Defect Characterization in Crystalline Solids

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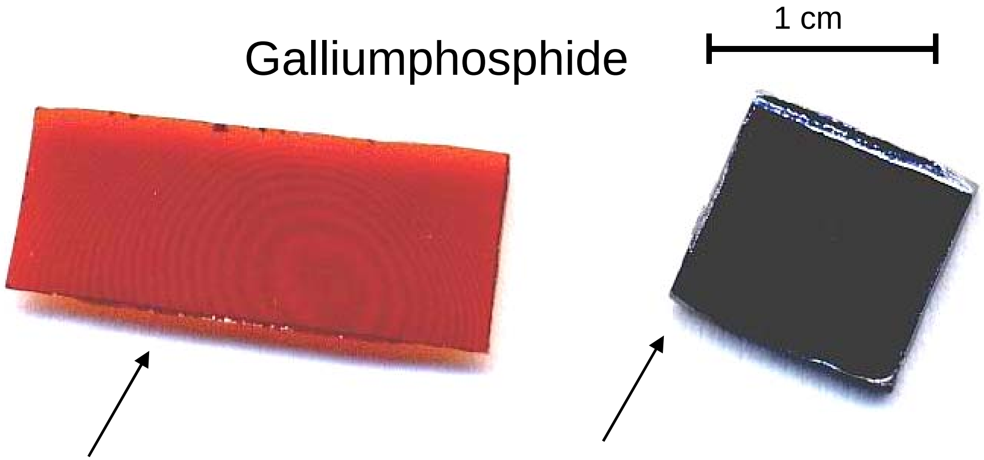
- Why are nano-defects important at all?
- Defects in metals and semiconductors
- Positron beam applications

Point defects determine properties of materials



without vacancies
transparent

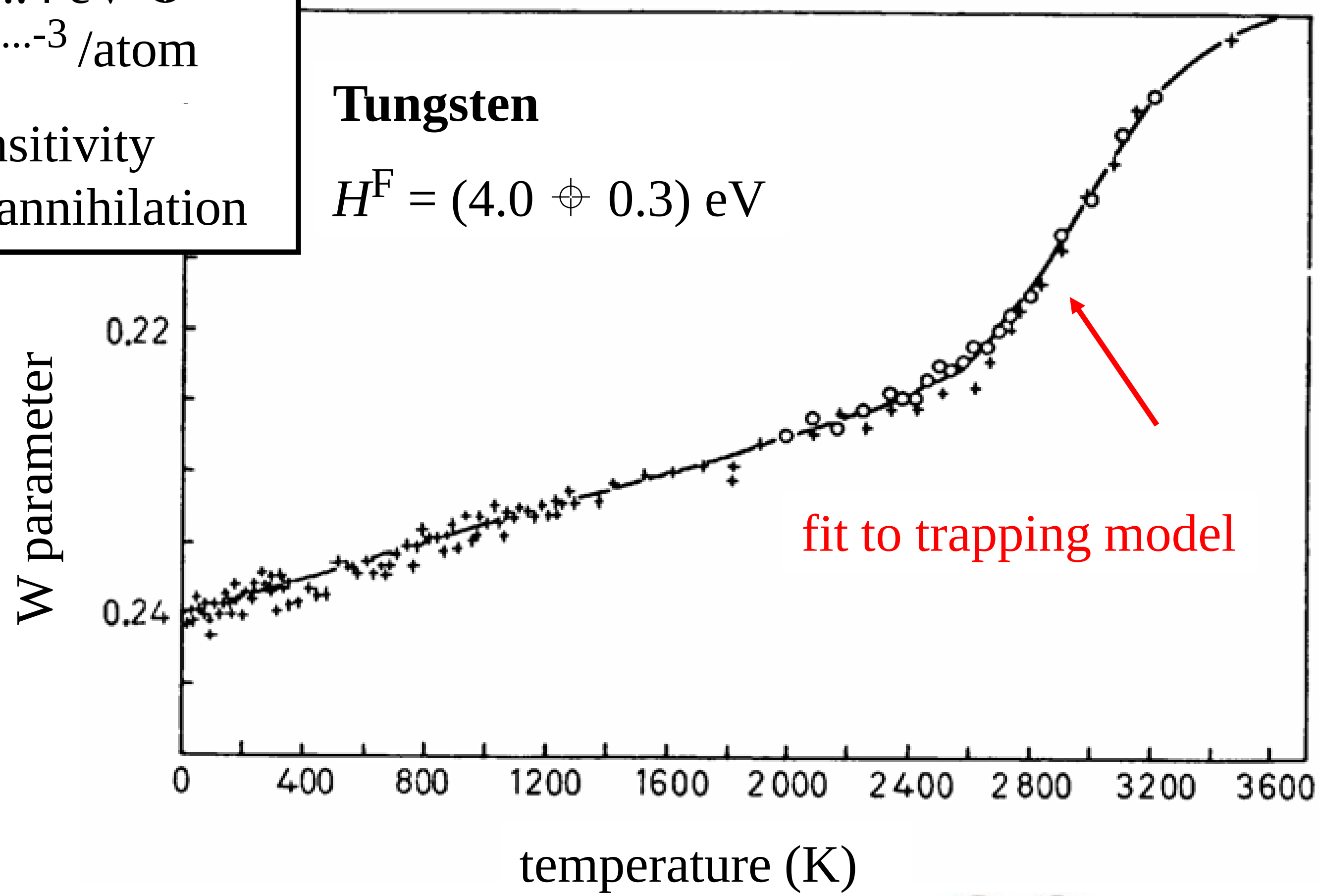
with 0.001% vacancies
opaque
1 vacancy in 100000 atoms

- Point defects determine electronic and optical properties
- electric conductivity strongly influenced
- Point defects are generated by irradiation, by plastic deformation or by diffusion, …
- Metals in high radiation environment -> formation of voids -> embrittlement
- -> Properties of vacancies and other point defects must be known
- Analytical tools are needed to characterize point defects

Vacancies in thermal Equilibrium

- Vacancy concentration in thermal equilibrium:
- in metals $H^F \approx$ 1...4 eV $\Rightarrow$ at T_m [1v] $\approx 10^{-4...-3}$ /atom
- fits well to the sensitivity range of positron annihilation

