Electronic Properties of Graphene on Metallic and Semiconducting Surfaces

Ivana Vobornik
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Istituto Officina dei Materiali

APE Beamline(**s**) (Elettra synchrotron):
Advanced **P**hotoelectric **E**ffect Experiments
in a ***full size surface science laboratory***

Diracland – a romance in two dimensions

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Advanced **P**hotoelectric **E**ffect Experiments
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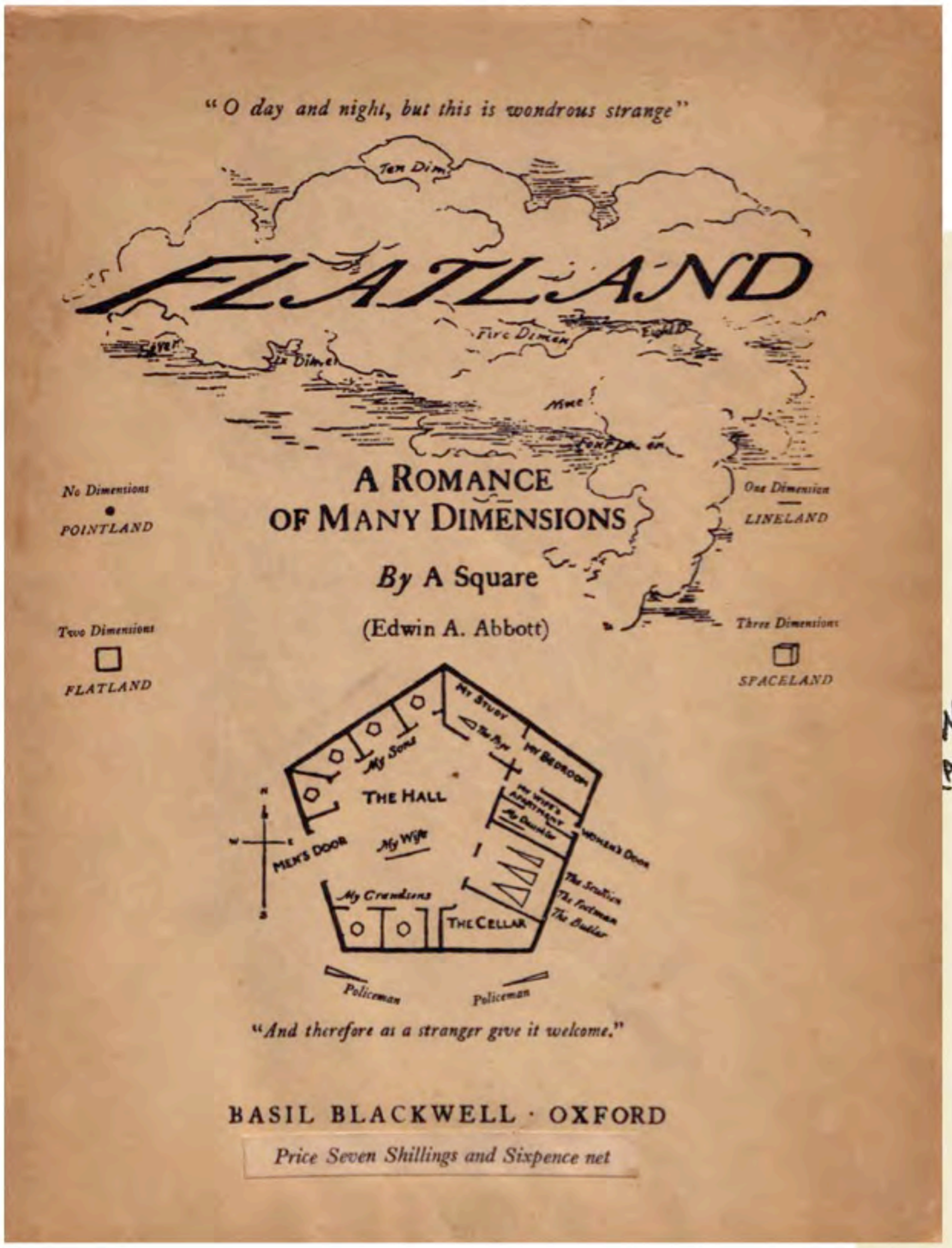
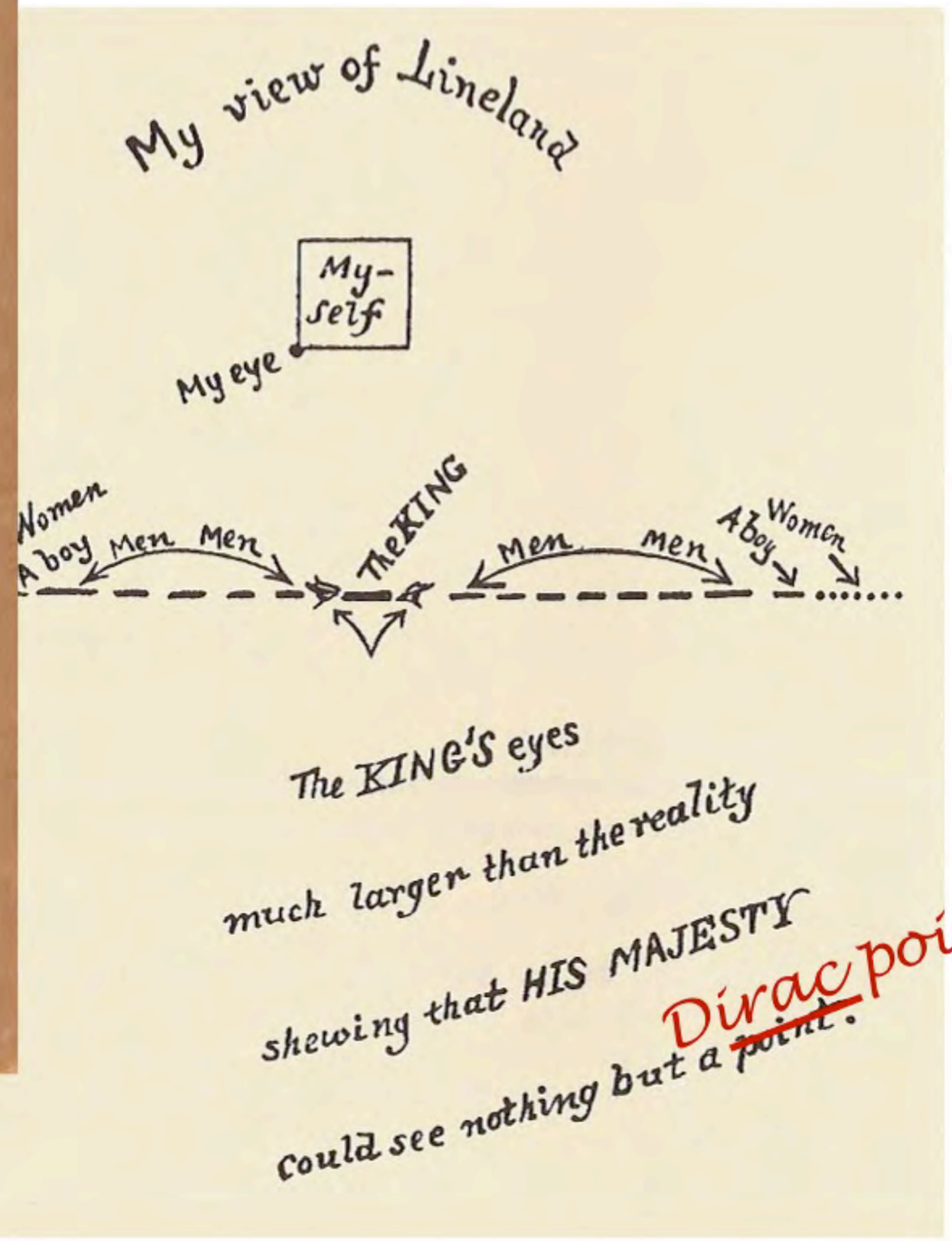
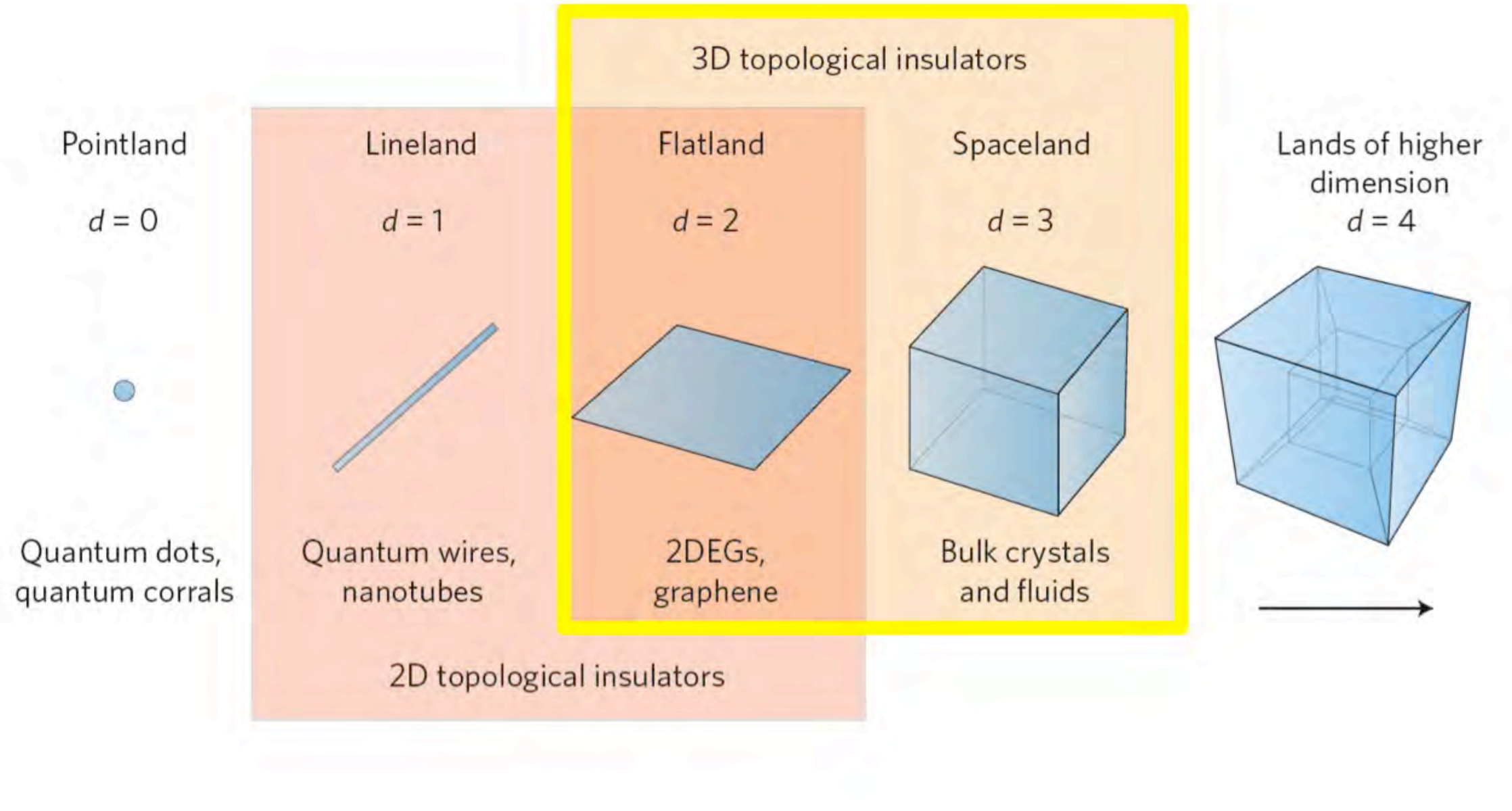
A Romance of Many Dimensions





Physics today



Hari C. Manoharan, Nature Nanotechnology 5, 477 (2010), news and views

Outline

➔**Graphene on cubic SiC/Si and on Ir(111)**

***collaboration with V. Aristov**, Leibniz Institute, Dresden, D, Russian Academy of science, Moscow, Russia*

V. Aristov et al. Nano Letters **10**, 992–995 (2010)

***collaboration with P. Pervan**, IFS, Zagreb University, Croatia*

M. Kralj et al., in preparation

➔ **The role of topology**

➔ **Magnetism in topological insulators**

***collaboration with R.J. Cava**, Princeton University, USA*

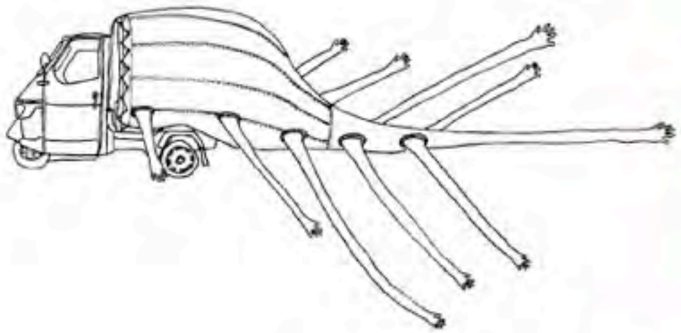
➢**Beamline APE** @ Elettra

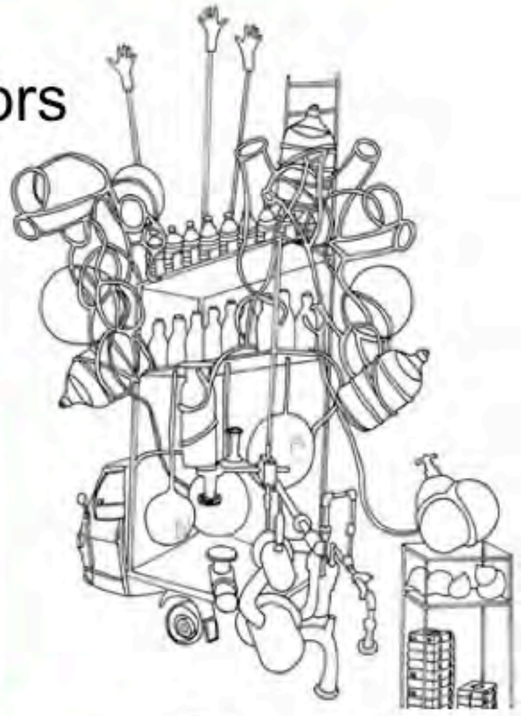
- tool for combined structural and spectroscopic studies of surfaces, interfaces, organic films, magnetic materials,…

