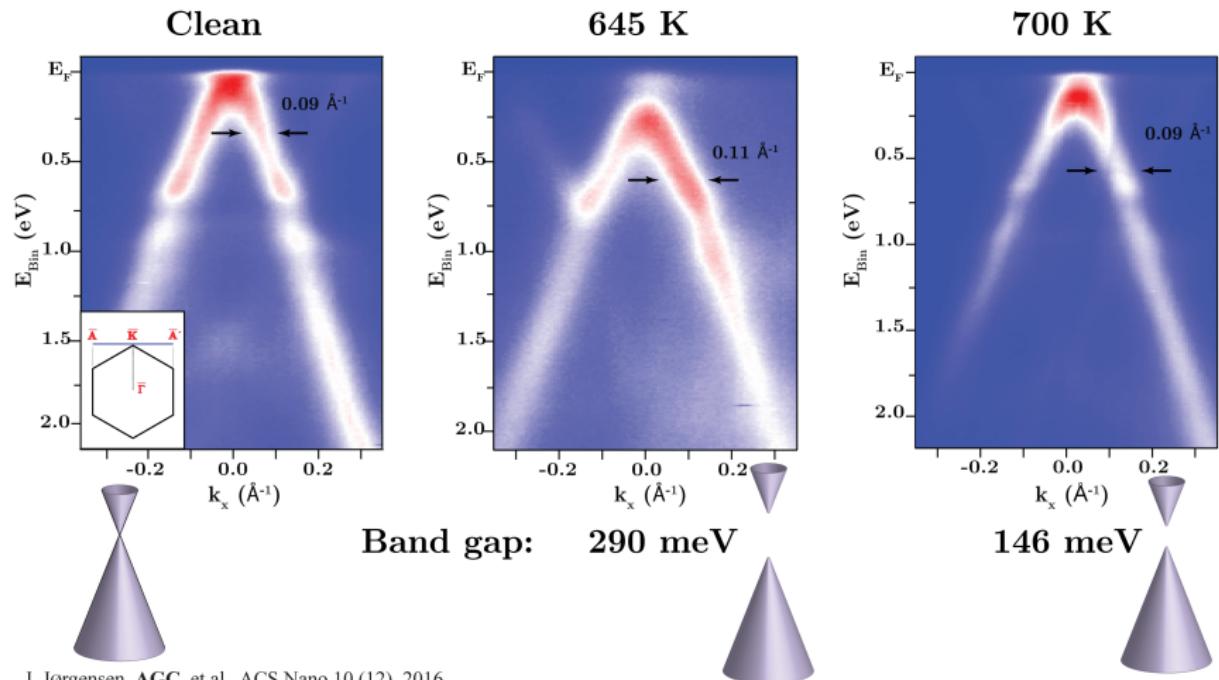
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Band gap opening following hydrogenation



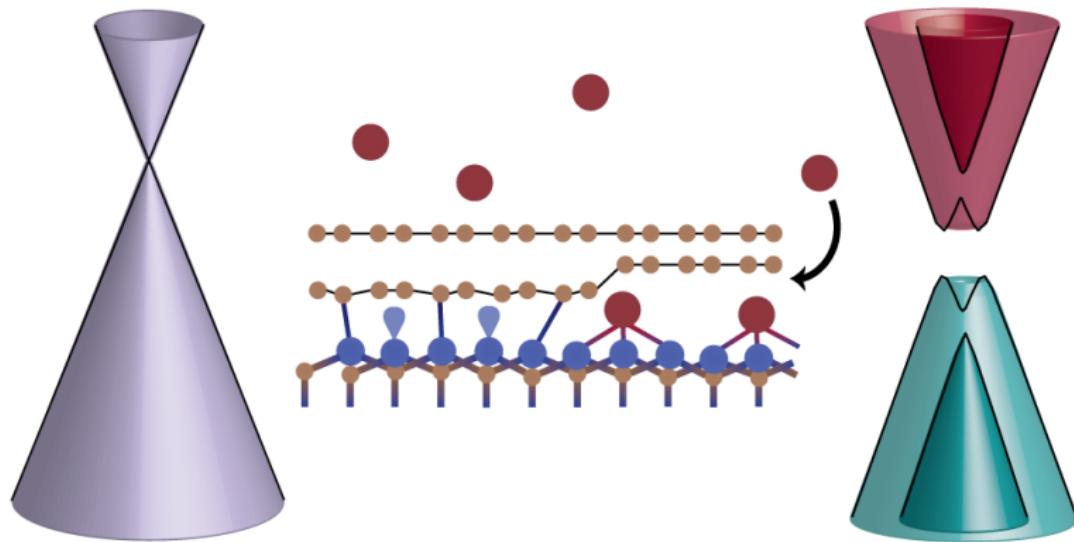
J. Jørgensen, AGC, et al., ACS Nano 10 (12), 2016

