Manipulation der atomaren Anordnung mit Epitaxie

↓

Ein Weg zur erweiterten Funktionalität von Halbleitermaterialien für nanoelektronische Anwendungen

A. Fissel

Laboratorium für Informationstechnologie

Motivation

Influence of materials on the properties of semiconductor devices:

- Doping
- Material combination
- Composition

→ **Problems:**

→ alloy scattering

→ no sharp interfaces (interdiffusion)

→ strain-induced defects

→ decomposition

change of the symmetry by strain

gap engineering

Crystal structure ?

Motivation

A lot of materials occur in different crystal structures (polymorphism) with different electronic properties, such as electronic band structure.
Semiconductor materials: CdS, ZnS, GaN, SiC (one-dimensional polymorphism)

New types of heterostructures or superlattice:
One material constituent in different crystal structures (heteropolytypic structures)
(wurtzite/zinc-blende or lonsdaleite/diamond heterostructures)

F. Bechstedt, P. Käckell, Phys. Rev. Lett. 75 (1995) 2180-2183.
S.-H. Ke et al., Phys. Rev. B 54 (1996) 8789-8793.
A. Fissel, Phys. Rep. 379 (2003) 149-255.

Motivation

Heteropolytypic structures are also under consideration for the most common semiconductor, silicon. (Only theory)

Further advantage of lonsdaleite/diamond, or at least non-cubic/cubic, Si heterostructures :

→Additional degree of freedom (Functionality)

combined with properties that can otherwise only be achieved by incorporating SiGe or SiGeC into Si technology

M. Murayama, T. Nakayama, Electronic Structures of Hetero-crystalline Semiconductor Superlattices, J. Phys. Soc. Jap. 61 (1992) 2419.
Ch.-Y. Yeh et al., Zinc-blende-wurtzite polytypism in semiconductors, Phys. Rev. B 46 (1992) 10086.
C. Persson, E. Janzen, Electronic band structure in hexagonal close-packed Si polytypes, J. Phys.: Condens. Matter 10 (1998) 10549.
C. Raffy, J. Furthmüller, F. Bechstedt, Properties of hexagonal polytypes of group-IV elements from first-principles calculations, Phys. Rev. B 66 (2002) 075201.
S.Q. Wang, H.Q. Ye, First-principle study on the londsdaleite phases of C, Si and Ge, J. Phys.: Condens. Matter 15 (2003) L197.

Outline

Introduction to polytypism

Properties of polytypes and heteropolytypic structures (SiC, Si)

Formation and stability of polytypes

Epitaxy of polytypes

Application and outlook

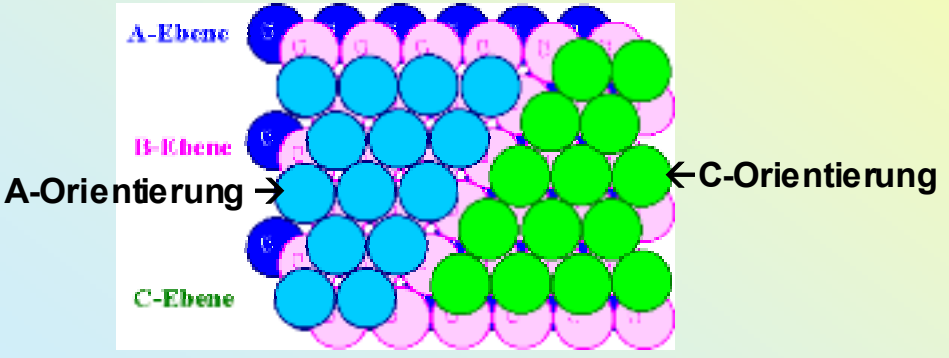
Introduction to polytypism

One-dimensional Polymorphism

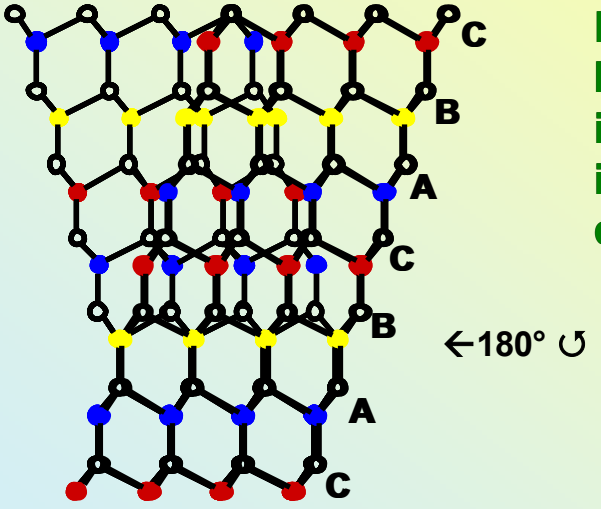
↓

Polytypism

Change of the stacking order only in one crystal direction



Motivation and Introduction

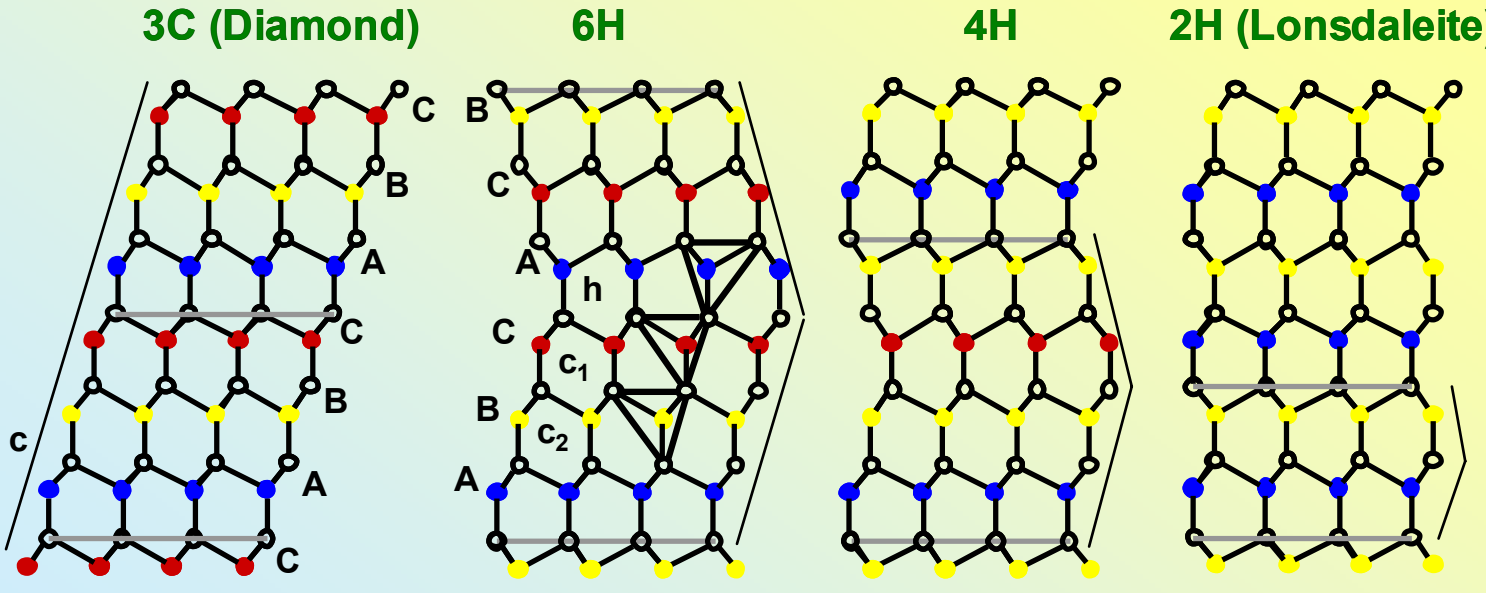


New stacking order (structure) can be described by a periodical introduction of 180° rotation twins in the cubic 3C-structure in [111] direction!

