Ion implantation and “Defect Engineering”

most important process of doping in Si planar technology

- **Advantages:**
  - fast, homogenous on large wafers, reproducible result
  - exact control of implanted amount of dopant (measurement of current); especially important for small dopant levels
  - excellent cleaning of dopants during implantation by mass separation
  - simple mask techniques with thick oxide-, nitride- und photo lacquer layers
  - doping through thin passivation layers
  - doping profile easily adjustable by multiple implantation (not possible by diffusion techniques)
  - very small device structures possible
- **Disadvantages:**
  - irradiation damage up to amorphisation
  - additional annealing steps necessary (defect annealing)
  - doping atoms often not at regular lattice sites after implantation (interstitial position); electrical activation necessary by additional annealing (diffusion of dopants, danger of impurities)
  - implantation only possible for near-surface region
  - Channeling leads to larger penetration depth of a fraction of dopant atoms

Some historical remarks about ion implantation

1952: bombardment of diods with He - improvement of blocking behavior (Ohl)

1955: attempt to dope Ge failed due to implantation defects (Cussins)

1957: first patent for ion implantation technique includes annealing step (Shockley)

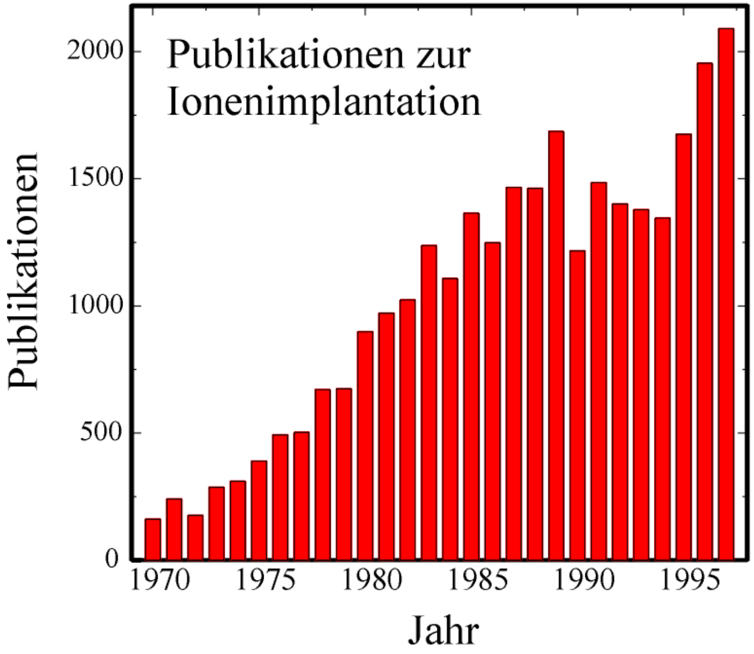
1962: radiation detectors made by P-implanted Si

1963: Lindhardt, Scharff und Schiøtt – LSS theory for ion penetration in solids

1963: experimental study of ion implantation in crystalline and amorphous solids

1965: breakthrough by many studies

increasing interest due to high technological importance



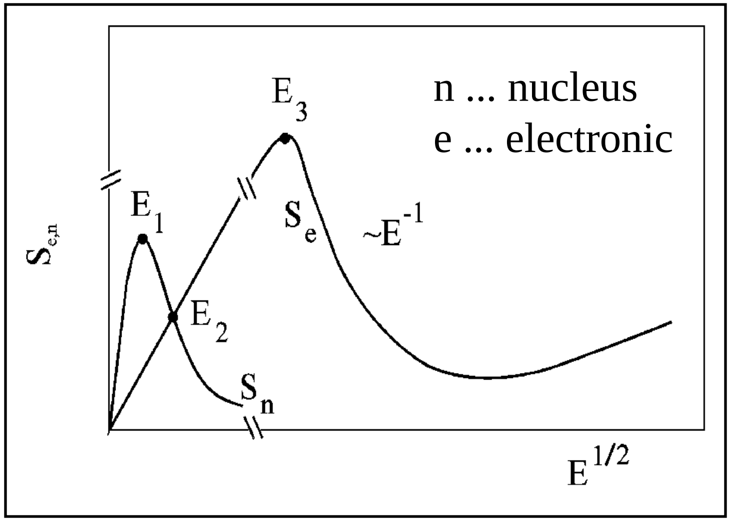
LSS-Theory

- LSS-Theory: interaction of ions with amorphous solids (1963: Lindhardt, Scharff und Schiøtt)
- no channeling effect considered (amorphous state), no diffusion and no defect interaction
- interaction mainly by elastic collisions with cores and inelastic interaction with electrons
- energy loss cross section (*Bremsquerschnitt*) S

$$S_{e,n} = -\frac{1}{N}\left[\frac{\mathrm{d}E}{\mathrm{d}z}\right]_{e,n}$$

N ... atomic density

z ... distance



for B in Si: E1=3, E2=17 and E3=1000 keV

for As in Si: E1=73, E2=800 and E3=10^5 keV

Interaction of ions with solids

- elastic interaction: classical scattering theory is a good approximation
- it is obtained by energy and momentum conservation during central impact:

$$T_m = 4\frac{m_1 m_2}{(m_1 + m_2)^2} E$$

T_m is maximum transferable energy during central stroke

- T_m becomes maximum for equal masses ($T_m = E$)
- electronic deceleration is function of ion energy
- it is possible by this theory to calculate implantation depth distributions

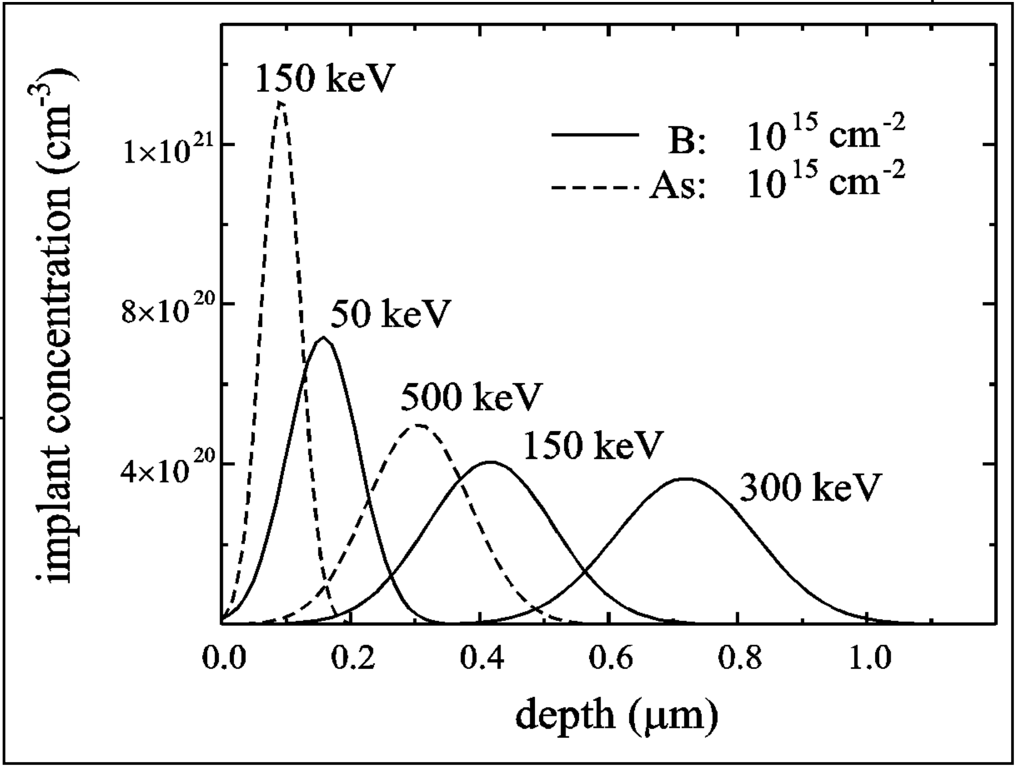
Implantation depth distributions of ions

$$N(x) = \frac{N_0}{\sqrt{2\pi}\Delta R_P} \exp\left[-\frac{(x - R_P)^2}{2\Delta R_P^2} \right]$$

- maximum doping is

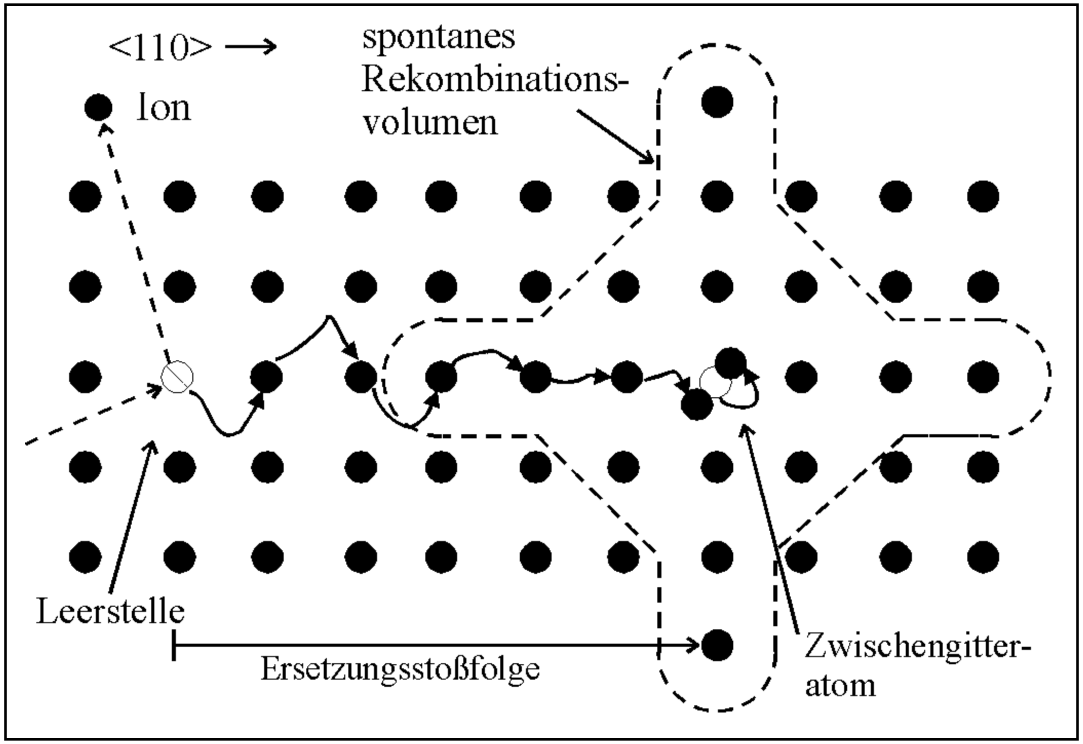
$$N_{max} = \frac{N_0}{\sqrt{2\pi}\Delta R_P}$$

- R_p ... **projected range** of implanted ion
- N_0 ... implanted dose



Implantation-induced defect generation

- when transferred energy > **displacement energy** (10 - 40 eV):
- **Frenkel pairs** are generated as result of a displacement cascade
- vacancy only stable, when it is located outside of recombination volume of interstitial atom (size of this volume is temperature dependent)
- primary ion generates many vacancies, but only a few survive