Band gap size can be tuned

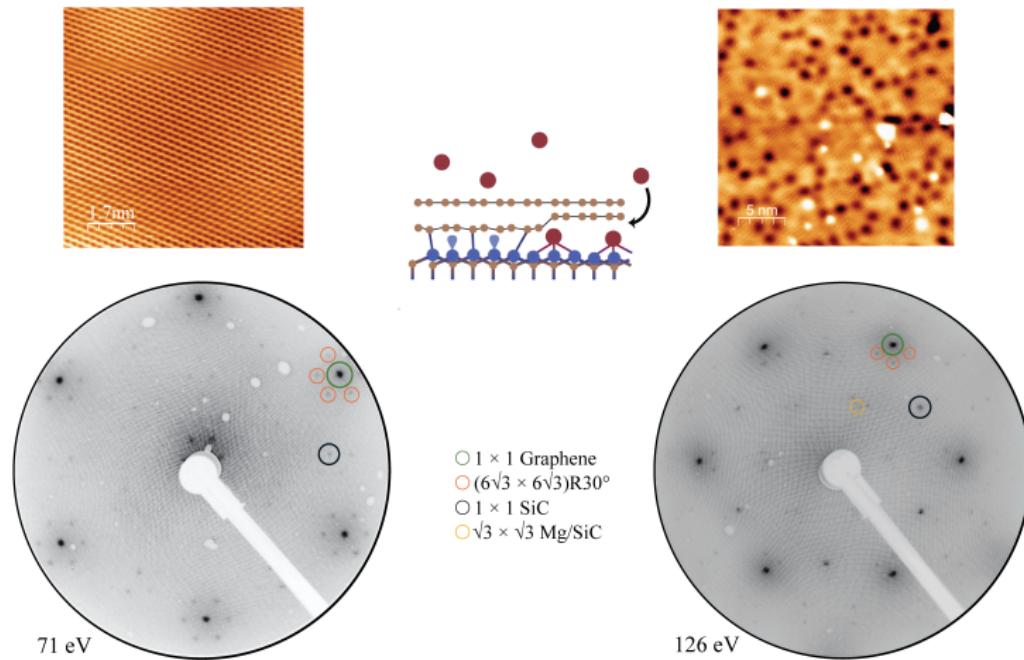


J. Jørgensen, AGC, et al., ACS Nano 10 (12), 2016

Graphene intercalation - n-doping (for transparent electrodes)



Mg - Graphene intercalation



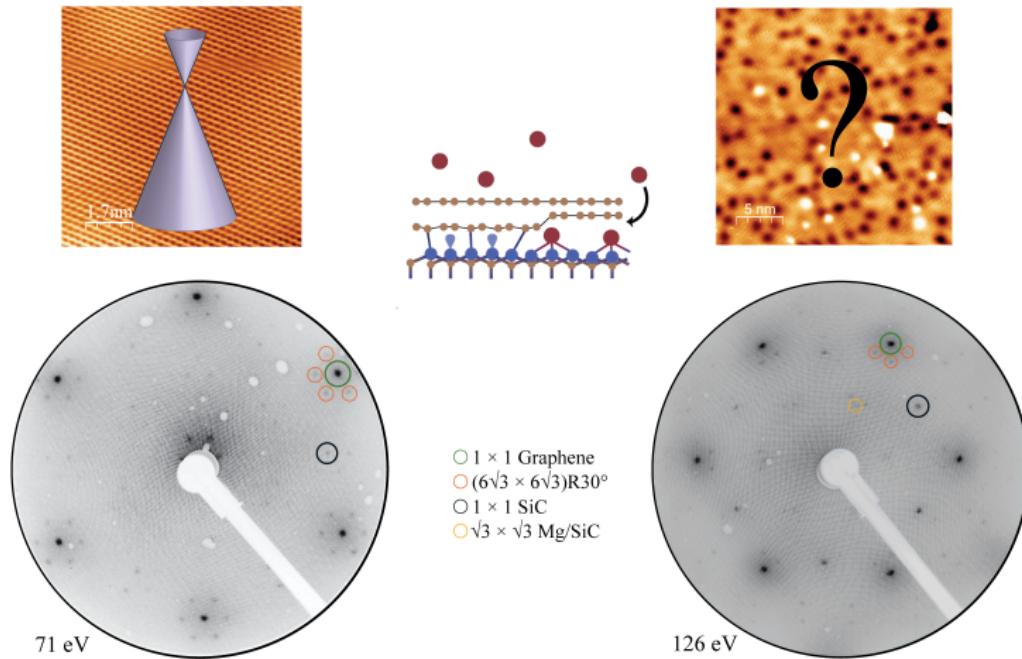
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

AGC, et al., Appl. Surf. Sci 541, 148612, 2021



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How does it affect the electronic structure?



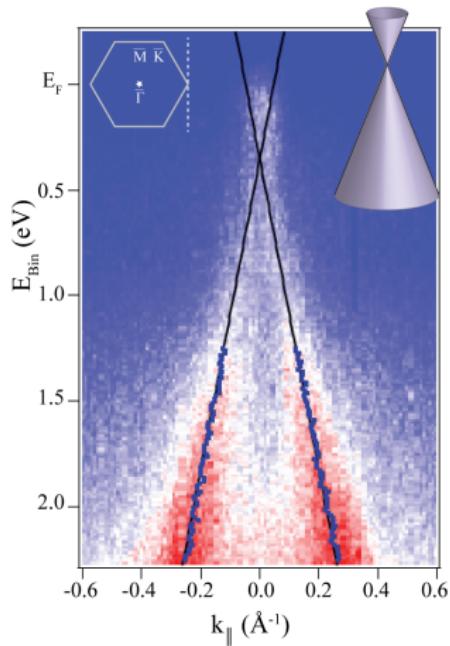
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