APE BeamlineS

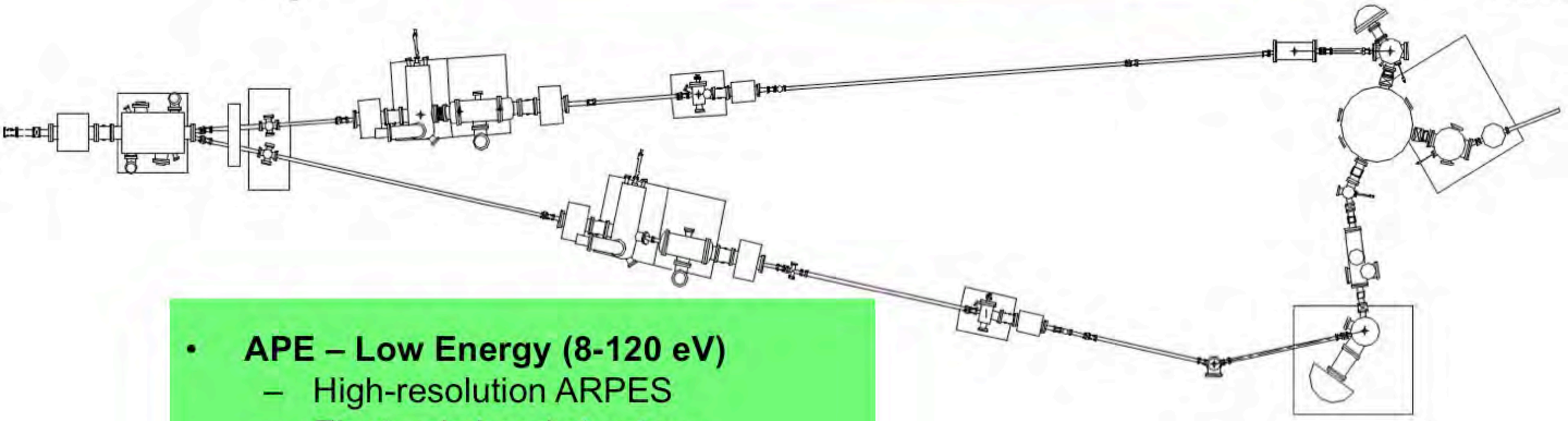
Two independent, off-axis, variable polarization (APPLE type) undulators

→ **two independent canted beamlines operating simultaneously**





- **APE – High Energy (150-1600 eV)**
  - XPS spectroscopy
  - X-ray absorption (XAS, XMCD, XMLD)



- **APE – Low Energy (8-120 eV)**
  - High-resolution ARPES
  - Electronic band structure
  - Fermi surface mapping
  - Fermi surface instabilities

APE Laboratory

Omicron EA125

APE-HE

Variable polarization photons 150-1600 eV

Distribution center

Users' docking ports

STM

Load-lock

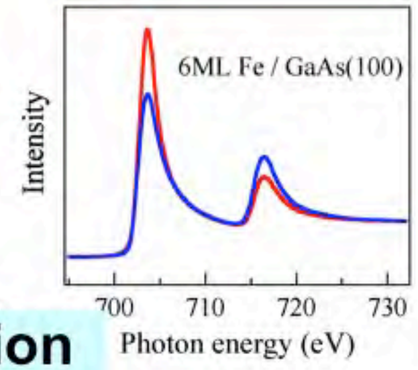
MO Kerr effect;
LEED/Auger
Sample growth and prep.

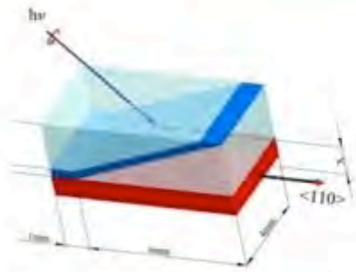
Sample preparation

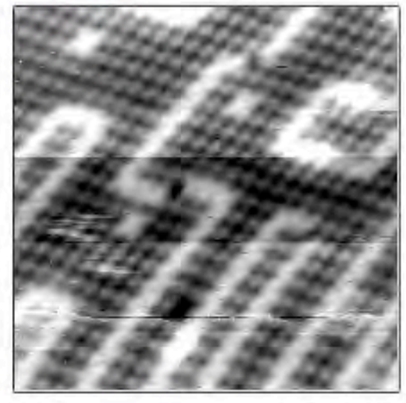
APE-LE

Variable polarization photons 8-120 eV

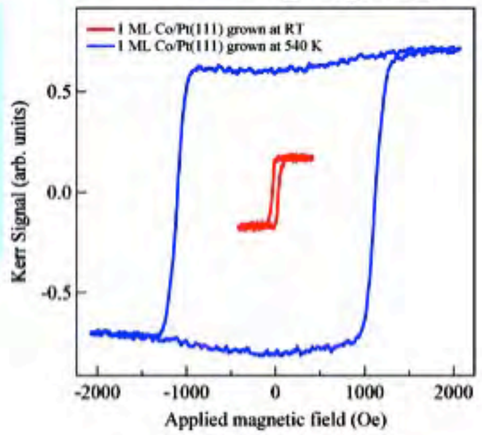
Scienta SES2002

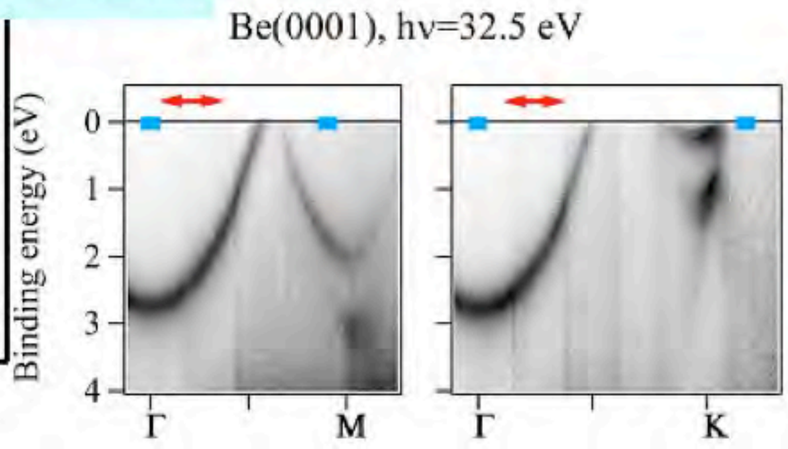


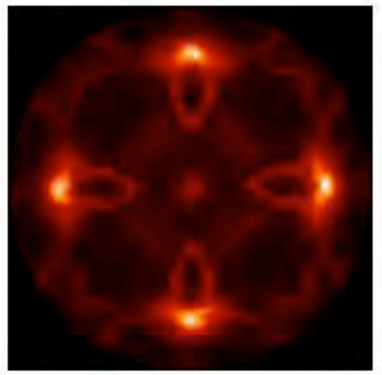




S segregation on Fe(100)







Fe(100) Fermi surface

Graphene in real life

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Radical fabric is one atom thick

A new class of material, which brings computer chips made from a single molecule a step closer, has been discovered by scientists.

Called graphene, it is a two-dimensional, giant, flat molecule which is still only the thickness of an atom.

The new class of material is much more stable than others

- **AIM:** mass production of graphene with **preserved and controlled properties**

- **PROBLEMS:**
  - → the original production method (mechanical exfoliation) results in **small graphene flakes**, not suitable for industrial scale applications
  - → The properties of **epitaxial graphen** are always to some extent **altered by the presence of the substrate**

Epitaxial graphene on metallic and semiconducting surfaces

➔**Epitaxial growth on Ir (111)**

➔Lattice-mismatch-induced moiré superstructure

➔Multiple Dirac cones and gaps in the band structure

➔**Epitaxial growth on 3C-SiC (β-SiC)**

➔Cubic SiC substrate (commercially available)

➔Graphene flakes decoupled from the substrate

Graphene on Ir(111)

➔ **Epitaxial growth on Ir (111)**

➔ **High structural quality** over mm scale

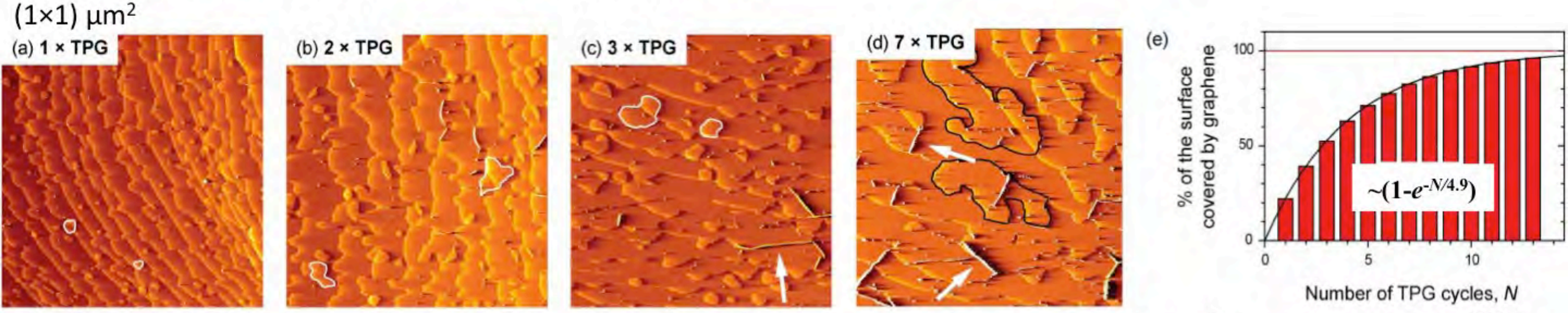
➔ **The solubility of C is insignificant** at graphene formation temperatures ➔ permits controlled growth by **hydrocarbon decomposition**

➔ Two growth modes:

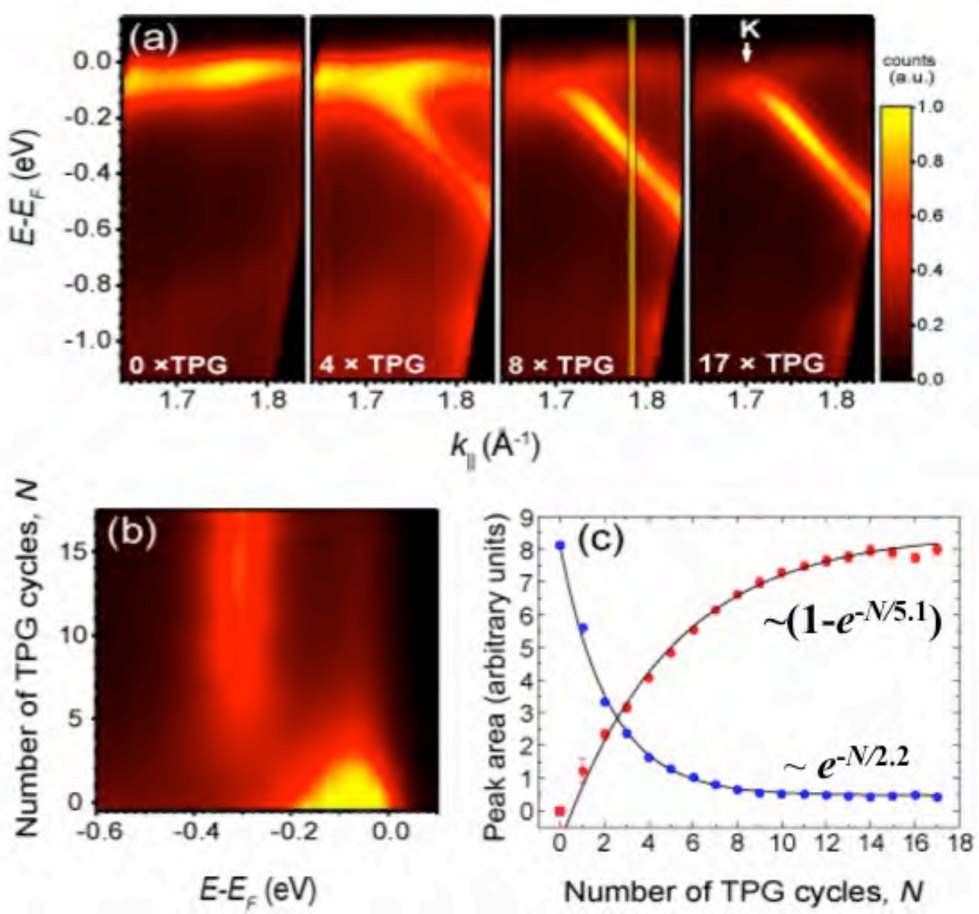
- **Direct exposure of the hot substrate** to a hydrocarbon (ethene)
- **Low temperature hydrocarbon exposure** followed by **thermal (~1500 K) decomposition** (Temperature Programmed Growth-TPG)

Graphene on Ir(111) – growth characterization STM, ARPES

➔**TPG growth on Ir (111):** >10 Langmuir ethene exposure per cycle (saturation at RT) and subsequent heating to 1470 K



➢Area (%) covered by graphene as a function of a number N of TPG cycles scales as $\mathbf{1\text{-}e^{-N/4.9}}$

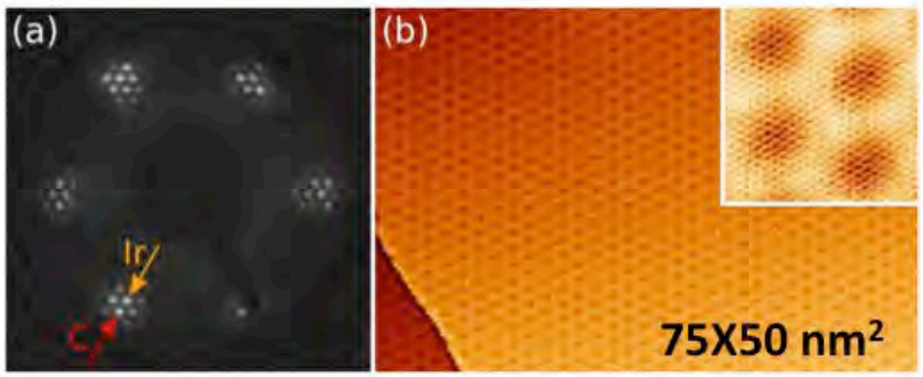


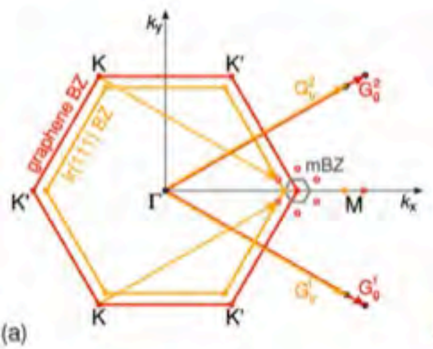
➢Progressive suppression if the Ir(111) SS signal and appearance of the Dirac cone