Distance of rotation twins (atomic double layers)	Description
5 ≤	Crystal structure
> 5	Twinning-superlattice
≫ 5	Twinned crystal

Polytypic structures

Stacking sequences in [111] and [0001]-direction for the most common closed-packed polytypes



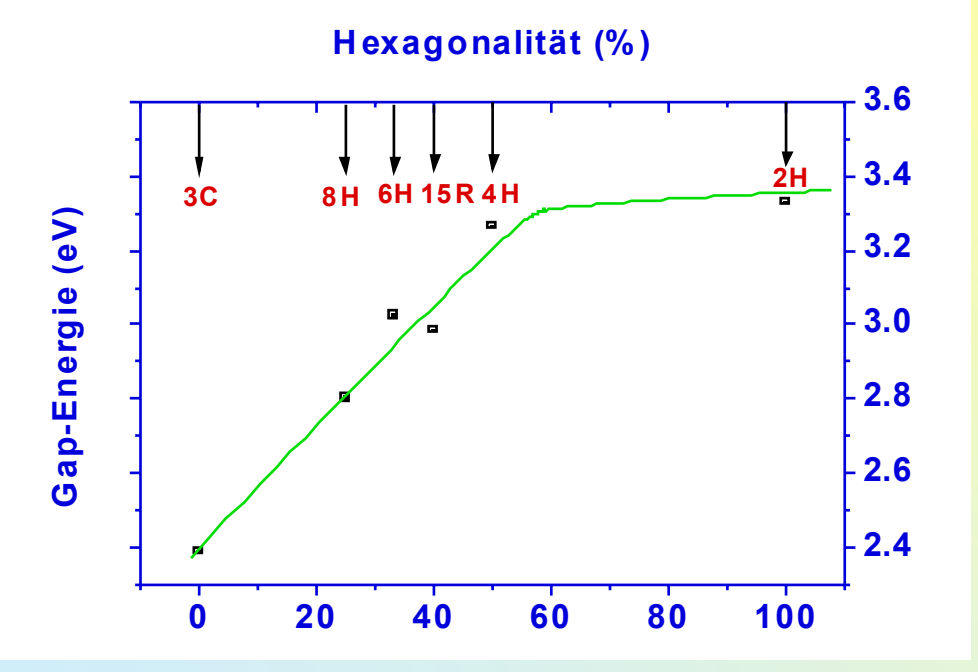
Orientation of the bilayers with cubic (c) or hexagonal (h) character
rotation of the sp^3 bonding tetrahedron

Andreas Fissel

Laboratorium für Informationstechnologie lfi

Properties of SiC-Polytypes

Gap energy as function of hexagonality

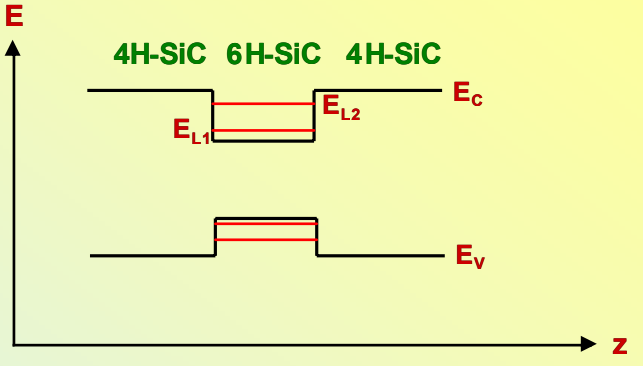


Properties of heteropolytypic SiC-structures

Typ I Heterostructure

Localization of carriers in both the conduction and valence band at the same place

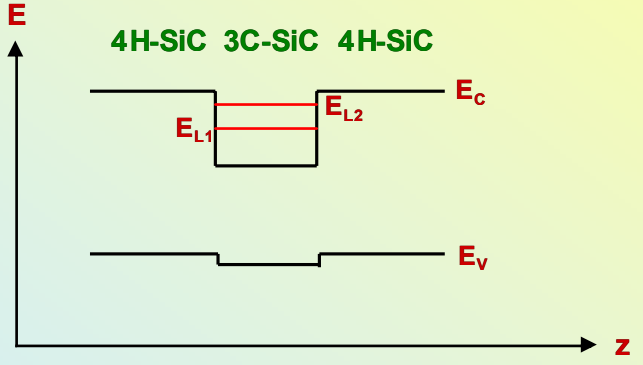
↳ **Quantum levels in the conduction and valence band**



Typ II Heterostructure

Localization of carriers at different places.
However, localization only in the Conduction band

↳ **No Quantum levels for holes**



Properties of Si polytypes

	2H-Si	4H-Si	6H-Si	3C-Si
Hexagonality	100 %	50 %	33 %	0%
a (Å) c (Å)	3.80 6.28	3.84 12.54	3.84 18.59	3.8403 9,4068
B (mbar)	0.99	0.93	0.95	0.95
E_g(eV)	0.99	1.13	1.16	1.17
D_{cf} (meV) D_{so} (meV)	300 33.7	144 30.1	102 28.0	 50.1
ΔE_V (meV)	235	157	135	

C. Persson, E. Janzen, J. Phys.: Condens. Matter 10 (1998) 10549.
C. Raffy, J. Furthmüller, F. Bechstedt, Phys. Rev. B 66 (2002) 075201.

1. Gap energy reduces with the hexagonality from 1.16 eV (6H) to 0.99 eV (2H).
2. Hexagonal polytypes: the threefold-degenerate valence-band maximum of cubic Si splits into a twofold and a lower onefold splittoff band. (crystal-field splitting increases with the hexagonality).
3. Electronic heteropolytypic structure should mainly governed by the valence-band discontinuity: 135 meV (3C/6H) and 235 meV (3C/2H).

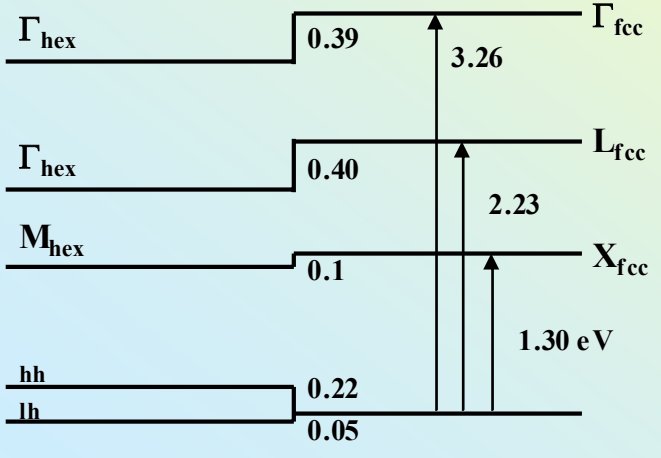
Properties of heteropolytypic Si-structures

Combination 3C/2H : type- I heterostructure

Combination 3C/4H and 3C/6H : type- II heterostructure

Localization: electrons in the cubic parts; holes in the hexagonal parts

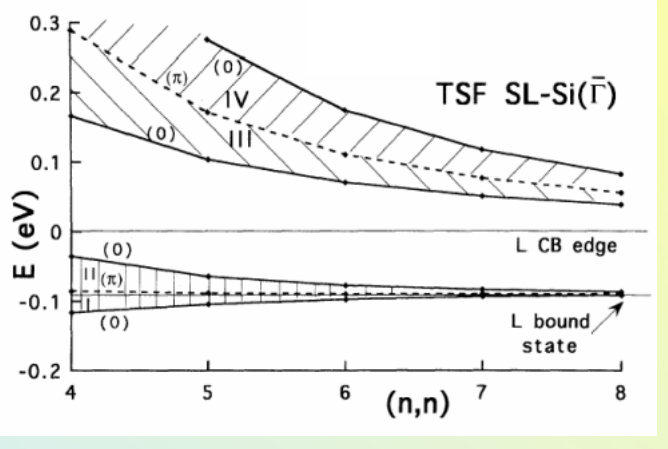
Band offsets for a lonsdaleite/ diamond-Si heterojunction*



Data by M. Murayama, T. Nakayama, J. Phys. Soc. Jap. 61 (1992) 2419.