AGC, et al., Appl. Surf. Sci 541, 148612, 2021



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Gr/SiC electronic structure



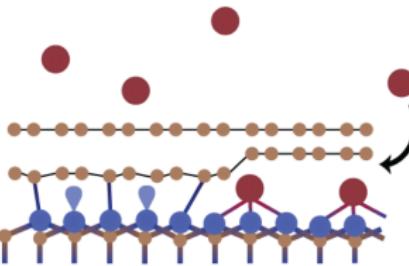
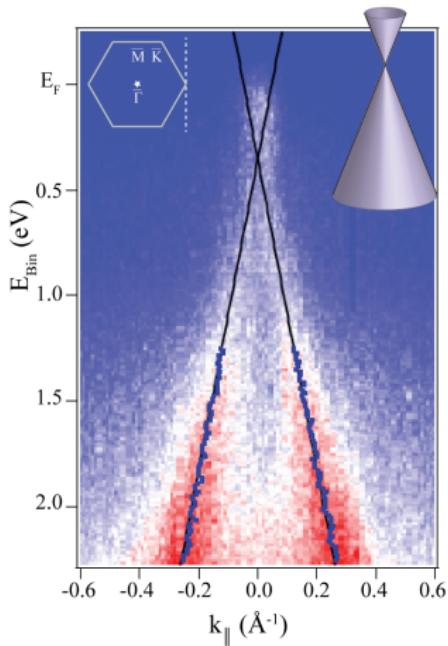
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

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Mg - Graphene intercalation

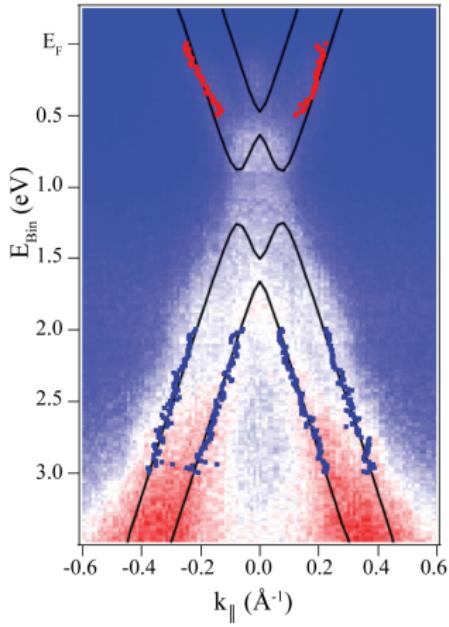
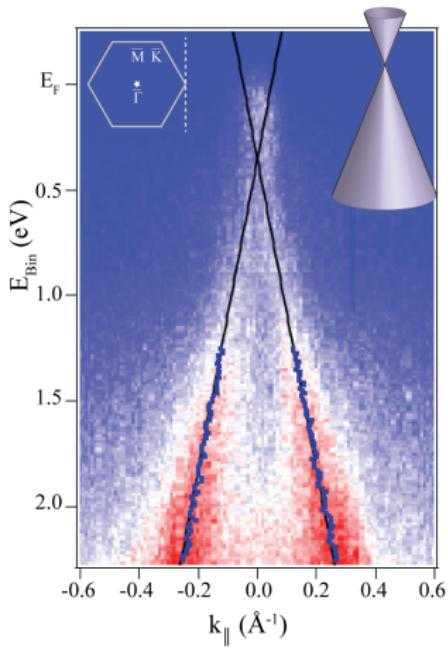


J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

AGC, et al., Appl. Surf. Sci 541, 148612, 2021



Mg - Graphene intercalation



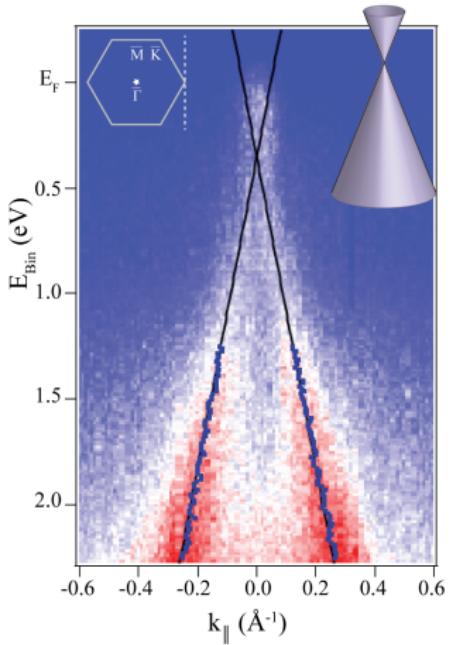
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AGC, et al., Appl. Surf. Sci 541, 148612, 2021

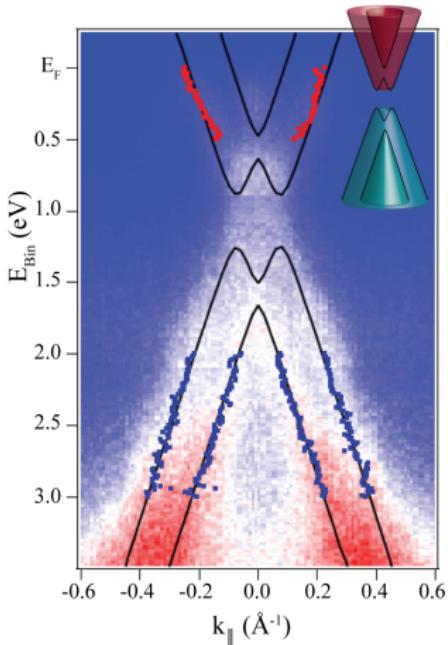


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Mg - Graphene intercalation creates bilayer graphene