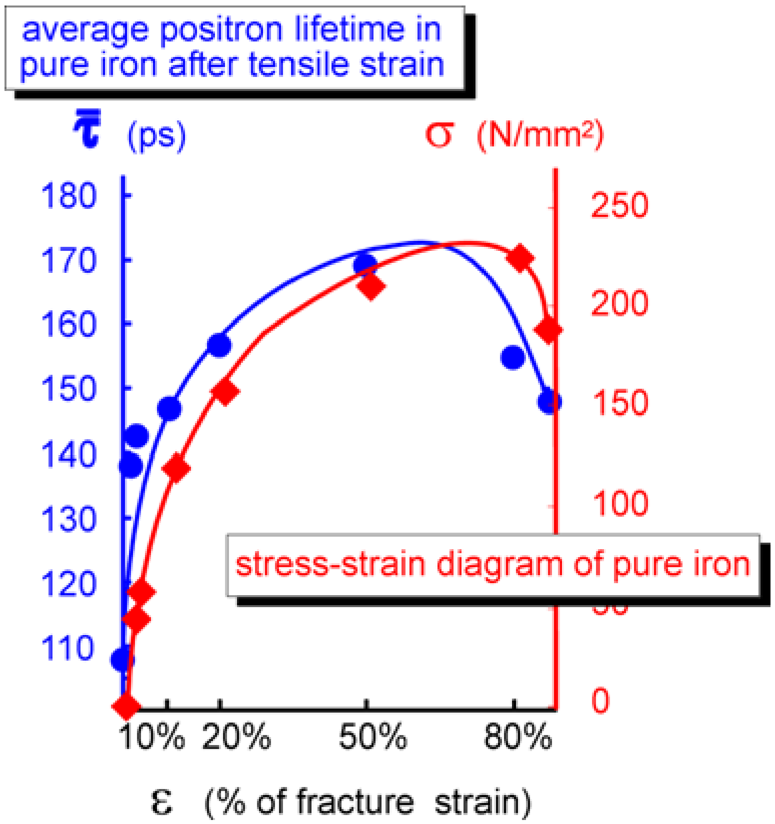
$$C_{1v}(T) = \exp\left(\frac{S_{1v}^F}{k}\right)\exp\left(\frac{H_{1v}^F}{kT}\right)$$

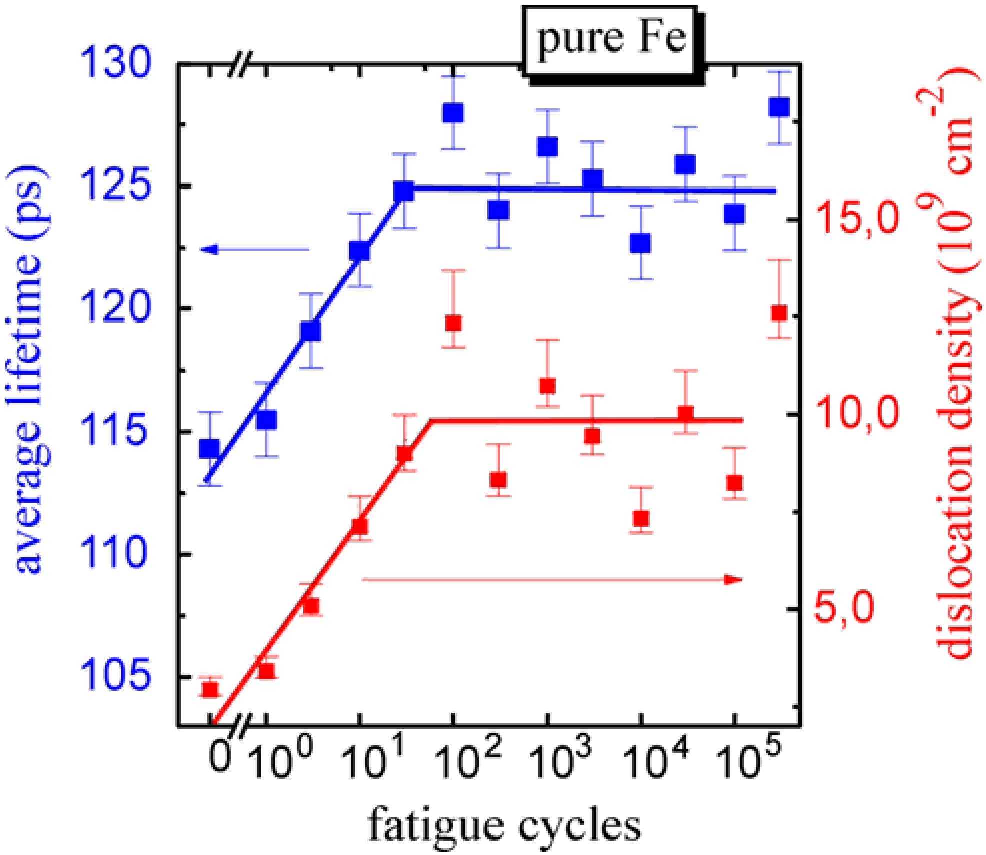


(Ziegler, 1979)

Defects in Iron after tensile strength and fatigue treatment

- extensive study of defects in mechanically damaged iron and steel
- Positrons are very sensitive: detection of defects already in the Hooks range of the stress-strain experiment
- Vacancy cluster and dislocations are detectable in both cases

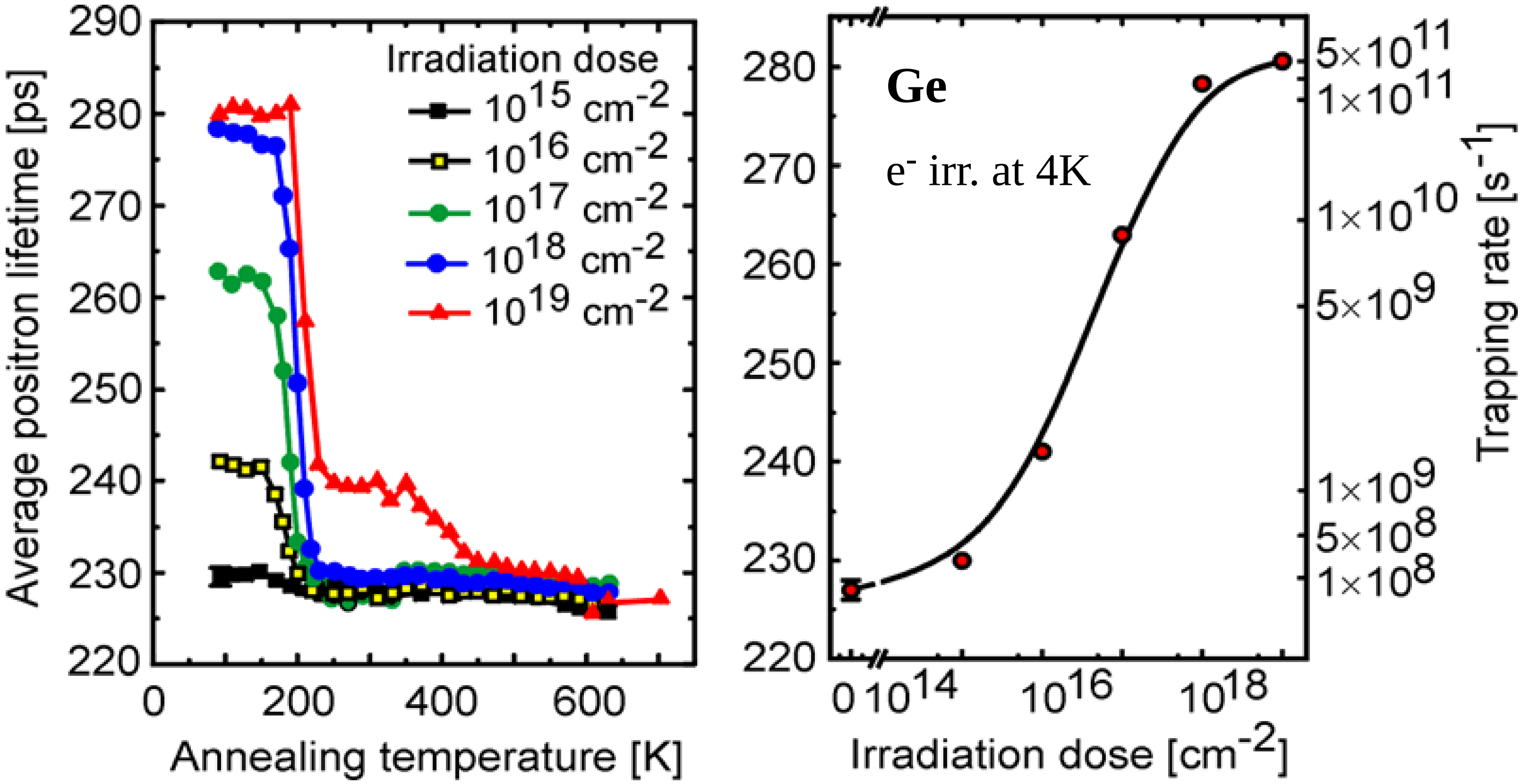




Somieski et al., J. Physique IV 5, C1/127-134 (1995)

