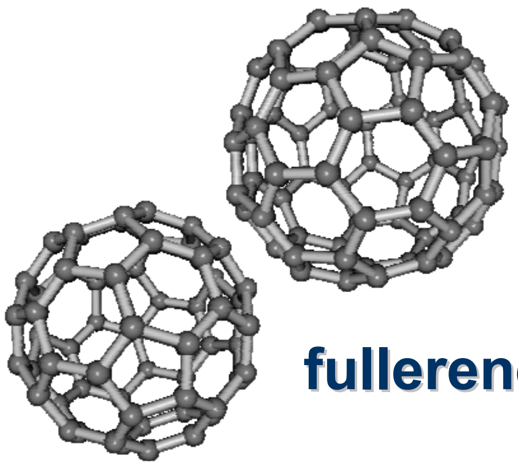
Photoelectron Spectroscopy of Graphene on SiC:

Growth, Interface, and Electronic Structure

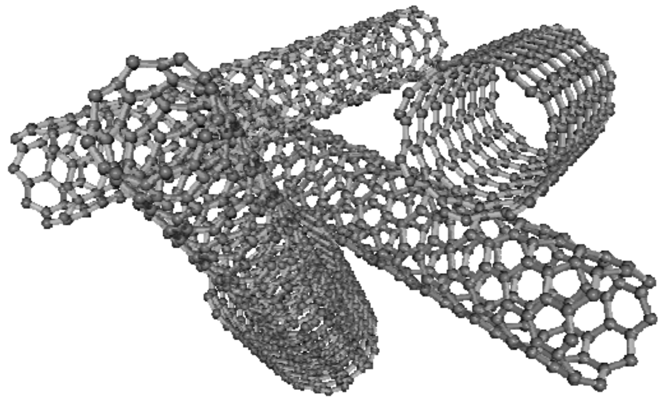
Thomas Seyller

Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie
Universität Erlangen-Nürnberg, Germany
http://www.tp2.uni-erlangen.de

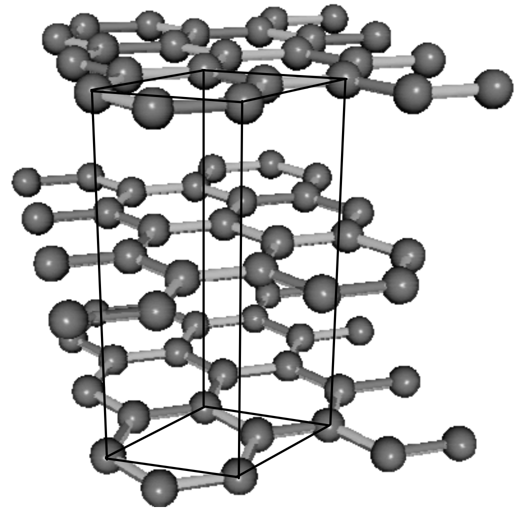
The many faces of sp²-bonded carbon



fullerenes

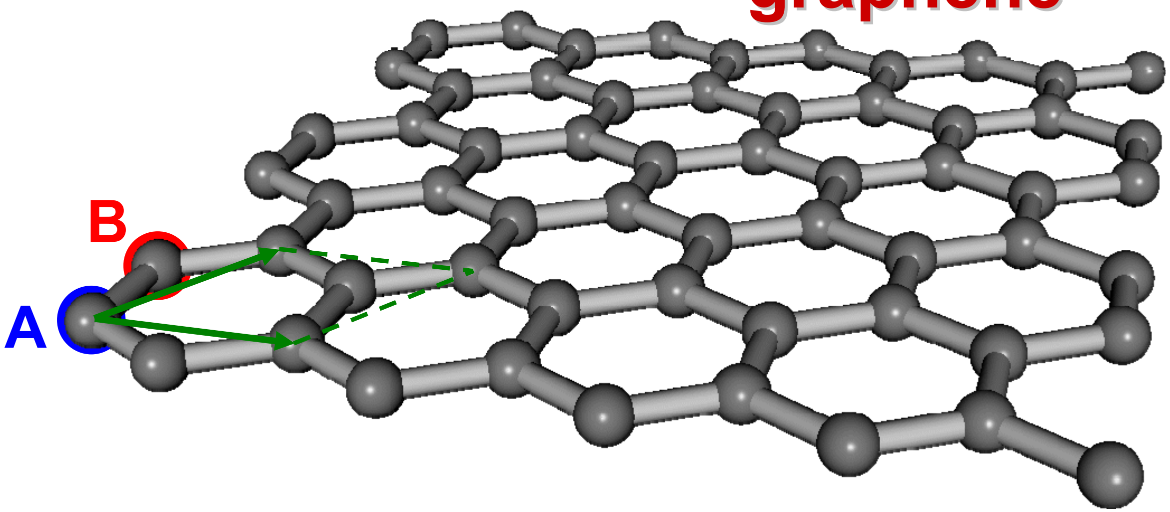


carbon nanotubes (CNTs)



graphite

graphene



deemed unstable

ZUR THEORIE DER PHASENUMWANDLUNGEN. II.

Von L. Landau.

(Eingegangen am 4. Februar 1937.)

Es wird die Unmöglichkeit der Existenz von Kristallen gezeigt, deren Dichtefunktion nur von einer oder zwei Koordinaten abhängt. Es wird die Frage des Überganges zwischen Flüssigkeit und Kristall untersucht und bewiesen, dass es zwischen diesen Phasen keine auf einer Kurve im *p*, *T*-Diagramm liegenden Curie-Punkte geben kann. Ferner wird die Natur der flüssigen Kristalle untersucht.

Landau, Phys. Z. Sowjetunion 11 (1937) 545-555

Friedrich-Alexander-Universität Erlangen-Nürnberg

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

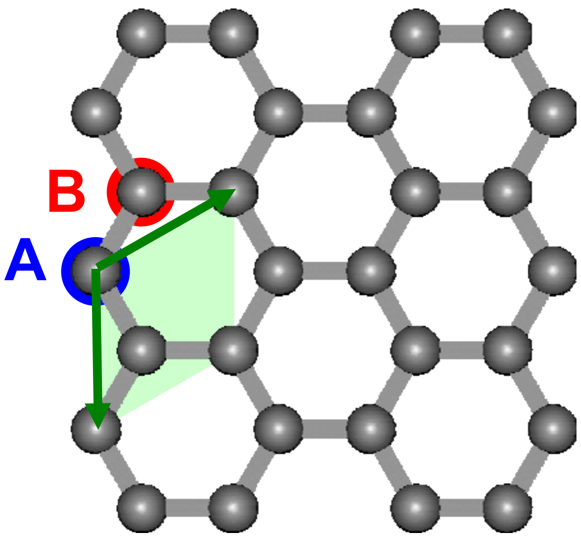
Electronic structure of graphene

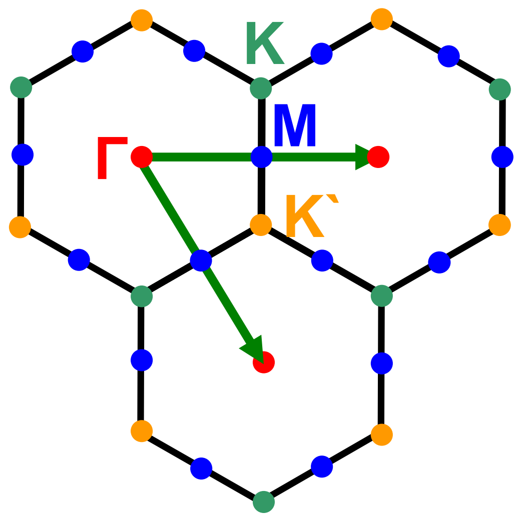
PHYSICAL REVIEW MAY 1, 1947

The Band Theory of Graphite

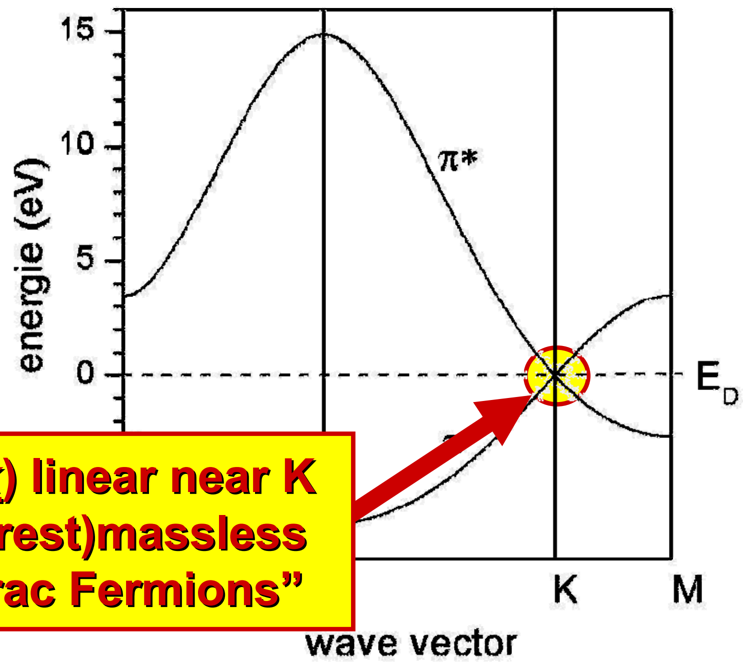
P. R. WALLACE*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

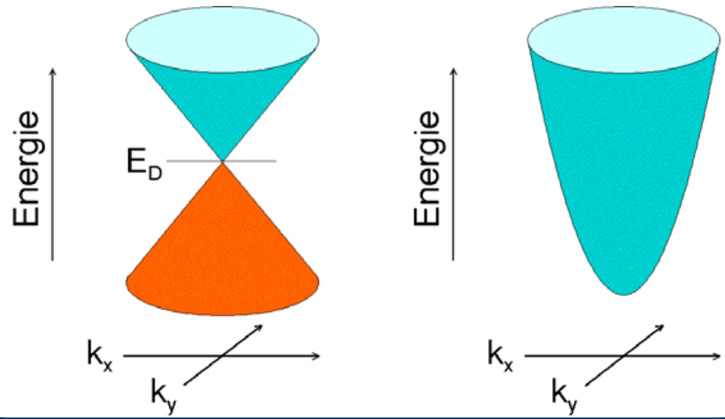
(Received December 19, 1946)