J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482
 AGC, et al., Appl. Surf. Sci 541, 148612, 2021

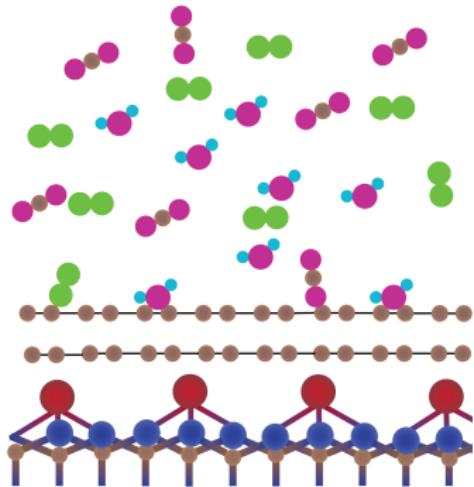


Band gap = 0.36 eV (absent in monolayer)
 Dirac point = 1.07 eV (0.35 eV in monolayer)
 Displacement field = 2.6 V/nm



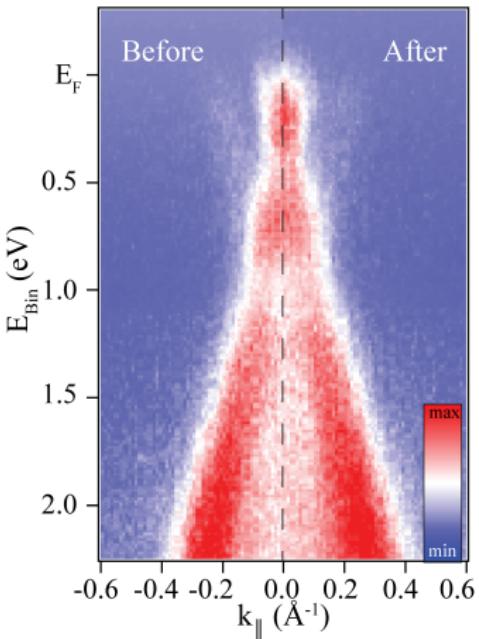
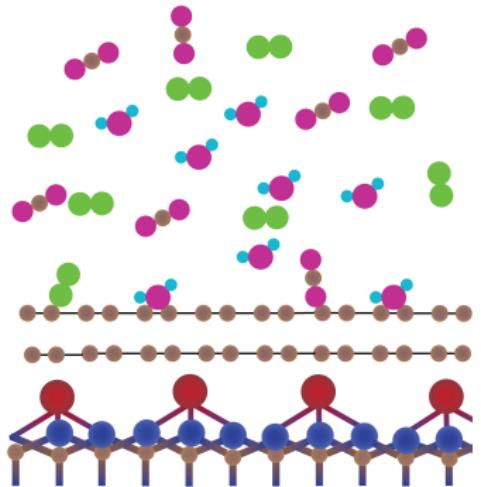
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What happens upon air exposure?



J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482
AGC, et al., Appl. Surf. Sci. 541, 148612, 2021

Before & After air exposure



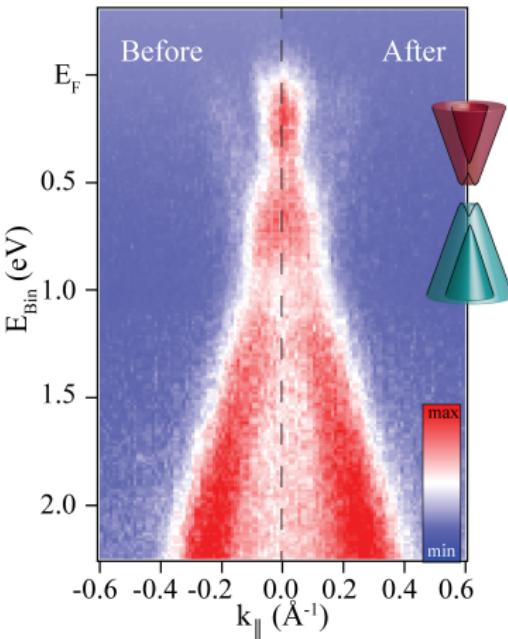
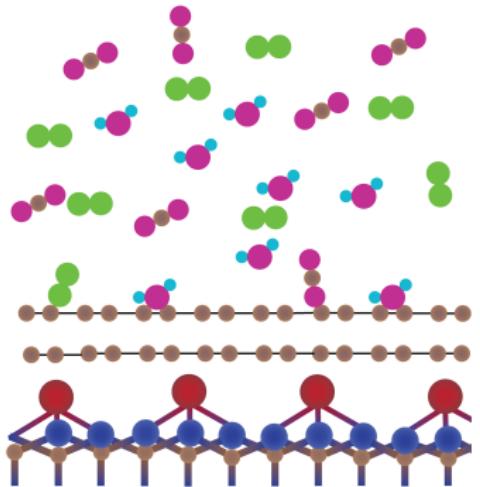
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

AGC, et al., Appl. Surf. Sci 541, 148612, 2021



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No significant changes to the band structure