Miniband structure for Si-based twin stacking-fault superlattices

(n-superlattice periodicity)



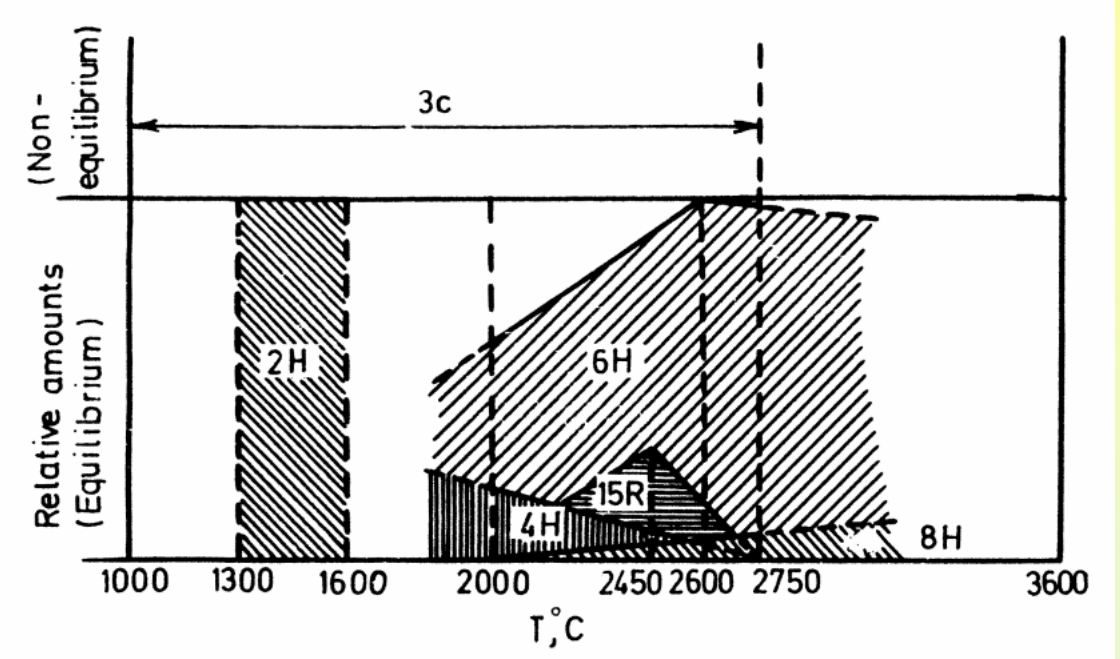
Z. Ikonic et al., Phys. Rev. B 48 (1993) 17181.

Andreas Fissel

Laboratorium für Informationstechnologie lfi

Occurence of SiC polytypes

Relative amount of polytypes in SiC crystals as function of growth temperature



W.F. Knippenberg, Philips Res. Rep. 18 (1963) 161.

Origins of polytype formation

1. Formation of polymers within the gas phase
2. Influence of dopants and impurities
3. Si/C-ratio
4. Influence of temperature and supersaturation
5. Influence of the surface structure
6. Stacking fault energy

Preparation of heteropolytypic structures by layer growth

Requirements: perfect layers
sharp interface between substrate and layer

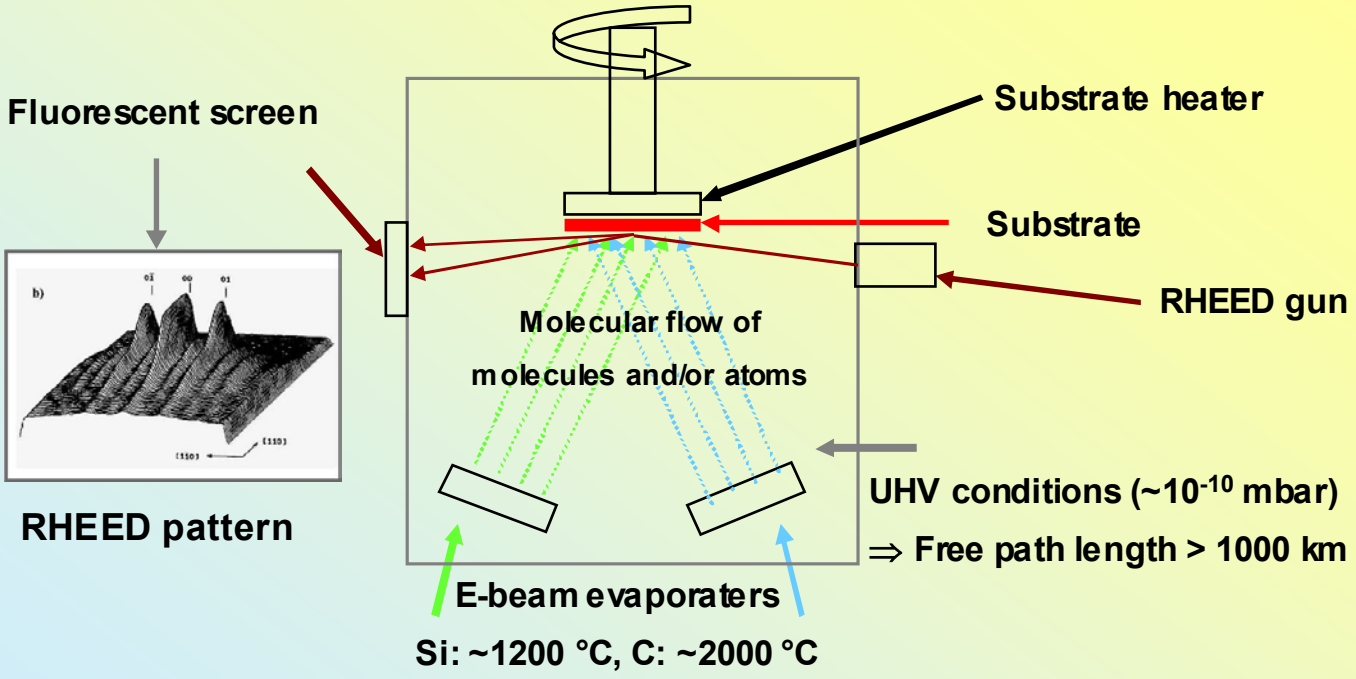
Method: Epitaxy (επι(epi) – upon; ταξιζ(taxis) – ordered)

Epitaxy = growth of a layer with a crystallographic relationship between film and substrate (demands matching in structure and lattice parameters)