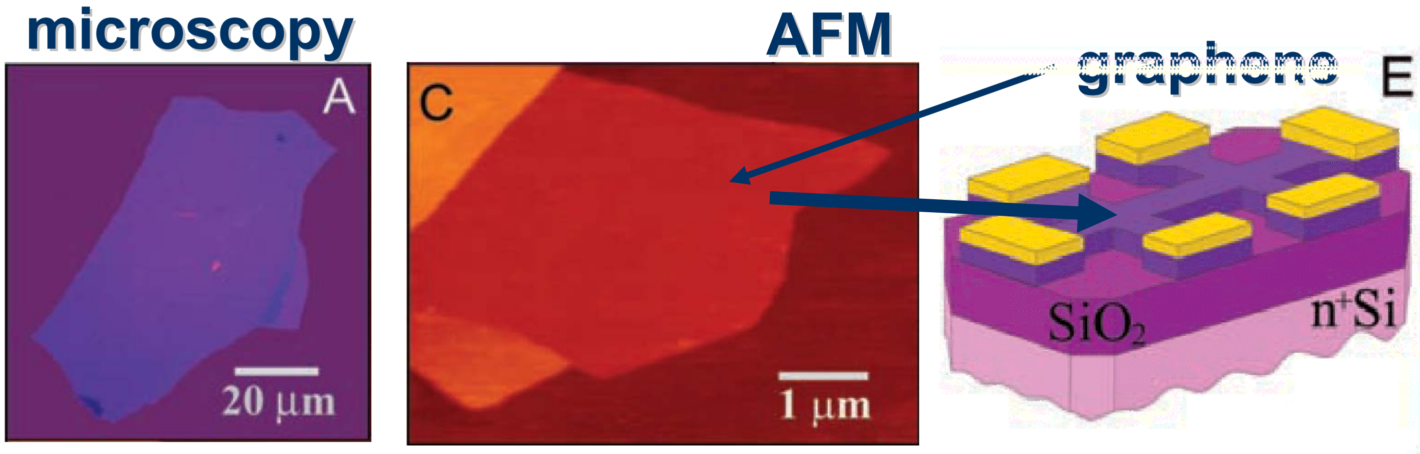
Tight binding π-band structure:

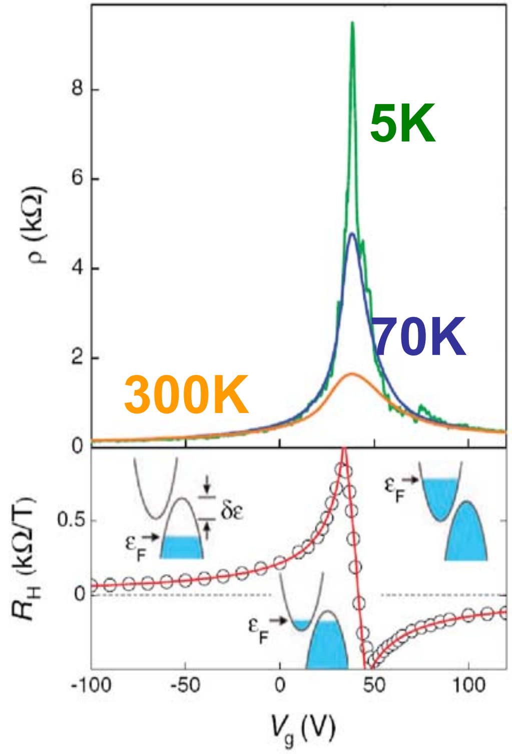




D.P. DiVincenzo and E.J. Mele: *Self-consistent effective mass theory for intralayer-screening in graphite intercalation compounds.* Phys. Rev. B 29, 1685(1984)

The discovery of graphene





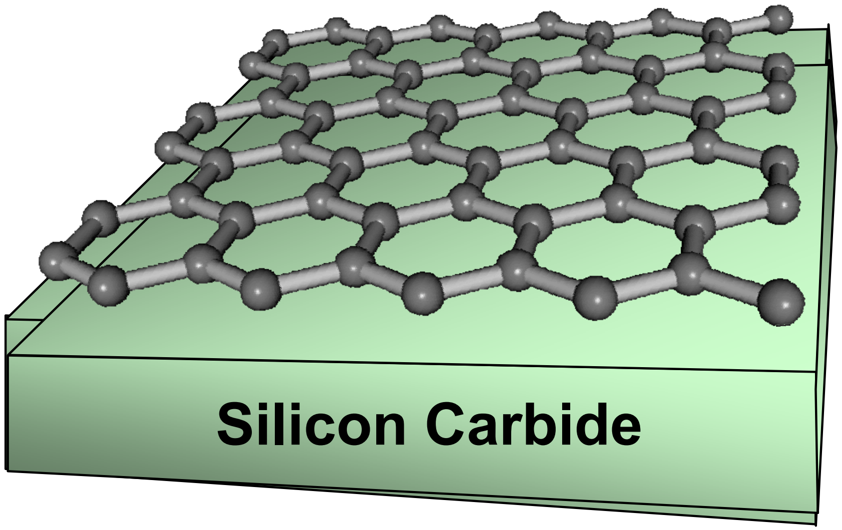
K.S. Novoselov et al.: *Electric Field Effect in Atomically Thin Carbon Films*, Science 306, 666 (2004)

Graphene obtained by exfoliation

Key properties of graphene*:
- **High mobilities µ**
- **Little dependence of µ on carrier concentration**
- **Little effect of chemical doping on µ**
- **Good contacts**

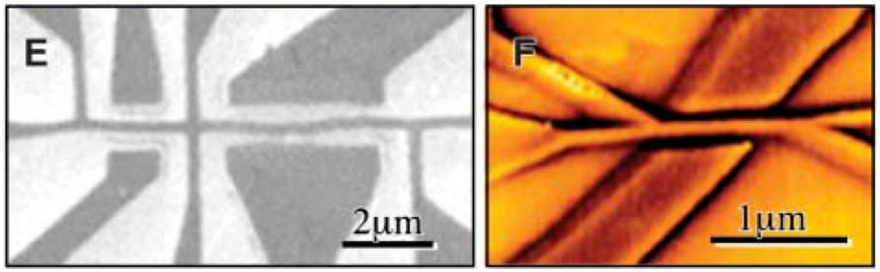
*A.K. Geim and K.S. Novoselov: *The Rise Of Graphene*, Nature Materials 6 (2007) 183.

Graphene and Few Layer Graphene by solid state phase separation of SiC



T ≥ 1150°C in vacuum

- A.J. van Bommel et al.: *LEED and Auger electron observations of the SiC(0001) surface*, Surf. Sci. 48 (1975) 463.
- I. Forbeaux et al.: *Heteroepitaxial graphite on 6H-SiC(0001): Interface formation through conduction-band electronic structure*, Phys. Rev. B 58 (1998) 16396.
- I. Forbeaux et al.: *High-temperature graphitization of the 6H-SiC(000$\bar{1}$) face*, Surf. Sci. 442 (1999) 9.



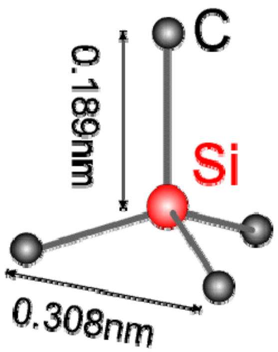
- **Mobility μ = 2.7 m^2/Vs**
- **Coherence length 1μm**
- **SdH-Oszillations**

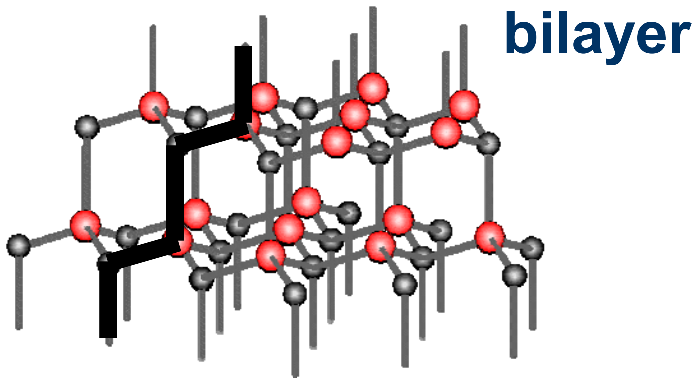
- C. Berger et al.: *Ultrathin epitaxial graphite: 2D electron gas properties and a route towards graphene-based nanoelectronics*, J. Phys. Chem. B 108 (2004) 19912.
- C. Berger et al.: *Electronic confinement and coherence in patterned epitaxial graphene*, Science 312 (2006) 1191.

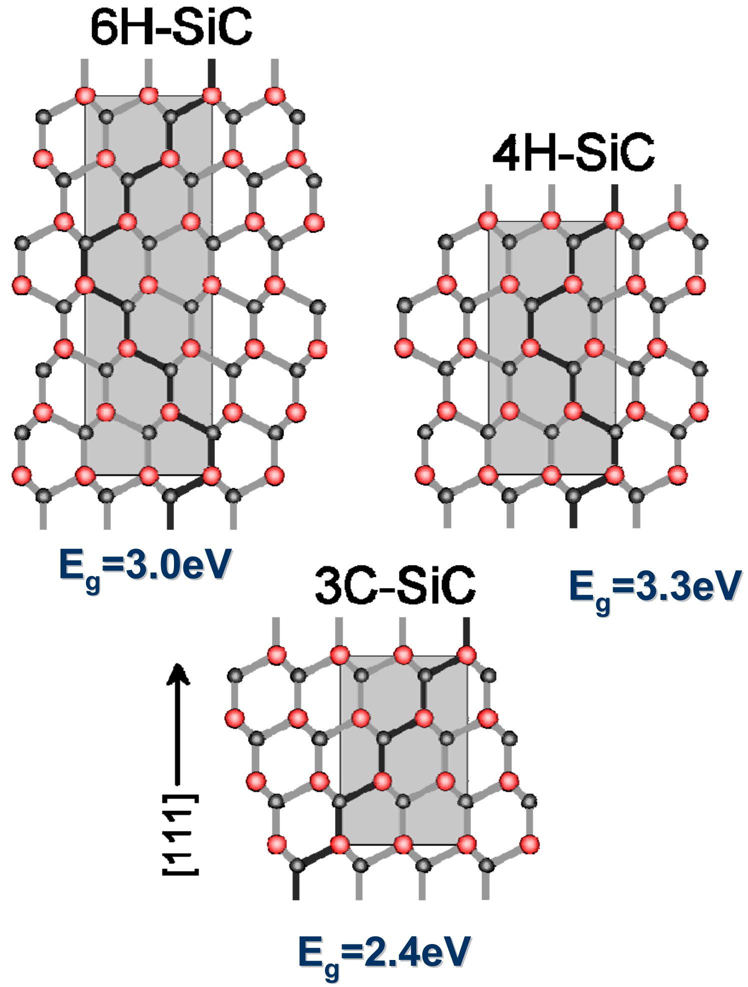
Friedrich-Alexander-Universität Erlangen-Nürnberg

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

What makes that combination interesting?