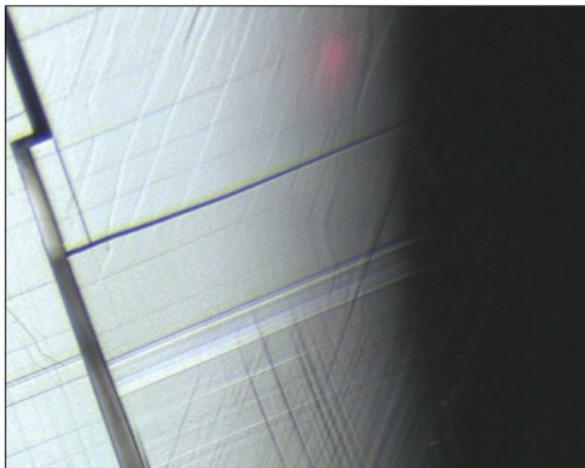
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15, 6464–6482

AGC, et al., Appl. Surf. Sci. 541, 148612, 2021



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PbSnSe - change in the electronic structure upon capping (protecting air sensitive materials)

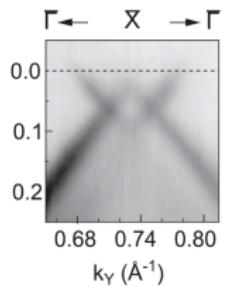


C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

Clean PbSnSe



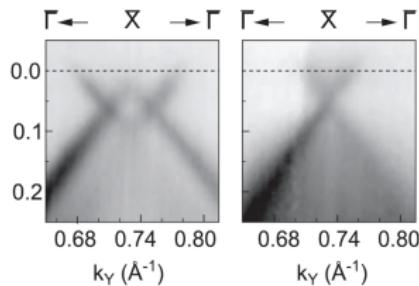
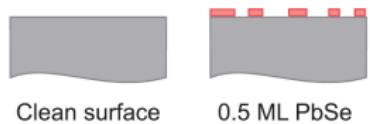
Clean surface



C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

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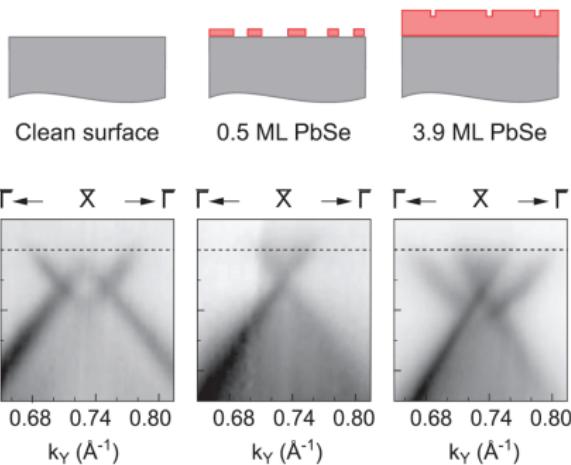
PbSnSe - Buried Interface



C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

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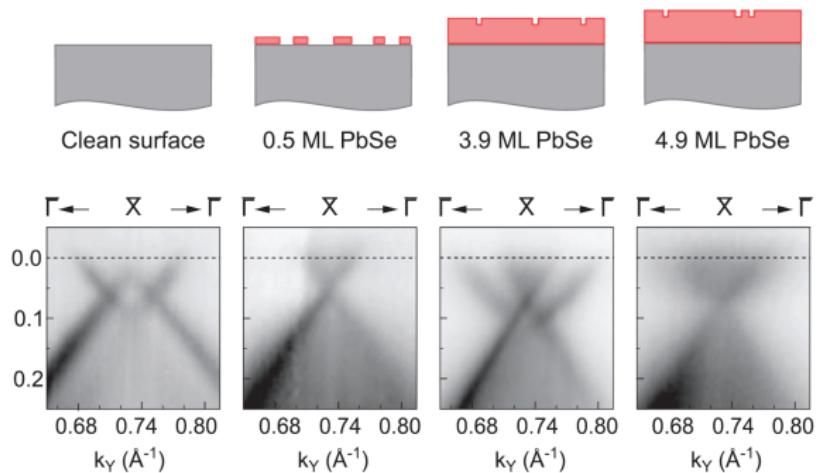
PbSnSe - Buried Interface