First report on heteroepitaxy

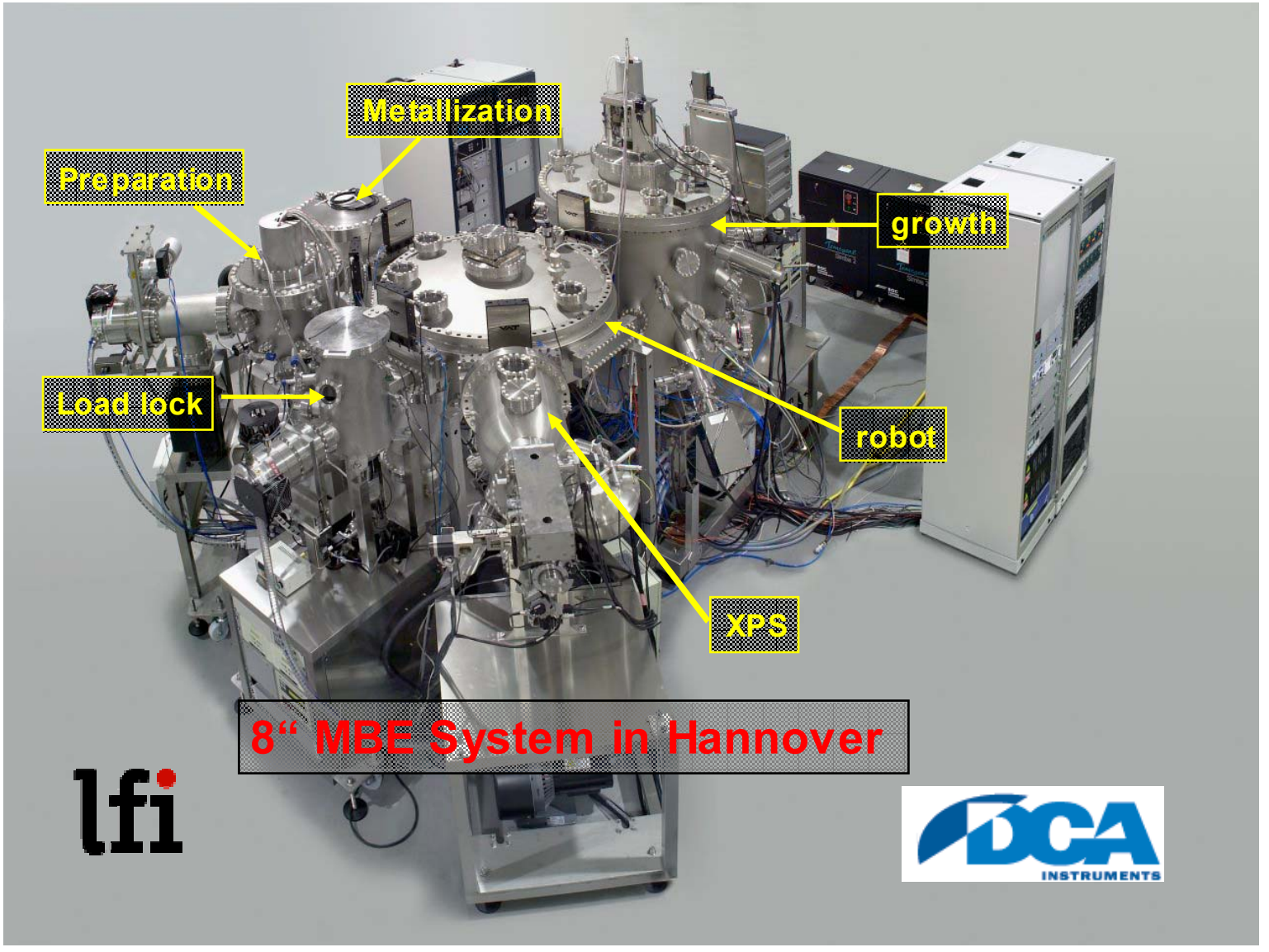
M.L. Frankenheim: Ann. Physik 37, 516 (1836):
Orientiertes Aufwachsen von Natriumnitrat ($NaNO_3$) auf Kalziumcarbonat ($CaCO_3$)

Molecular beam epitaxy (Equipment)



Advantages of UHV conditions:

- ⇨ no interaction between molecules and atoms in the chamber
- ⇨ Time for surface coverage by impurities >> Time to grow a monolayer
- ⇨ In situ growth monitoring by RHEED

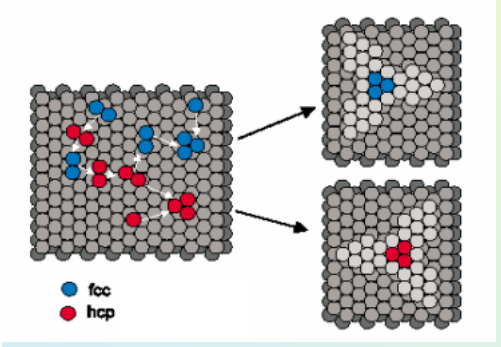

Metallization
Preparation
growth
Load lock
robot
XPS
8“ MBE System in Hannover
lfi
DCA
INSTRUMENTS

SiC polytype layer growth by epitaxy

Change of the structure needs formation of a new phase

⬇

Nucleation



Adsorption-Desorption

Si_2C SiC_2

C Si

Attachment-Detachment Attachment-Detachment

A B C B A B C B A

Andreas Fissel

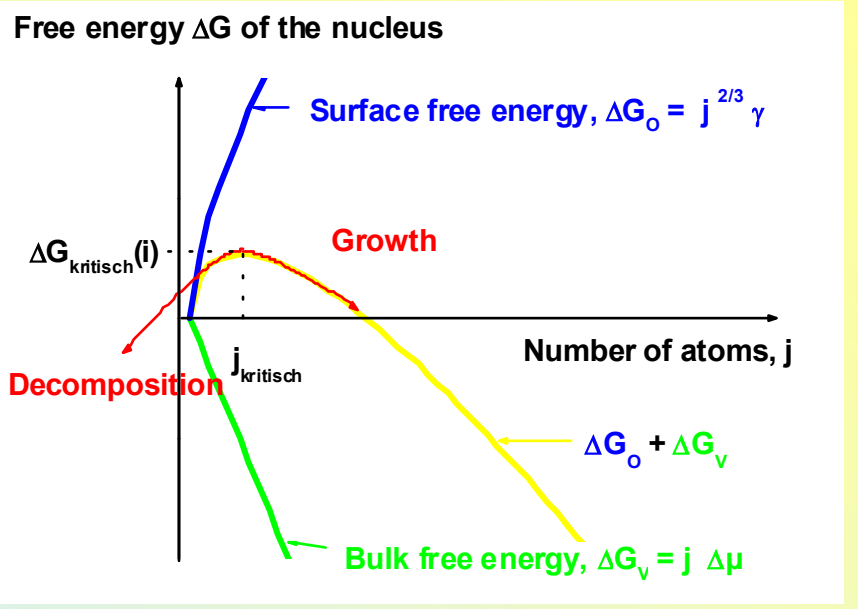
Laboratorium für Informationstechnologie lfi

Thermodynamic consideration

Growth needs a nucleus which is stable

Critical 2D-nucleus size:

$$l_{2,k} = \frac{4b^2\kappa_{11}}{3\Delta\mu}$$



b – Bonding length

k_{11}-specific edge energy

Δμ - chemical potential change (= kTlnS),

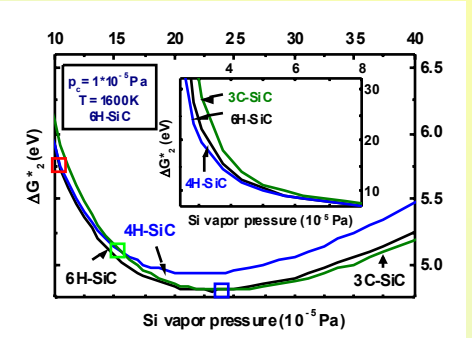
T = 1600 K, Supersaturation (S) = 10 → $l_{2,k}$ = 3.5 nm = **260 Atoms/Monolayer**