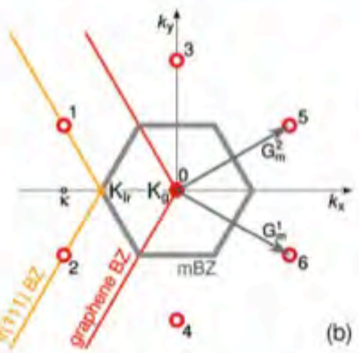
Ir: $\sim e^{-N/2.2}$

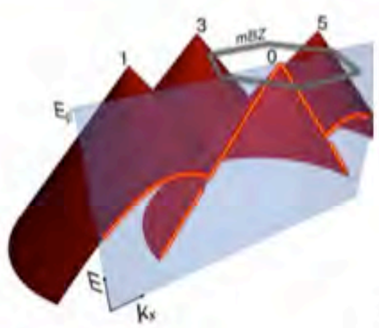
Graphene: $\sim 1\text{-}e^{-N/5.1}$

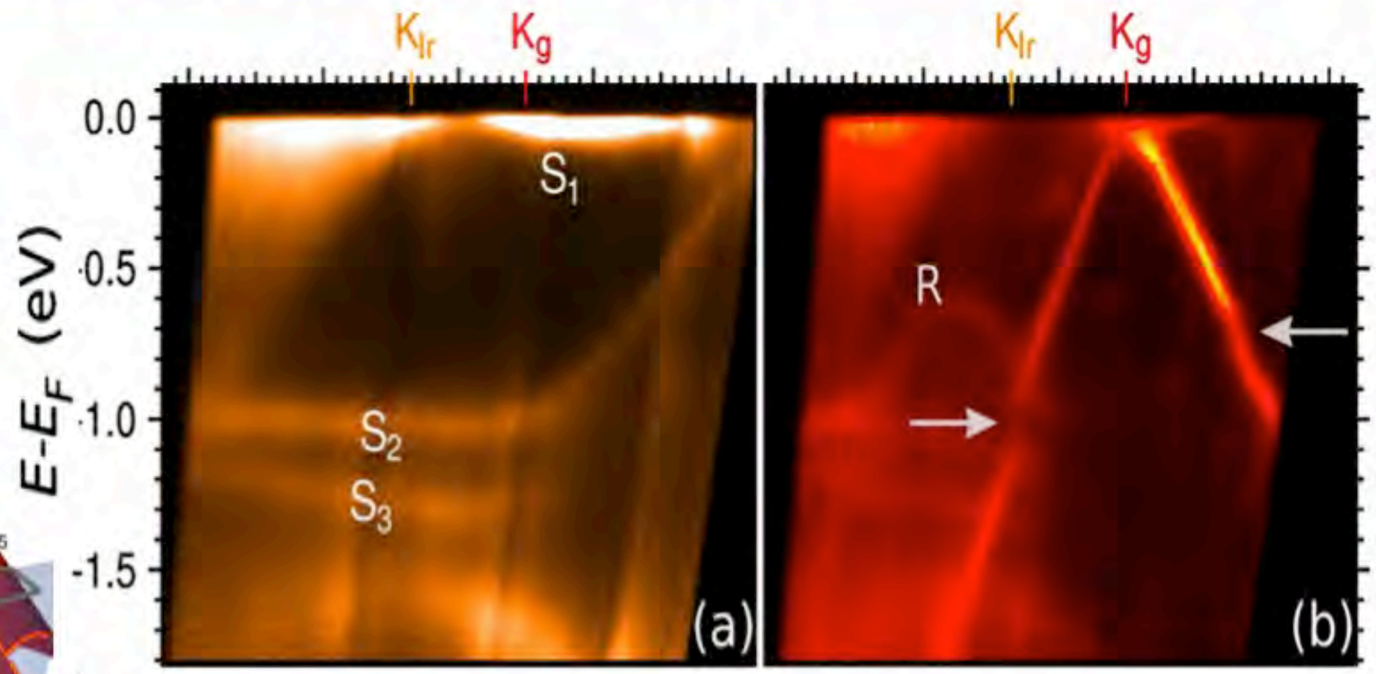
Graphene on Ir(111) – lattice mismatch











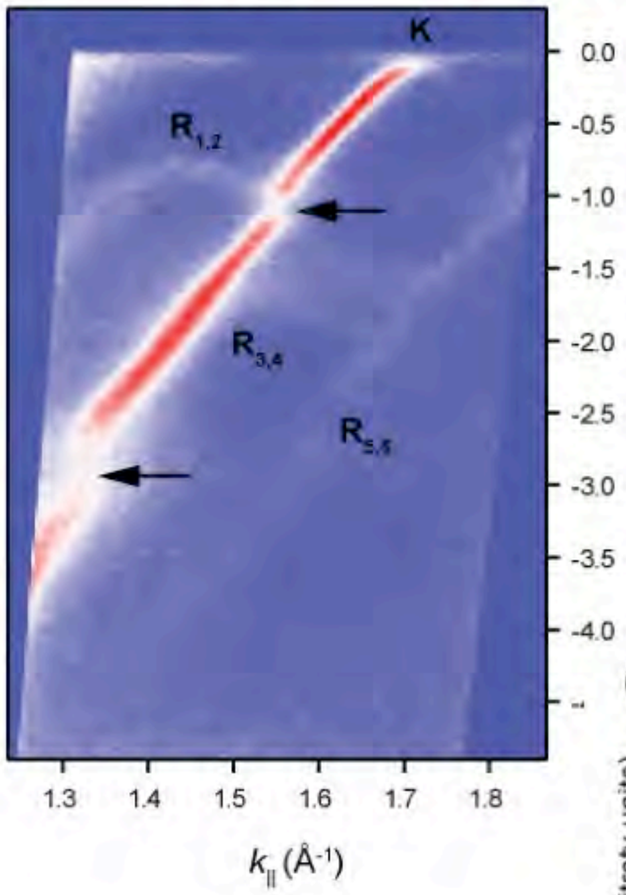
- The lattice mismatch between graphene and Ir(111) results in moiré superstructure → a corresponding superperiodic potential exists and gives rise to the **opening of gaps** in the band structure
- Graphene **superlattices** could be used for tuning the propagation velocity and the density of charge carriers, which is of practical interest in building graphene based electronic components
- Gap at E_F was found in hydrogenated graphene/Ir(111) (R. Balog et al., Nature Materials 9, 315–319 (2010))

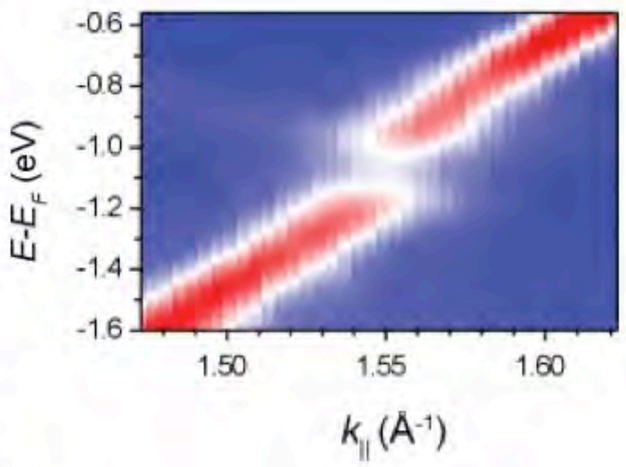
I. Pletikosic et al., Phys. Rev. Lett. 102, 056808 (2009), M. Kralj et al., in preparation

Graphene on Ir(111) – cook book

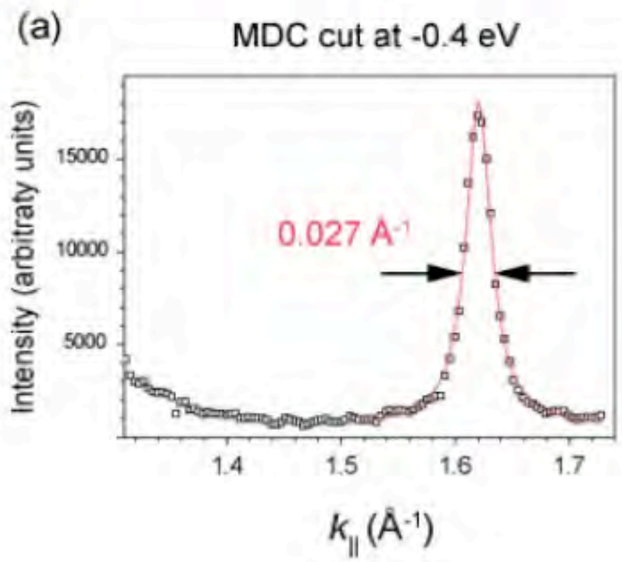
- Temperature programmed graphene growth (TPG) on Ir (111)
  high quality graphene / long preparation procedure

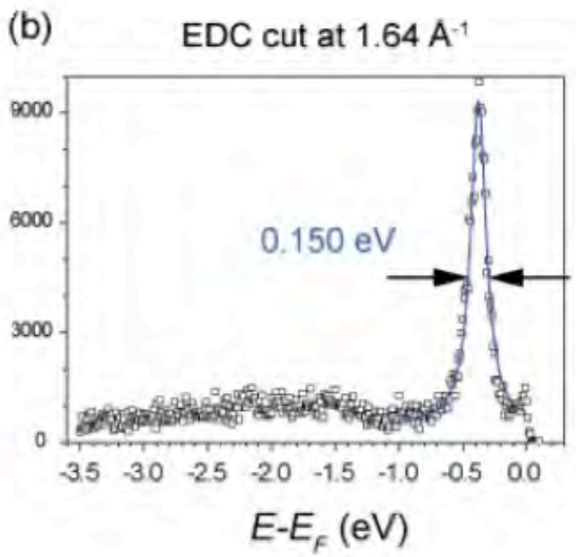
➔TPG cycle + CVD 5min.; 6X10^{-6} Pa ethene @ 1150K

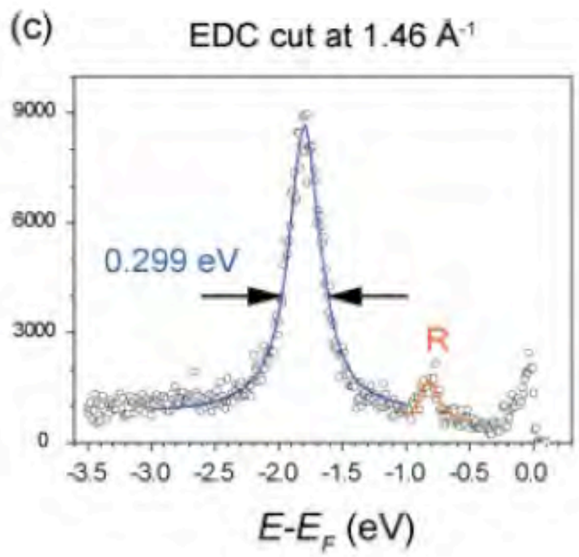




- **Decreased preparation time**
- **High quality** maintained



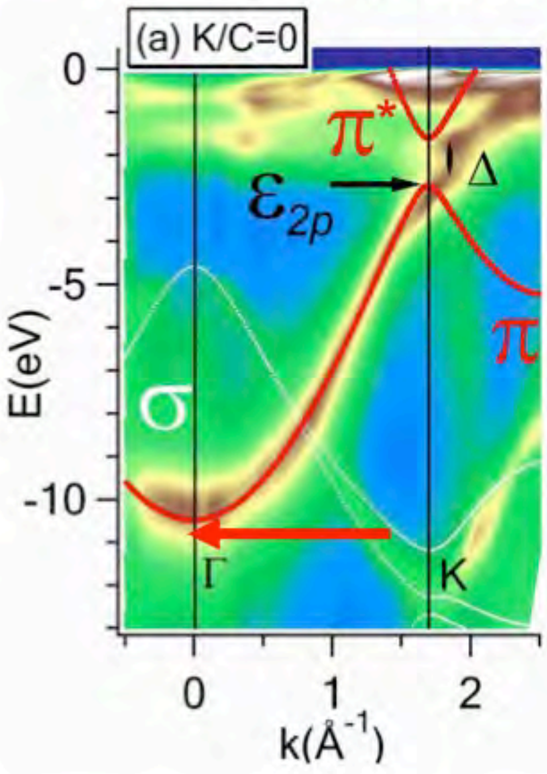




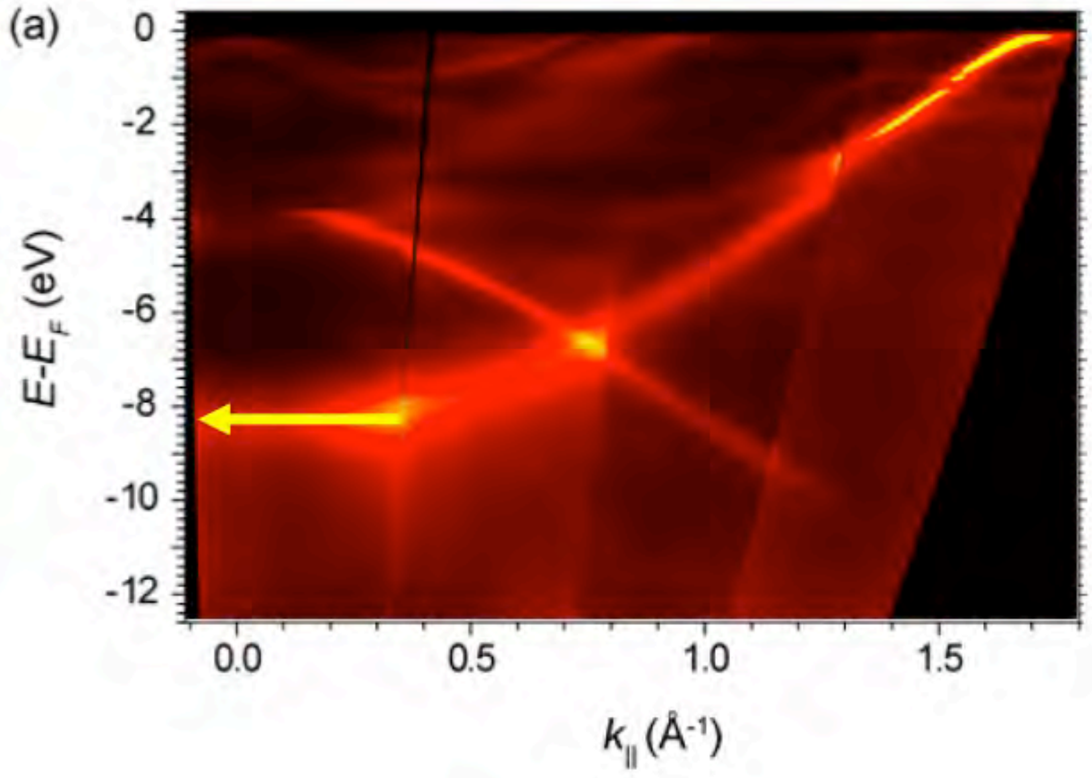
Graphene on Ir(111) vs. Ni(111) and SiC(0001)

Ni(111)

A. Grüneis & D. V. Vyalikh
PRB 77, 193401 (2008)

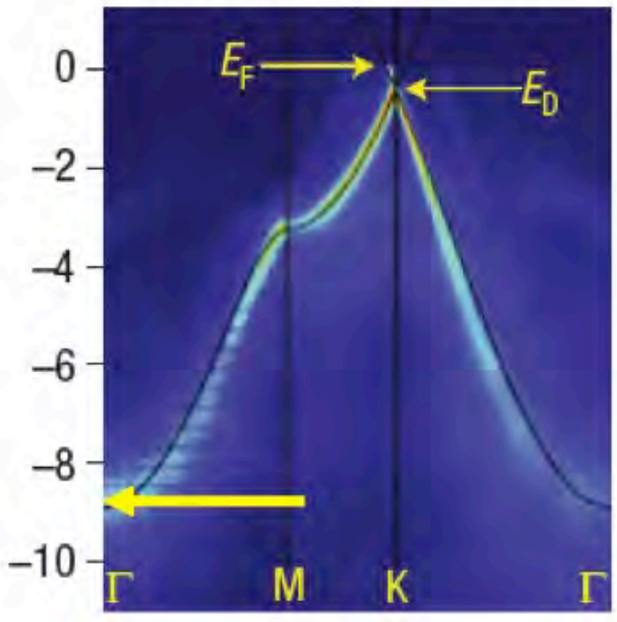


Ir(111)