C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

University of Groningen

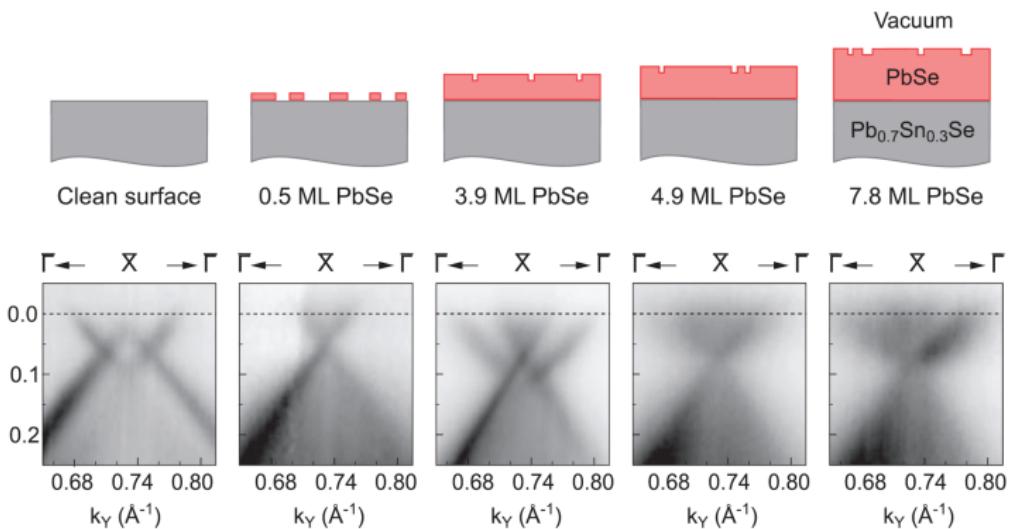
PbSnSe - Buried Interface



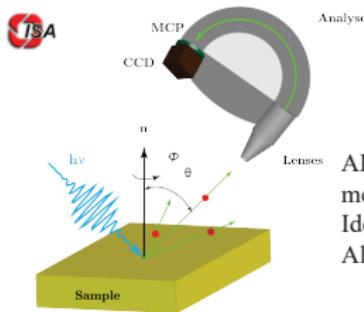
C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

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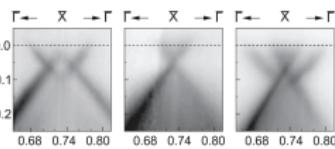
PbSnSe - Buried Interface



Summary

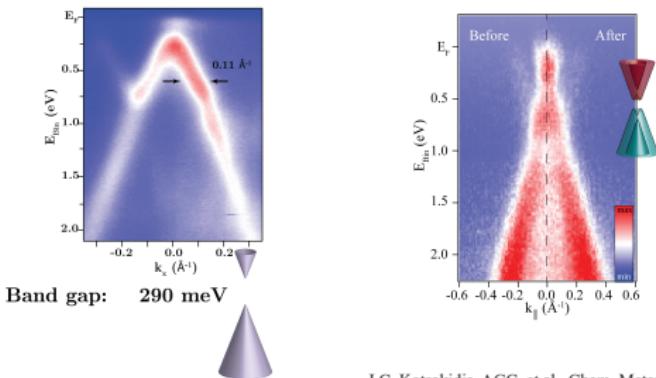


ARPES - a powerful technique to measure electronic structure
Ideal for 2D materials
Also works for 3D



C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

2D (Graphene): Tailoring properties by adsorption and intercalation
645 K



J. Jørgensen, AGC, et al., ACS Nano 10 (12), 2016

J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15
AGC, et al., Appl. Surf. Sci. 541, 148612 (2021)

[@CaboAntonija](mailto:a.grubisic-cabo@rug.nl)



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groningen



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 Mark Edmonds
 Jimmy Kotsakidis
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 Yuefeng Yin
 Nikhil Medhekar

Craig M. Polley
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 Tomasz Story
 Małgorzata Trzyna



Philip Hofmann
 Liv Hornekær
 Jill A. Miwa
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 Marco Bianchi
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 Richard Balog
 Line Kyhl
 Albert Bruix
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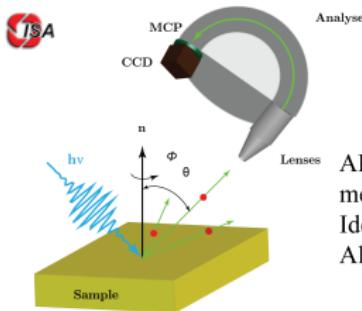
Australian
Synchrotron

Anton Tadich
 John Riley
 Eric Huwald
 Amadeo L. Vazquez de Parga
 D. Kurt Gaskill
 Rachael Myers-Ward
 Matthew DeJarlid
 Shojan P. Pavunny
 Marc Currie
 Kevin M. Daniels

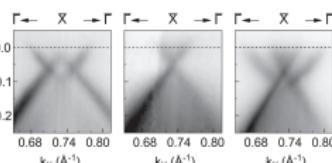


Thank you for your attention!

Summary

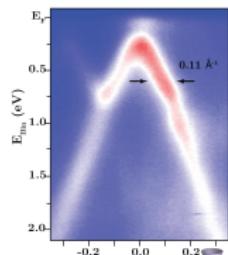


ARPES - a powerful technique to measure electronic structure
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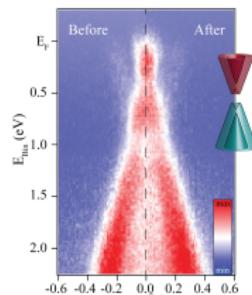
C. M. Polley, ... AGC et al., ACS Nano 12 (1), 617-626 (2018)