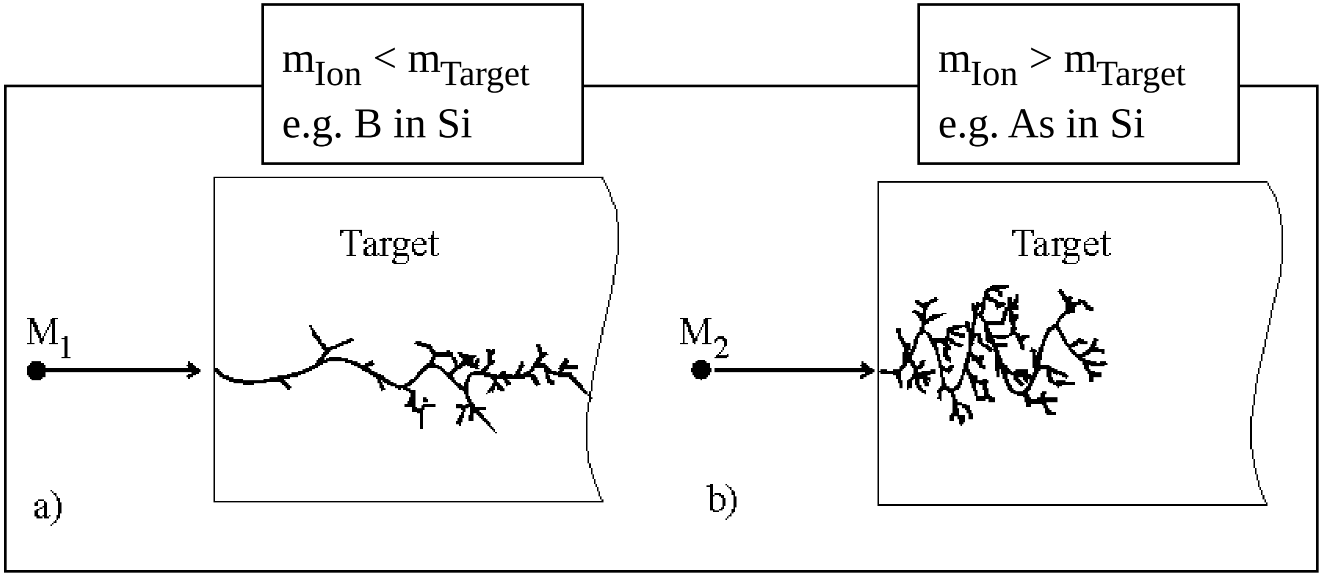


Depth distribution of atomic displacements

- electrons (e.g. 1 MeV) generate in Si just one Frenkel pair (bad energy transfer due to very different masses)

$$T_m = 4\frac{m_1 m_2}{(m_1 + m_2)^2}E$$

- ions transfer much more energy → generation of defect cascades
- sub-cascades appear
- heave ions: deposed energy density is larger, implantation depth smaller
- implantation damage = f (mass ratio Ion/target atom; energy; dose; dose rate; temperature)



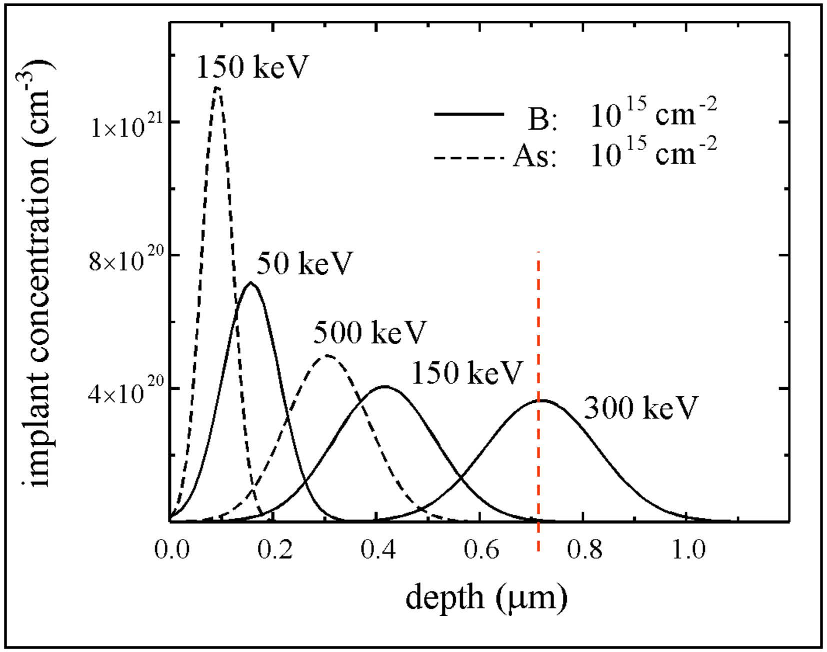
$m_{Ion} < m_{Target}$

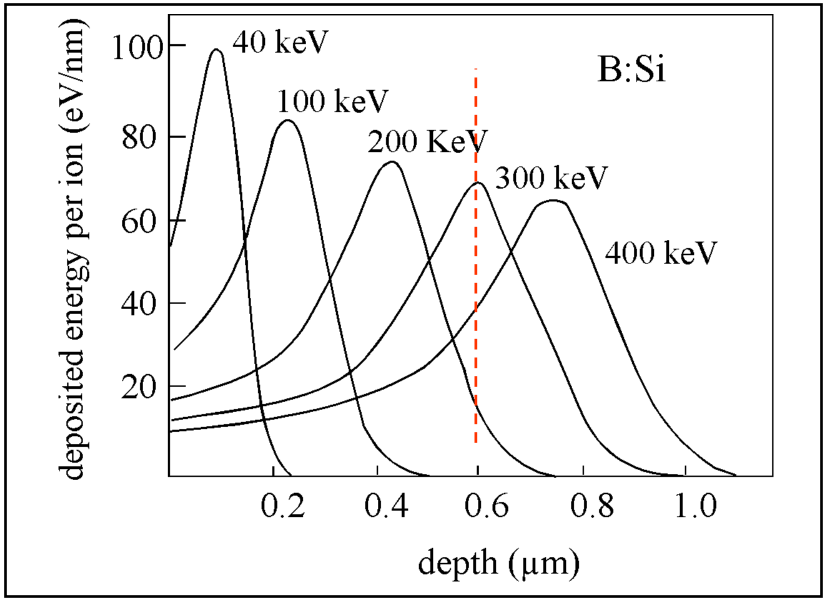
e.g. B in Si

$m_{Ion} > m_{Target}$

e.g. As in Si

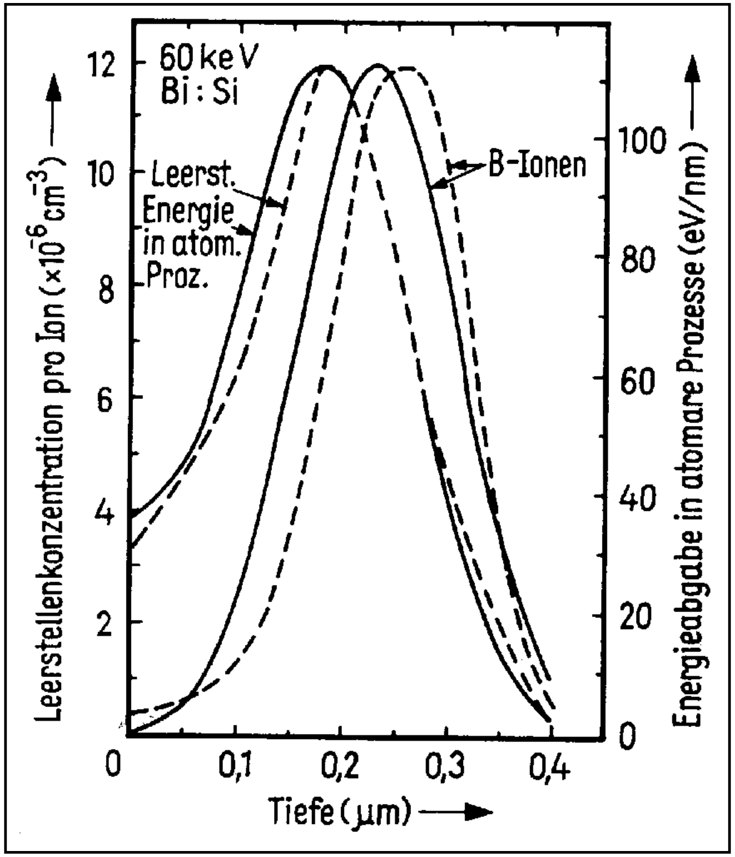
Depth distribution of atomic displacements





- depth distribution of defects can be determined by Monte-Carlo-methods
- TRIM: **TR**ansport of **I**ons in **M**atter (DOS)
- SRIM: **S**topping and **R**ange of **I**ons in **M**atter (Windows)
- does not take into account defect annealing, diffusion, dose rate effects and channeling →
- defect concentration too large, but distribution can sufficiently be calculated
- maximum of defect density before maximum of implanted ions

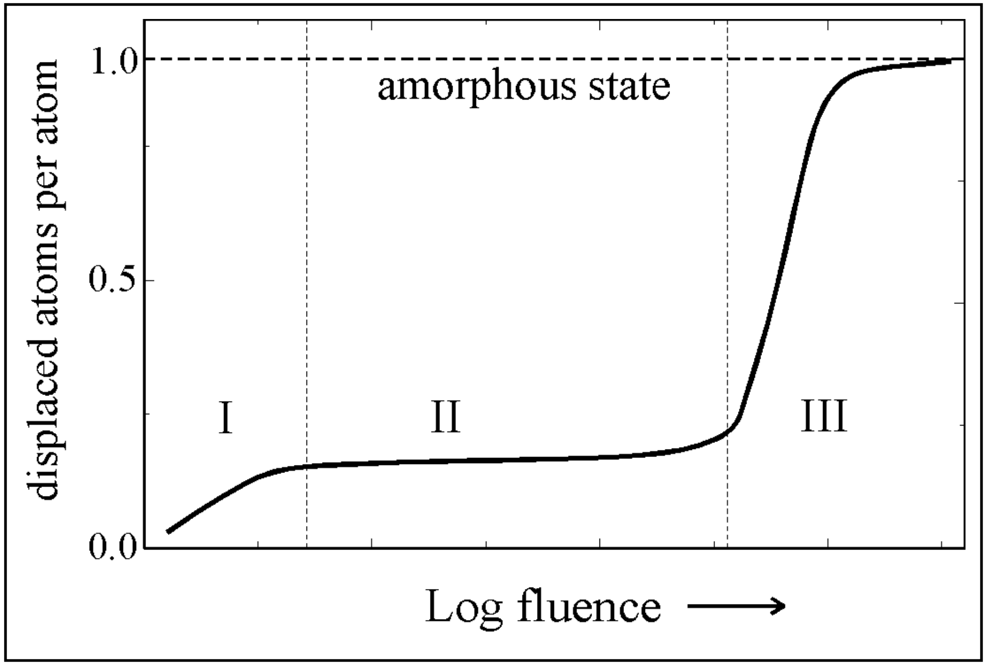
Depth distribution of atomic displacements