↓

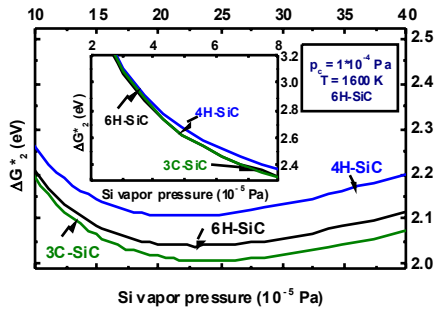
Thermodynamic consideration is justified

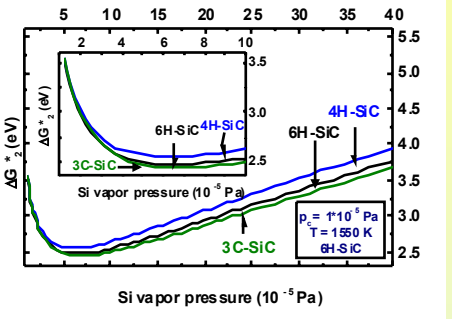
Nucleation energy as function of Si chemical potential

Chemical potential



Temperature





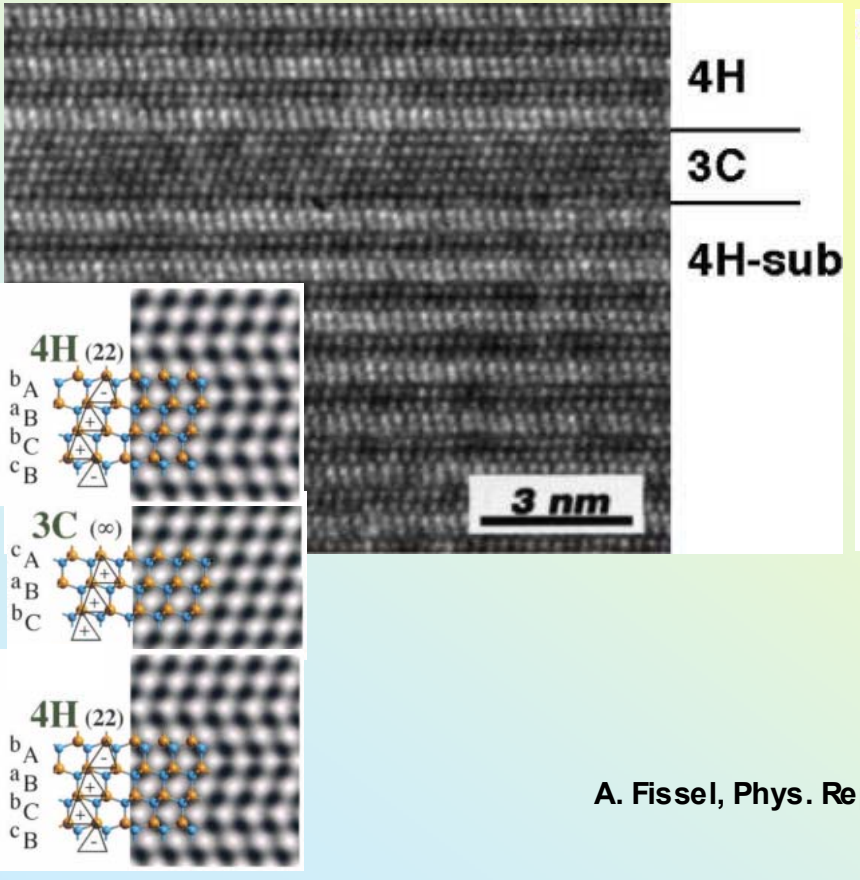
4H-Growth: higher temperature, more C-rich condition

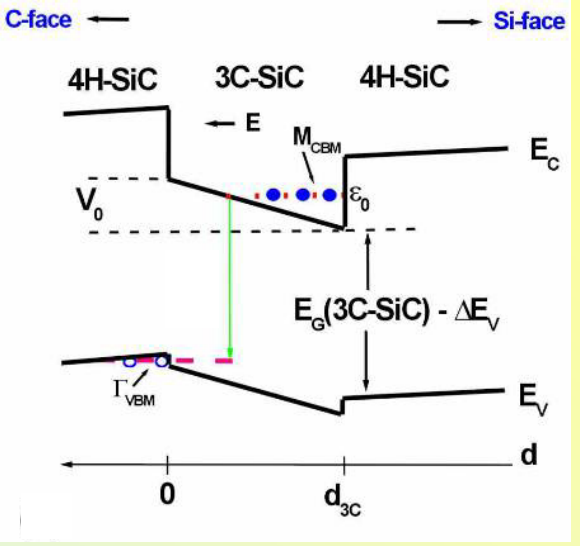
6H-Growth: higher temperature, more Si-rich conditions

3C-Growth: lower temperature, Si-rich conditions, higher growth rates

A. Fissel, J. Cryst. Growth 212 (2000) 438.

Heteropolytypic SiC-structure

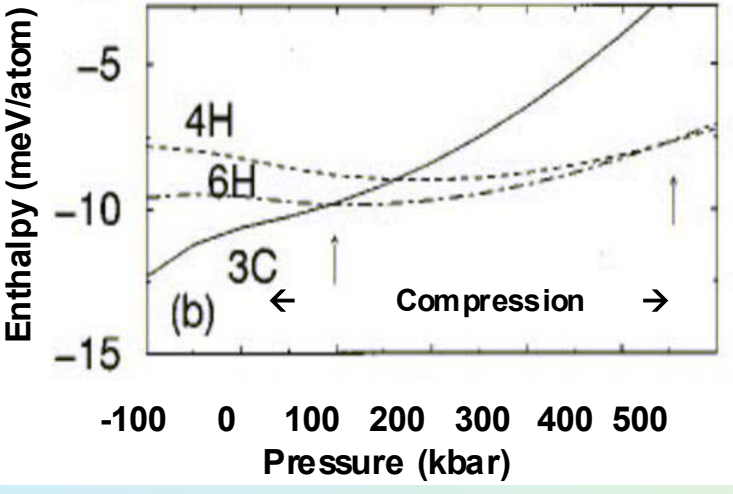




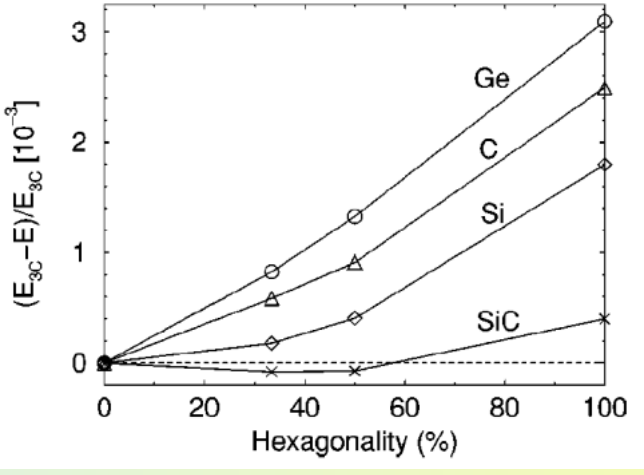
A. Fissel, Phys. Rep. 379 (2003) 149.