Silicon Carbide

- commercially available
- technology established
- high thermal stability and thermal conductivity
- chemically inert
- wide band gap (insulating or conducting)

Well known in Erlangen

- SFB 292 “Mehrkomponentige Schichtsysteme”
- Forschergruppe “SiC als Halbleitermaterial: Alternative Wege in Züchtung und Dotierung”

>15 years experience: growth, defects, devices, surfaces, interfaces

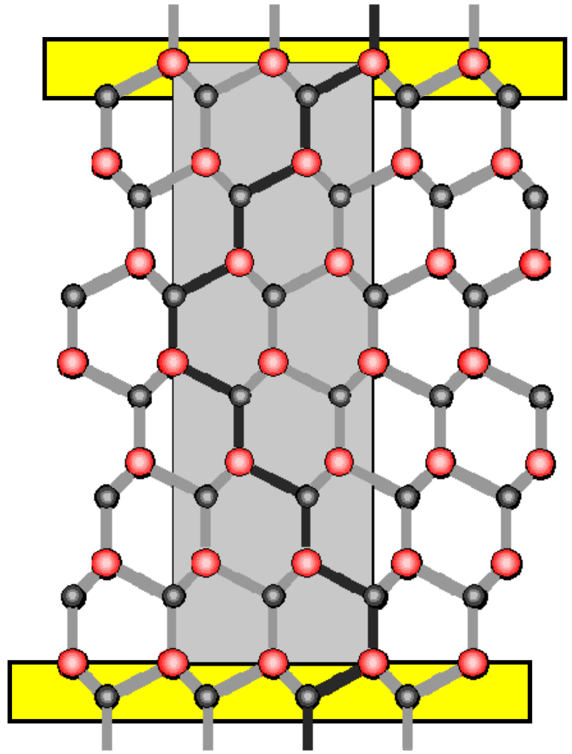
PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Topics

Graphene and FLG on SiC(0001)