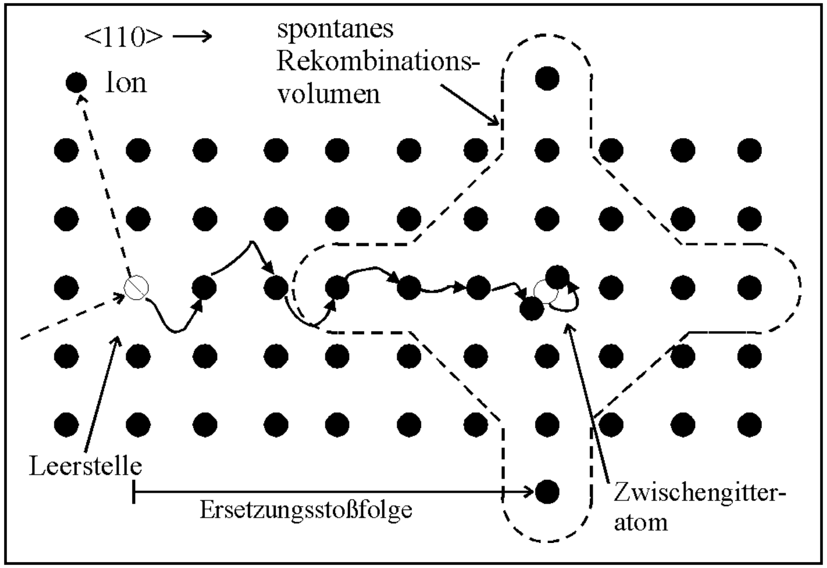


- SRIM is rather rough due to many simplifications
- however, comparison with more sophisticated simulations and experiments shows no strong deviations
- more difficult: simulations for ion implantation in compound semiconductors (e.g. InP)
- there are simulation programs which take into account the defect interaction and the crystal structure (e.g. Crystal-TRIM)

Defect evolution according to Hecking

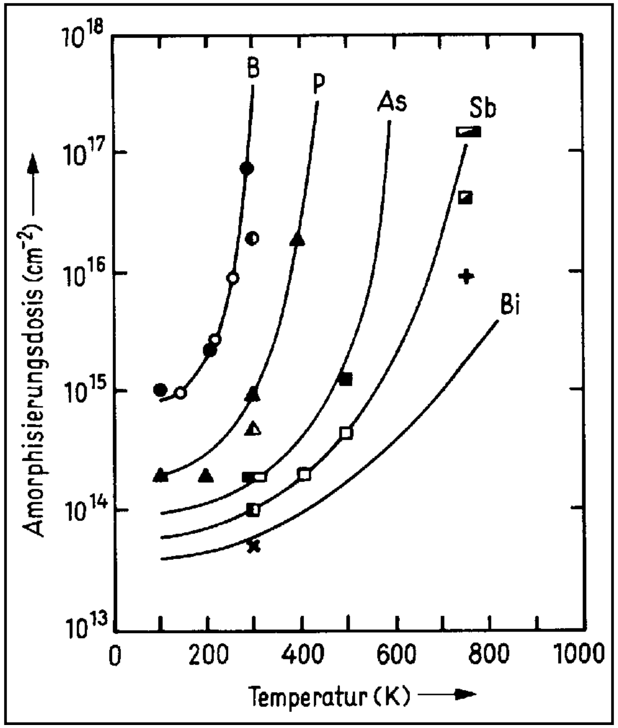
- coexistence of crystalline and amorphous phases; relative fraction changes with implantation dose
- Range I – weak damage: defect density increases continuously
- Range II – medium damage: equilibrium between defect generation and annihilation of defects
- Range III – strong damage: collapse-like amorphization during further accumulation of defects (depend on dose and dose rate!)



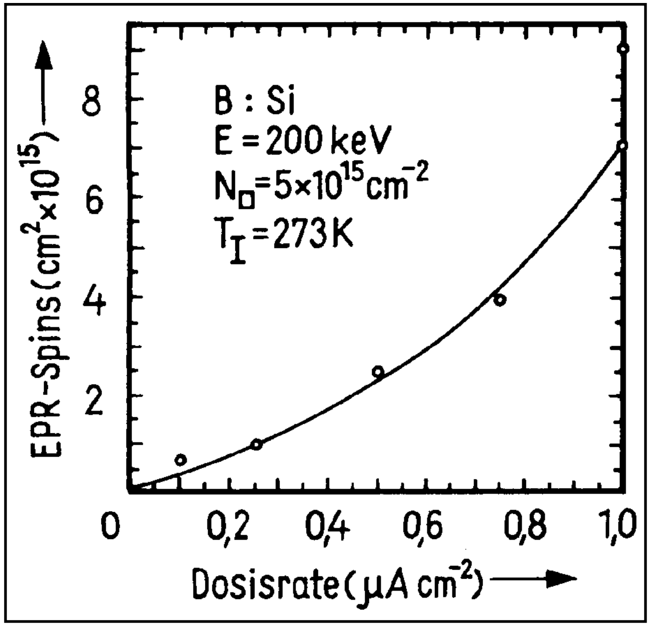


Amorphization dose is function of temperature and dose rate

- most simple assumption for calculation of amorphization dose: all target atoms must be moved ones
- however, real dose is even larger due to defect annealing during implantation
- no amorphization for B implantation in Si for T > 300K due to defect interaction and annealing



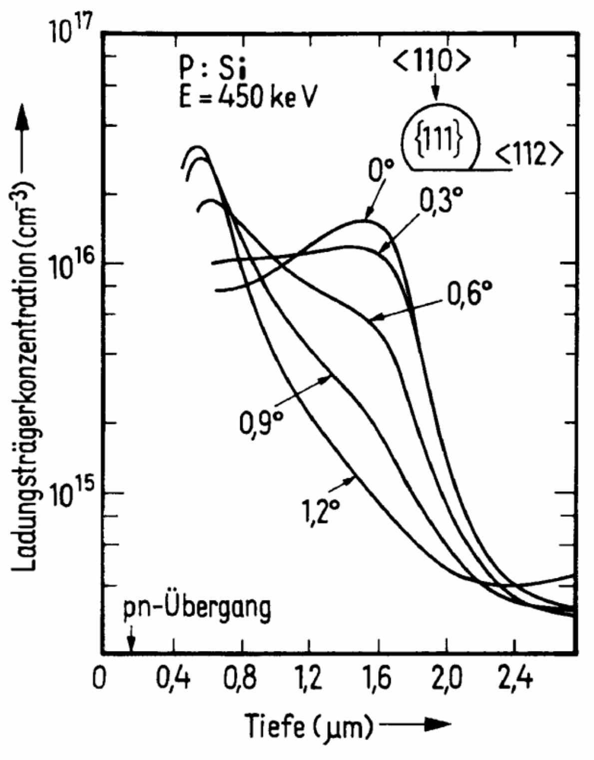
amorphization dose = f (T)



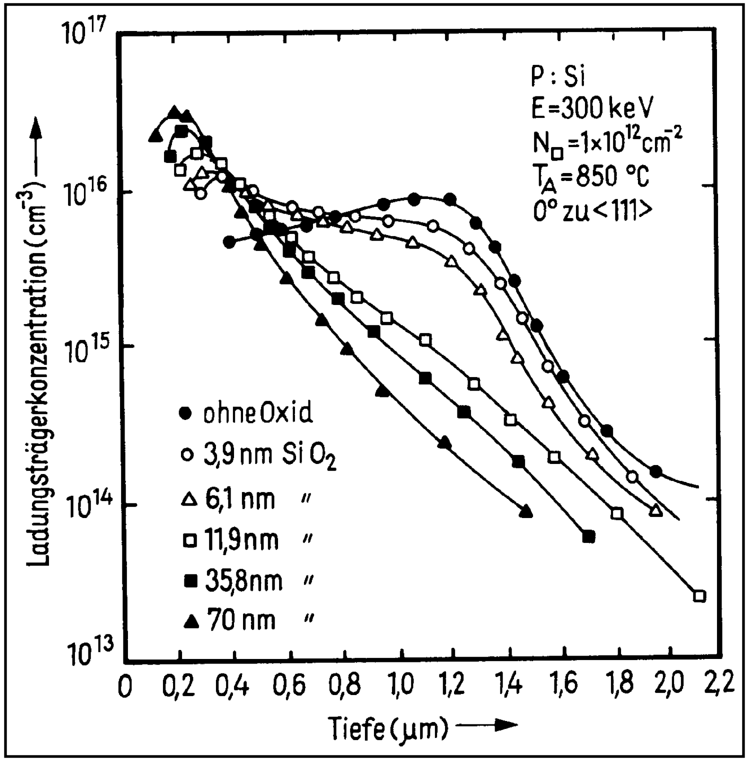
influence of dose rate on defect generation

Channeling effect

- Ions penetrate deep along low-index axis into the crystal → **channeling effect**
- penetration depth can be 10 times larger compared to a „random“ direction
- in case of amorphous oxide cap layer: ions will be scattered, only a few will “find” the channels
- in semiconductor technology: tilt angle 7°... 10° to avoid channeling



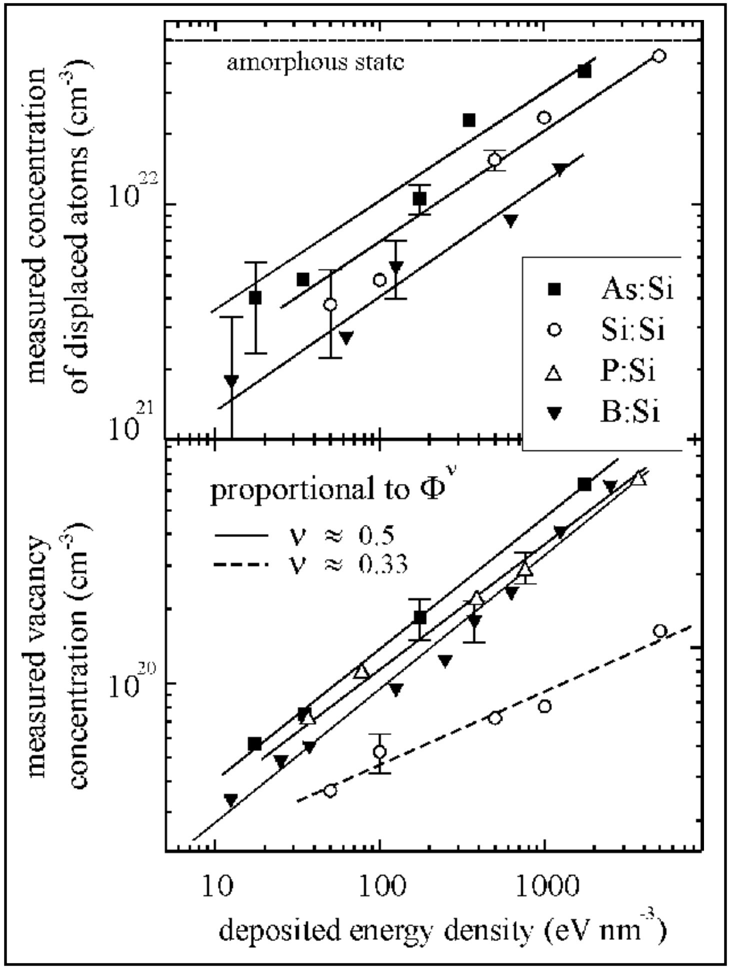
Channeling effect during tilt for a 450keV-P-implantation in Si <111>



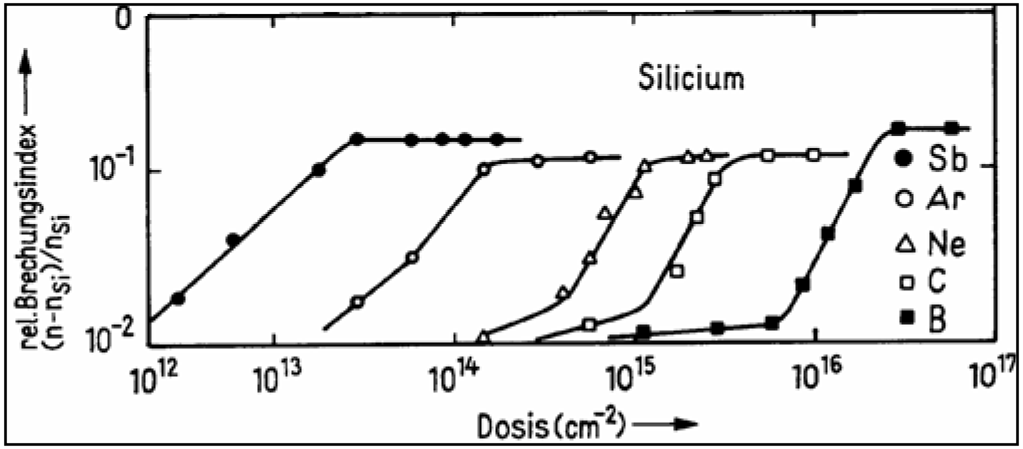
dependence of channeling effect on oxide coverage for 300 keV P ions