2D (Graphene): Tailoring properties by adsorption and intercalation
645 K



Band gap: 290 meV

J. Jørgensen, AGC, et al., ACS Nano 10 (12), 2016



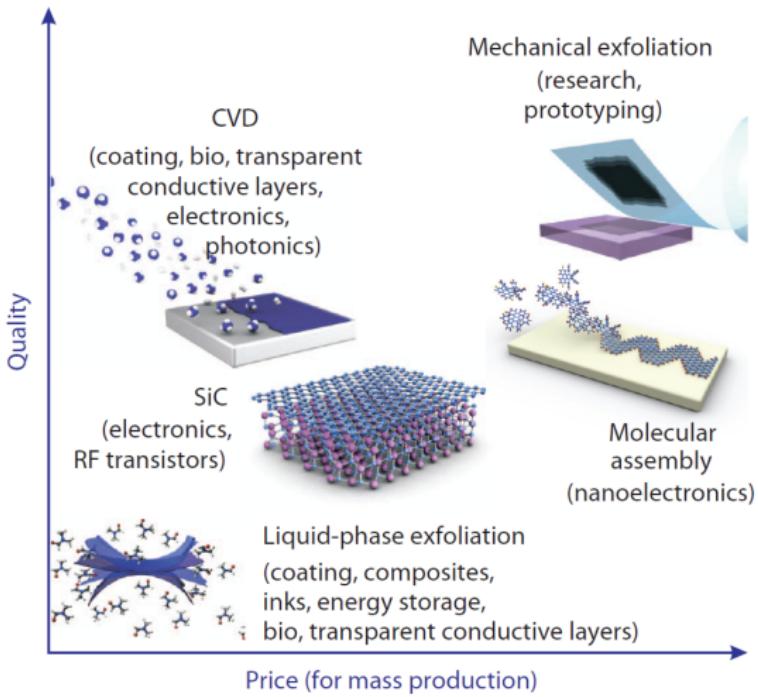
J.C. Kotsakidis, AGC, et al., Chem. Mater. (2020), 32, 15
AGC, et al., Appl. Surf. Sci. 541, 148612 (2021)

[@CaboAntonija](mailto:a.grubisic-cabo@rug.nl)



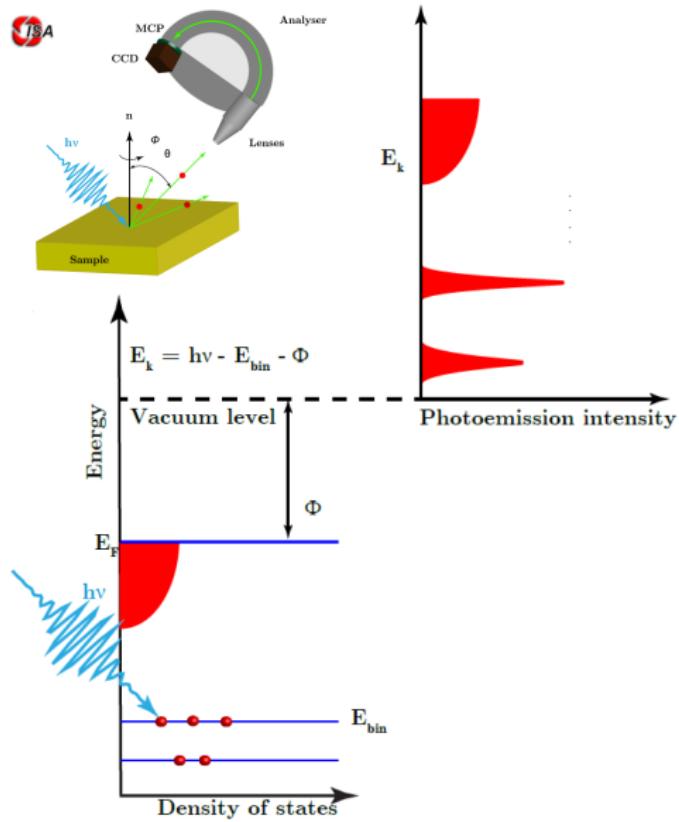
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2D Materials

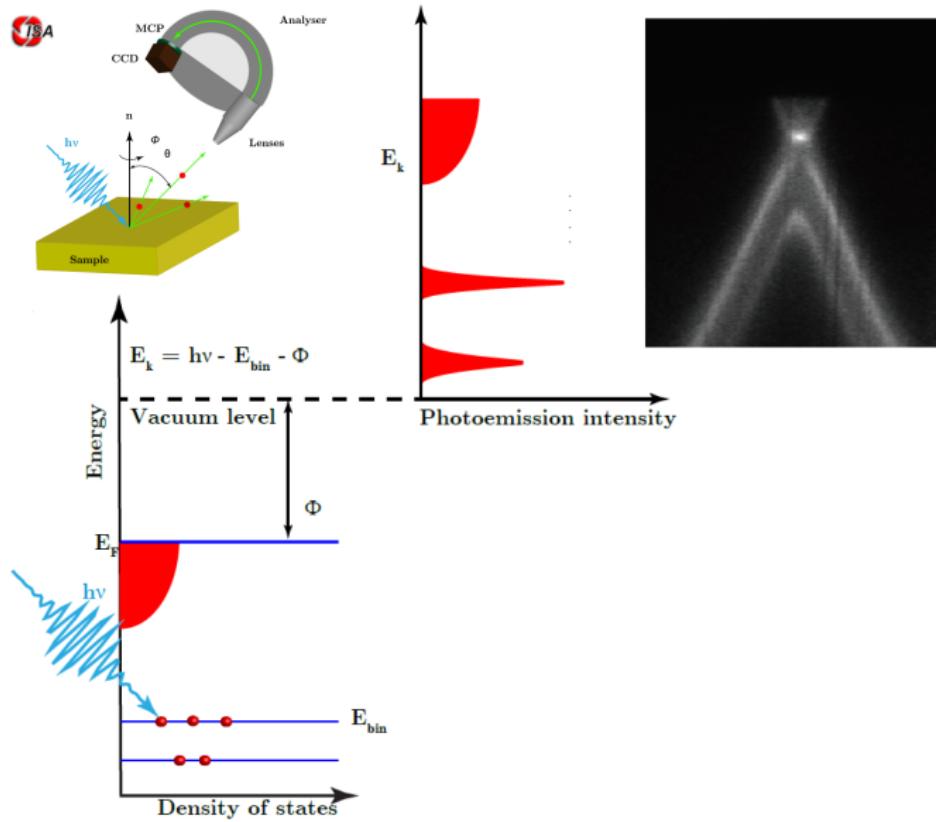


After K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim.
Nature, 490:192–200, 2012