Defects in electron-irradiated Ge

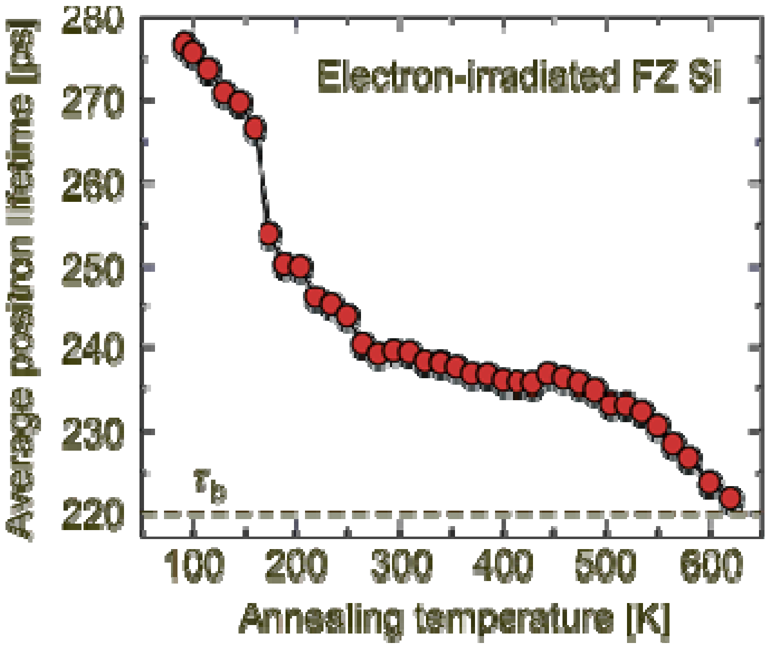
- Electron irradiation (2 MeV @ 4K) induces Frenkel pairs (vacancy - interstitial pairs)
- steep annealing stage at 200 K
- at high irradiation dose: divacancies are formed (thermally stable up to 400 K)

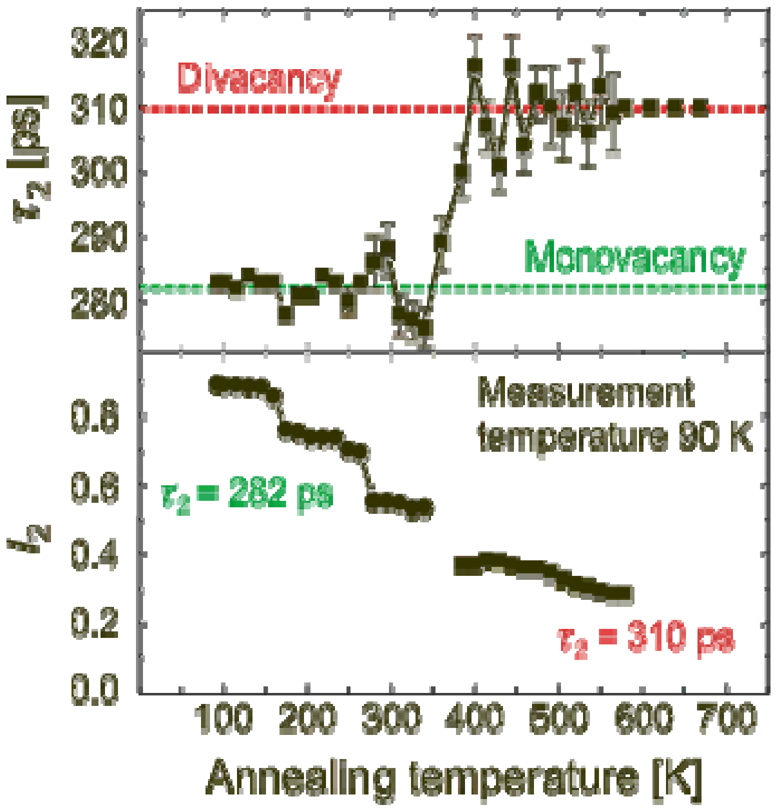


(Polity et al., 1997)

Electron irradiation of Si

- low-temperature electron irradiation was performed at 4K (E_{e-}=2 MeV)
- annealing stage of monovacancies at about 170 K
- moving V_{Si} partly form divacancies
- divacancies anneal at about 550…650 K