Defect generation in Si during weak damage

- defect density is function of dose: [defect] $\propto \Phi^{0.5}$
- exception: Si into Si, because implanted Si-ions are built-in on lattice site immediately: $[Si_V]$ smaller
- e.g. boron ends at interstitial position, needs additional annealing to be B_{Si}



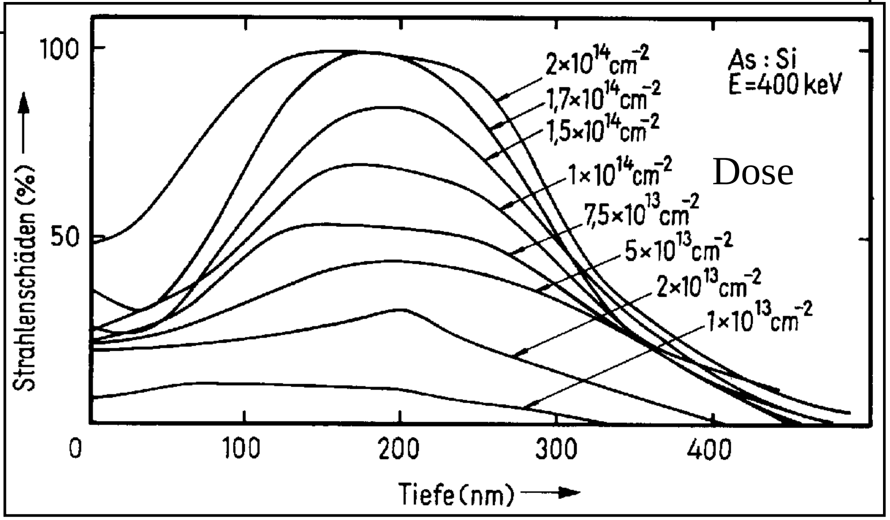
S. Eichler, PhD Thesis, Halle 1998



Si divacancies (optically detected)

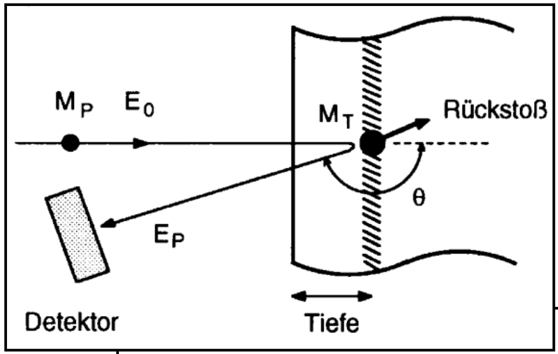
Change of material properties by ion implantation

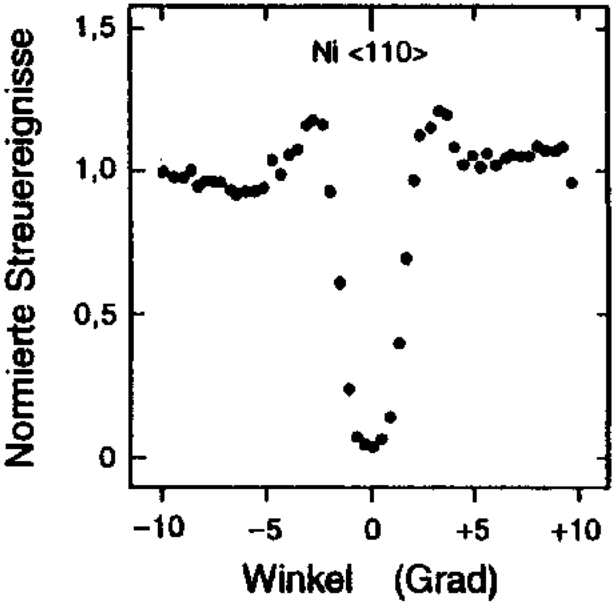
- many material properties change during implantation
- decrease of minority carrier lifetime: 10^{12} cm^{-2} B in Si → $\tau = 10^{-9}$ s
- free charge carriers are compensated; $\rho = 10^{6} \ldots 10^{9}$ Ωcm obtainable
- carrier mobility decreases too; may become smaller than 1 cm^2/Vs (normal $>10^3$)
- optical transmission becomes smaller by additional energy levels in the band gap
- refraction index (*Brechungsindex*) changes (thus also reflection index): light propagates in an inner layer (integrated light pipe)
- SIMOX: hidden SiO_2 isolation layer can be done by oxygen implantation and annealing
- for high doses: density- and volume change
- change of elastic and plastic properties (embrittlement of reaction pressure vessel steel in nuclear power plants)

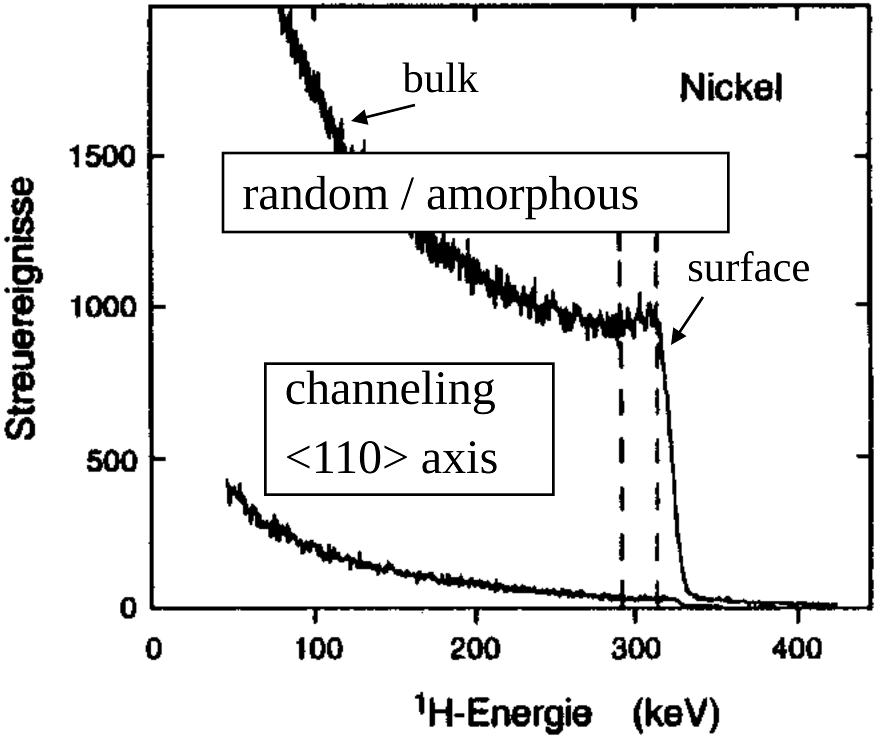


Detection of defect density by observation of reflection coefficient; depth information obtained by layer-by-layer removal

Defect detection by RBS (Rutherford Backscattering)







bulk

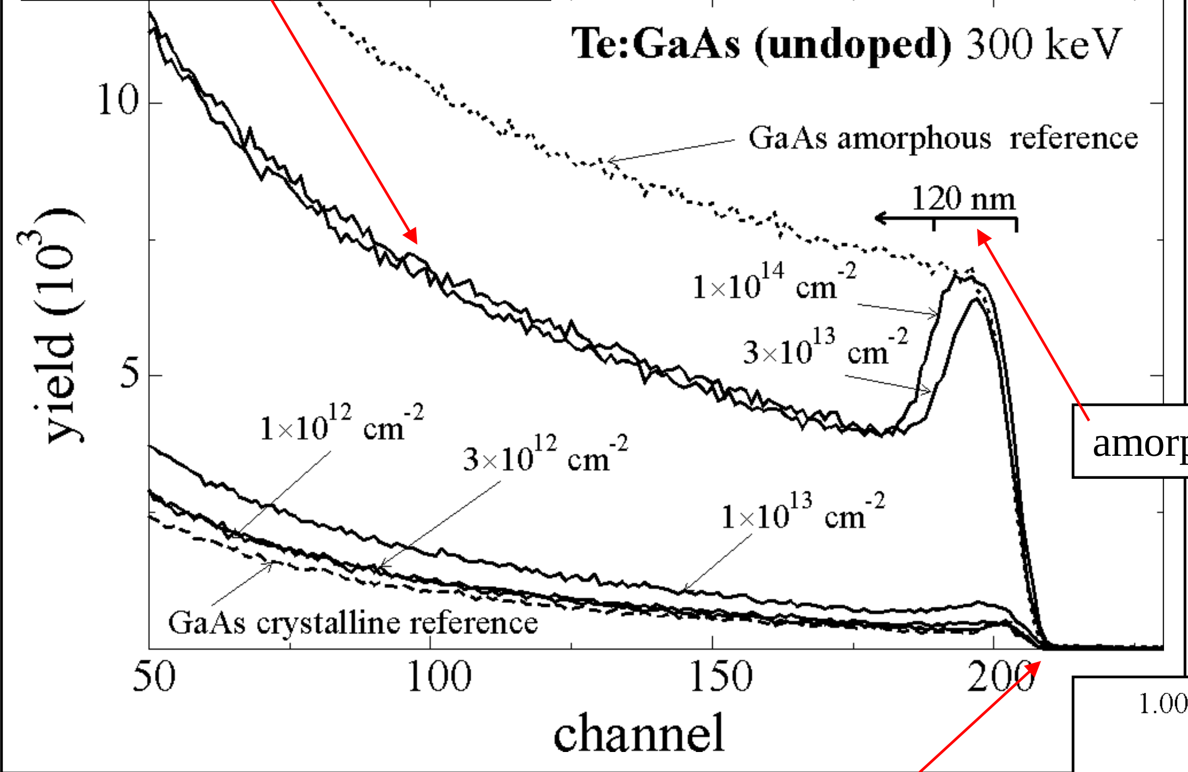
random / amorphous

surface

channeling

<110> axis

Defects after ion implantation

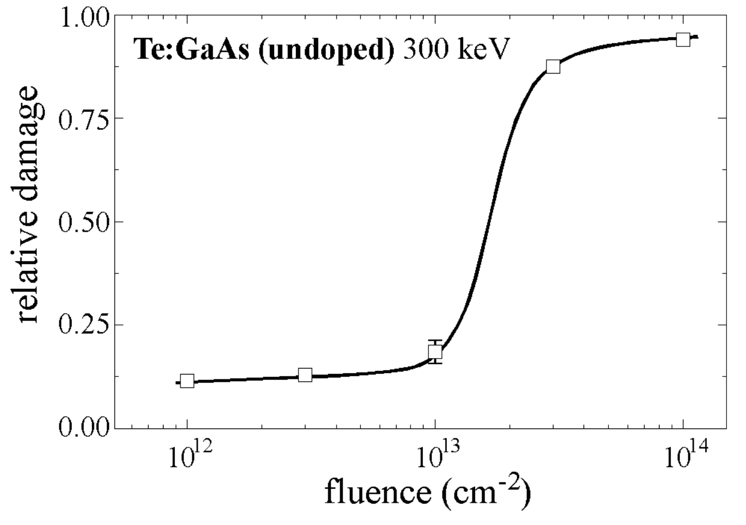


crystalline bulk of sample

amorphous layer near surface

Amorphization by ion implantation and subsequent defect annealing can easily be studied by RBS