SiC(0001)

A. Bostwick et al.,
Nat. Phys. 3, 36 (2007)



- The position of the π band vertex at Γ gives a measure of the **hybridization with the substrate**
- Graphene/Ir(111) is comparable to graphene/SiC

Graphene on Cubic SiC/Si Wafers

➔**The choice of substrate**

➔**Comparable lattice structure** (Ni(111), SiC(0001), Ir(111), Ru(0001))

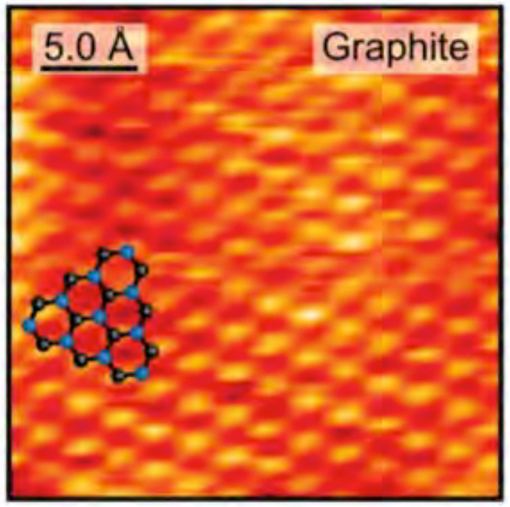
➔**Interaction with the substrate** either through structural modulation or band hybridization

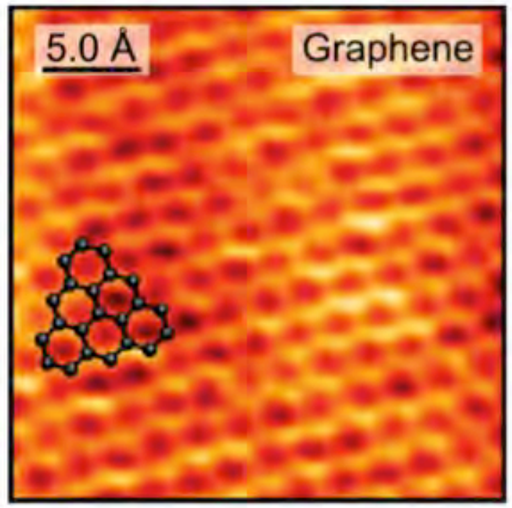
➔**Apparent lattice mismatch - cubic SiC/Si**

- Easily grown on commercially available Si(001) wafers by CVD ($\sim 1\mu m$ SiC films doped with nitrogen (n-type doping) at 10^{17} cm^{-3}; iterative cycles of Si deposition followed by thermal annealing resulting in c(4x2) Si-rich surface; subsequent Si sublimation at ~1200°C C-rich **(graphene)** surfaces)

➔**Interaction with the substrate almost negligible !**

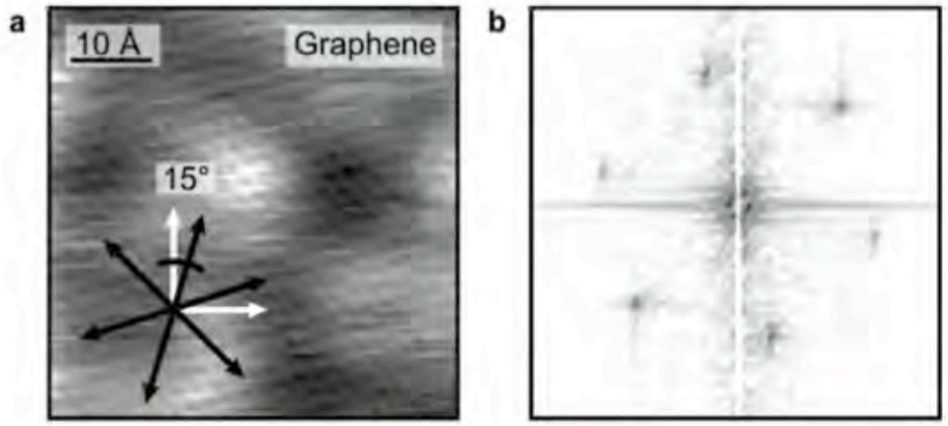
Graphene on Cubic SiC/Si Wafers





Graphite structure:
The two nonequivalent atom sites (black and blue)

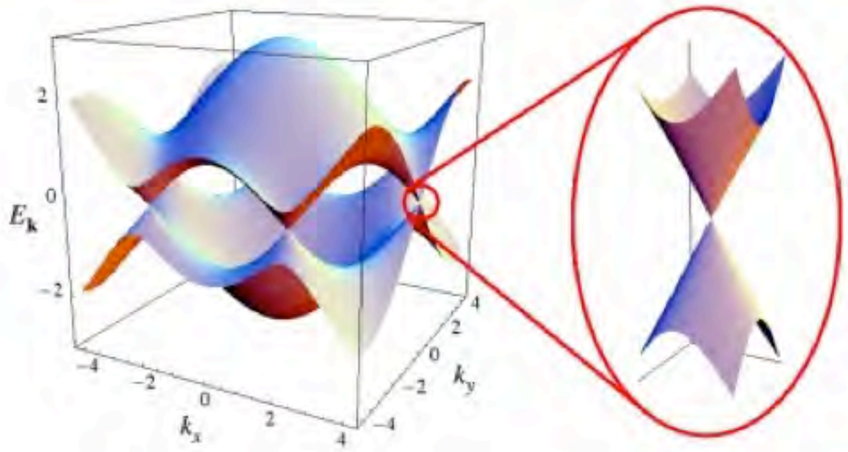
Graphene structure:
All carbon atom sites are equivalent. Hence the characteristic honeycomb pattern shows up.

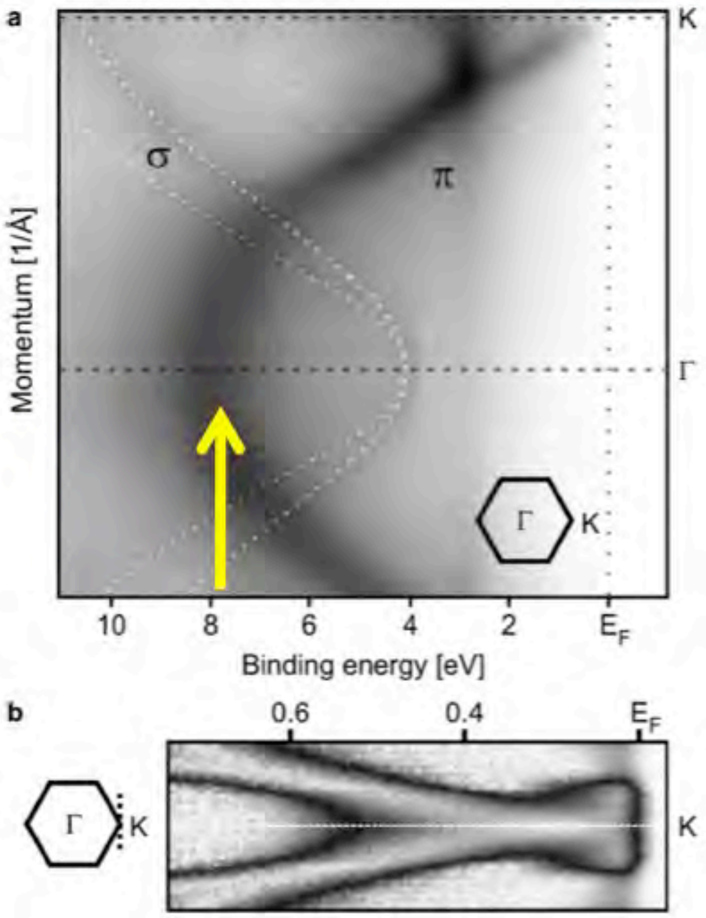


Graphene organization on cubic SiC:
Graphene [11-20] direction parallel to [110] direction of the substrate

V. Aristov et al. Nano Letters 2010, **10**, 992–995

Graphene on Cubic SiC/Si Wafers



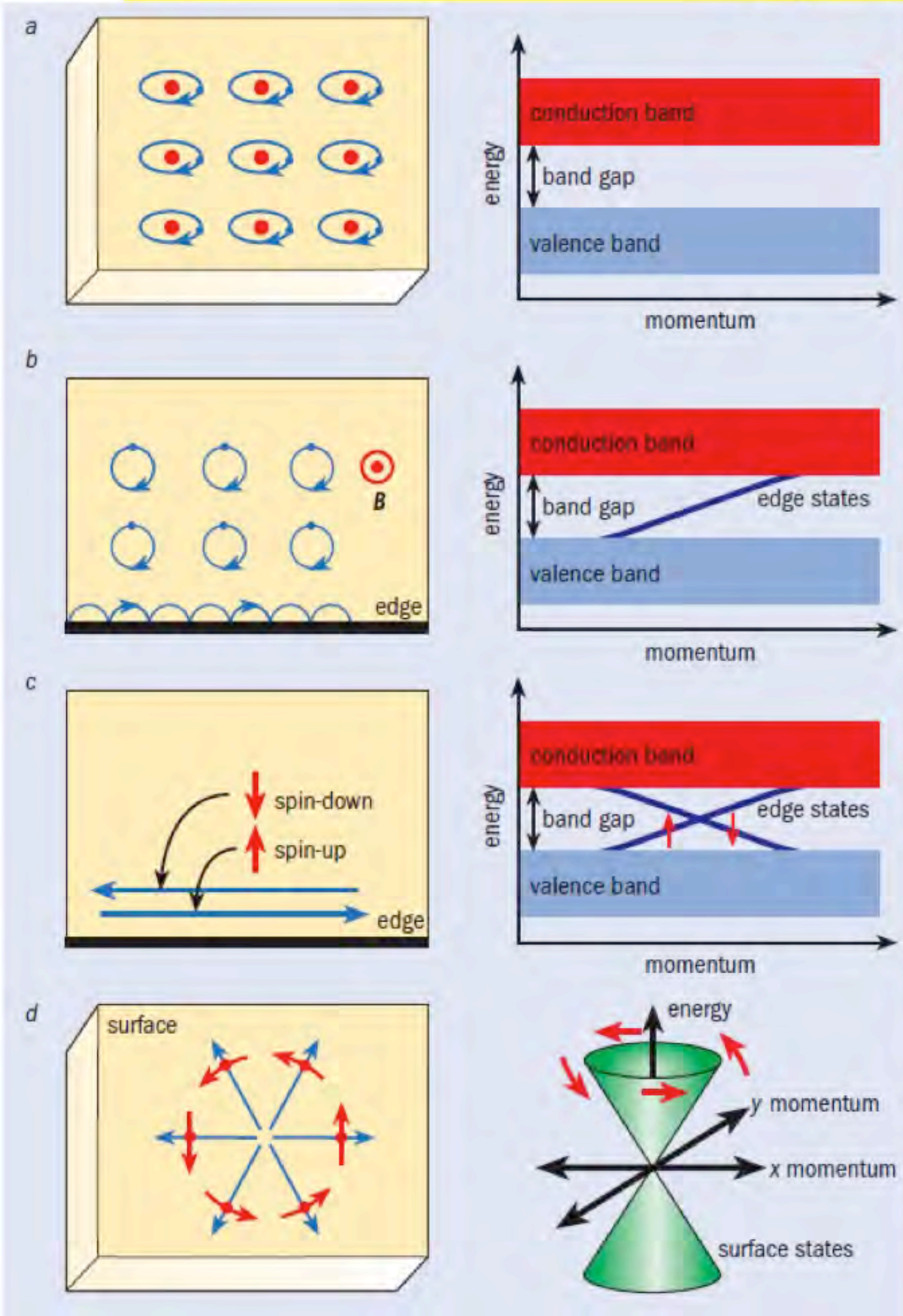


- **Despite apparent lattice mismatch, graphene can be grown on β-SiC/Si**
  cheap and commercially available wafers

- **Very weak interaction with the substrate**
  – likely because of the lattice mismatch

V. Aristov et al. Nano Letters 2010, **10**, 992–995
Among top-20 most downloaded Nano Letters in 2010 2nd semester

Topology matters



Insulating state – characterized by an energy gap between filled and empty states

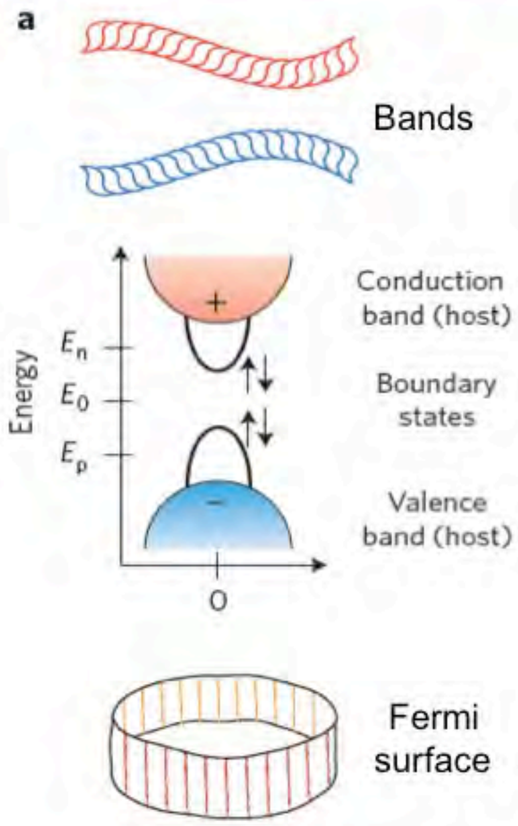
Quantum Hall state – the circular motion of the electrons, induced by the **applied magnetic field** is interrupted by the sample boundary; the skipping orbits at the edge lead to perfect conduction along the edge