- Growth
- Interface
- Electronic structure

Si-face



C-face

People

Friedrich-Alexander-Universität Erlangen-Nürnberg

- K.V. Emtsev
- F. Speck
- Th. Seyller
- L. Ley

Fritz-Haber-Institut der Max-Planck-Gesellschaft

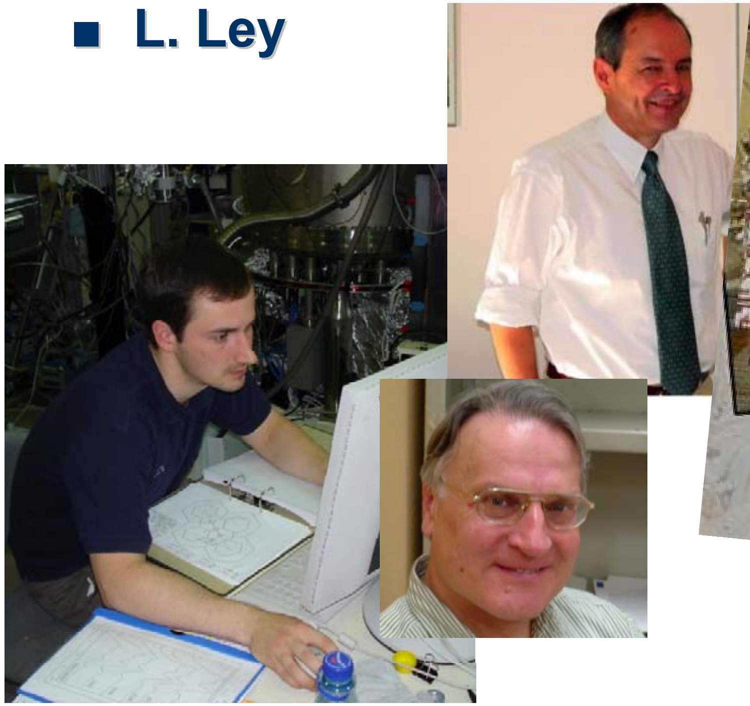
- T. Ohta
- K. Horn

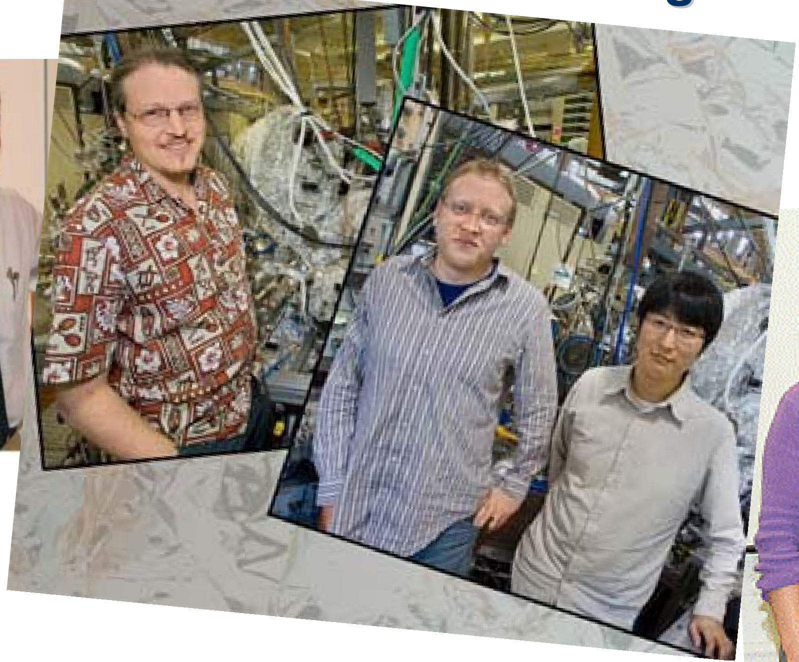
ALS Advanced Light Source

- A. Bostwick
- J.L. McChesney
- E. Rotenberg

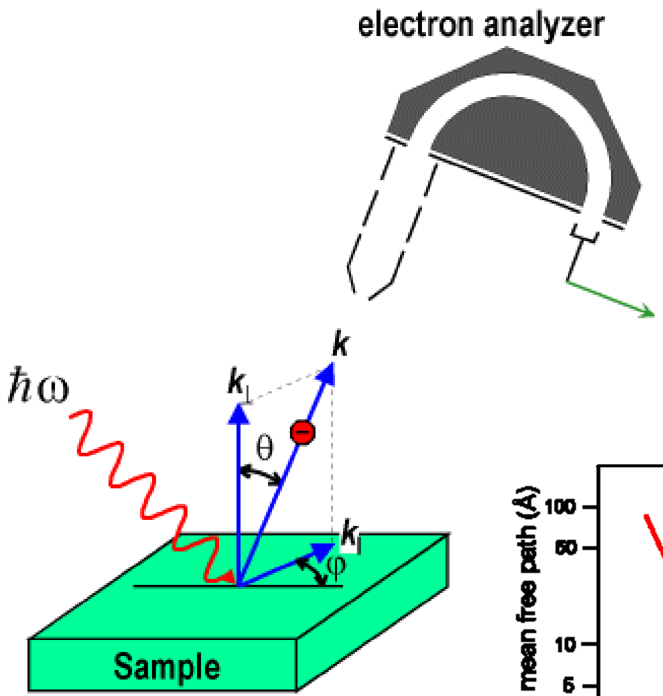
La Trobe University

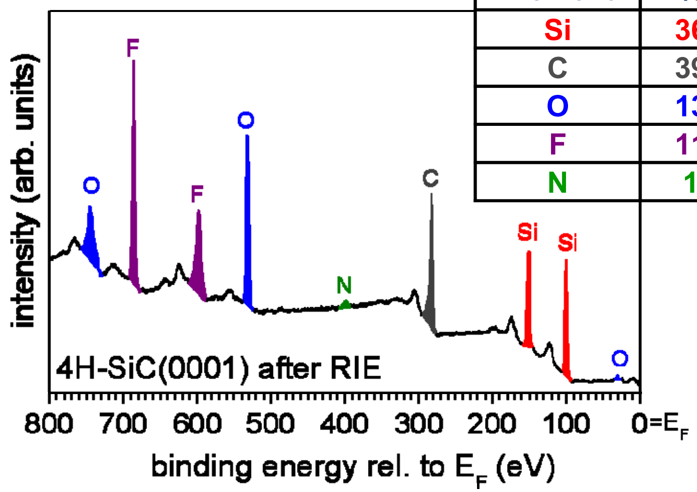
- J. Riley
- E. Huwald



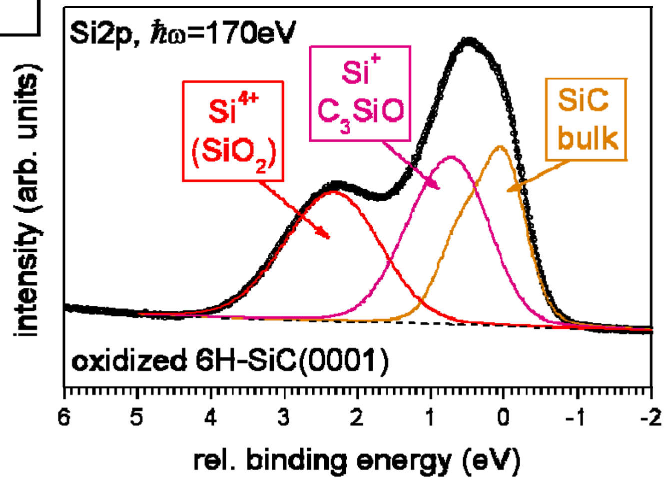


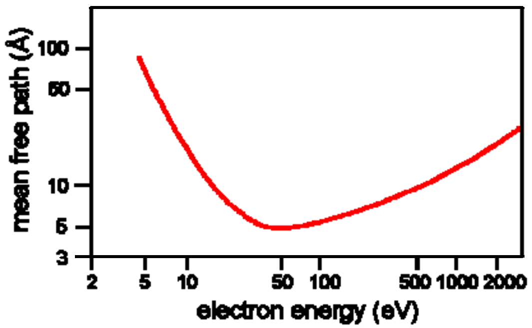
Photoelectron spectroscopy

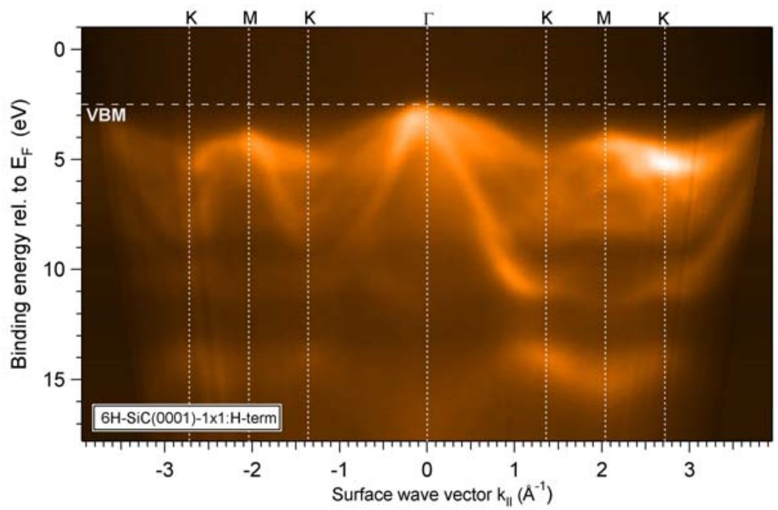


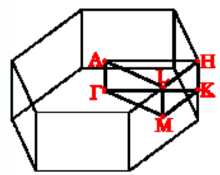


Element	%
Si	36
C	39
O	13
F	11
N	1









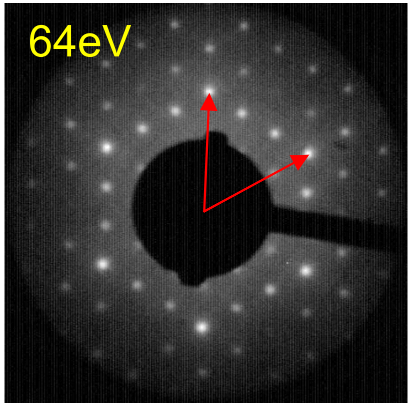
- Surface sensitive
- Element specific and quantitative
- Bond configurations
- *k*-resolved: band structure

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

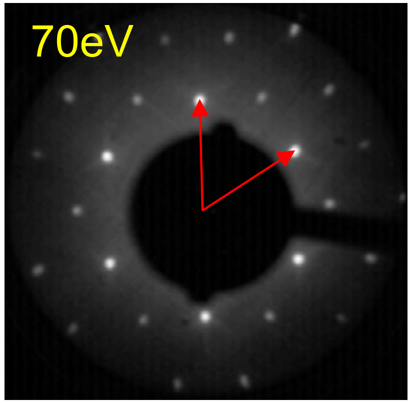
FLG growth by solid state graphitization

Starting point:
well ordered and clean
Si-rich (3×3)

LEED images

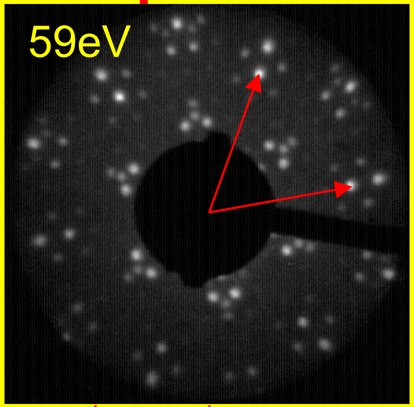


(3×3)

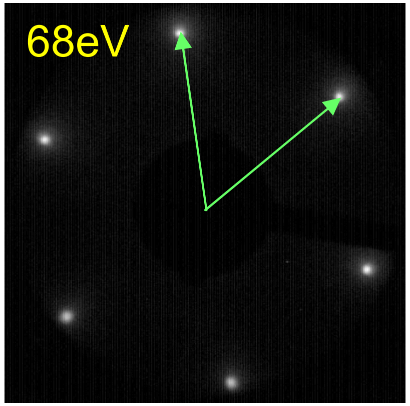


(√3×√3)R30°

important



(6√3×6√3)R30°



$(1\times1)_{graph}$

temperature

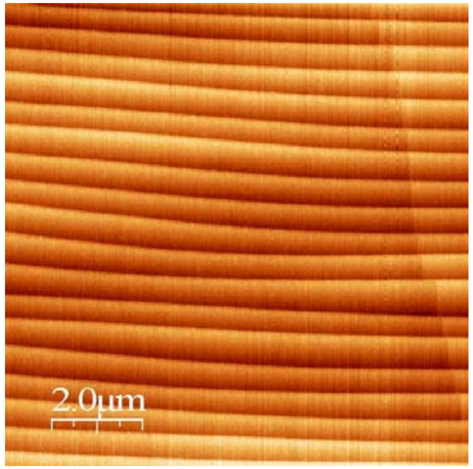
950°C

1050°C

1150°C

1400°C

also possible to start here

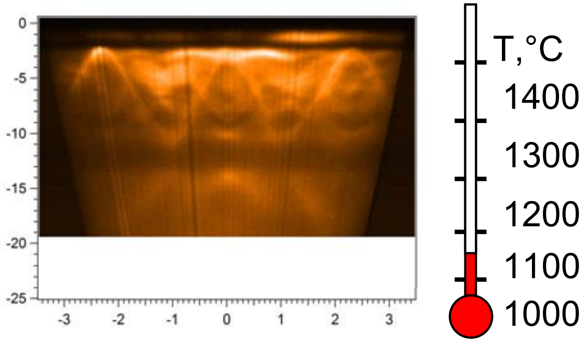


Th. Seyller, K.V. Emstev, et al.:
Structural and electronic properties of graphite layers grown on SiC(0001),
Surf. Sci. 600 (2006) 3906.

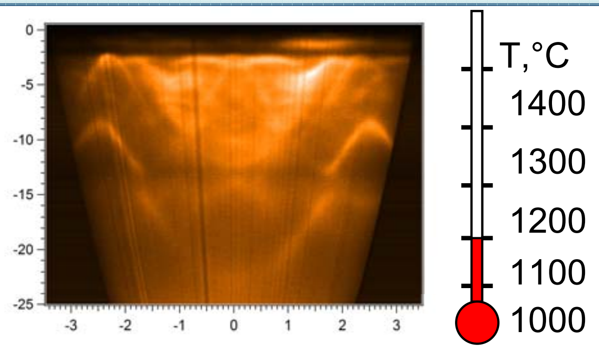
Friedrich-Alexander-Universität Erlangen-Nürnberg

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

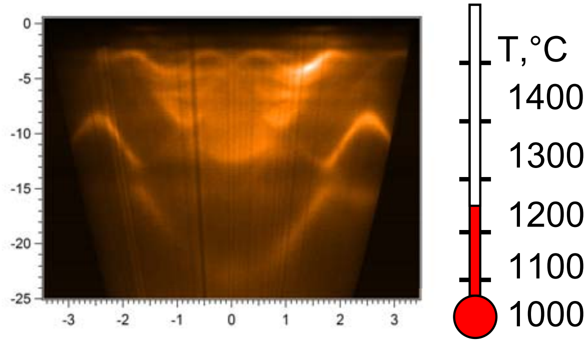
FLG growth by solid state graphitization



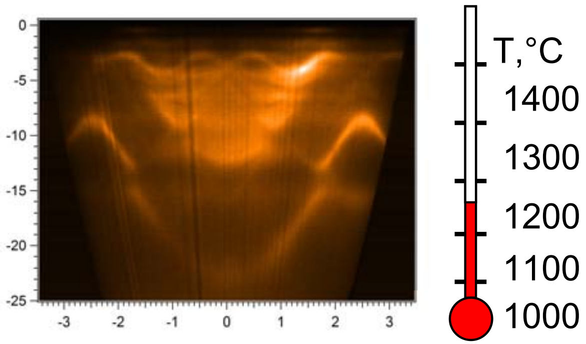
(√3×√3)



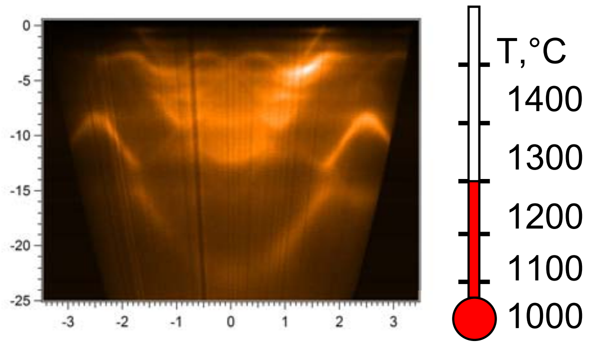
(1-x) (√3×√3) + x (6√3×6√3)



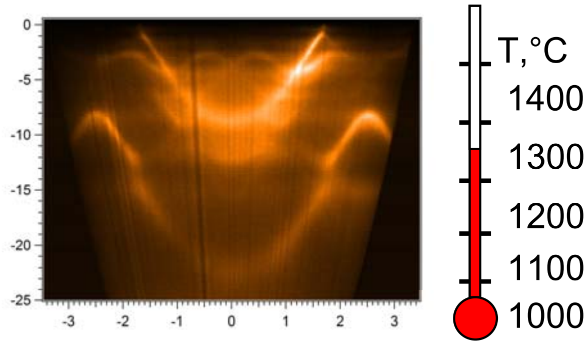
x (√3×√3) + (1-x) (6√3×6√3)