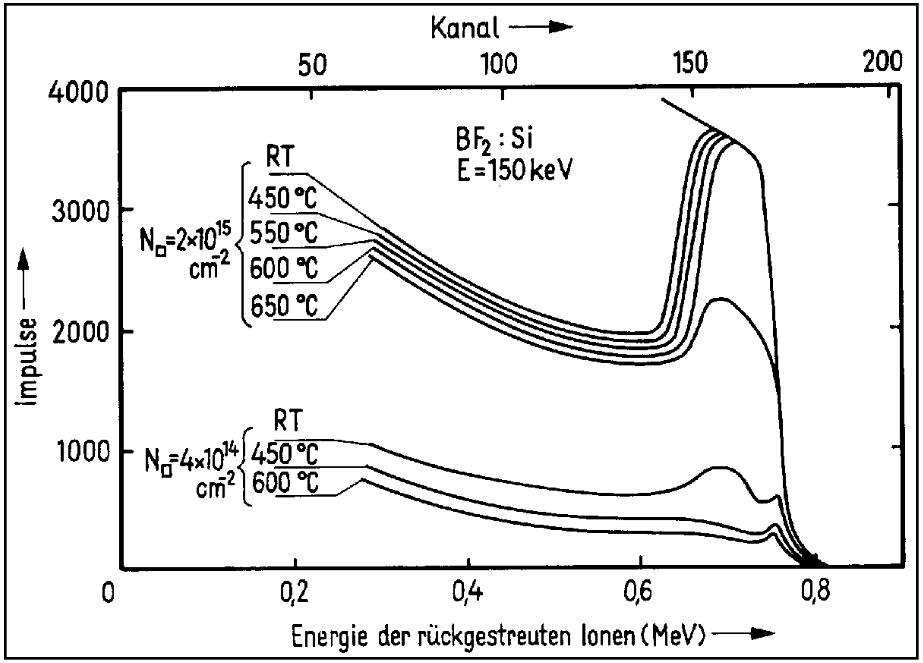
- elastic scattering from surface provides maximum energy of observed ions
- is not equal to maximum energy of probe ion (often H^+ or He^+) due to collision law

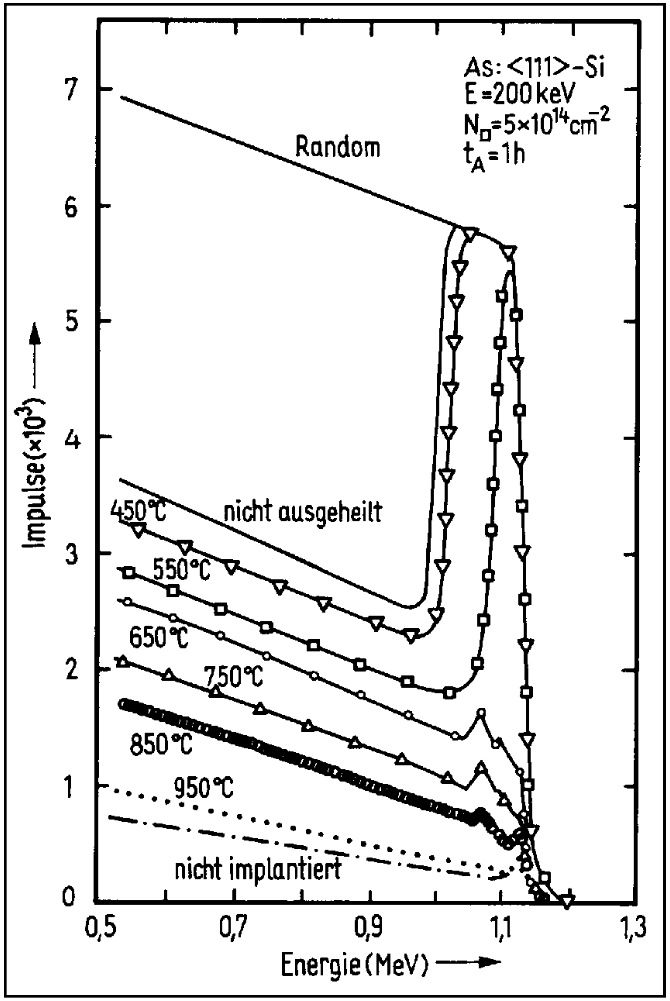


Annealing of implantation defects

- implantation-induced defects must be annealed; for Si at 900° to 1000°C (often by infrared light as „rapid thermal annealing“ - RTA)

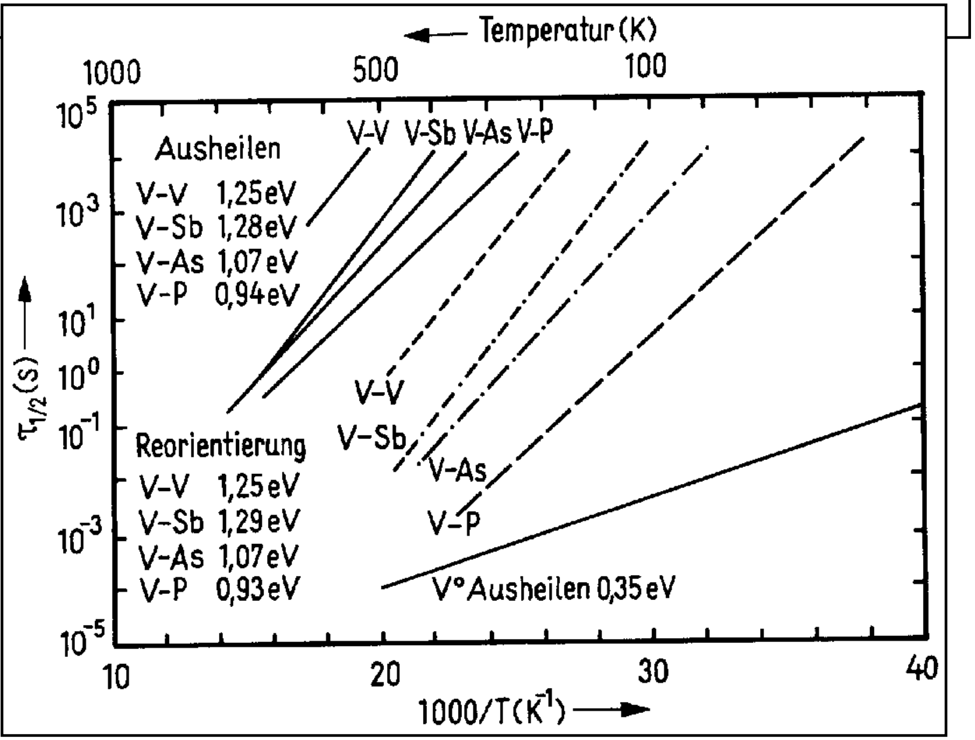
- amorphous layers may have very good crystalline properties after annealing treatment
- high defect density can easily be measured by Rutherford-backscattering during annealing treatment





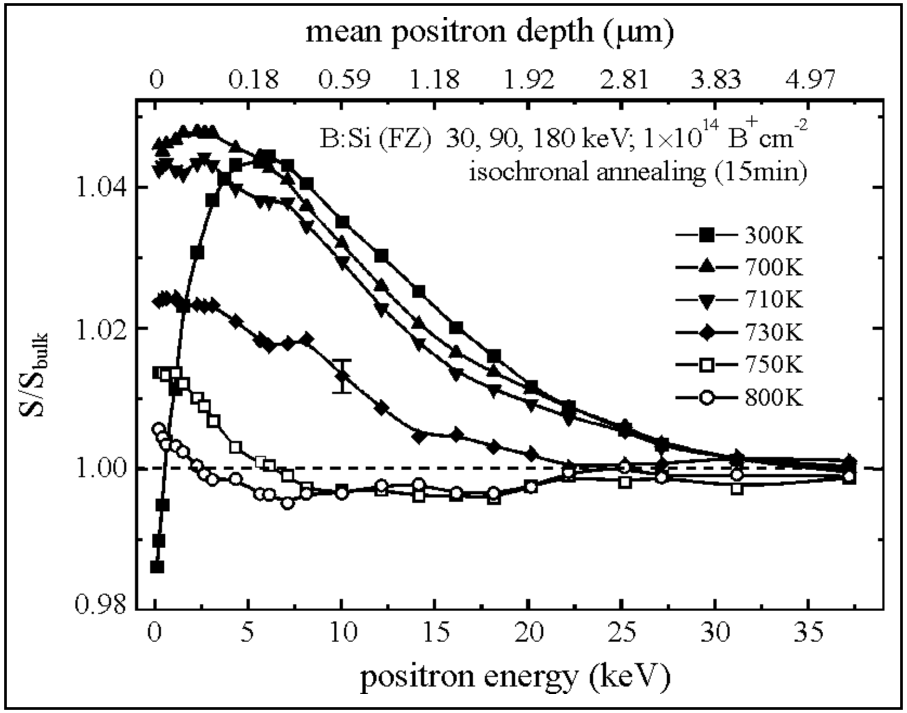
Annealing of implantation defects in Si

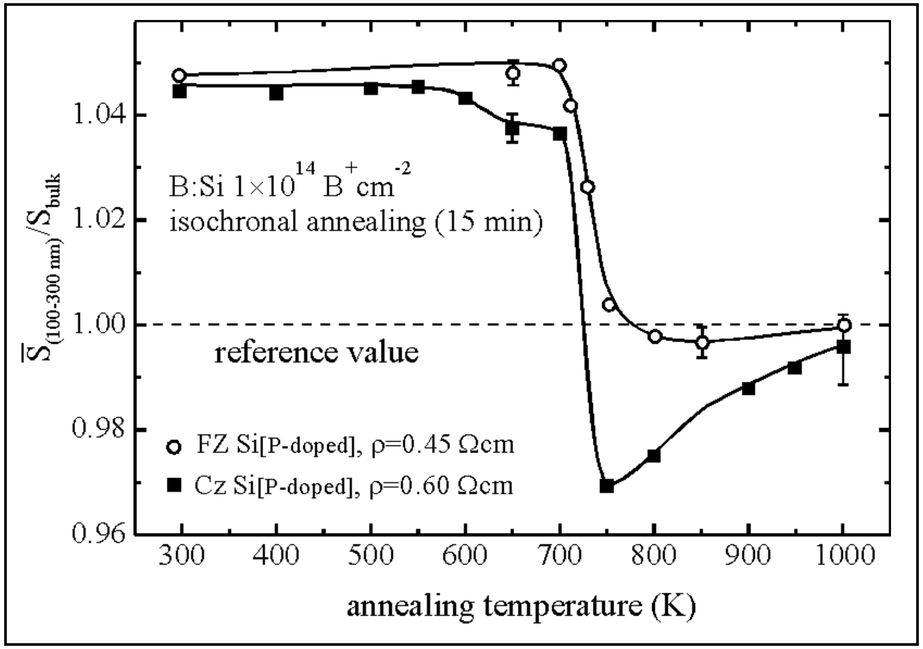
below RT:	monovacancies and interstitials
200 - 300 K:	clustering of vacancies (formation of divacancies); formation of dislocation rings
400 - 500 K:	E-center annealing (dopant atom-vacancy-complex) of group V atoms
around 500 K:	E-centers of group III atoms
around 550 K:	divacancies
600 - 1000 K:	epitaxial recrystallization of amorphous layers (from crystalline side)
>1200 K:	dislocation loops
1683 K:	melting point