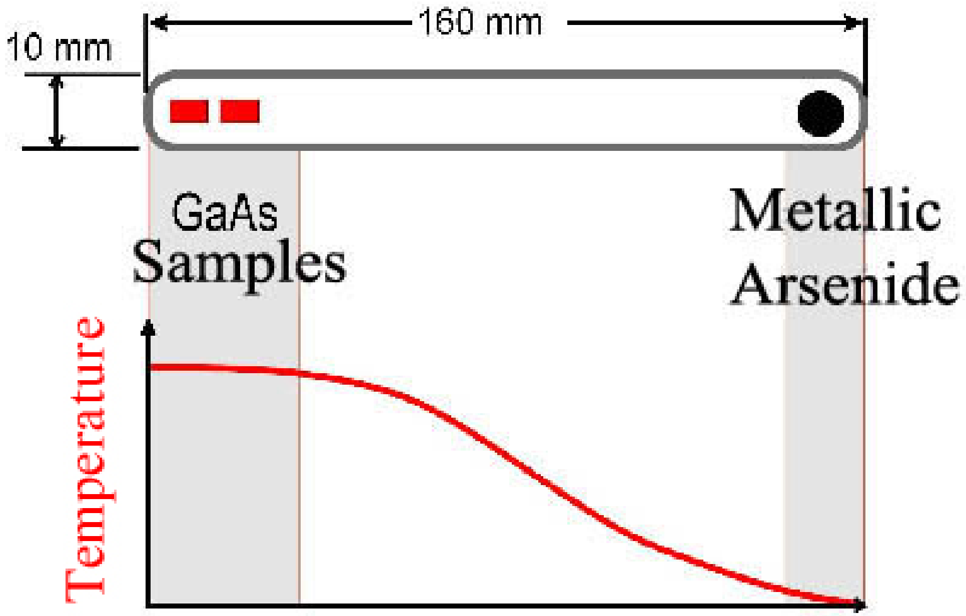




Polity et al., Phys. Rev. B **58** (1998) 10363

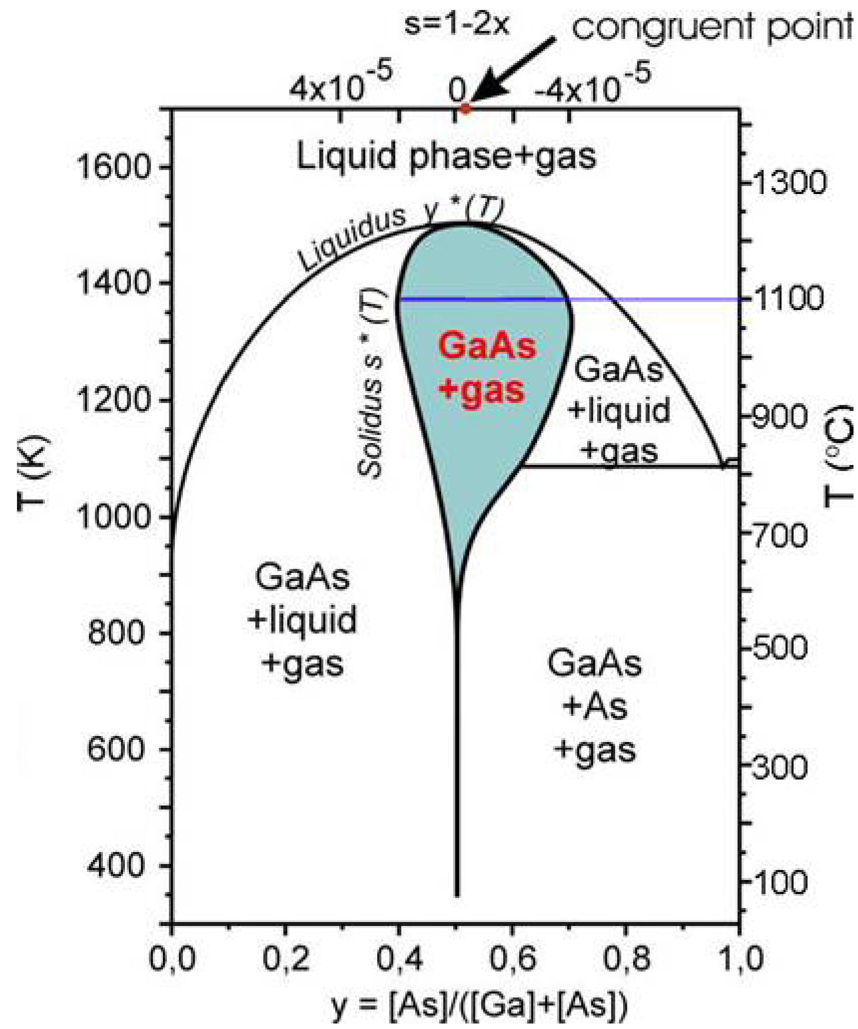
GaAs: annealing under defined As-partial pressure

- two-zone-furnace: Control of sample temperature **and** As partial pressure allows to navigate freely in phase diagram (existence area of compound)
- Measurements near equilibrium after quenching of samples



T_{sample}: 1100° C

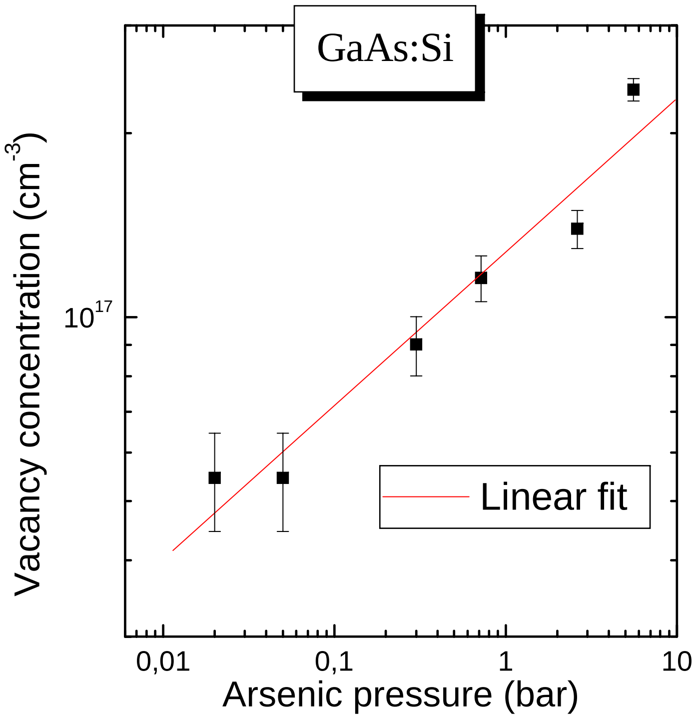
T_{As}: determines As-partial pressure



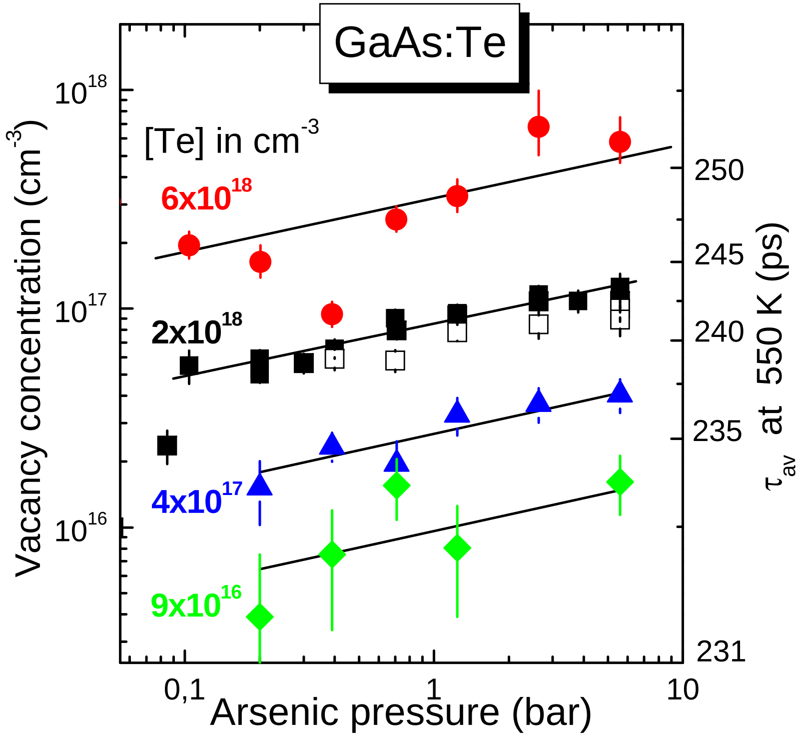
H. Wenzl et al., J. Cryst. Growth **109**, 191 (1991).