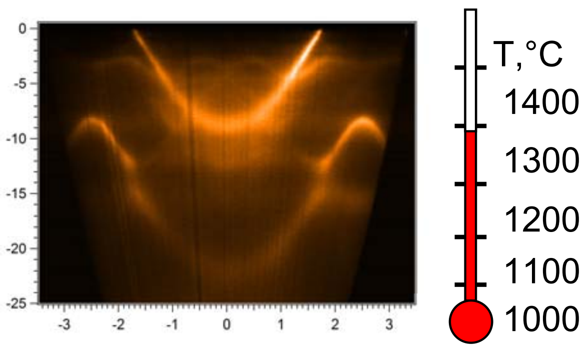
(6√3×6√3)



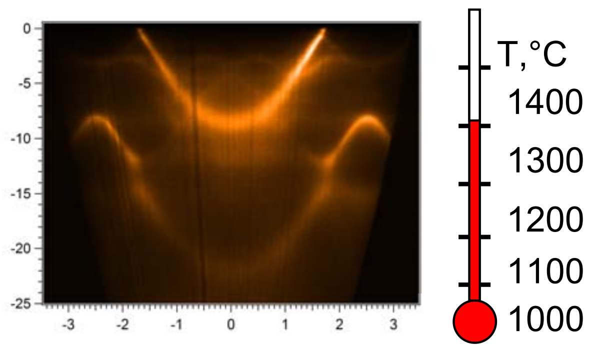
(6√3×6√3) + x graphene



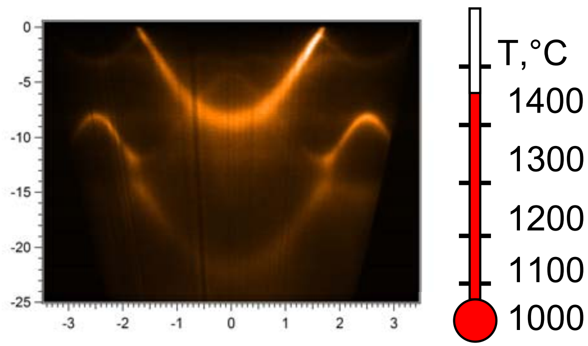
(6√3×6√3) + x graphene



Graphene



Graphene + x Bilayer Graphene



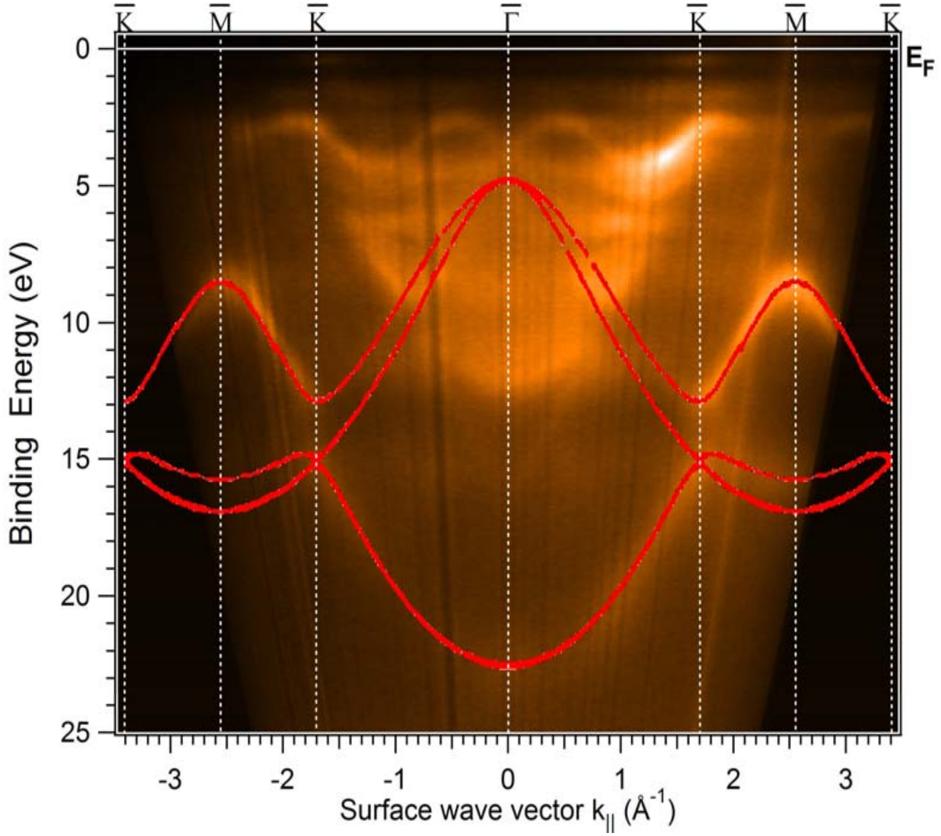
Bilayer Graphene

Friedrich-Alexander-Universität
Erlangen-Nürnberg

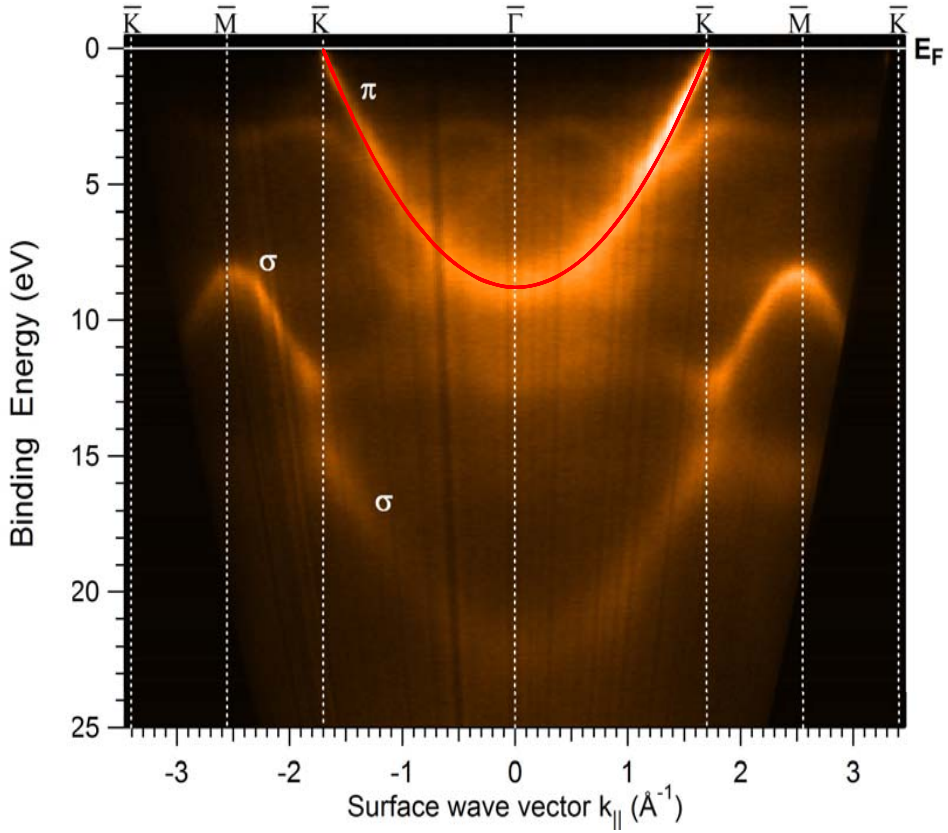
PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Electronic structure of the (6√3×6√3) reconstruction

(6√3×6√3)



graphene



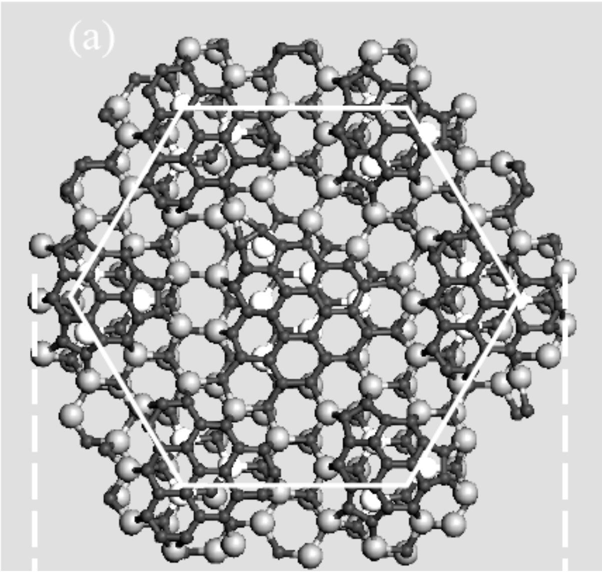
Characteristic σ-bands of graphene!
Deformed π-band!

Calculation: R. Ahuja, et al.: *Electronic structure of graphite: Effect of hydrostatic pressure*, Phys. Rev. B 51 (1995) 4813.

K.V. Emtsev, T. Seyller, F. Speck, L. Ley, P. Stojanov, J.D. Riley, R.C.G. Leckey: *Initial stages of the graphite-SiC(0001) interface formation studied by photoelectron spectroscopy*, cond-mat/0609660

Models for the $(6\sqrt{3}\times6\sqrt{3})$ reconstruction

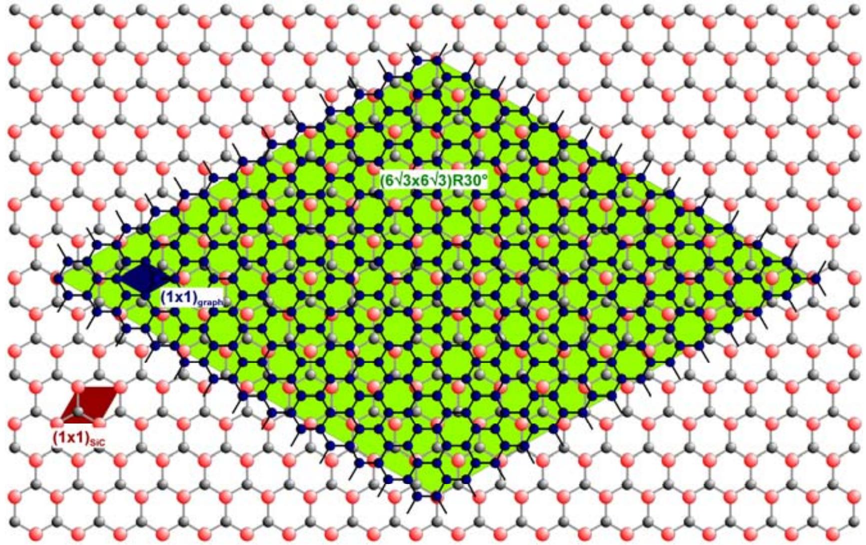
Self-organized graphitic islands arranged in (6×6) structure