Formation of Si polytypes

Enthalpy as function of pressure (H = E + pV)



Relative lattice energy versus hexagonality

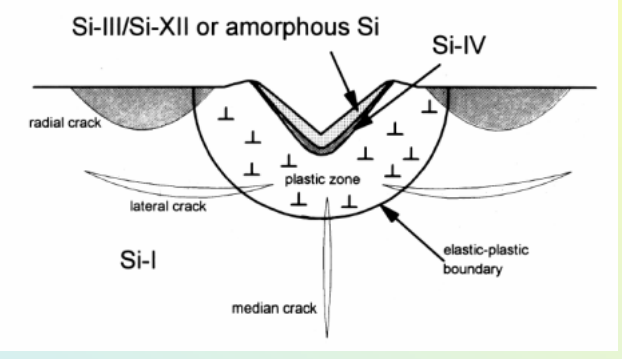


C. Raffy, J. Furthmüller, F. Bechstedt, Phys. Rev. B 66 (2002) 075201.

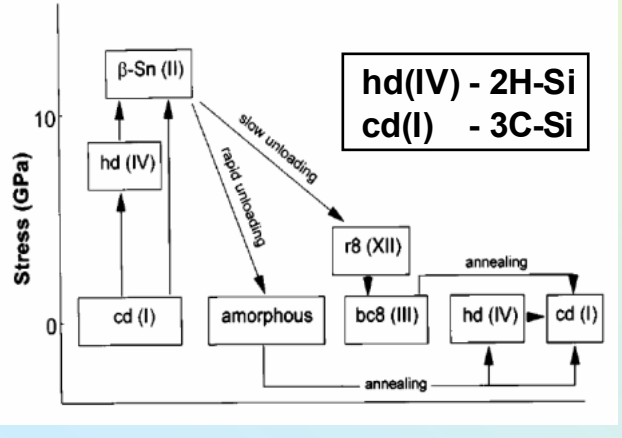
Si exhibits a high stacking fault energy

→Formation of bulk non-cubic Si only under conditions far away from the equilibrium, like diamond (high pressure, high temperature).

Formation and stability of non-cubic silicon



Appearance of Si phases in the vicinity of indents on Si



Appearance of Si phases as function of the applied stress and post-treatment

A. Kailer, Y.G. Gogotsi, K.G. Nickel, J. Appl. Phys. 81 (1997) 3057.

Introduction of stacking disorder in Si

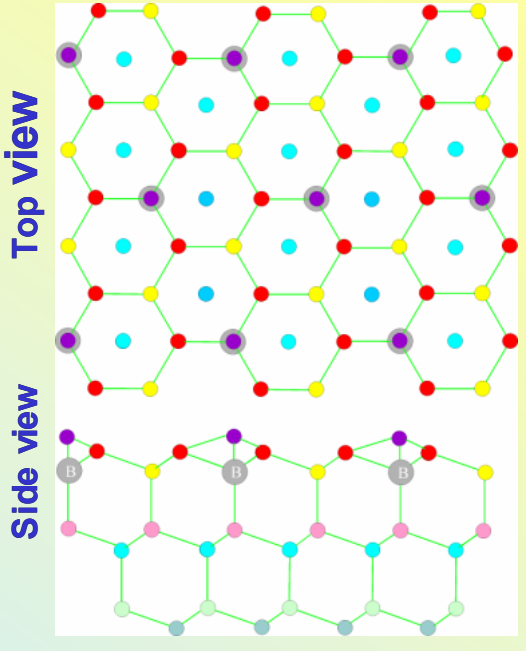
Surface-induced stacking transition was reported for Si epitaxy on Si(111) (√3x√3)R30°-reconstructed due to 1/3 ML subsurface boron.

R.L. Headrick et al., Influence of surface reconstruction on the orientation of homoepitaxial silicon films, Phys. Rev. Lett. 65 (1990) 1128-1131.

Influence of subsurface boron:

1. Subsurface strain by the short Si-B bonds (0.0141 Å per atomic percent of boron in silicon)
2. Surface passivation through charge transfer from the Si adatom to the substitutional B.

Surface structures of Si(111) with 1/3 ML subsurface boron

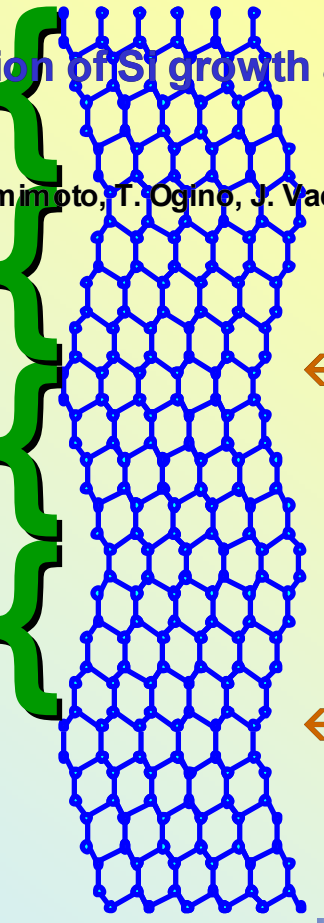


Si(111)-B:(√3x√3)R30°(B_5 site)

Si polytype growth: Basic Approach

Change of stacking order by repetition of Si growth and boron coverage circles on Si(111)!?

(First not very successful attempt: H. Hibino, K. Sumimoto, T. Ogino, J. Vac. Sci. Technol. A 16 (1998) 1934.)



Boron coverage:

1. Only initial deposition and annealing
2. Deposition and annealing

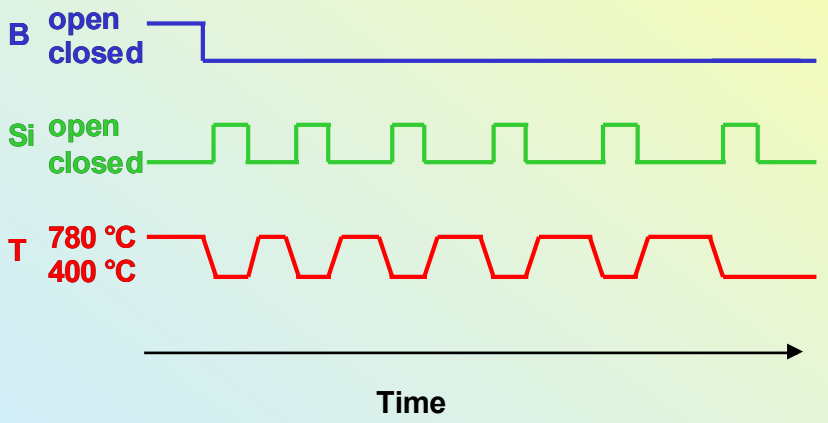
Andreas Fissel

Laboratorium für Informationstechnologie lfi

Si polytype growth: First Experiments

Initial deposition and afterwards annealing

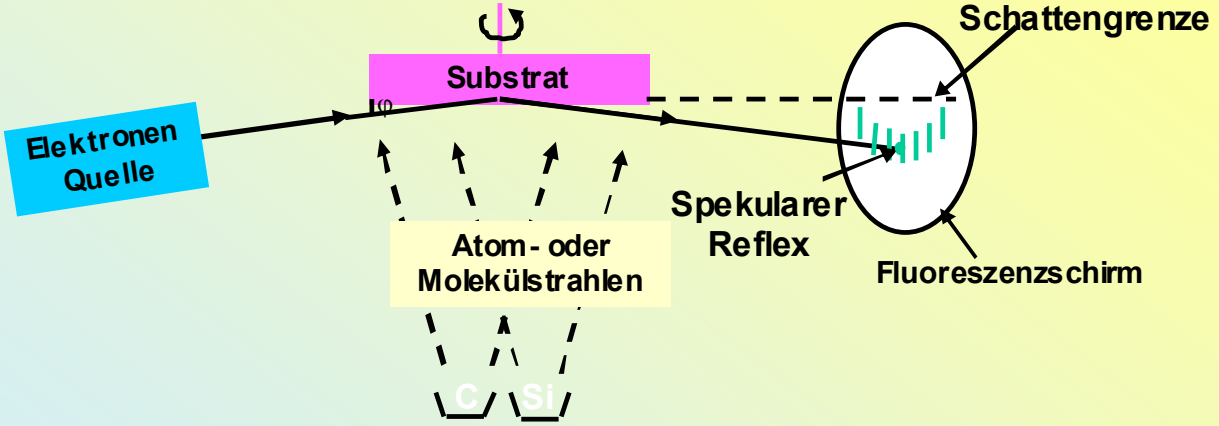
Growth and preparation regime



2.5 nm per circle

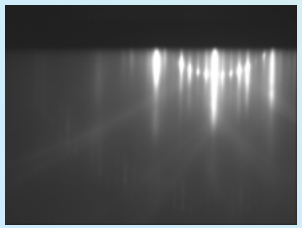
Si polytype growth: First Experiments

Control of surface conditions by electron diffraction

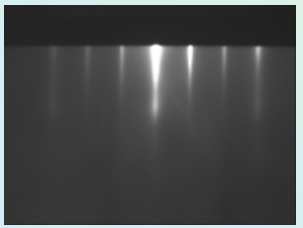


RHEED-Pattern

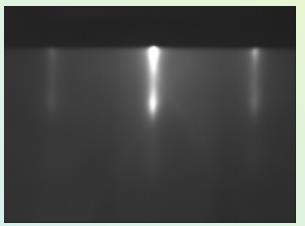
(7x7)-Si(111) (before B deposition)



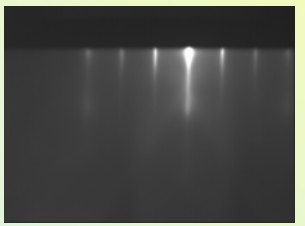
(√3x√3) B-induced (after B deposition)



(1x1)-Si(111) (after 4 ML Si deposition)

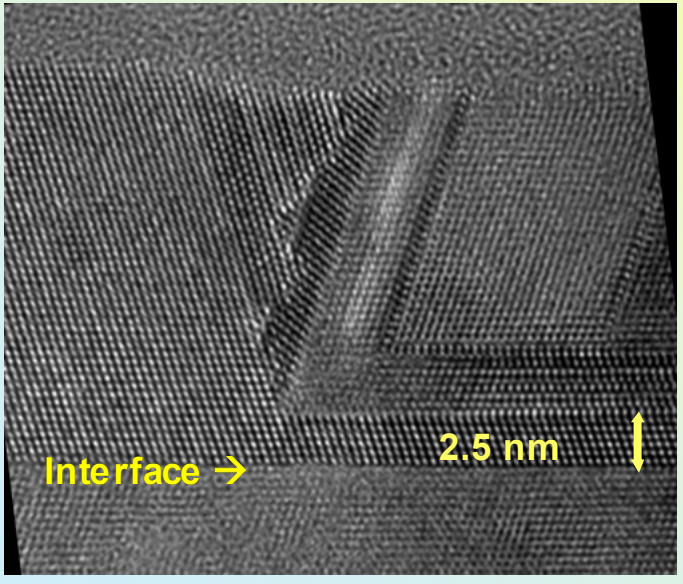


(√3x√3)B-induced (after annealing)



Si polytype growth: First Experiments

Si deposition on surfaces with only initially 1/3 ML B
(no further B-supply during the annealing circles)



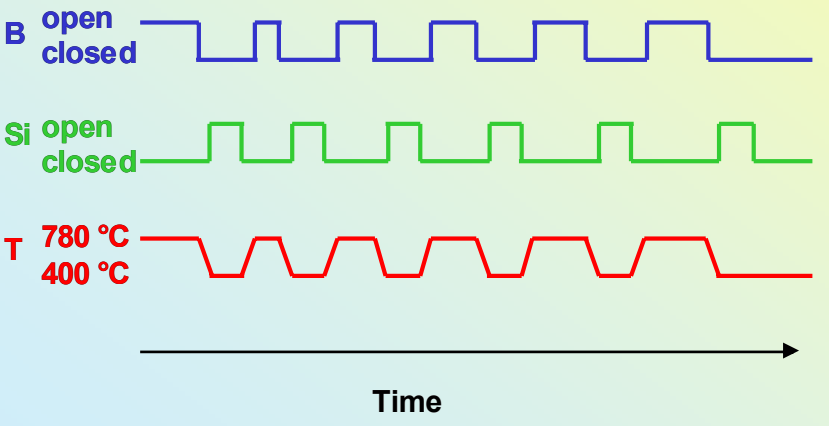
Cross-sectional TEM micrograph

- Stacking conversion in the substrate-layer interface
  (no change for coverages below 1/3 ML boron and vicinal substrates)
- Repeated change in stacking direction only partially

Si polytype growth: First Experiments

Boron deposition and annealing

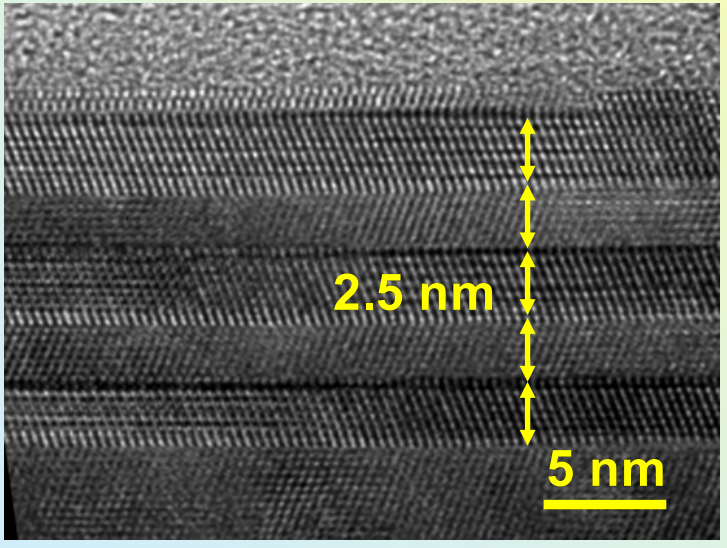
Growth and preparation regime



2.5 nm per circle

Si polytype growth: First Experiments

Si deposition on surfaces with initially 1/3 ML B and deposition after each annealing cycle