GaAs: Annealing under defined As pressure

Si_{Ga}-V_{Ga}



Te_{As}-V_{Ga}



J. Gebauer et al., Physica B 273-274, 705 (1999)

Thermodynamic reaction:

$1/4\ As_4^{gas} \leftrightarrow As_{As} + V_{Ga}$

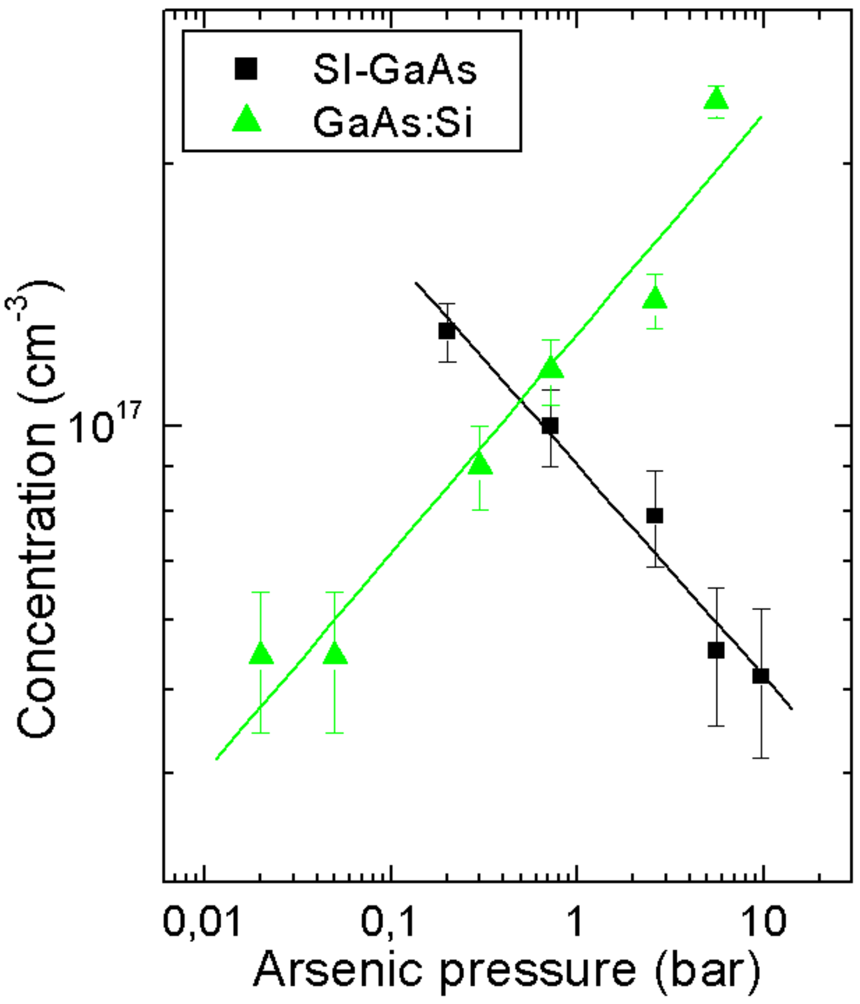
Mass action law:

$[V_{Ga}] = K_{VG} \times p_{As}^{1/4}$

Fit: $[V_{Ga}\text{-Dopant}] \sim p_{As}^{n}$

$\rightarrow n = 1/4$

Comparison of doped and undoped GaAs



Bondarenko et al., 2003

Thermodynamic reaction:

$$As_{As} \leftrightarrow V_{As} + 1/4As_4^{gas}$$

Mass action law:

$$[V_{As}] = K_{VAs} \times p_{As}^{-1/4}$$

Fit: $[V\text{-complex}] \sim p_{As}^{n}$

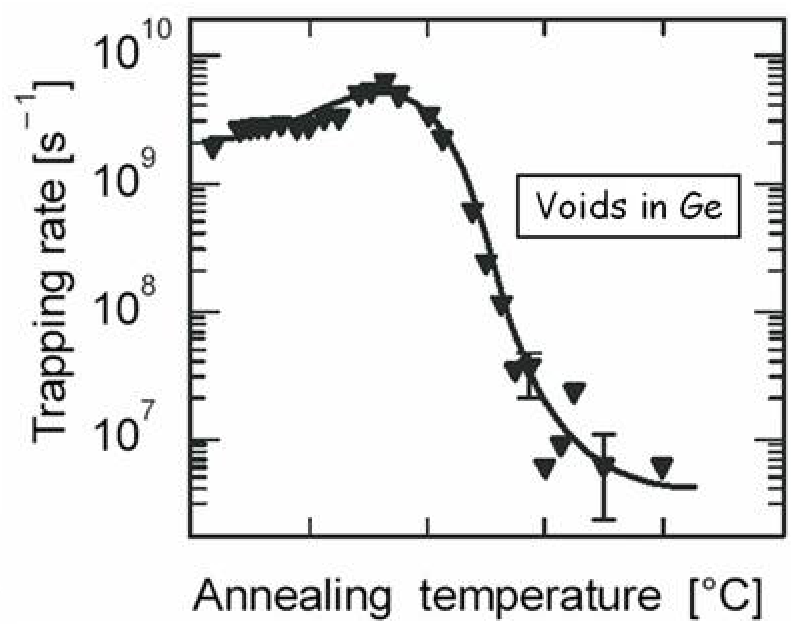
$\rightarrow n = -1/4$

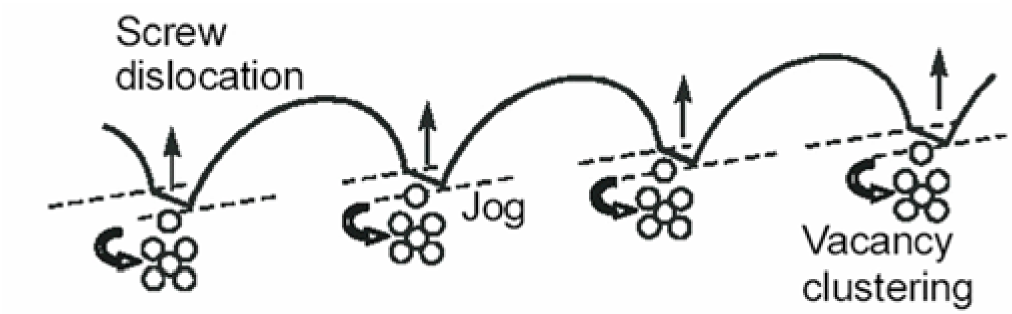
↓

undoped GaAs: As vacancy

Vacancy clusters in semiconductors

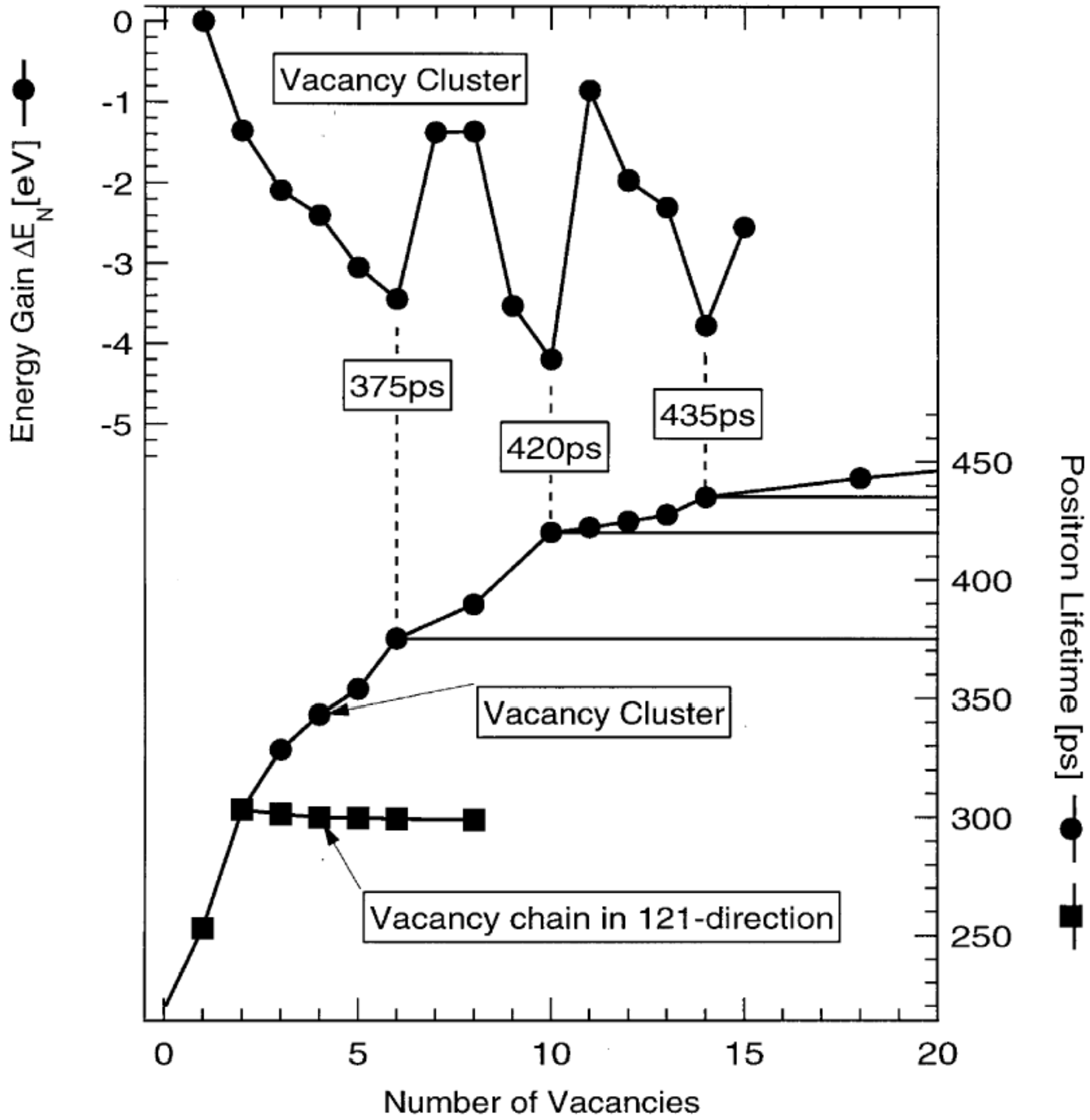
- vacancy clusters were observed after ion/neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) -> positron lifetime increases distinctly
- example: plastically deformed Ge
- lifetime: τ = 525 ps
- reason for void formation: **jog dragging mechanism**
- trapping rate of voids disappears during annealing experiment





Krause-Rehberg et al., 1993

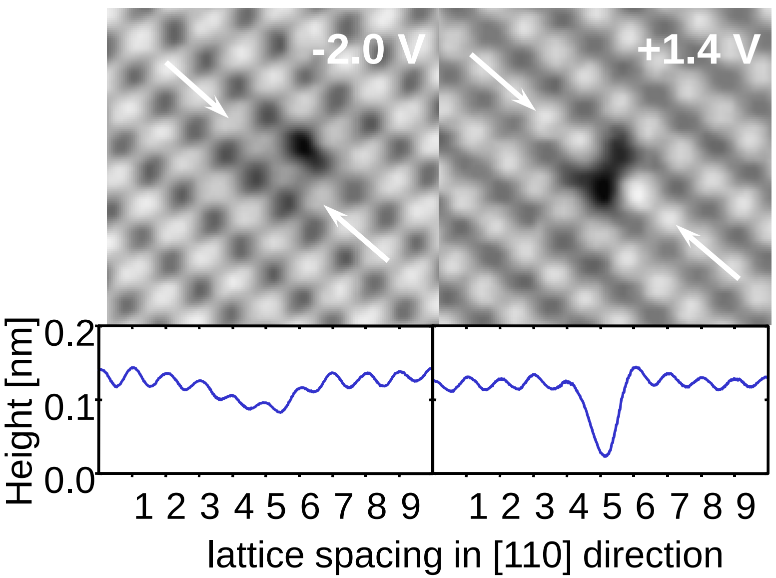
Theoretical Calculation of Vacancy Clusters in Si

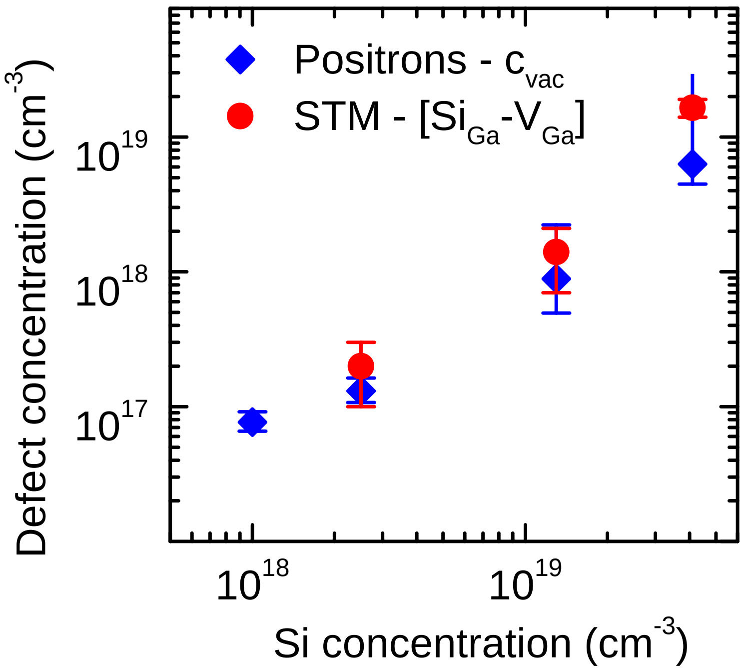


- there are cluster configurations with a large energy gain
- „Magic Numbers“ with 6, 10 und 14 vacancies
- positron lifetime increases distinctly with cluster size
- for n > 10 saturation effect, i.e. size cannot be determined

T.E.M. Staab et al.,
Physica B 273-274 (1999) 501-504

Identification of V_{Ga}-Si_{Ga}-Complexes in GaAs:Si





- Scanning tunneling microscopy at GaAs (110)-cleavages planes (by Ph. Ebert, Jülich)
- Defect complex identified as **V_{Ga}-Si_{Ga}**