Annealing of implantation defects in Si

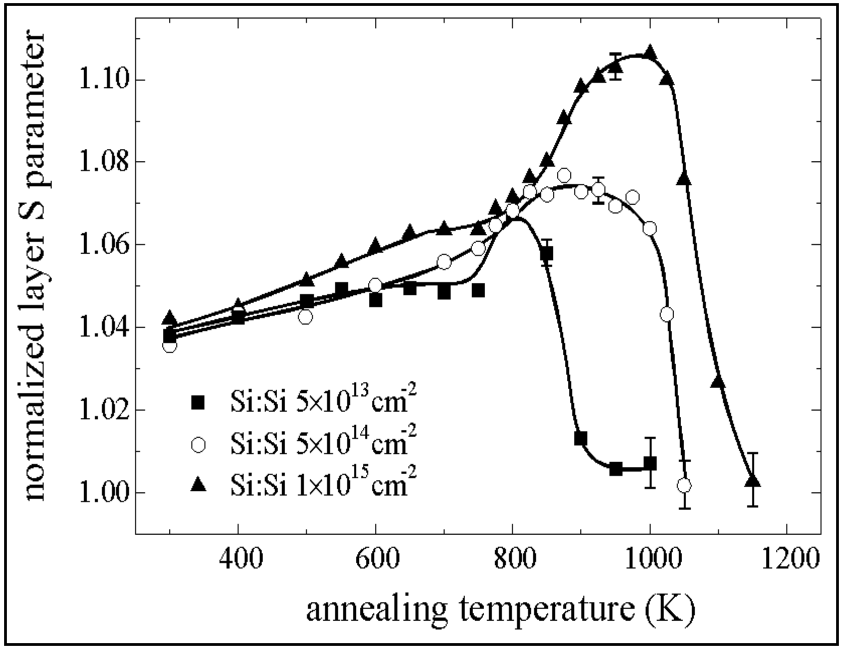
- Positron Annihilation is very sensitive for detection of open-volume defects
- main annealing stage at 750 K (vacancies, divacancies and E-centers are annealed before)
- different annealing behavior for Cz-Si (contains up to 10^{18} cm^{-3} oxygen)
- obviously oxygen is part of defect complex in Cz-Si

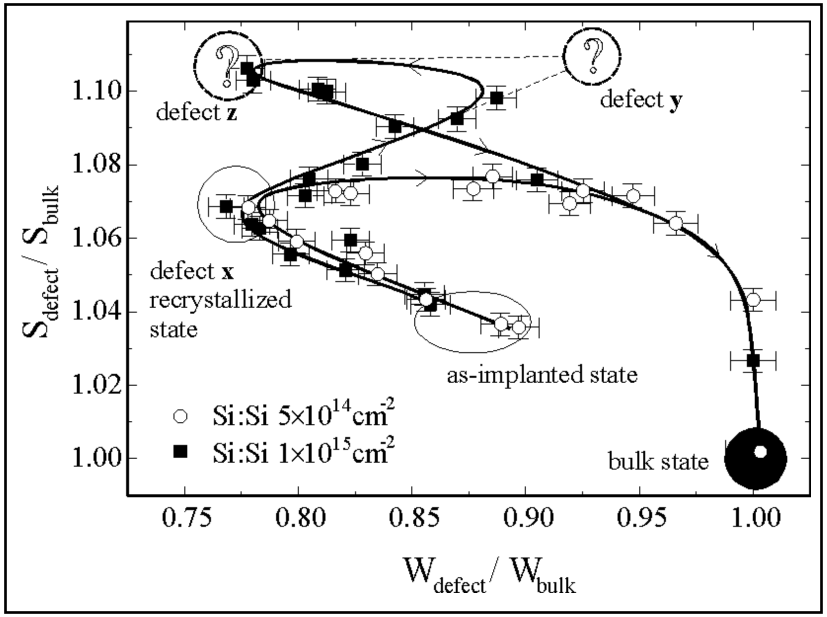




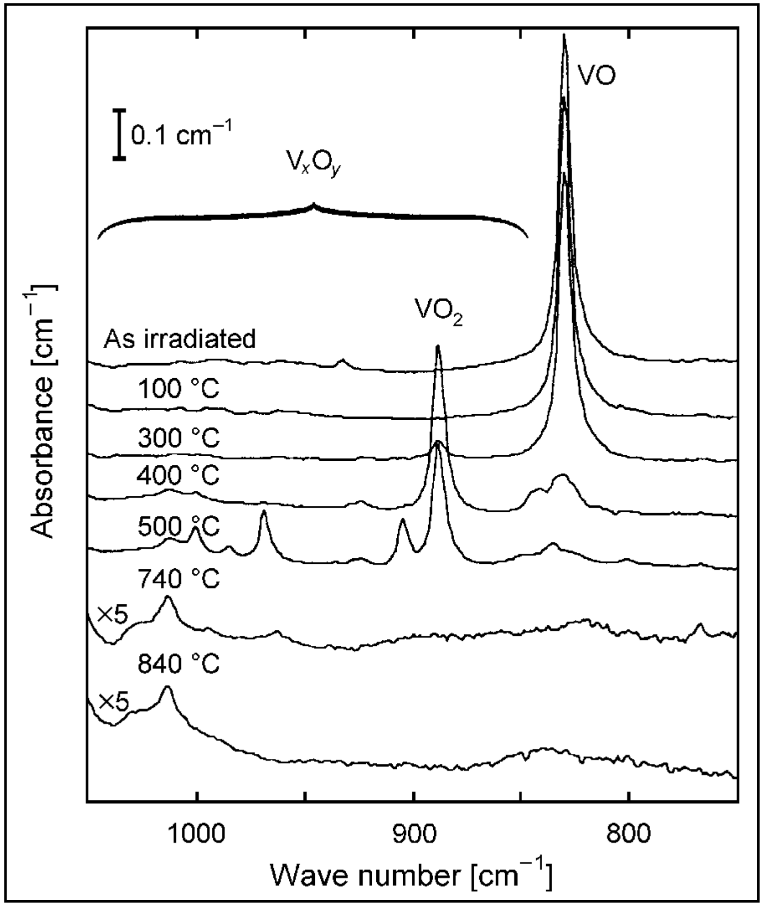
Defect reactions during annealing

- during annealing: defect reactions take place
- so-called “S-W-Plot” of positron annihilation shows a sequence of different open-volume defects
- behavior in Cz-Si rather complicated: defect complexes are formed and dissolved during heating





Oxygen-vacancy-complexes in Cz-Si



- Infrared absorption of electron irradiated Cz-Si during annealing (Ikari, 1995)
- VO = so-called A-center anneals at RT
- many different V_xO_y complexes are formed in a sequence

Defect reaction during annealing

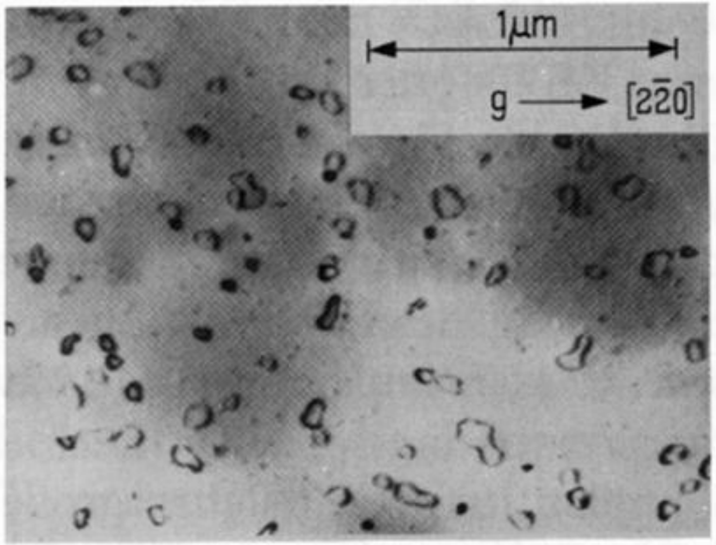
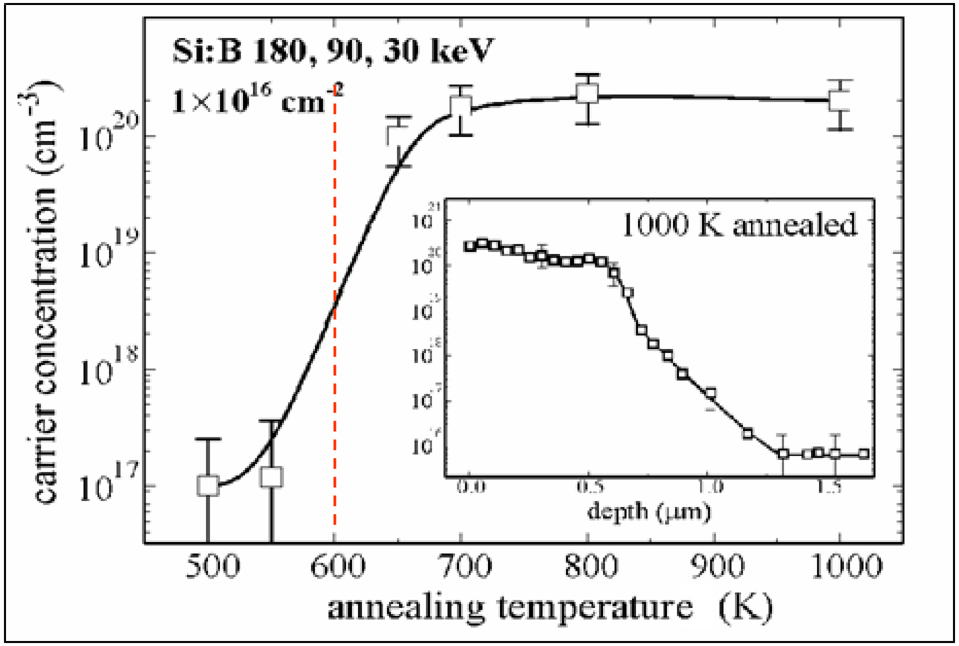
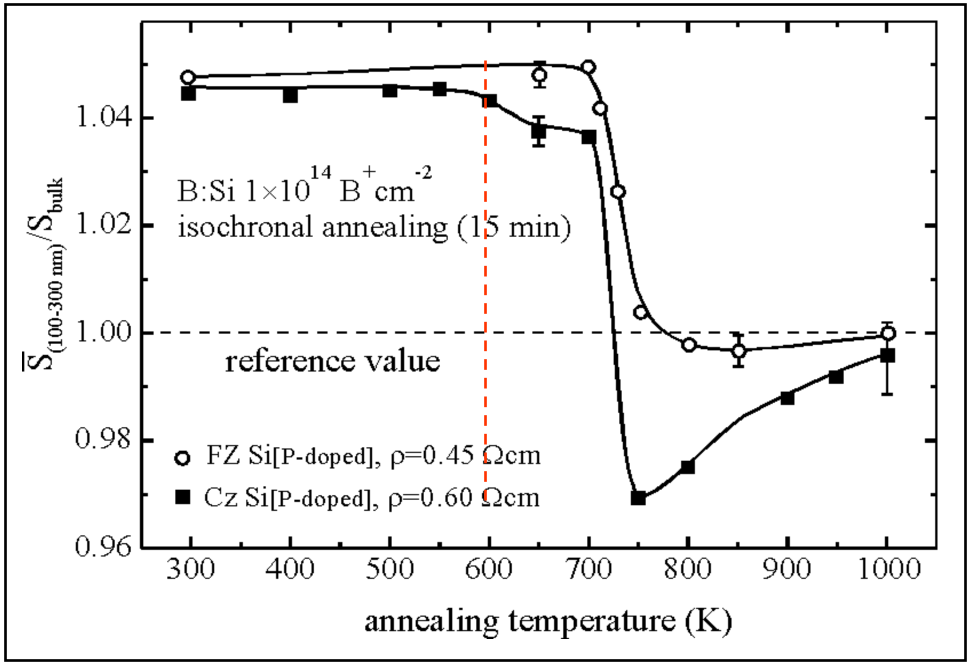