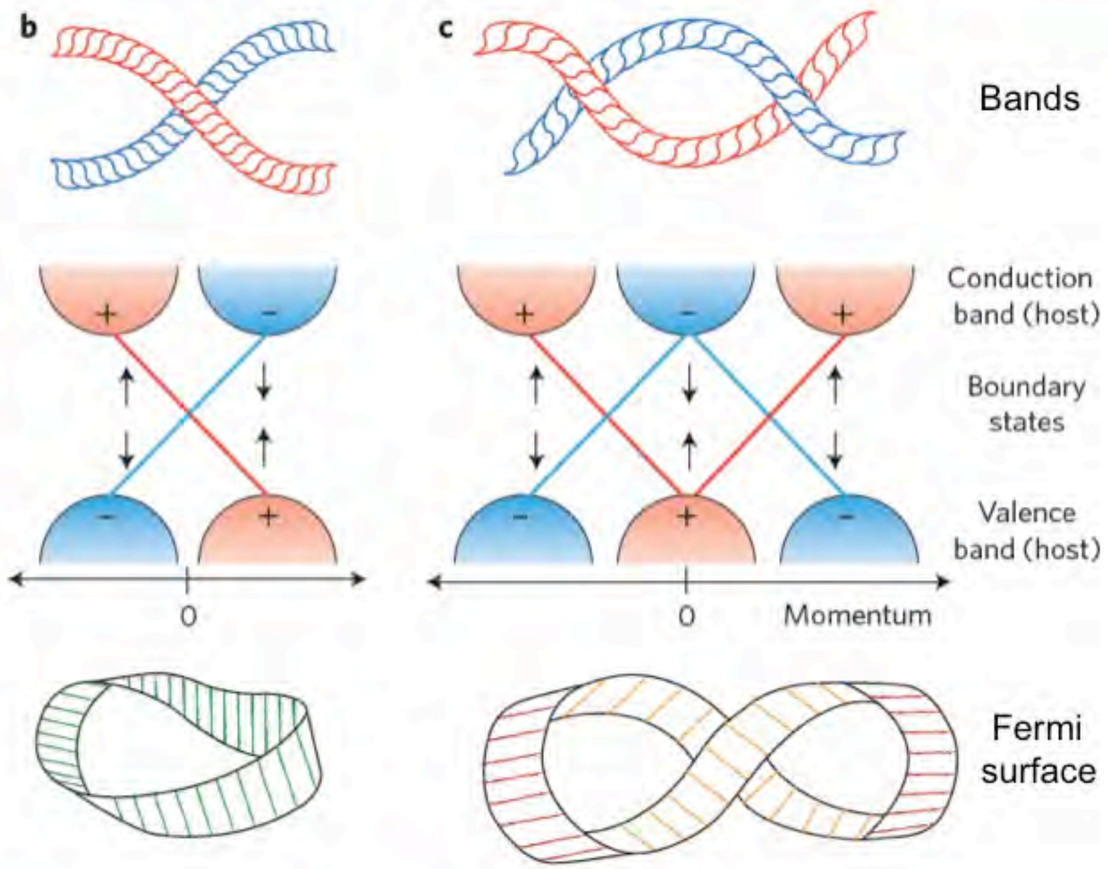
Quantum spin Hall state – instead of the applied field – **spin-orbit coupling** results in the two edge modes with opposite spins related by **time reversal symmetry**

3D case – electronic motion in any direction; direction of the motion determines the spin and vice versa; **Dirac dispersion**

C. Kane & J. Moore, Physics World, Feb.2011, 32

The role of the S-O interaction





➔Without spin-orbit interaction

Valence (antibonding orbitals, antisymmetric wave functions) and conduction (bonding orbitals, symmetric wave functions) bands; spin up and down electrons have the same energies

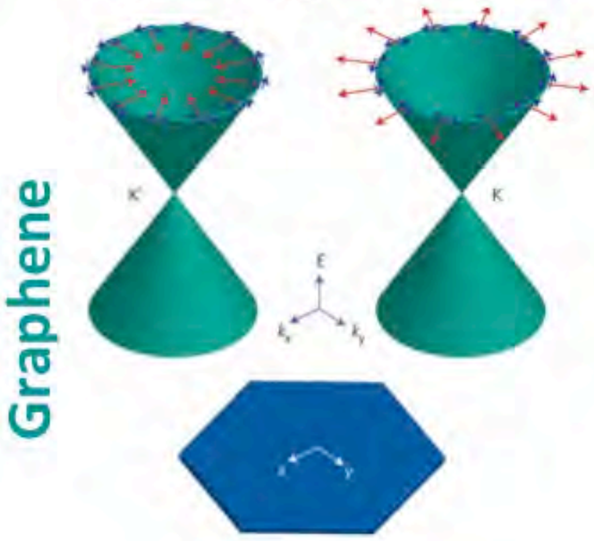
➔With spin-orbit interaction

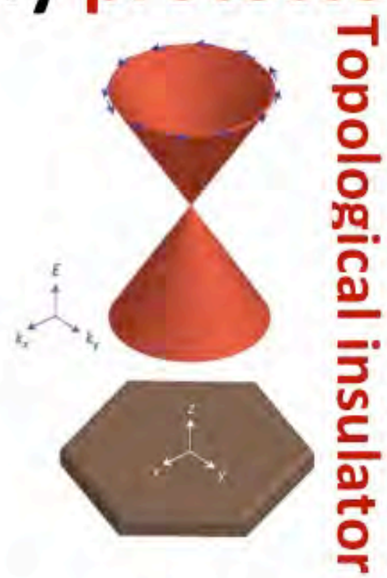
The **inversion** of symmetric and antisymmetric states may occur (topological twisting);
the number of twists determines **the number of Dirac cones**;
if **odd** – backscattering is forbidden
when **time-inversion symmetry** is preserved

H.C. Manoharan, Nature Nanotechnology 5, 477 (2010), news&views

Graphene vs. topological insulators

Topologically trivial vs. topologically protected





Graphene:

4 Dirac cones; charges with opposite spins have nearly the same energy (2 overlapping cones); both sets of cones characterized by **pseudospin**

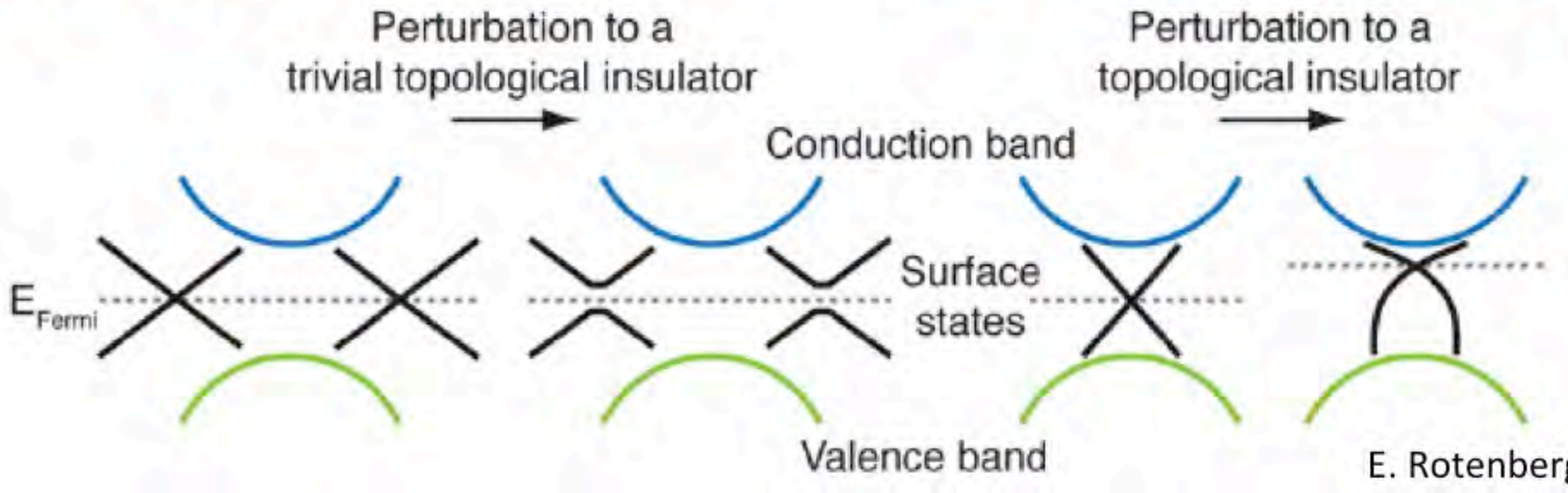
Protection against scattering – **pseudospin** (lattice determined);

change in the lattice – gap at the Dirac point

TIs:

Dirac cone describes the surface of the insulator with **large spin-orbit coupling**; the spin circulates around the constant energy contour in momentum space;

Surface states are preserved as long as the time inversion symmetry is preserved!

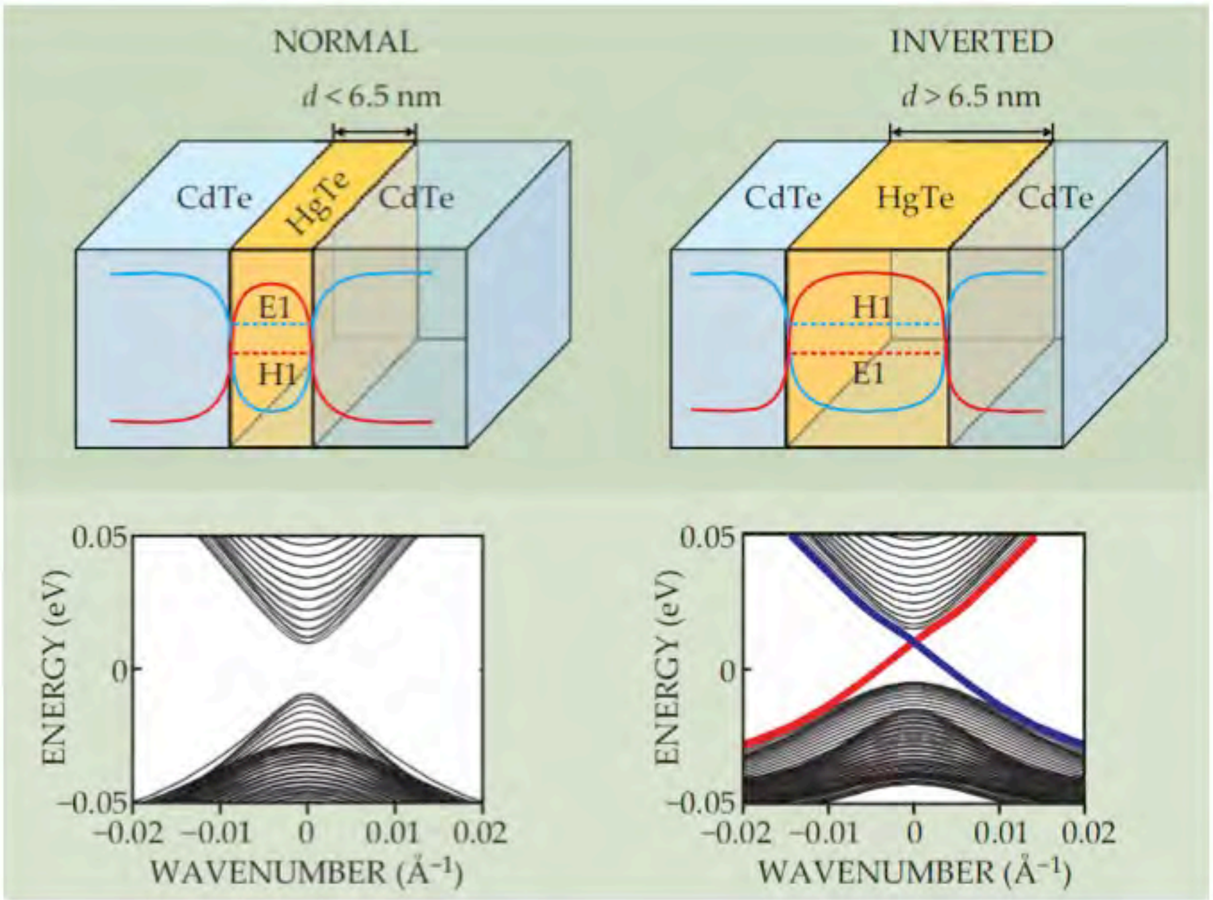


E. Rotenberg, Nat. Physics 7, 8 (2011)

Materials

2D:

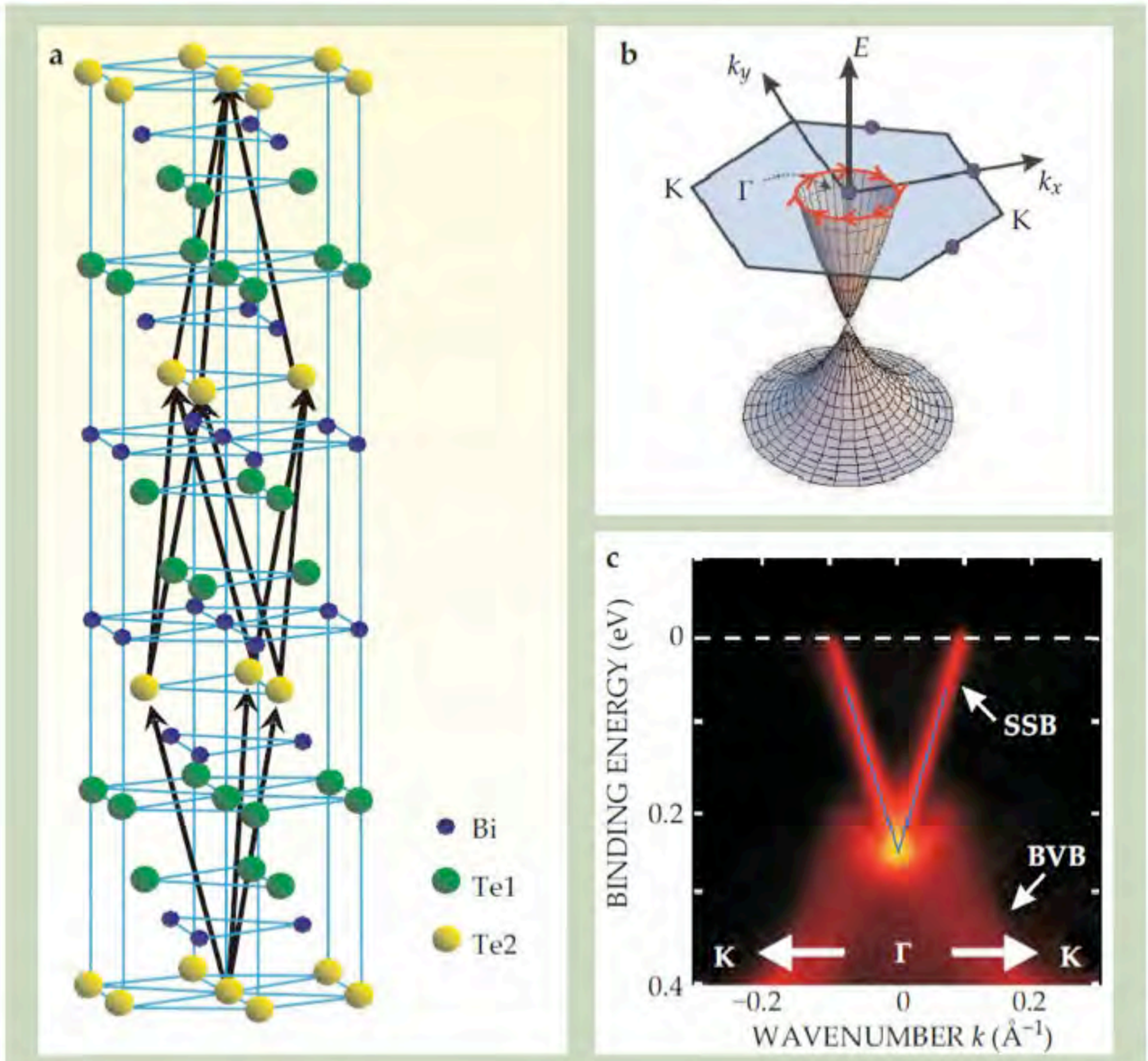
HgTe quantum well states



M. Konig et al., Science 318, 766 (2007)

3D:

BiSb, Bi_2Te_3, Bi_2Se_3, surface states

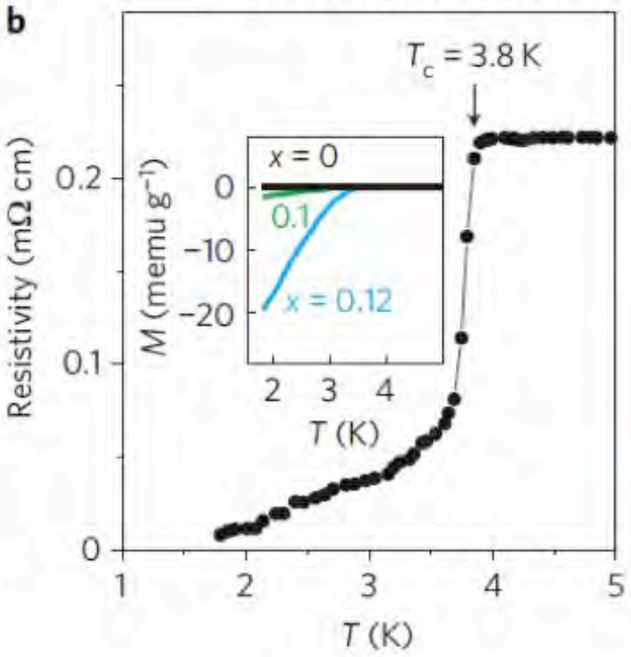


X-L Qi, S-C Zhang, Physics Today, Jan.2010, 33

Doping topological insulator

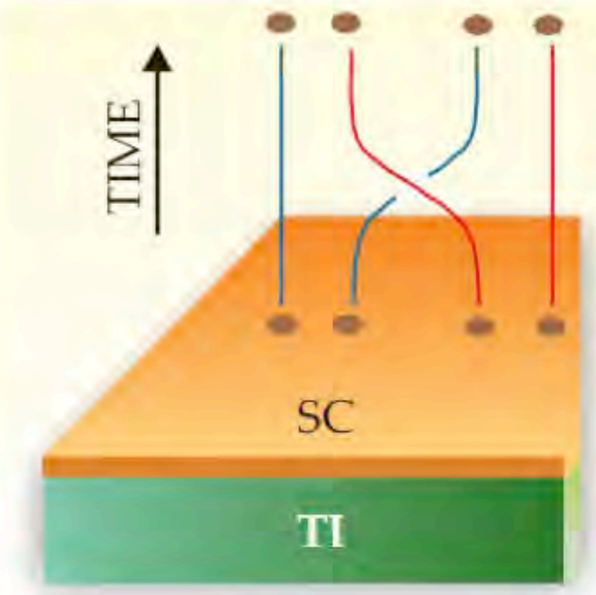
- **Superconductivity**
  - Cu doping in Bi_2Se_3 (Wray et al., Nat. Physics 6, 855 (2010)) – bulk superconductivity

interplay between topological and broken-symmetry order



bulk superconducting pairing occurs in the presence of a two-dimensional topological surface state

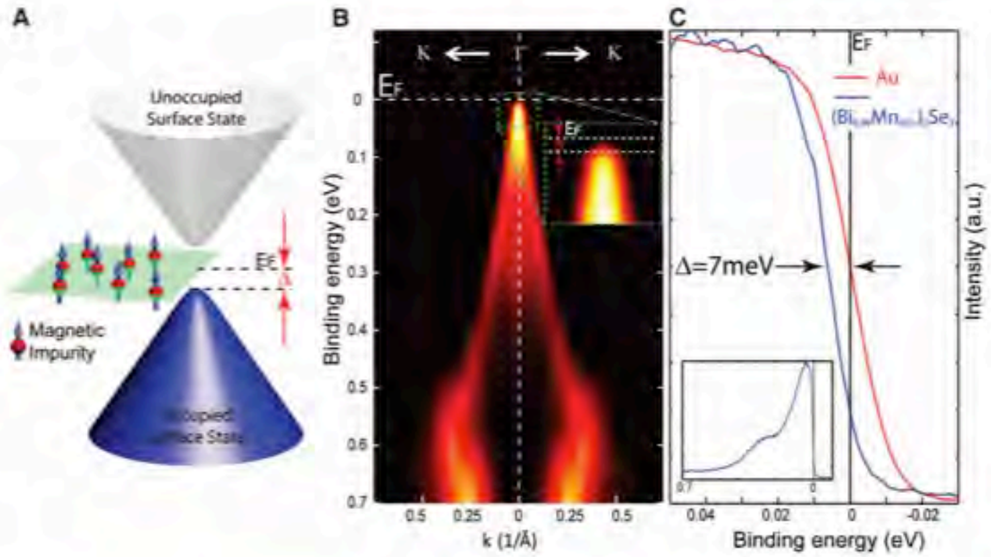
➔possible realization of **Majorana fermions**



Doping topological insulator

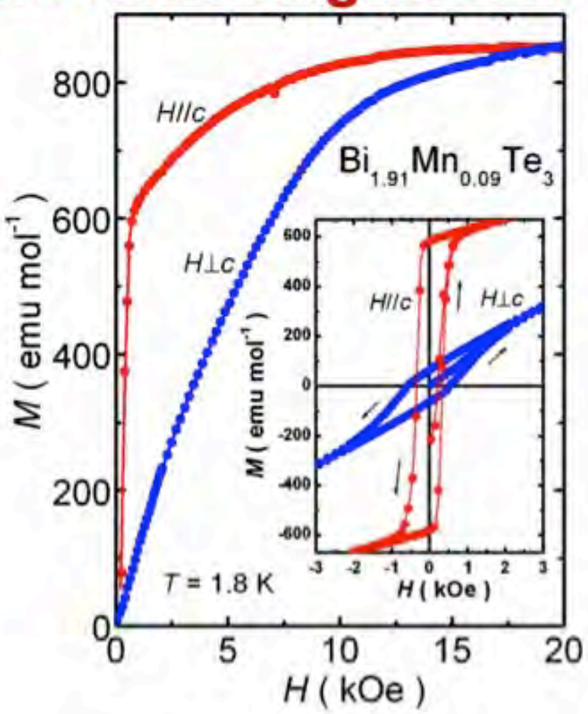
➢Ferromagnetic impurities

Magnetic impurities **break time-reversal symmetry – gap** in the surface state opens (Y.L. Chen et al., Science 329, 659 (2010); L.A. Wray et al., Nat. Physics 7, 21 (2011))



➔The surface turns into **quantum Hall insulator; dissipationless switching of the magnetic moments** (I. Garate & M. Franz, PRL 104, 146802 (2010))

➢Bulk ferromagnetism – diluted Mn doping

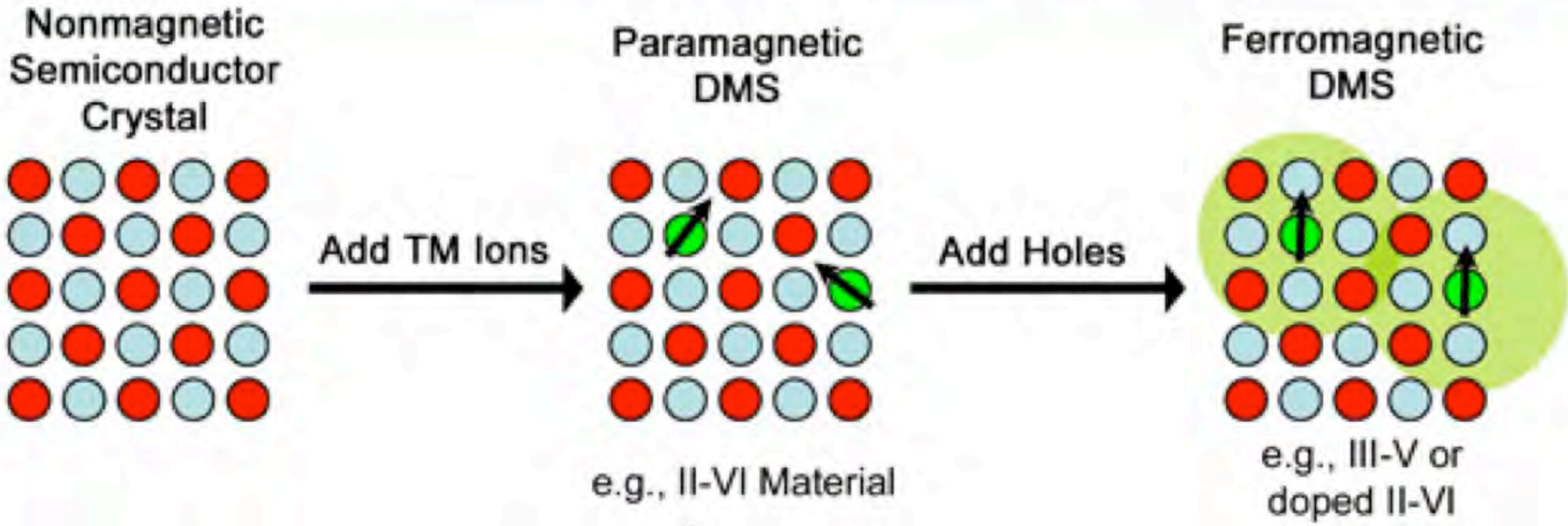


➢Mn doping (Y.S. Hor et al., PRB 81, 195203 (2010))

The Mn magnetic moments (bulk) **align ferromagnetically at T_C~12 K**, with easy magnetization axis perpendicular to the surface

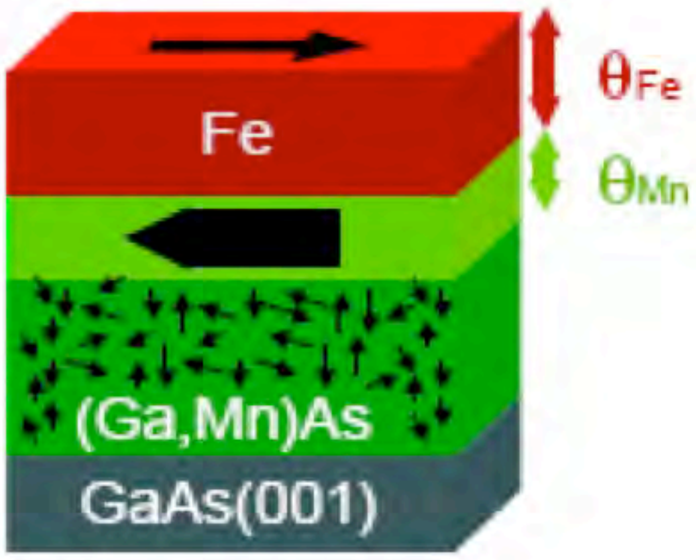
Can magnetism in Tis be controlled?

Ferromagnetic semiconductors - model system: $Ga_{1-x}Mn_xAs$



Highest Curie temperature ≈170K → Unsuitable for spintronics applications

A.H. Macdonald et al., Nature Mat. 4, 195 (2005)



Magnetic proximity effect – Fe layer on top of $Ga_{1-x}Mn_xAs$

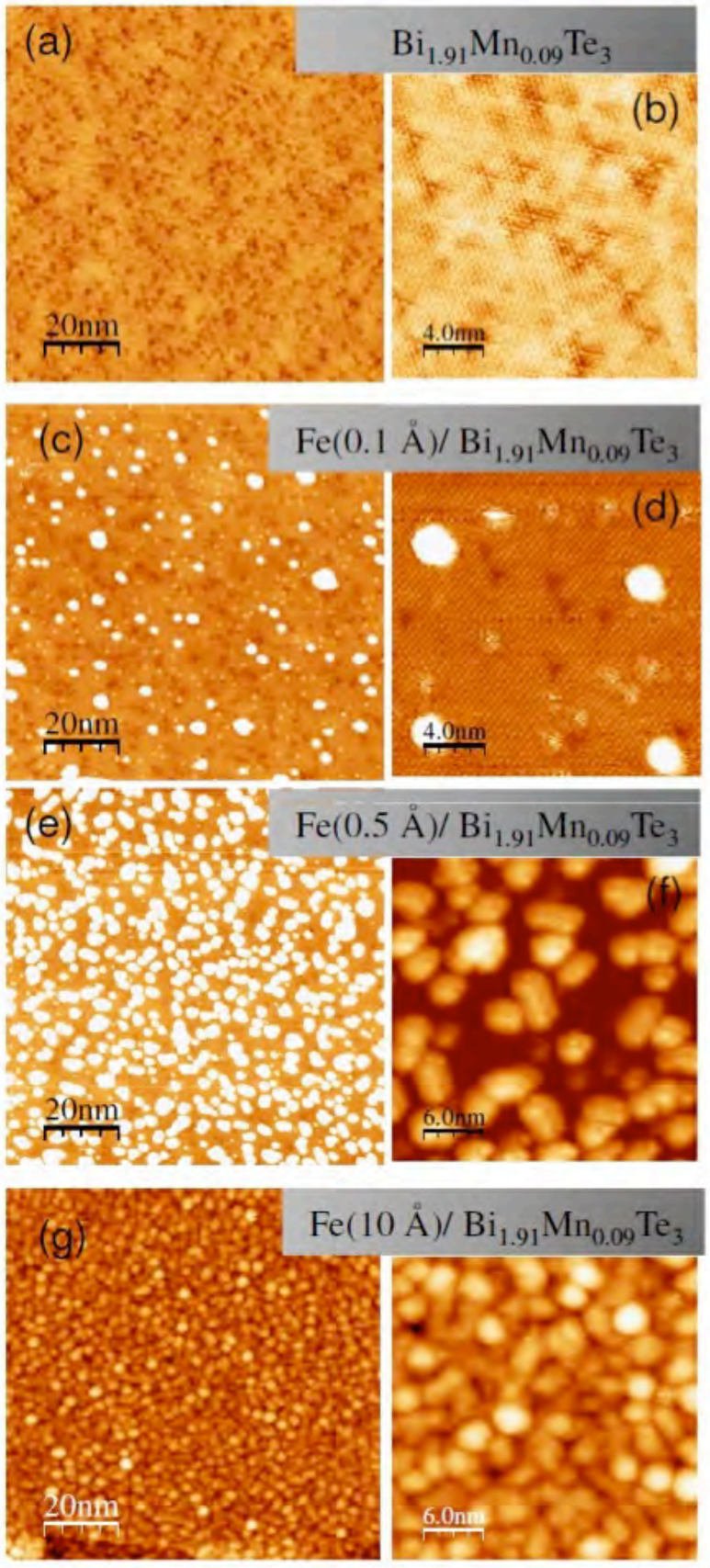
→ **Mn magnetized anti-parallel to Fe**

→ **Interface Mn ferromagnetic at RT**

Selected for **Viewpoint, Physics** 1, 43 (2008)

F. Maccherozzi *et al.* Phys. Rev. Lett. **101**, 267201 (2008)

Fe on $Bi_{2-x}Mn_xTe_3$ (9% Mn doping)