- Quantification → Agreement

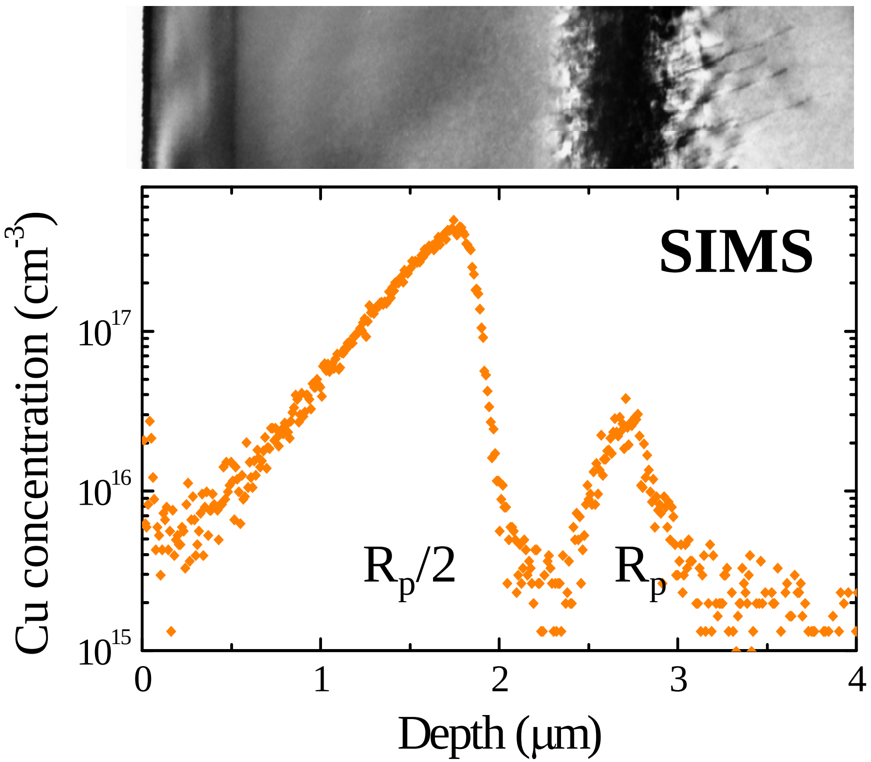
Mono-Vacancies in GaAs:Si are V_{Ga}- Si_{Ga}-complexes

Gebauer et al., Phys. Rev. Lett. **78** (1997) 3334

Defects after high energy Si self-implantation - the Rp/2 Effect

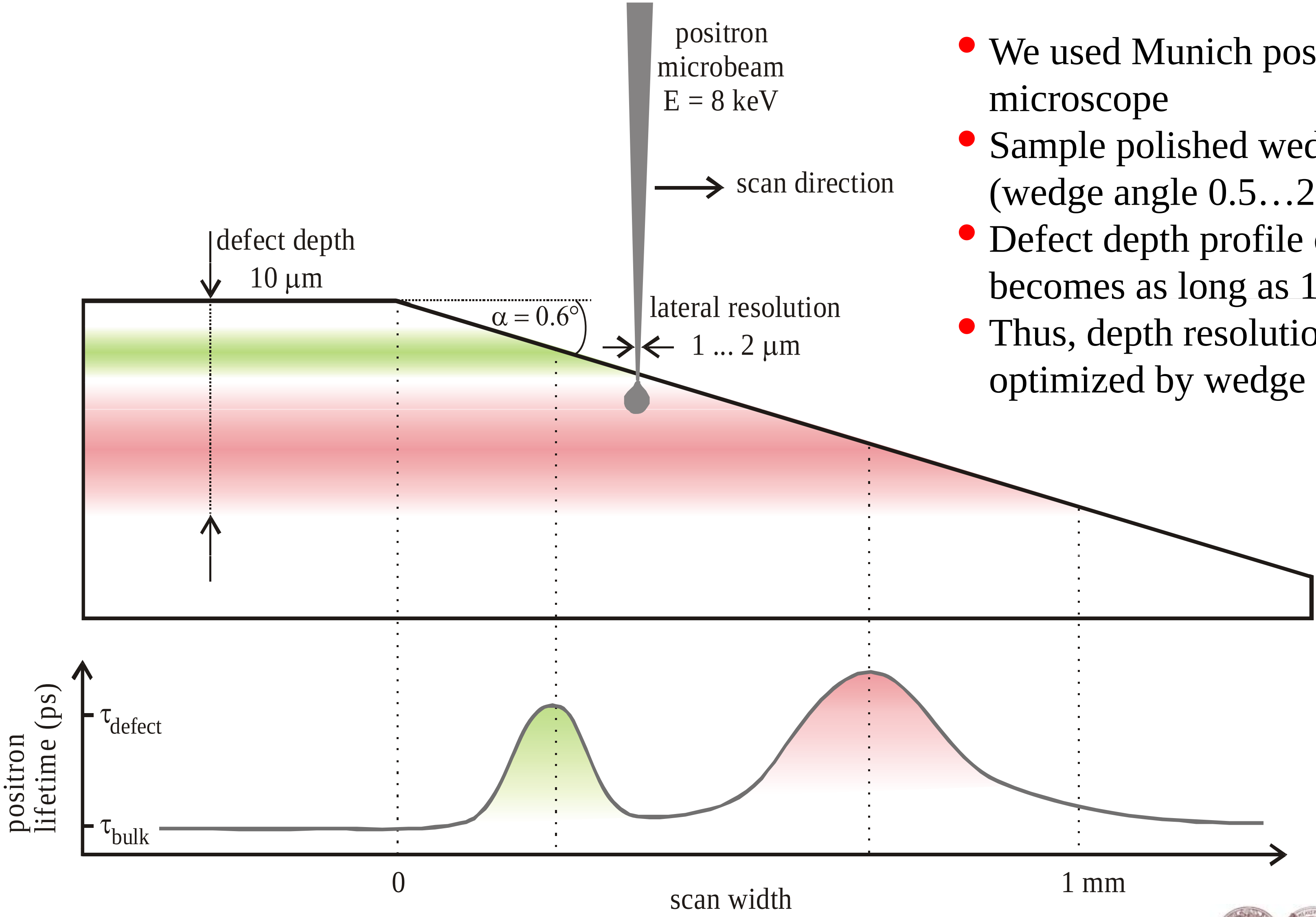
- After high-energy self-implantation of Si (3.5 MeV; 5 ×10^{15} cm^{-2}) and RTA (900°C, 30s): two new getter zones appear at R_p and $R_p/2$ (R_p = projected range of Si^+)
- Zones become visible after Cu in-diffusion from rear side of sample (Cu implantation and diffusion annealing at 600°C)

TEM image by P. Werner, MPI Halle



- at R_p: gettering by interstitial type dislocation loops
- Formed due to interstial excess Si after implantation and RTA annealing
- Although gettering appears, no defects visible by TEM at $R_p/2$
- **What is the nature of these defects?**