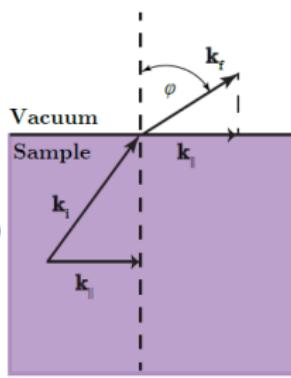
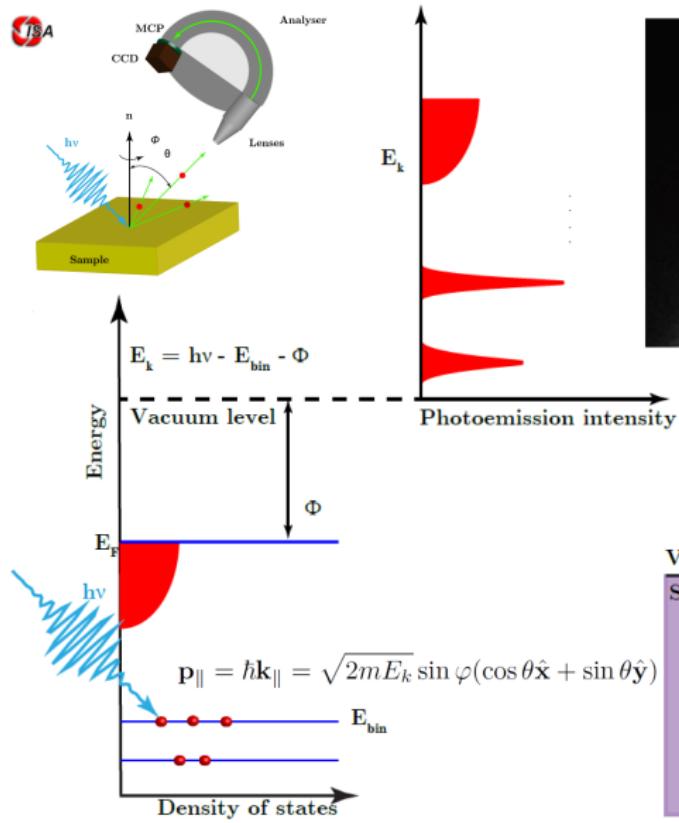
Photoemission



Photoemission



Photoemission



Where can one do ARPES?

- ARPES light sources span a large energy range: 6 – 3000 eV

Where can one do ARPES?

- ARPES light sources span a large energy range: 6 – 3000 eV
- Laser sources: 6 – 11 eV, variable light polarisation, very high energy resolution, but not tunable. Small spot size (tens of μm).
- Laser + High Harmonic Generation:

Where can one do ARPES?

- ARPES light sources span a large energy range: 6 – 3000 eV
- Laser sources: 6 – 11 eV, variable light polarisation, very high energy resolution, but not tunable. Small spot size (tens of μm).
- Laser + High Harmonic Generation: 11 – 100 eV, variable polarisation, lower energy resolution, several available energies. Small spot size (tens of μm).
- Gas (He, Xe, Ne, Ar...) discharge lamp: 21.2, 40.8, 8.4, 9.6, 11.6 eV and more (depending on the gas), energy resolution high (with monochromator), unpolarised light. Large spot size (100 μm to 1 mm).
- Synchrotron: Tunable energy, available energies depend on the synchrotron and the selected endstation (use specific).



Where can one do ARPES?

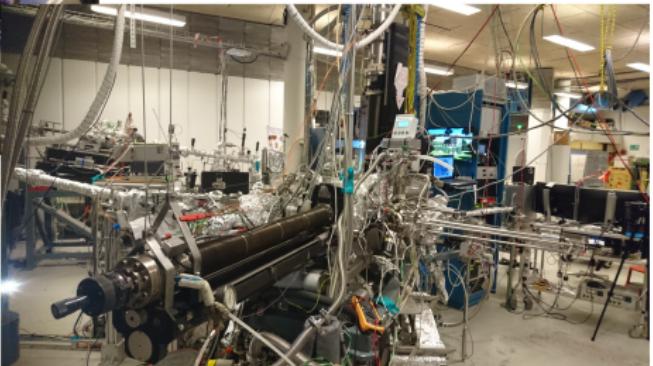
- ARPES light sources span a large energy range: 6 – 3000 eV
- Laser sources: 6 – 11 eV, variable light polarisation, very high energy resolution, but not tunable. Small spot size (tens of μm).
- Laser + High Harmonic Generation: 11 – 100 eV, variable polarisation, lower energy resolution, several available energies. Small spot size (tens of μm).
- Gas (He, Xe, Ne, Ar...) discharge lamp: 21.2, 40.8, 8.4, 9.6, 11.6 eV and more (depending on the gas), energy resolution high (with monochromator), unpolarised light. Large spot size (100 μm to 1 mm).
- Synchrotron: Tunable energy, available energies depend on the synchrotron and the selected endstation (use specific). Energy resolution can be high to low, depending on the endstation and need. Several fixed polarisations. Spot size usually medium (100-200 μm), with specialised end stations having even $<1\mu\text{m}$ spot size.



ASTRID2 & Australian Synchrotron



How it looks



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