Fig. 6.19 Interstitielle Versetzungsschleifen in Silicium, das mit 2×10^{16} cm^{-2} Arsen bei 40 keV durch 10 nm SiO_2 implantiert und bei 970°C für 30 min ausgeheilt wurde [456]

- Implantation leads first to supersaturation (*Übersättigung*) of atoms on interstitial positions
- simple reaction to diminish the distortion energy: formation of dislocation loops during annealing
- annealing at 800°C: diameter ca. 20nm, density 300 ... 650 μm^{-2}
- further annealing leads to larger dislocation structures

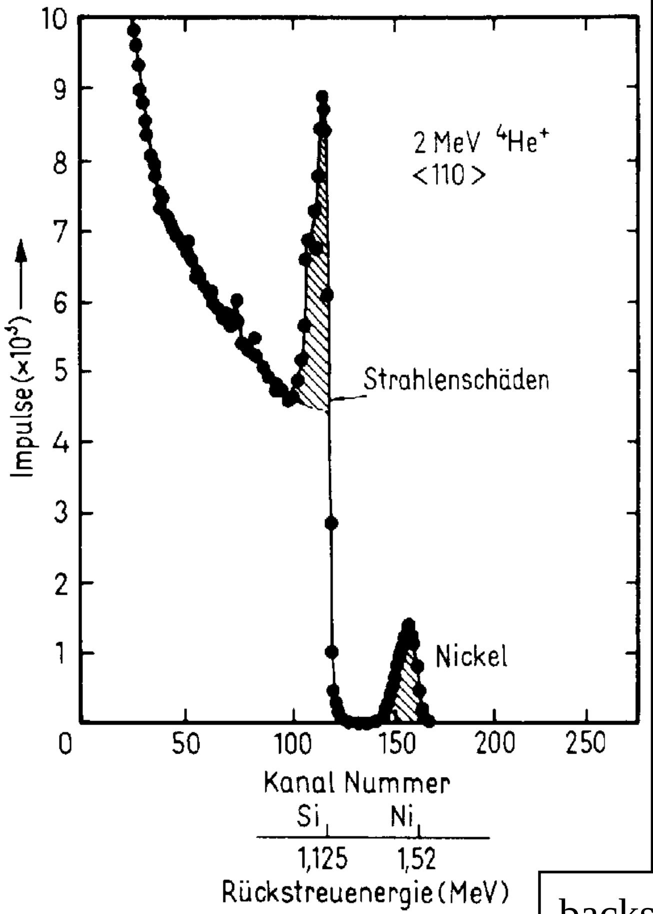
Electrical activation of carriers





- implanted dopant atoms are not electrically active after implantation, e.g. B is not immediately active as an acceptor
- reason: dopant atoms are first on interstitial positions
- there they do not act as shallow dopant
- moreover: occupation of defect levels in band gap lead to compensation of carriers
- to reduce both effects: annealing
- activation of carriers for B:Si at about 600 K, is temperature of divacancy annealing

Gettering of impurities

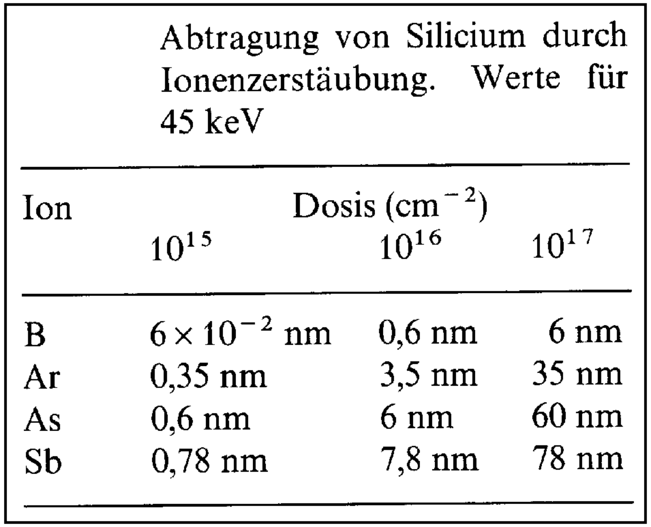


- most important ways of gettering:
  - capture by lattice defects
  - decrease of diffusivity by forming chemical bounds
- irradiated Si layer getters rather good
- Example: 10^{16} cm^{-2} 100 keV-Si-Ionen in Si
- getter experiments show that Cu und Ni getters easily, but Fe, Co und Au only slowly
- Differences due to solubility and diffusion
- result: Ar-radiation damage getters better than P-implantation at T<1000°C

backscattering spectra (2 MeV He-Ions); radiation damage from front side, and Ni in-diffusion from back side

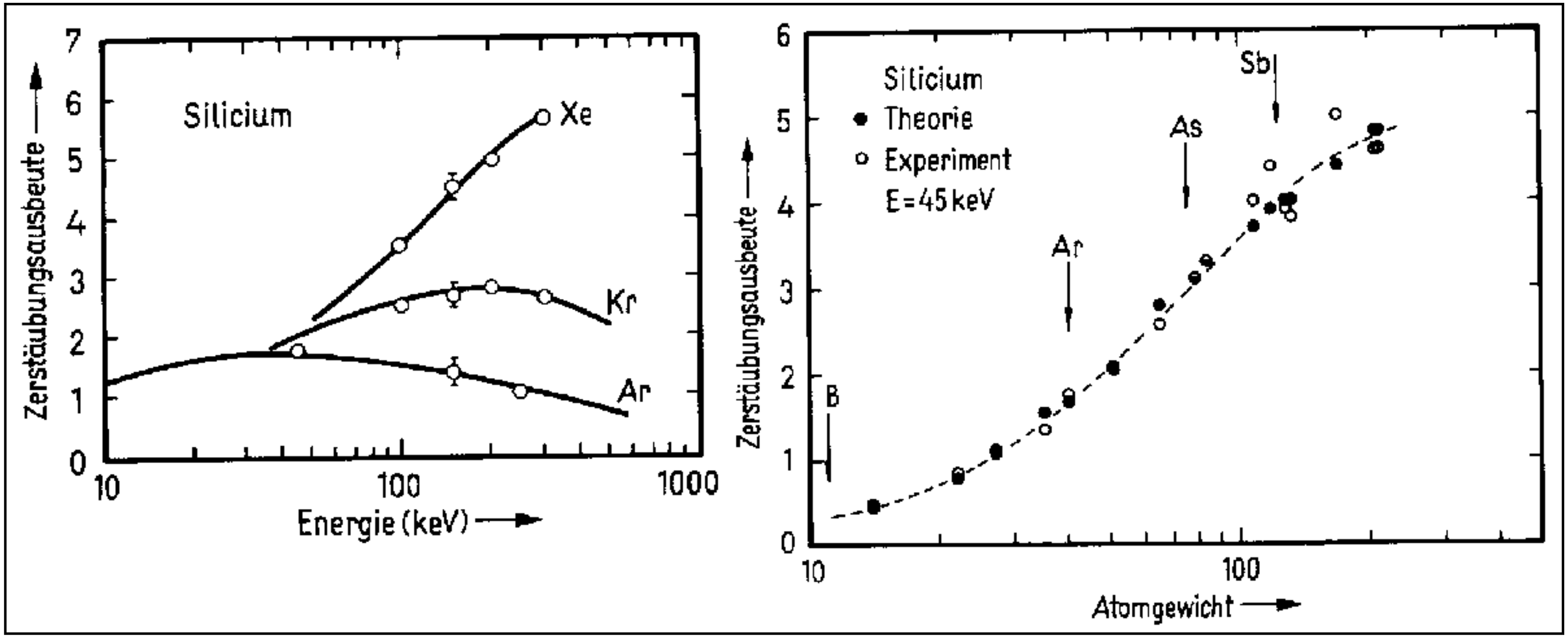
Problem: sputtering of material by ion implantation

- ions are also used to remove surface layers: sputtering (cleaning; depth profiles for chemical analysis with SIMS or AES)
- mostly no direct process
- energy deposited under surface leads to emission of atoms from surface



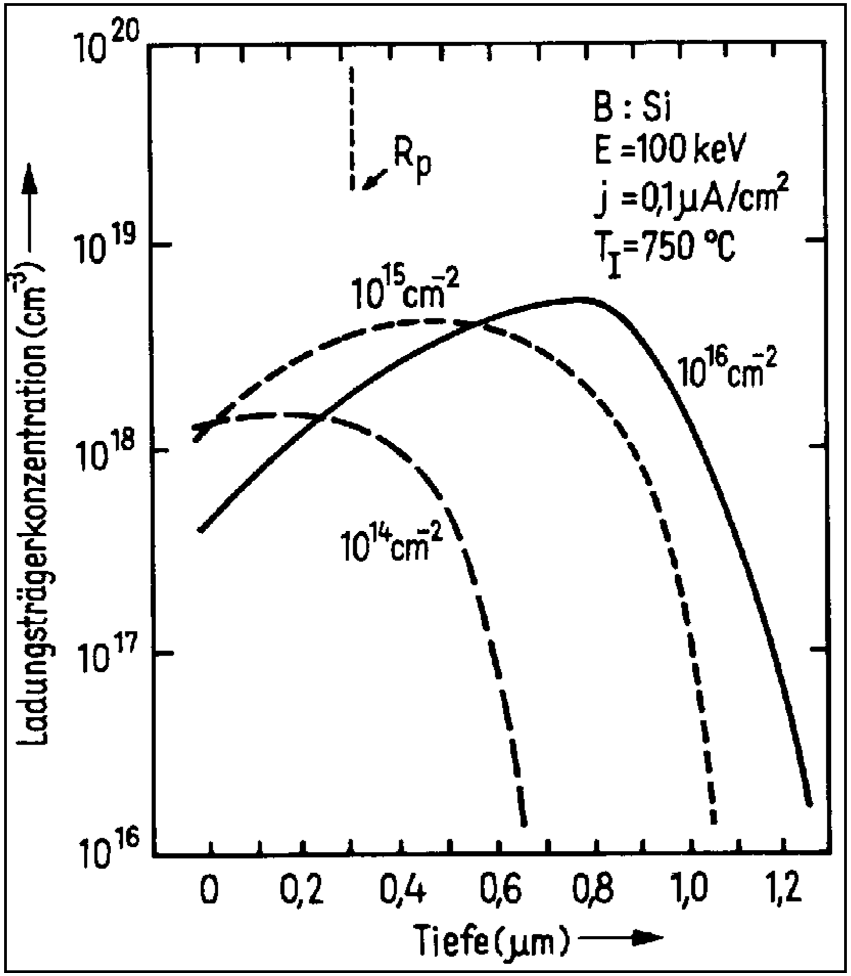
Abtragung von Silicium durch Ionenzerstäubung. Werte für 45 keV

Ion	Dosis (cm^{-2}) 10^{15}	10^{16}	10^{17}
B	6×10^{-2} nm	0,6 nm	6 nm
Ar	0,35 nm	3,5 nm	35 nm
As	0,6 nm	6 nm	60 nm
Sb	0,78 nm	7,8 nm	78 nm