W. Chen et al.; *Atomic structure of the 6H–SiC(0001) nanomesh,* Surf. Sci. 596 (2005) 176.

Incompatible with observed σ-bands

Graphene on top of (1×1)* or $(\sqrt{3}\times\sqrt{3})$ surface bound by Van der Waals forces**

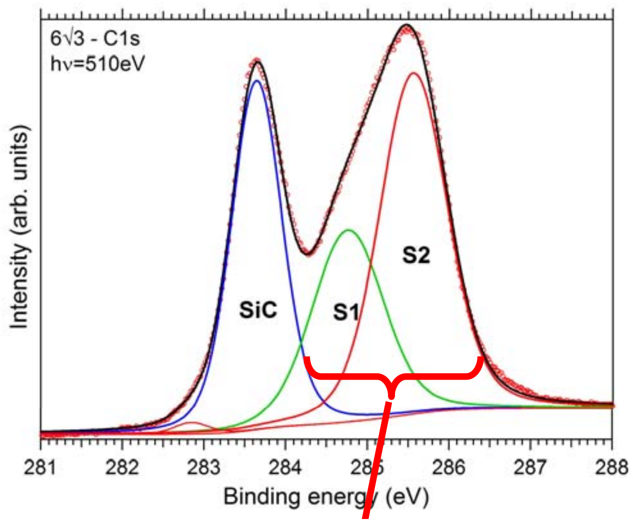


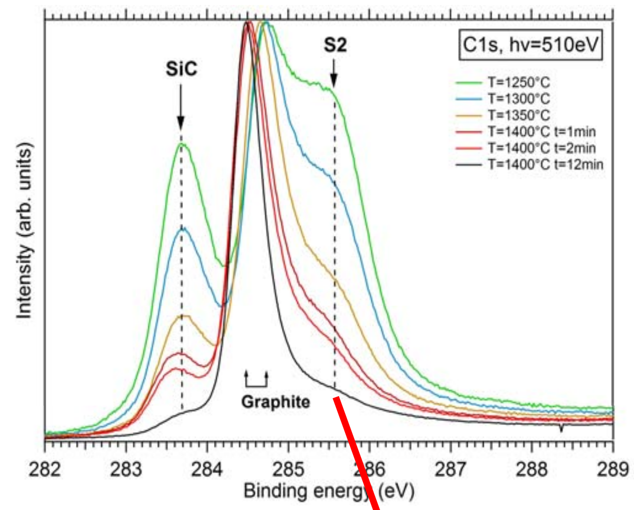
*Van Bommel et al.: *LEED and Auger electron observations of the SiC(0001) surface*, Surf. Sci. 48 (1975) 463.
**Forbeaux et al.: *Heteroepitaxial graphite on 6H-SiC(0001)*, Phys. Rev. B 58 (1998) 16396.

Incompatible with distorted π-bands

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Core level spectroscopy

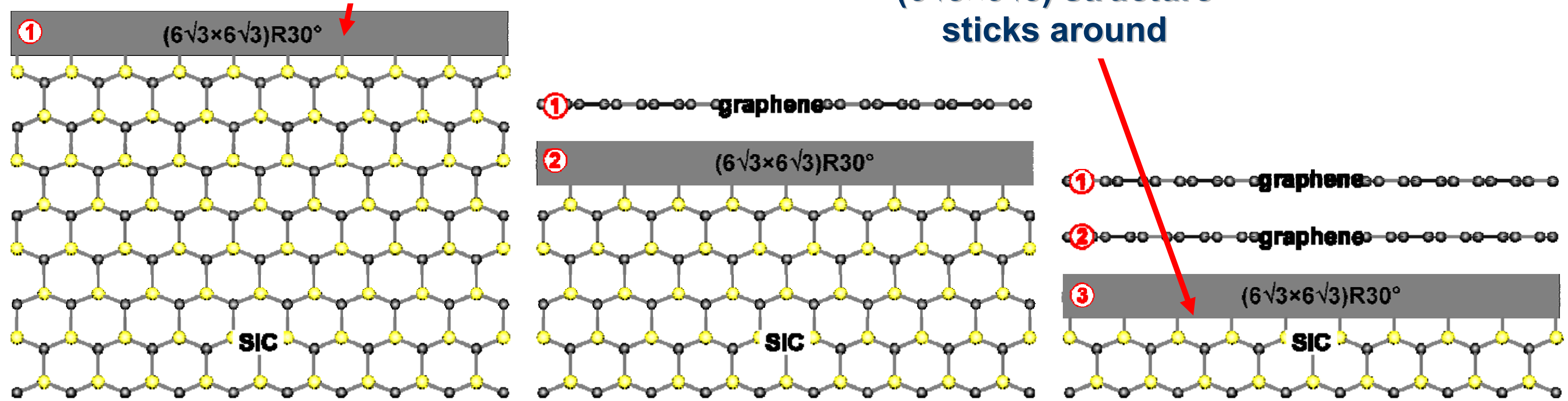




intensity corresponds to 1ML sp^2-networked carbon

(6√3×6√3) structure sticks around

3 layers SiC for 1 graphene layer

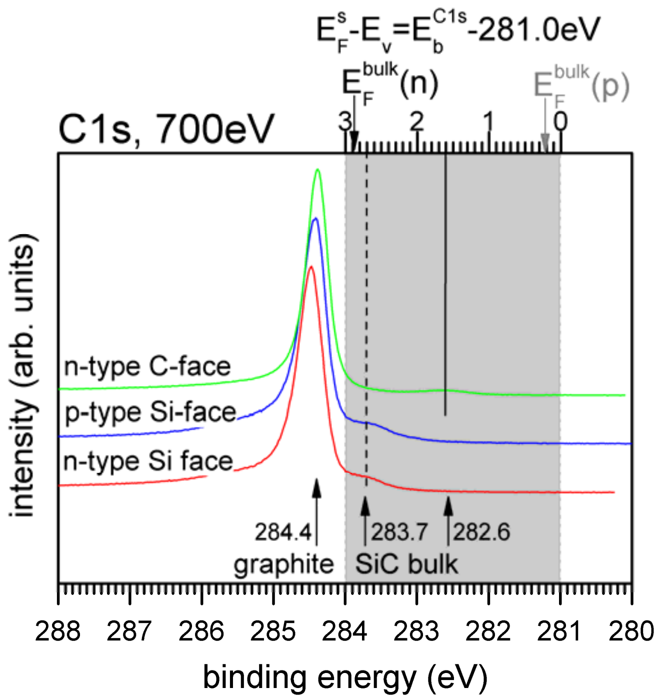


K.V. Emtsev et al., cond-mat/0609660

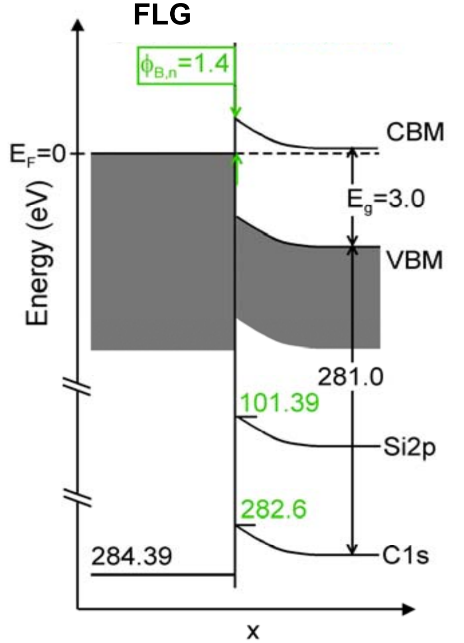
Friedrich-Alexander-Universität Erlangen-Nürnberg

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Band alignment between 6H-SiC and FLG