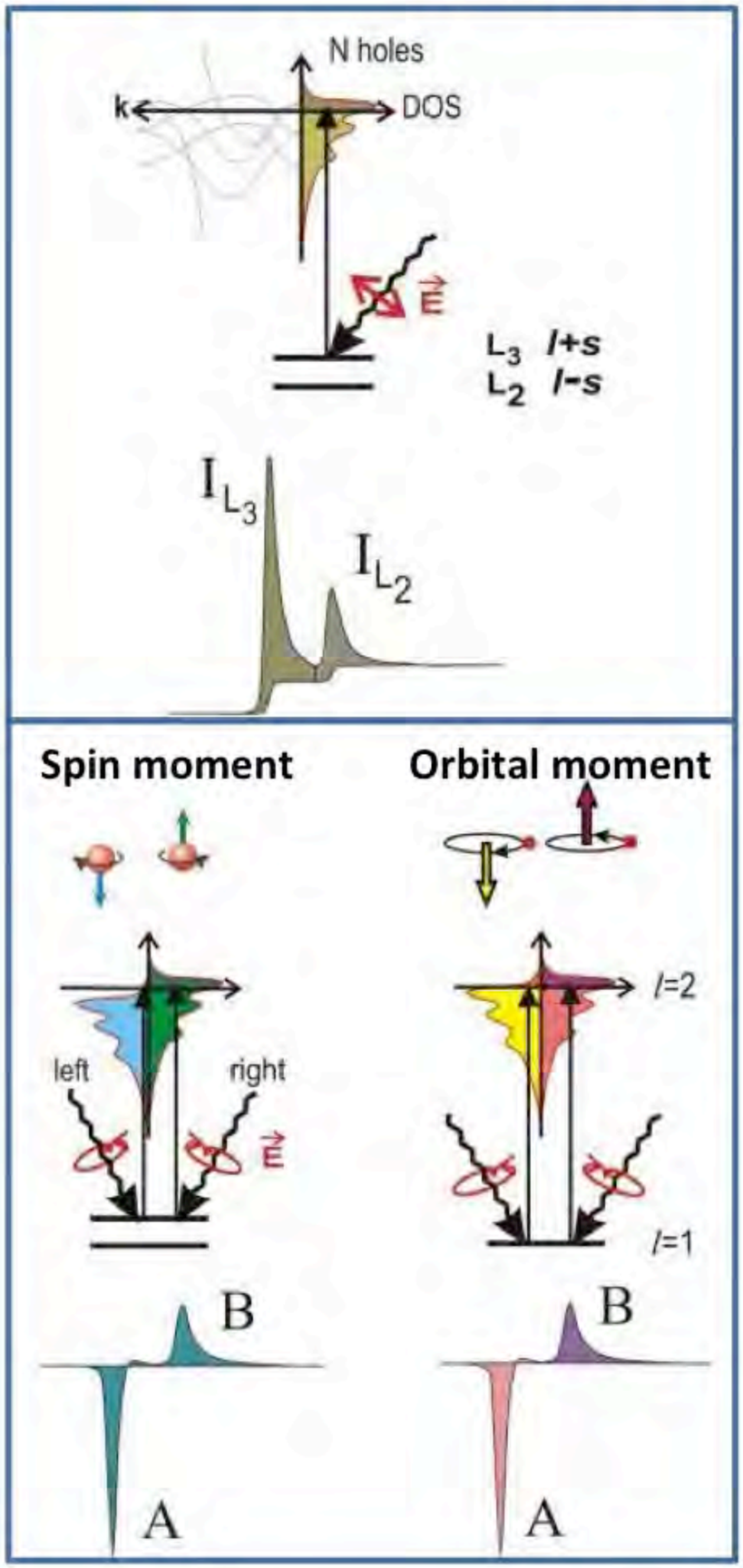
Mn content at the surface 3.5%, less than nominal 9%
➔ higher dilution of Mn in the surface region

Fe atoms are randomly distributed
➔no preferential nucleation sites

No long range Fe order (no LEED)

@ > 6Å Fe film is in-plane magnetized

Element selective magnetic properties - XMCD



X-ray Absorption Spectroscopy (XAS)

- The total intensity is proportional to the **number of empty 3d valence states**
- Two-peaks originate from the **spin-orbit interaction** (between the unpaired spin and orbital angular momentum)

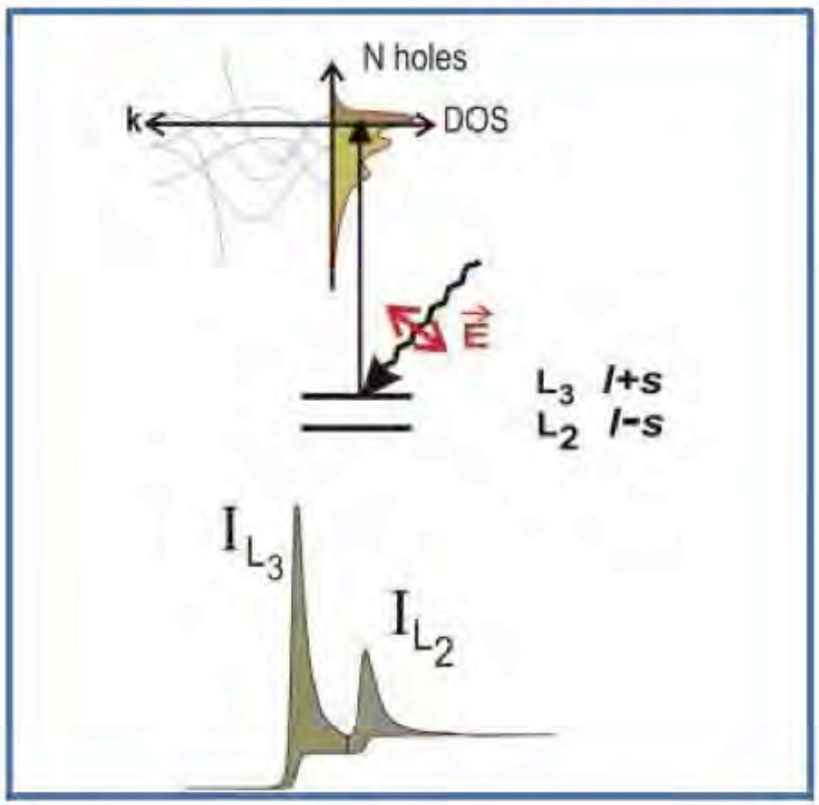
X-ray Magnetic Circular Dichroism (XMCD)

- The **d shell has a spin moment** which is given by the imbalance of spin-up and spin-down electrons
- The photon helicity couples to the core-shell electron spin
- Spin-up/down photoelectrons from the p core shell can only be excited into spin-up/down d hole states

XMCD gives a measure of the direction of the atomic magnetic moment of a ferromagnet relative to the helicity of the X-rays.

J. Stöhr, S. Anders, IBM J. RES. DEVELOP. VOL. 44 N. 4

Element selective magnetic properties - XMCD



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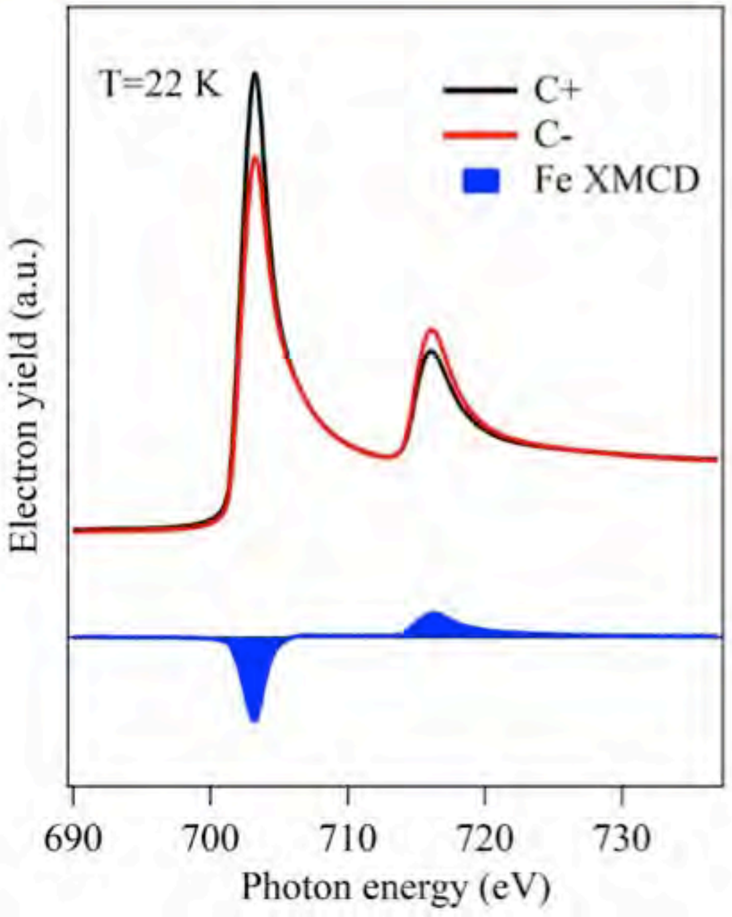

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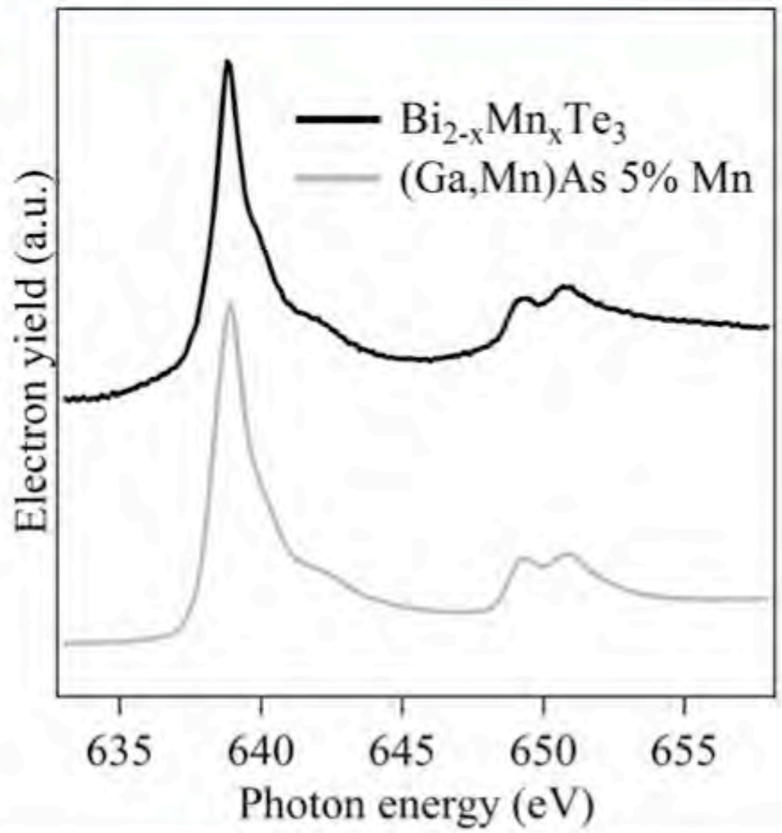
J. Stöhr, S. Anders, IBM J. RES. DEVELOP. VOL. 44 N. 4