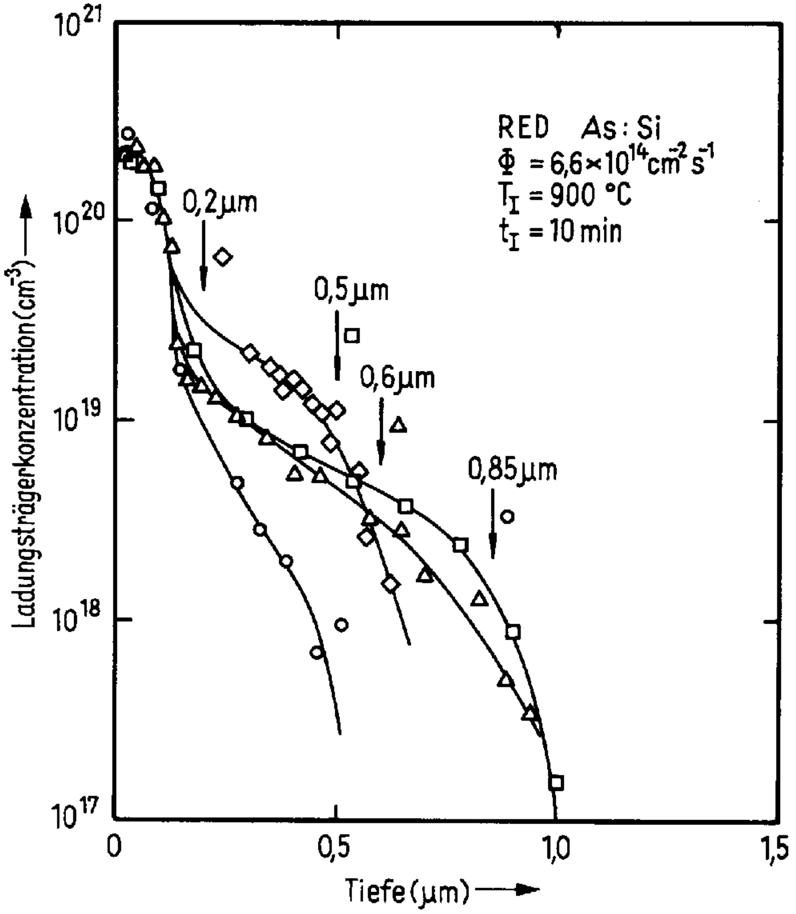
Problem: diffusion during annealing

- dopant atoms may diffuse during annealing of implantation-induced defects
- also during activation and defect annealing
- diffusivity is increased due to radiation damage



- R_P is expected depth of implantation
- defect-enhanced diffusion during 750°C-annealing

Problem: diffusion during annealing



Strahlungsbeschleunigte Diffusion von Arsen in Silicium durch Protonenbeschuß bei 900 °C für 10 min abhängig vom Ort der Leerstellengeneration, der durch einen Pfeil gekennzeichnet ist

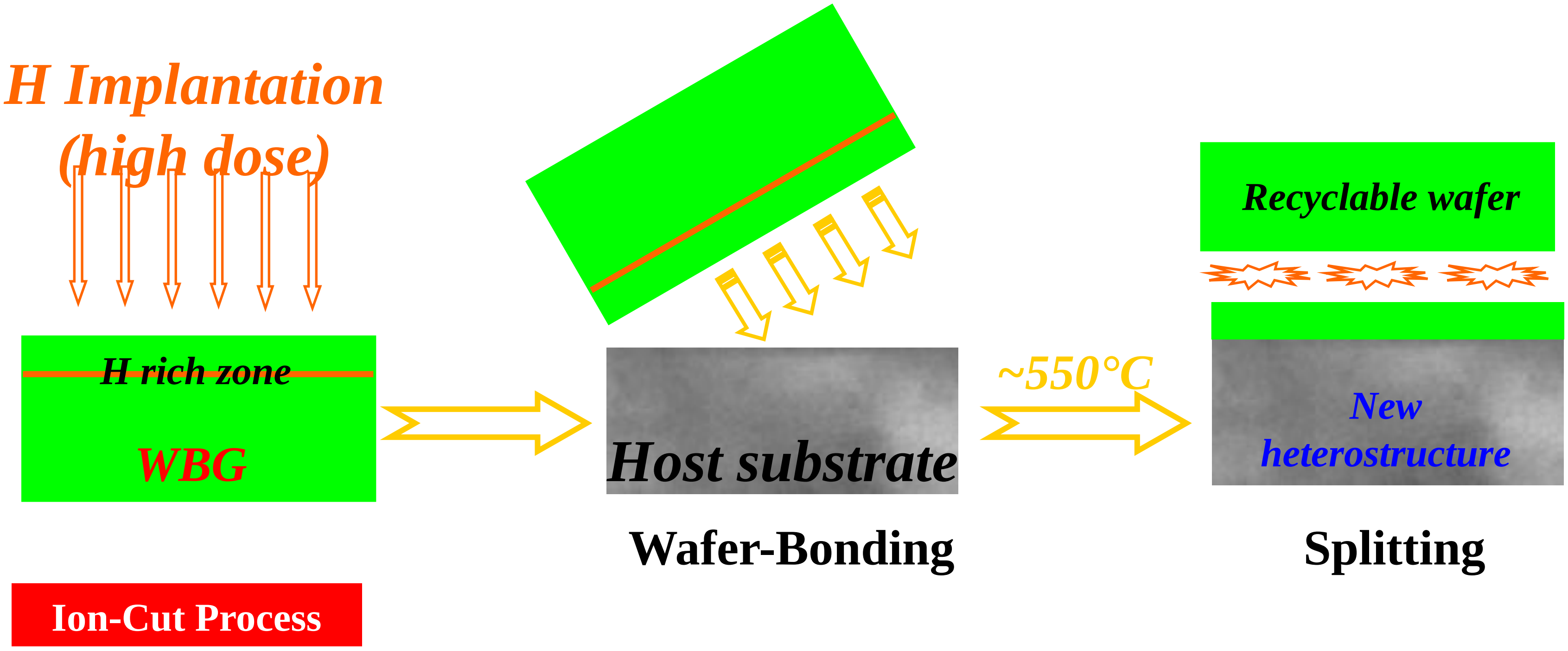
- proton irradiation provides sharp defect peak (depth is controlled by energy)
- shows clearly defect-induced diffusion
- experiment: diffusion in As:Si
- As is found in large depth, when proton irradiation creates defects in such a depth
- when defect depth is too large: effect disappears

Literature about ion implantation:

- Ryssel/Ruge: „Ionenimplantation“, Teubner 1978
- H. Ryssel, H. Glawischnig „Ion Implantation Techniques“, Springer, Heidelberg 1982; ISBN: 3540118780

Application: Ion-cutting and wafer bonding of GaN-Wafers

- proton irradiation creates defect-rich zone
- thin layers of GaN can be put on any substrate
- one wafer can be used to produce many layers



H Implantation (high dose)

H rich zone

WBG

Host substrate

~550°C

Recyclable wafer

New heterostructure

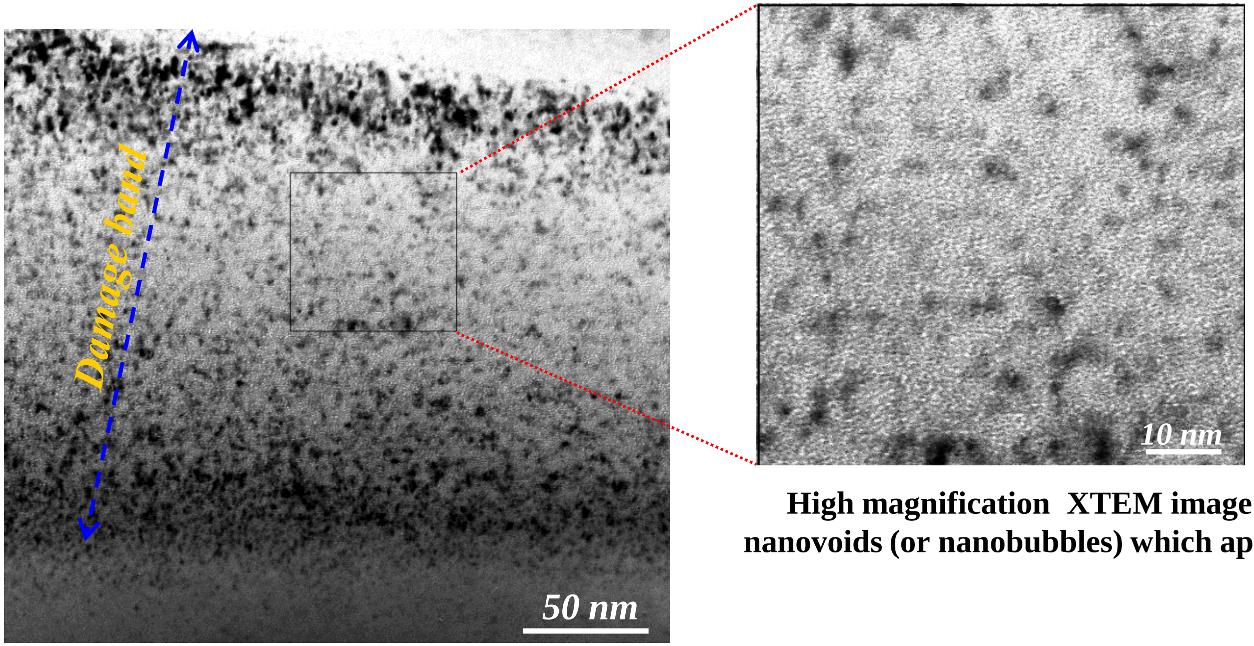
Wafer-Bonding

Splitting

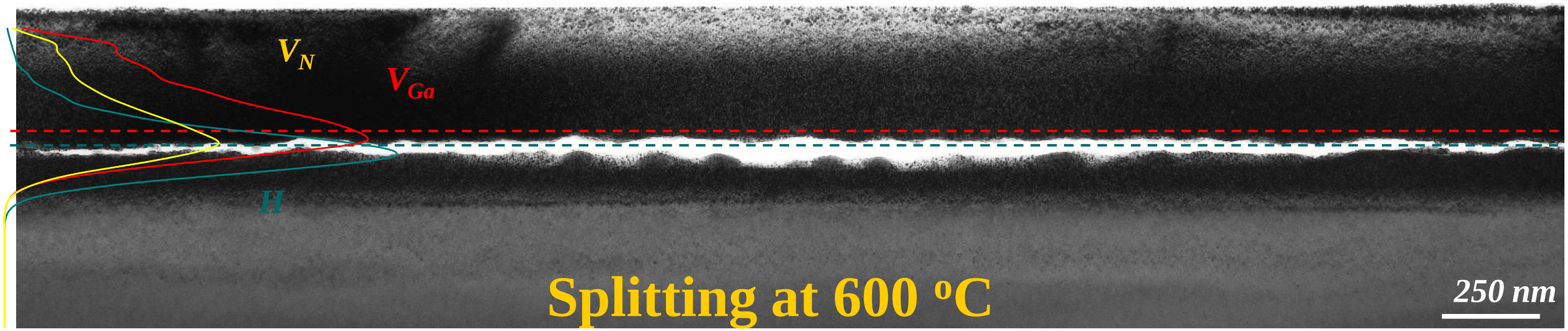
Ion-Cut Process

(current research of MPI Halle 2007: Dr. O. Moutanabbir)

As-implanted GaN:
2.6 10^{17} H^{+}/cm^{2} at
50 keV



High magnification XTEM image showing nanovoids (or nanobubbles) which appear bright.



Splitting at 600 °C