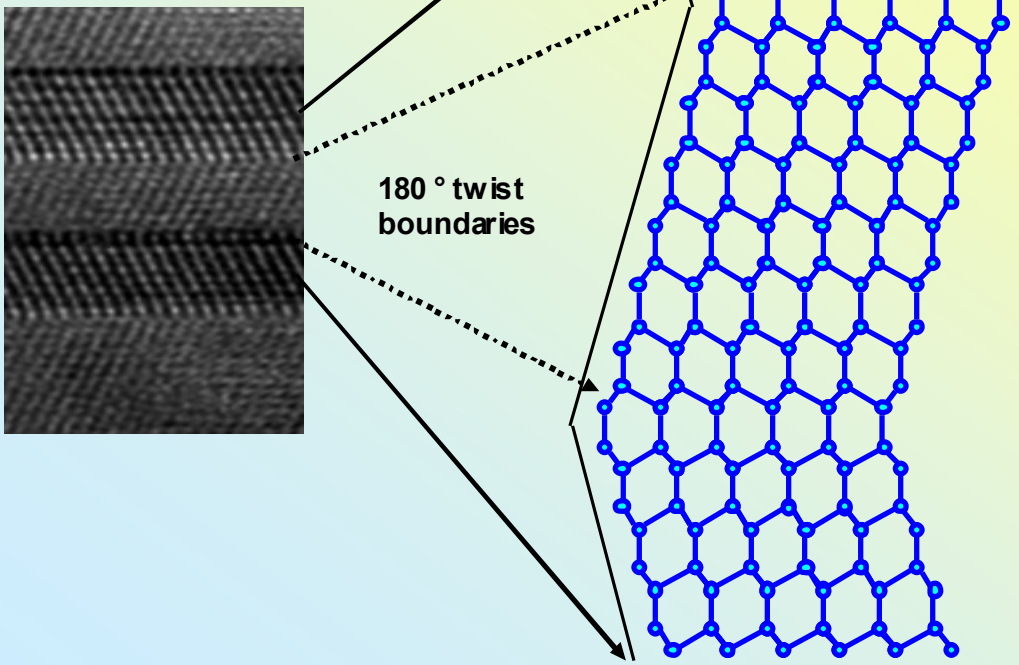


High-resolution cross-sectional TEM micrograph

Growth of twinning-superlattice structure with eightfold periodicity corresponding to 2.5 nm Si

A. Fissel, C. Wang, E. Bugiel, H.J. Osten; *Epitaxial Growth of non-cubic Silicon;* Microelectronics Journal 36 (2005) 506-509.

Crystal structure model of the superlattice sequence



Type of Bonding

Diamond

Lonsdaleite (twin boundary)

Diamond

Lonsdaleite (twin boundary)

Diamond

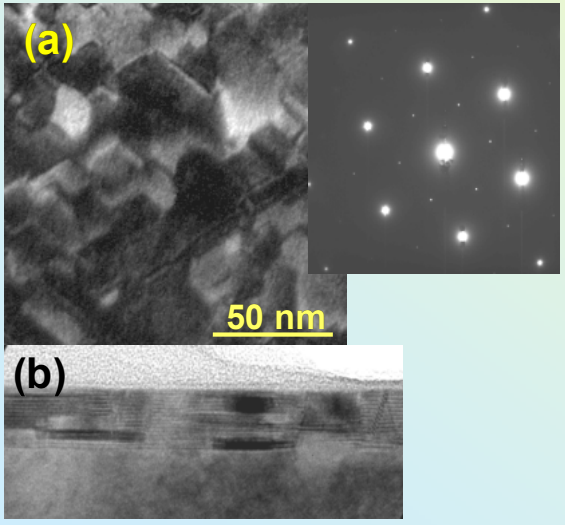
Andreas Fissel

Laboratorium für Informationstechnologie lfi

Si polytype growth: First Experiments

Homogeneity and size of superlattice regions

(a) Plan-view TEM image with SAED [111] pattern with sharp {220} spots and slight 1/3{422} superstructure spots due to twinning,
(b) cross-sectional TEM image with lower magnification.



Size of superlattice domains
→ 0.1 µm (corresponding to the distance of step edges)

Homogeneity influenced by:
1. the step density (partly step flow growth mode)
2. Nucleation on neighbouring terraces shifted by an atomic double step
3. Inhomogeneous boron surface segregation

Application of heteropolytypic and quantum-well structures

- **HEMT:** High Electron Mobility Transistor
  Carriers separated from doped region
  ⇨ high mobility of the carriers
- **HBT:** Hetero-Bipolar Transistor
  Material of the base with smaller gap
  ⇨ high current amplification and cut-off frequency, lower operation voltage
- **RTD:** Resonant tunnelling-diode
  Material of the base with smaller gap
  ⇨ high current amplification and cut-off frequency, lower operation voltage
- **Laser:** Quantum-well and quantum-Dot Structures
  Carriers are trapped in the lower gap region
  ⇨ lower threshold current only slightly dependent on temperature
  ⇨ Inter-subband transitions
- **Solar cells:** Multi-quantum well structures
  ⇨ higher efficiency

First, properties have to be investigated !

Heteropolytypic SiC resonant-tunneling devices

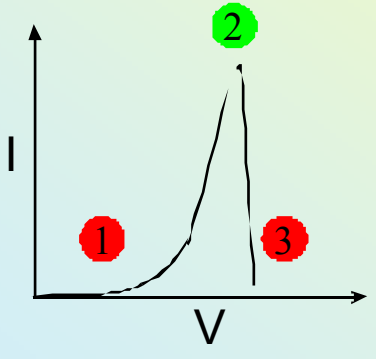
Double barrier structure:

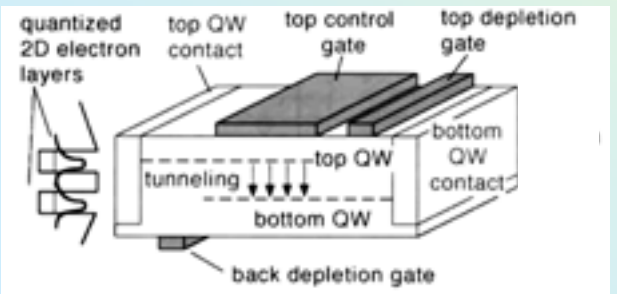
Discrete energy levels in the quantum-well

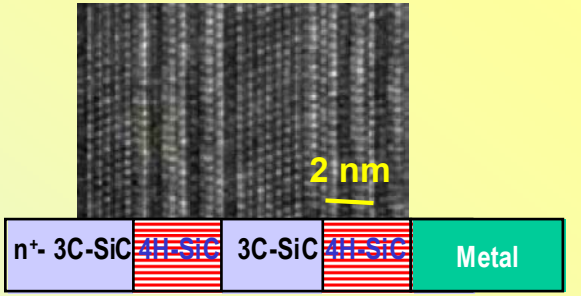
Tunnelling through thin barriers

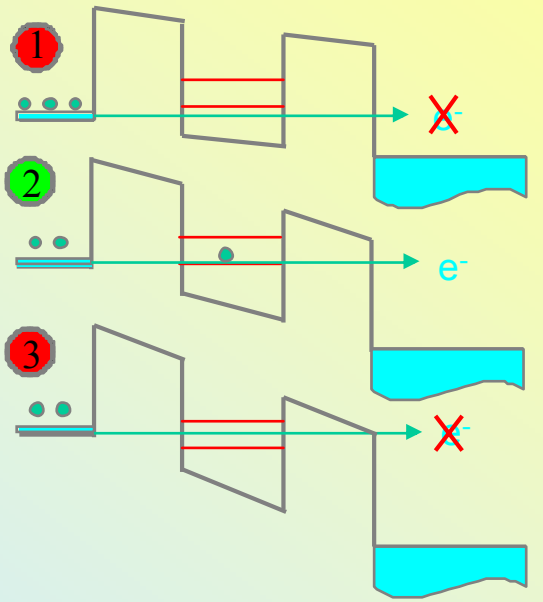
Current peak at resonance voltage

Negative differential resistance









Andreas Fissel

Laboratorium für Informationstechnologie lfi