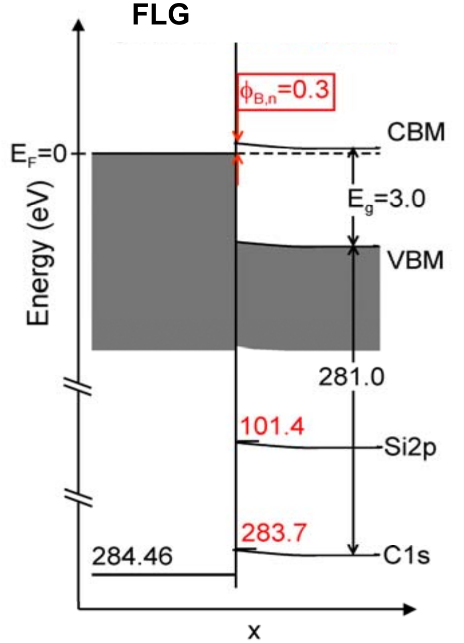


n-type C-face



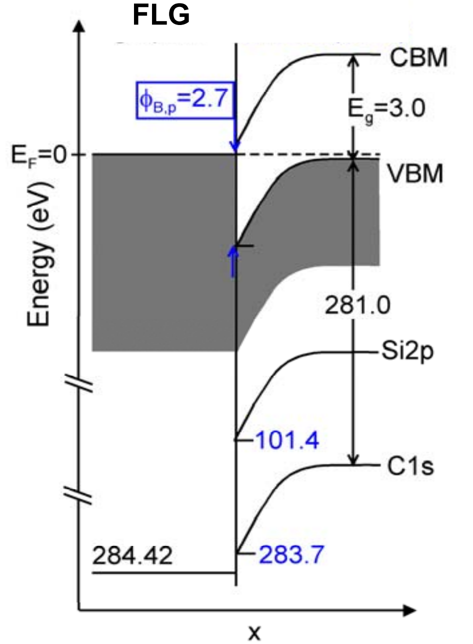
$\Phi_{B,n}$=1.4eV

n-type Si-face



$\Phi_{B,n}$=0.3eV

p-type Si-face

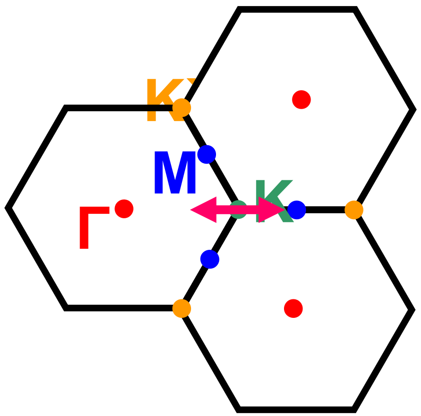


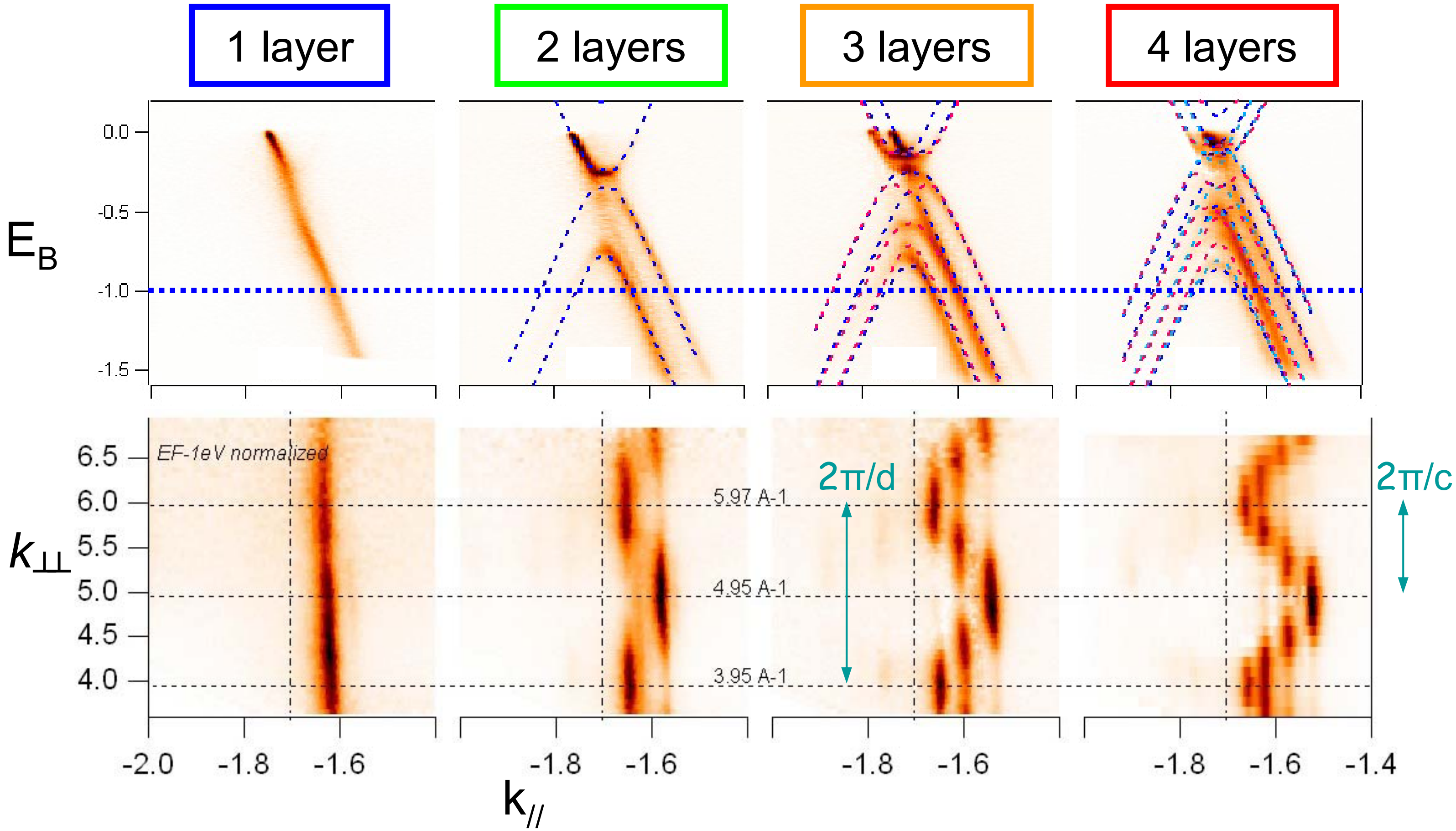
$\Phi_{B,p}$=2.7eV

Predictions for 4H-SiC: 1.7eV | 0.6eV | 2.7eV

Th. Seyller et al., cond-mat/0610220

Pure-2D to quasi-2D conversion with # of layers

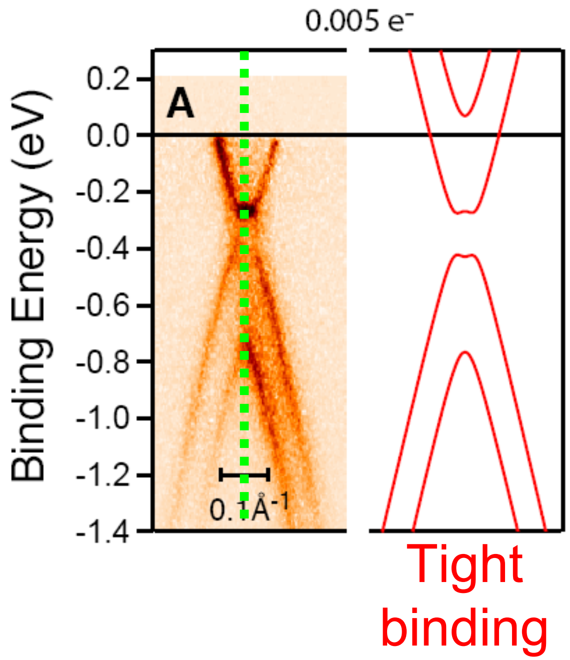




- Possibility of different stackings: Bernal (ABA) and rhombohedral (ABC)
- Interlayer interaction changing the nature of wave function from pure-2D (single layer) to quasi-2D (multilayers)
- Intensity oscillations correspond to out-of-plane periodicity of graphene layers - analogy to quantum well states

T. Ohta et al., under review

Evolution of tight binding parameters



$$H = \begin{pmatrix} \alpha_1 & \beta_0 & & & & \\ \beta_0^T & \alpha_2 & \beta_s & & & \\ & \beta_s^T & \alpha_3 & \beta_0 & & \\ & & \beta_0^T & \alpha_4 & \beta_s & \\ & & & \beta_s^T & \dots & \\ & & & & & \alpha_n \end{pmatrix}$$

with $\alpha_i = \begin{pmatrix} E_i & v\pi^\dagger \\ v\pi & E_i \end{pmatrix}$

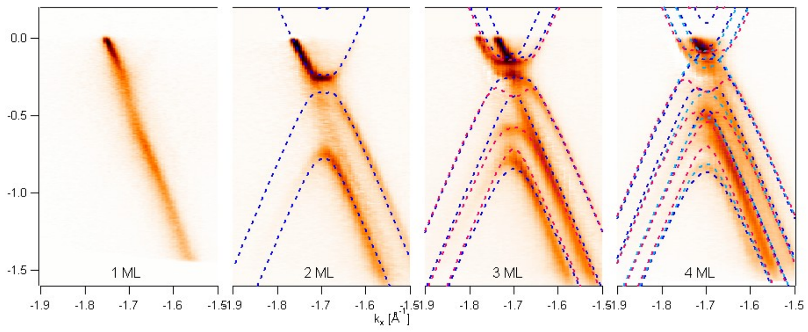
and $\beta_s = \gamma_1 \begin{pmatrix} 0 & s \\ 1-s & 0 \end{pmatrix}$

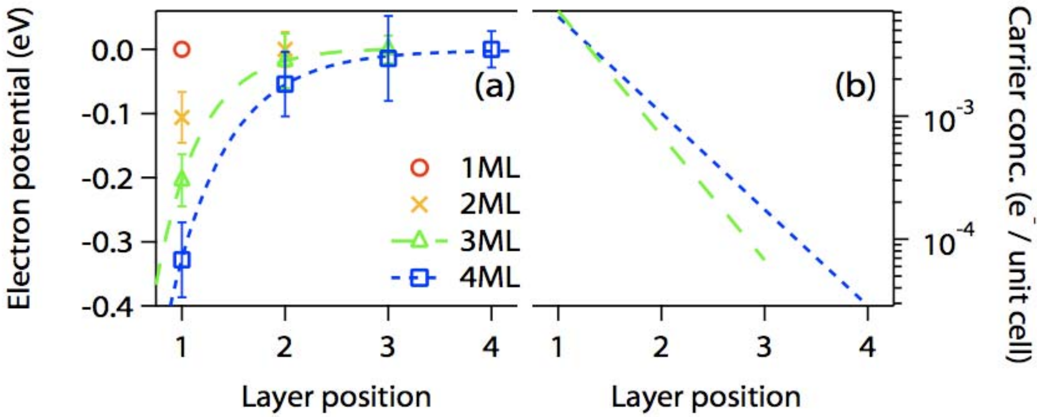
E_1: on-site Coulomb energy
$\pi = p_x + ip_y$
γ_1: nearest neighbor hopping integral across the layer
v band velocity
s = 0 Bernal (ABA), 1 rhombohedral (ABC) stacking
α and β operate on (A,B) sublattices

E. McCann, V. Fal'ko,
Phys. Rev. Lett. 96, 086805 (2006).

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Quantitative evaluation of band structure

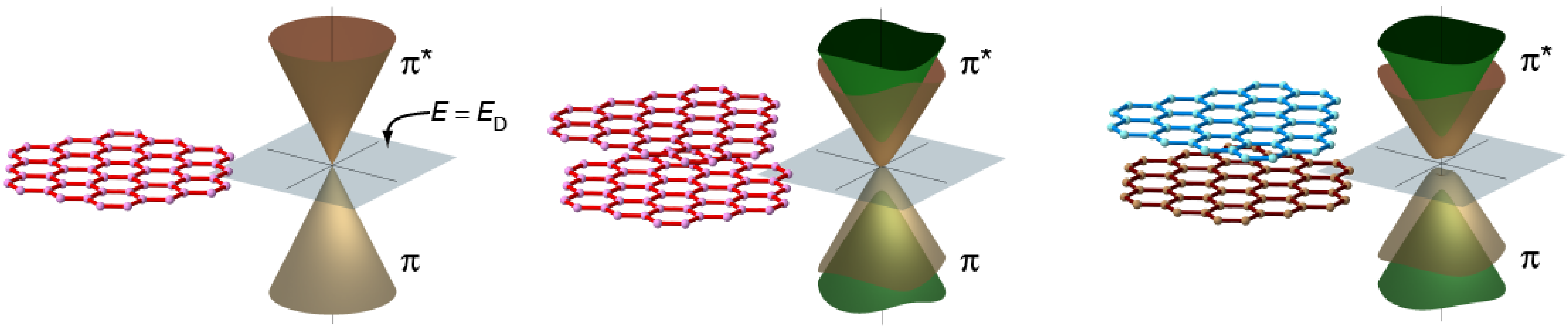




N	v (10^6m/sec)	n (10^{13} cm^{-2})	E_D (eV)	E_1 (eV)	E_2 (eV)	E_3 (eV)	E_4 (eV)	γ_1 (eV)
1	1.1	6.0	-0.44	-0.44				
2	1.05	8.1	-0.30	-0.35	-0.24			0.48
3	1.02	8.0	-0.21	-0.34	-0.16	-0.14		0.48
4	1.02	7.7	-0.15	-0.37	-0.10	-0.06	-0.05	0.45
inf	0.91							0.35