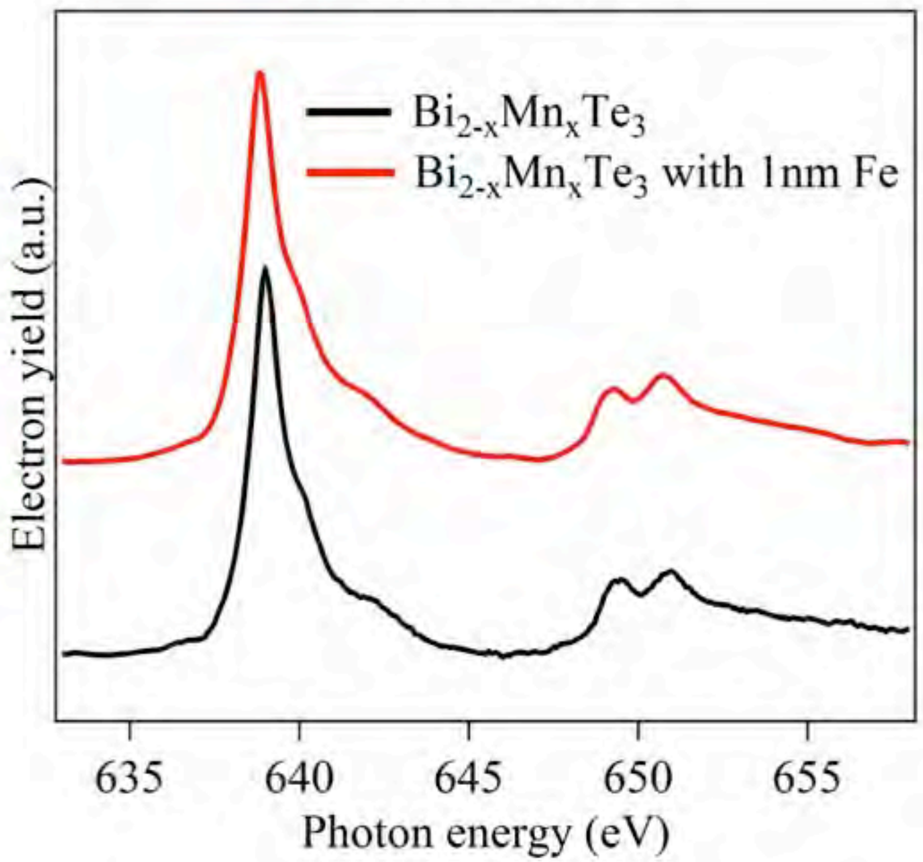
Mn XAS

$Bi_{2-x}Mn_xTe_3$ vs. (Ga,Mn)As



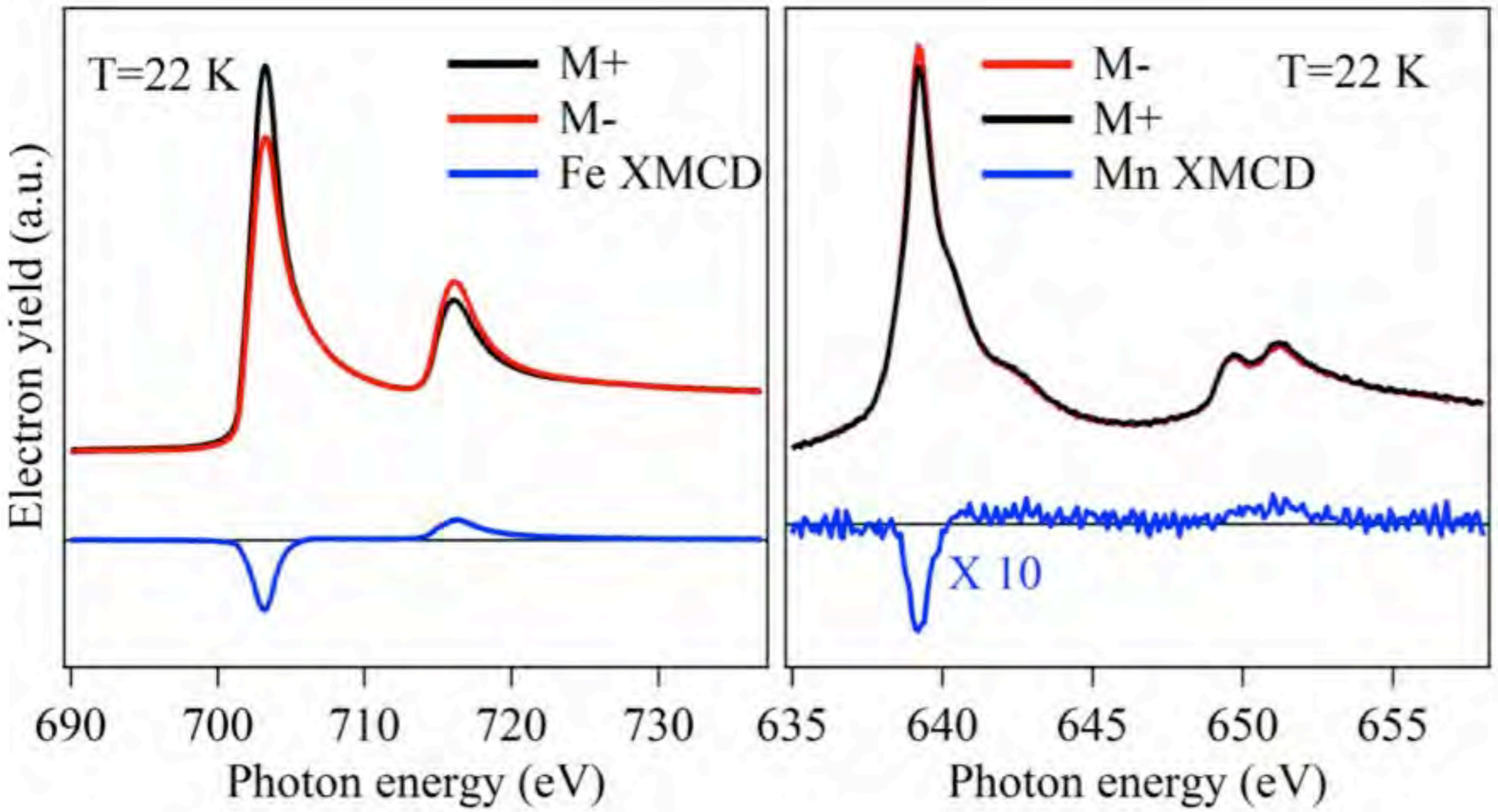
Characteristic spectra of **dilute Mn systems**, with no trace of oxidation and/or contamination

Before and after Fe deposition



Same spectral line-shape before and after Fe deposition ➔ **no Fe alloying**

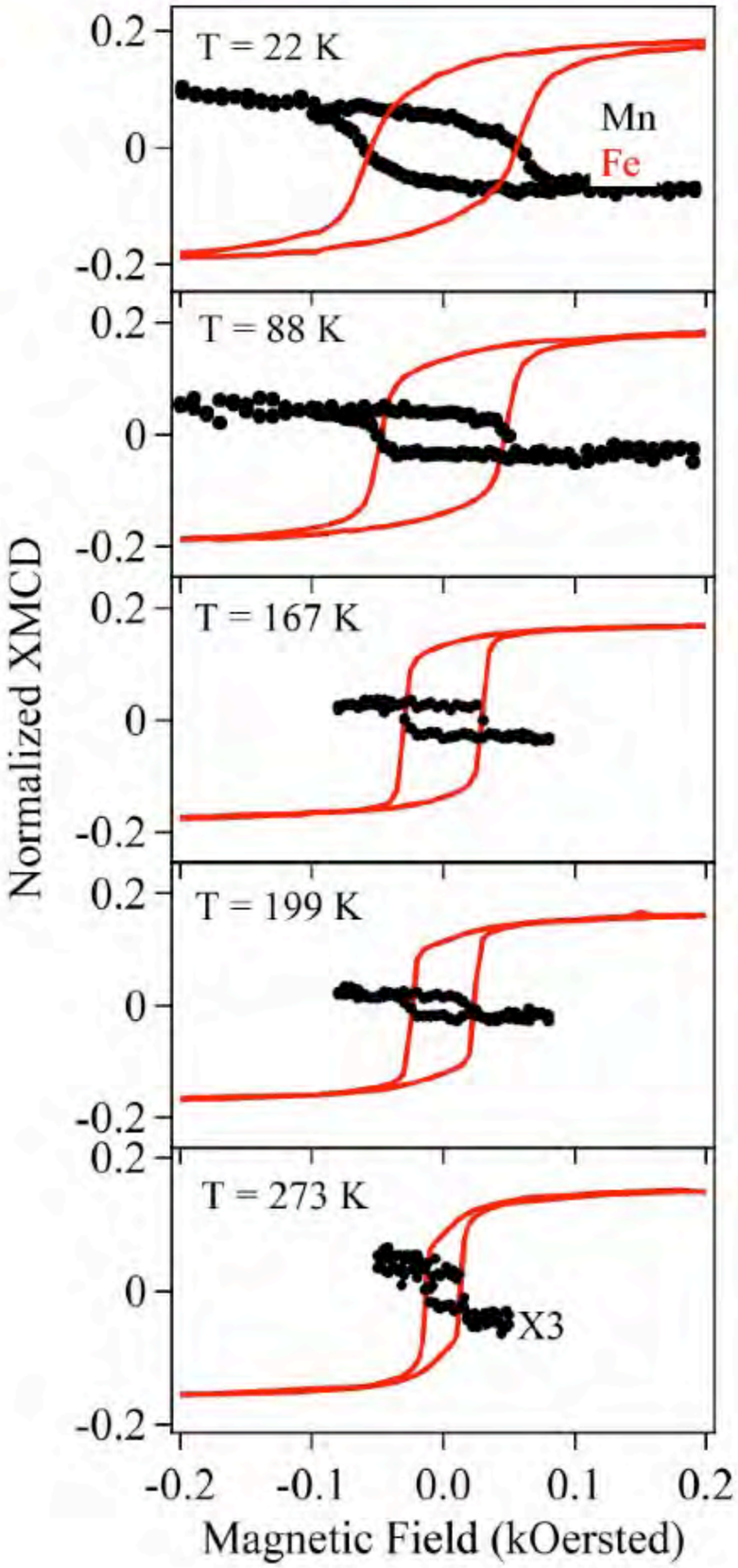
Fe and Mn XMCD



➔ Mn shows **clear dicroic signal** at 22K (larger than bulk T_C)

➔ **Mn is magnetized in-plane and antiferromagnetically coupled to Fe**

Fe and Mn Hysteresis Loops in Fe/BiMnTe



➔ **The in-plane Mn magnetization is finite at room temperature!**

Both the magnetic signal (height of the loops) and the coercive field (width of the loops) decrease with increasing temperature, suggesting a **robust magnetic coupling**.

Summary

Graphene

➔ Combined spectroscopies coupled to scanning tunneling microscopy allow to discriminate between different growth mechanisms and to evaluate graphene-substrate interaction

Topological Insulator

➔ Magnetic proximity effect allows to magnetize the topological surface even at room temperature

Topological properties of both graphene and TIs bring into material physics exciting new (old) concepts that we still need to learn how to deal with in order to explore them in future electronic devices!

Collaborators

- **CNR-IOM, TASC, Trieste, Italy**
  - Manju Unnikrishnan
  
  - Jun Fujii
  
  - Damjan Krizmancic
  
  - Piero Torelli
  
  - Giancarlo Panaccione
  

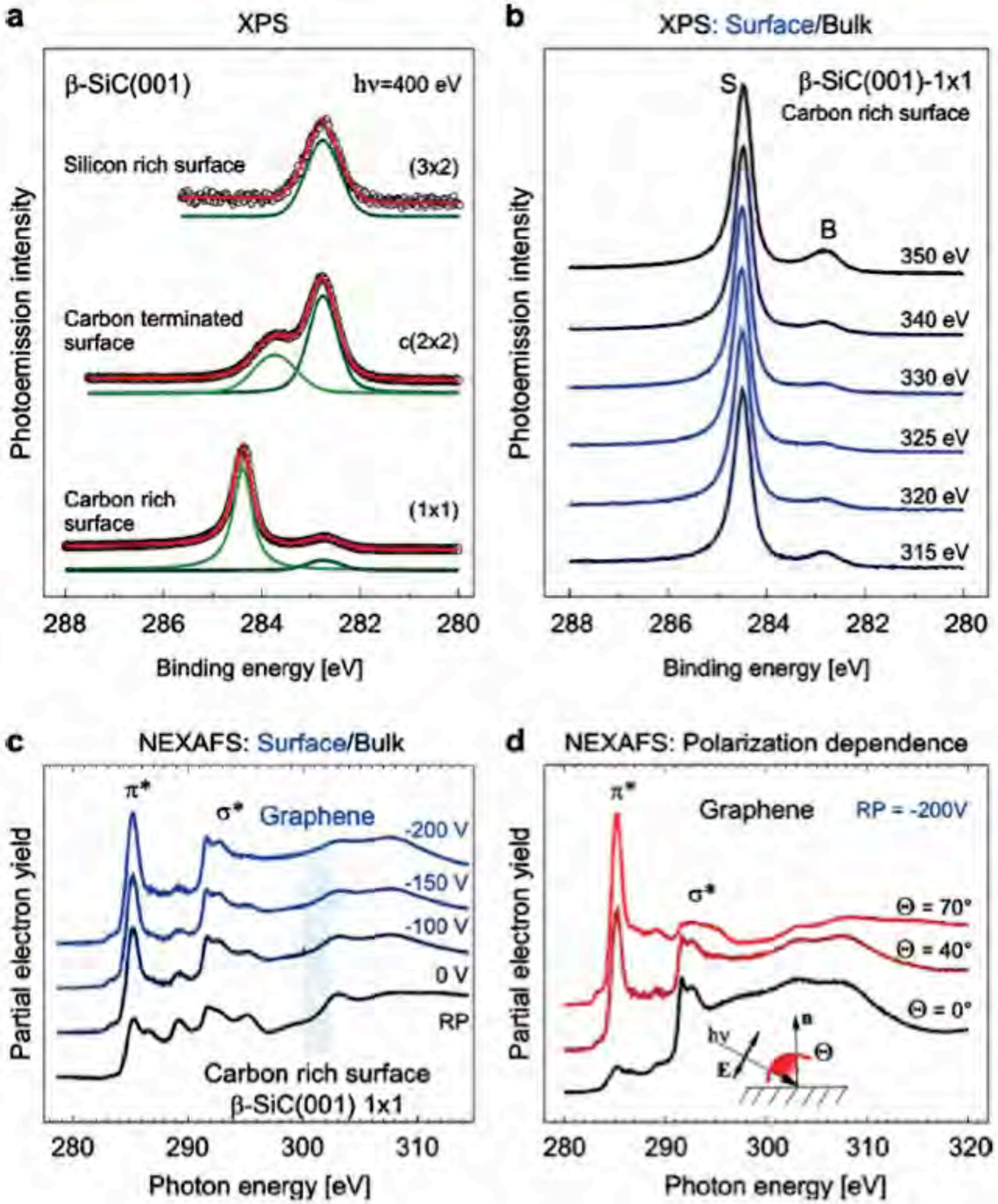
- **Princeton University, USA**
  - Robert J. Cava
  

- **Leibniz Institute, Dresden, Germany**
  Russian Asademy of Sciences
  - Victor Yu. Aristov
  

- **IFS, Zagreb, Croatia**
  (+Uni. Köln, T. Michely**)**
  - Petar Pervan
  
  - Marko Kralj
  

Extra slides

Graphene on Cubic SiC/Si Wafers



Core-level photoemission and near-edge X-ray absorption fine structure spectroscopy. (a) C 1s photoemission taken from the

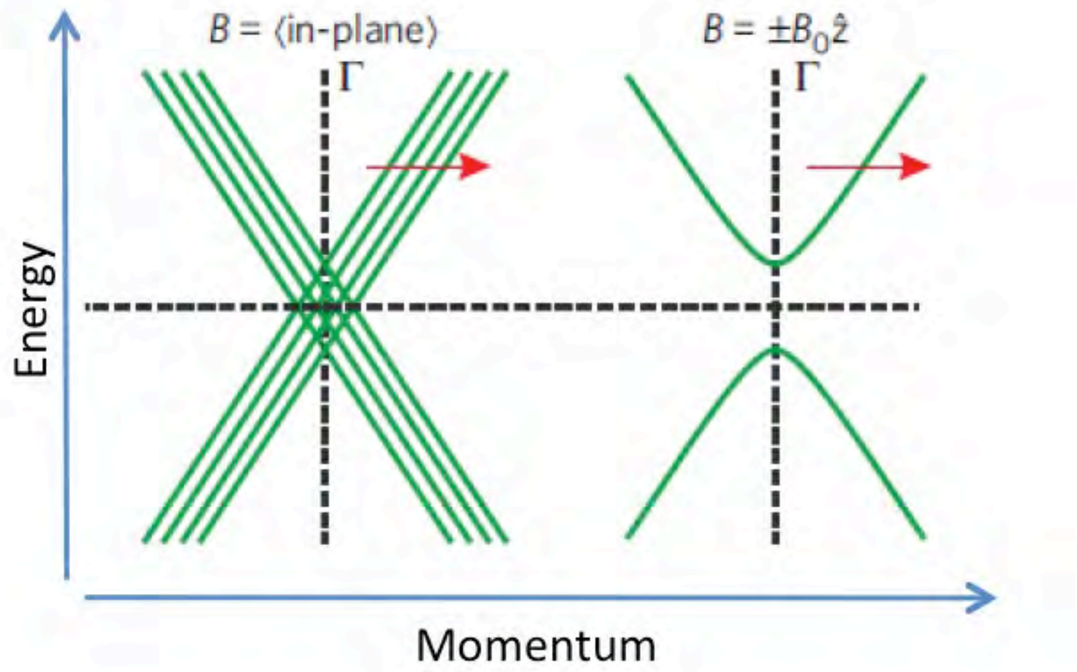
-SiC(001) at different stages of the surface preparation procedure using *hv) 400 eV photon energy. (b) C 1s photoemission of the* C-rich -SiC(001) 1 × 1 surface as a function of photon energy. As *hv is tuned away from the most surface sensitive regime at 325 eV,*

component B rises which proves its bulk origin. The binding energy

of the surface component S equals that found for graphene or graphite. (c) C 1s NEXAFS spectra recorded with increasing retard potential in order to separate bulk and surface features. At the most

surface sensitive regime (RP) -200 eV) the spectral shape equals those found for graphene/graphite. (d) With changing incidence angle Θ of the linearly polarized light, a strong anisotropy is found.

The behavior of the resonances suggests that the *π* orbitals are* collectively oriented parallel to the surface normal and the *σ orbitals perpendicular, as expected for graphene/graphite.**


B = ⟨in-plane⟩
Γ
B = ±B0ẑ
Γ
Energy
Momentum