Controlling π-π* gap in bilayer graphene

Single layer | Bilayer

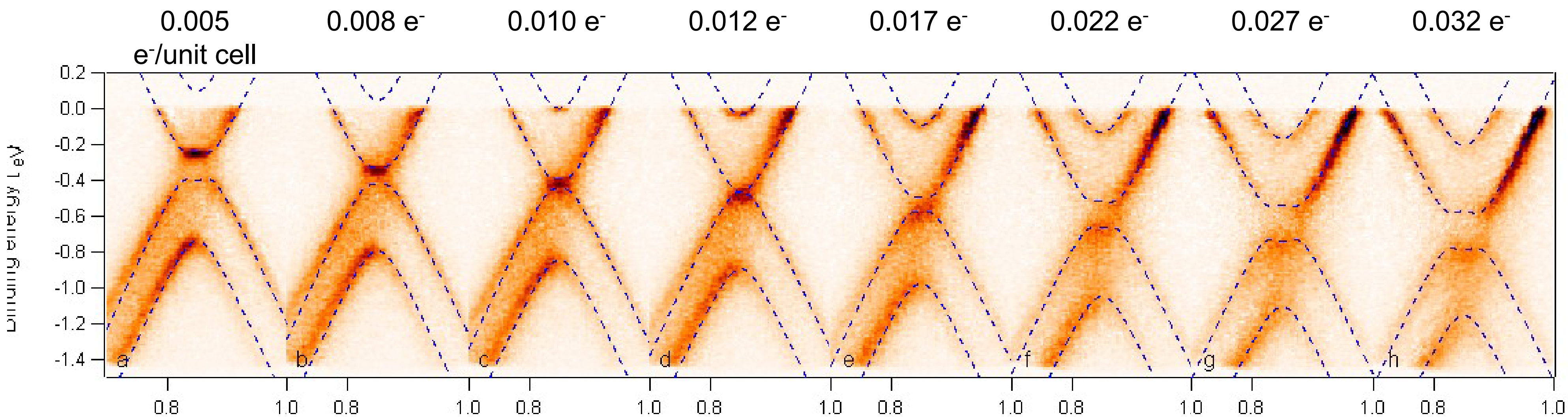


Theory: E. McCann, V.I. Fal'ko: *Landau-level Degeneracy and Quantum Hall Effect in a Graphite Bilayer*. Phys. Rev. Lett., 96 (2006) 086805.

Experiment: T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg: *Controlling the Electronic Structure of Bilayer Graphene*. Science 313 (2006) 951.

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Evolution of π bands on surface doping

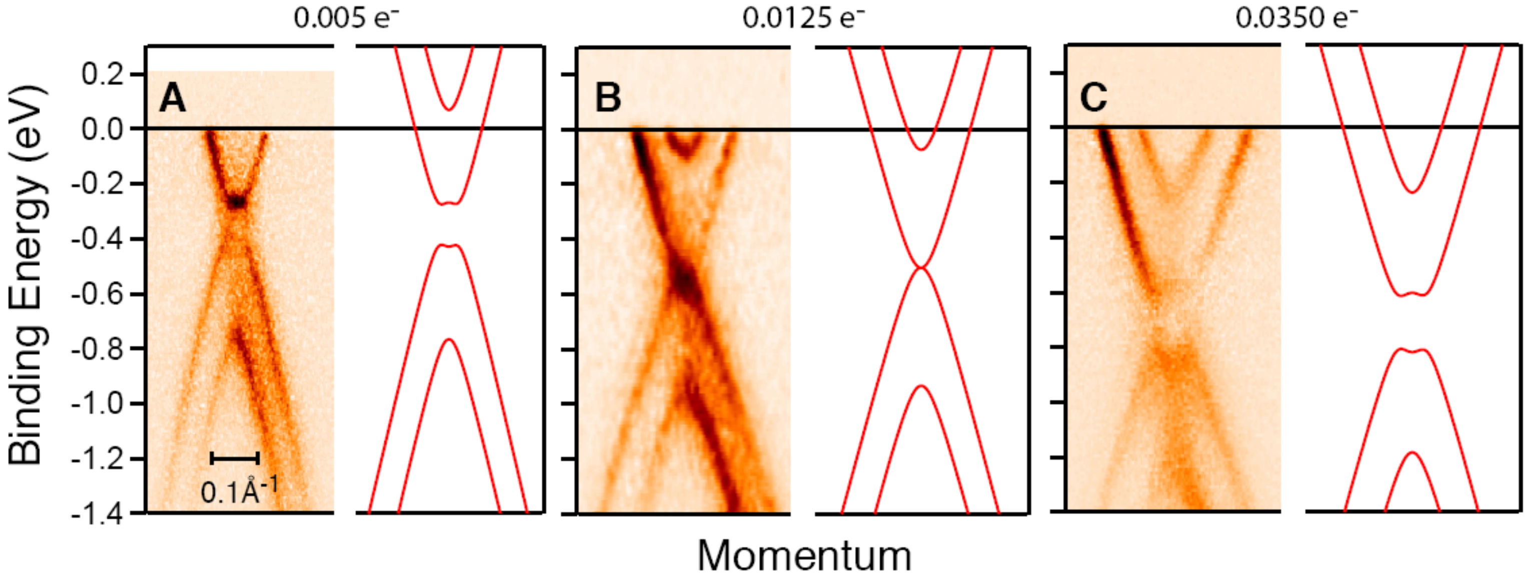


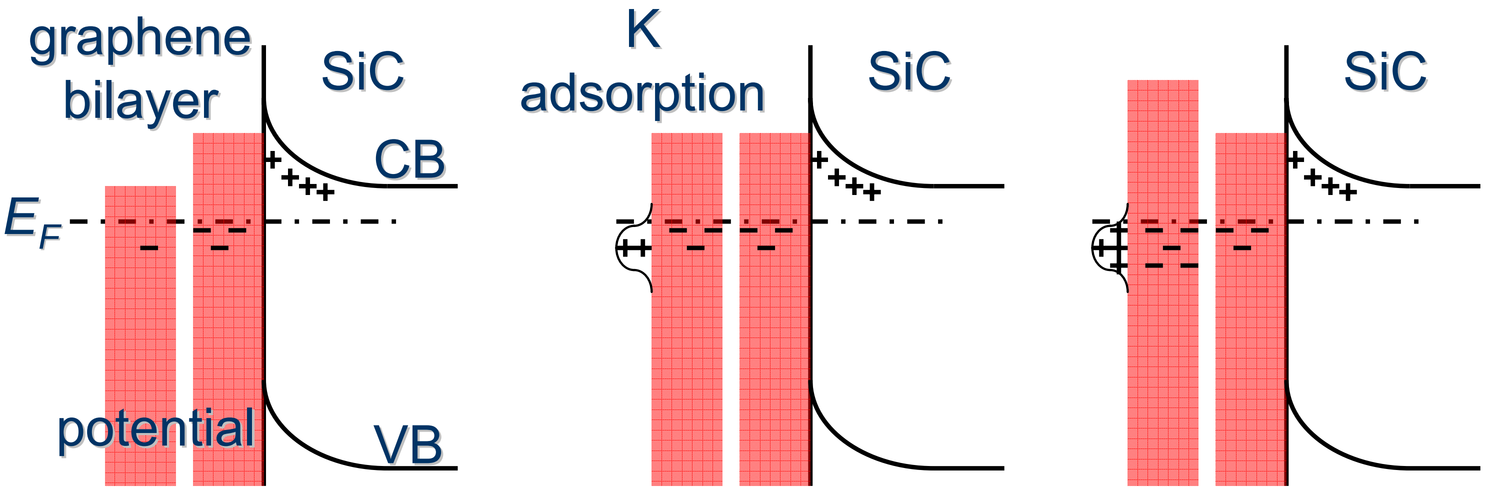
- Deposition of potassium
- Shift of π band due to increased total carrier density
- Continuous closing/reopening of the gap

Theory: E. McCann, V.I. Fal'ko: *Landau-level Degeneracy and Quantum Hall Effect in a Graphite Bilayer*. Phys. Rev. Lett., 96 (2006) 086805.

Experiment: T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg: *Controlling the Electronic Structure of Bilayer Graphene*. Science 313 (2006) 951.

Closing and re-opending of the π-π* gap





Non-equal charge distribution due to short interlayer screening length

Friedrich-Alexander-Universität Erlangen-Nürnberg

PD. Dr. Thomas Seyller
Lehrstuhl für Technische Physik
Institut für Physik der Kondensierten Materie

Summary

Characterization of ultra-thin graphitic layers on SiC by photoelectron spectroscopy:

- Individual graphene layers can be counted
- $(6\sqrt{3}\times6\sqrt{3})$ is '0th' graphene layer
- $(6\sqrt{3}\times6\sqrt{3})$ makes up interface between SiC(0001) and FLG
- $(6\sqrt{3}\times6\sqrt{3})$ responsible for odering of graphene in Si-face
- Barriers determined
- Controll of π-π* gap in bilayer graphene through relative potential
- Many-body interactions: e-ph, e-e, el-pl lead to considerable renormalization of bands

➡ **O 29.1. Invited talk by E. Rotenberg: *Many-body interactions in clean and alkali-adsorbed graphene***

A. Bostwick, T. Ohta, Th. Seyller, K. Horn, E. Rotenberg:
Quasiparticle dynamics in graphene, Nature Physics 3 (2007) 36.