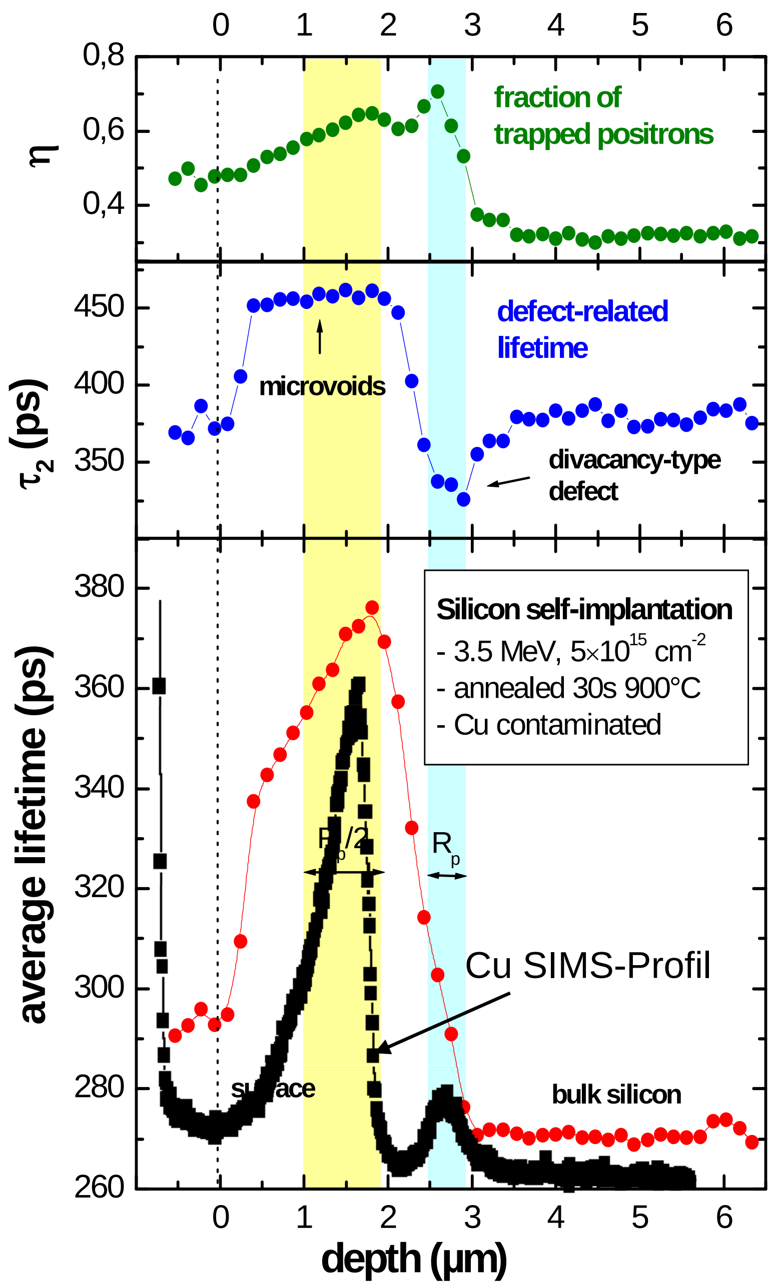
Improved depth resolution by using a positron microbeam



- We used Munich positron microscope
- Sample polished wedge-like (wedge angle 0.5…2°)
- Defect depth profile of 10 µm becomes as long as 1 mm
- Thus, depth resolution con be optimized by wedge angle

First defect-depth profile using a positron microprobe

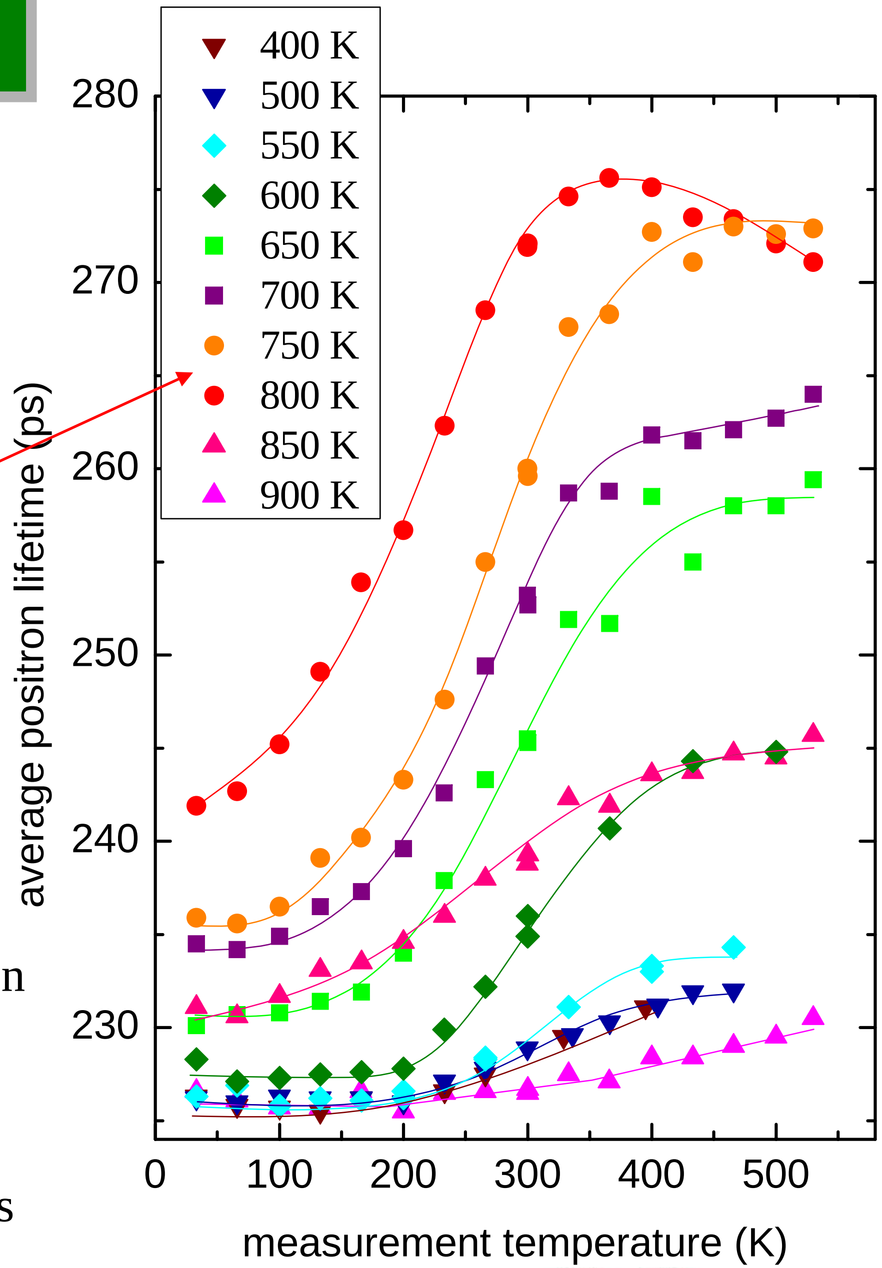
- 45 lifetime spectra were recorded along wedge
- Because of beam diameter - depth resolution of 155 nm is obtained at $\alpha = 0.81°$
- Positron implantation energy: 8 keV ⇒ mean information depth 400 nm
- Optimum depth resolution
- Both defected regions well visible
    - Vacancy clusters with increasing density down to 2 µm ($R_p/2$ region)
    - At R_p region: lifetime τ_2 = 330 ps; open volume corresponds to a divacancy; must be stabilized or being part of dislocation loops



R. Krause-Rehberg et al., Appl. Phys. Lett. **77** (2000) 3932

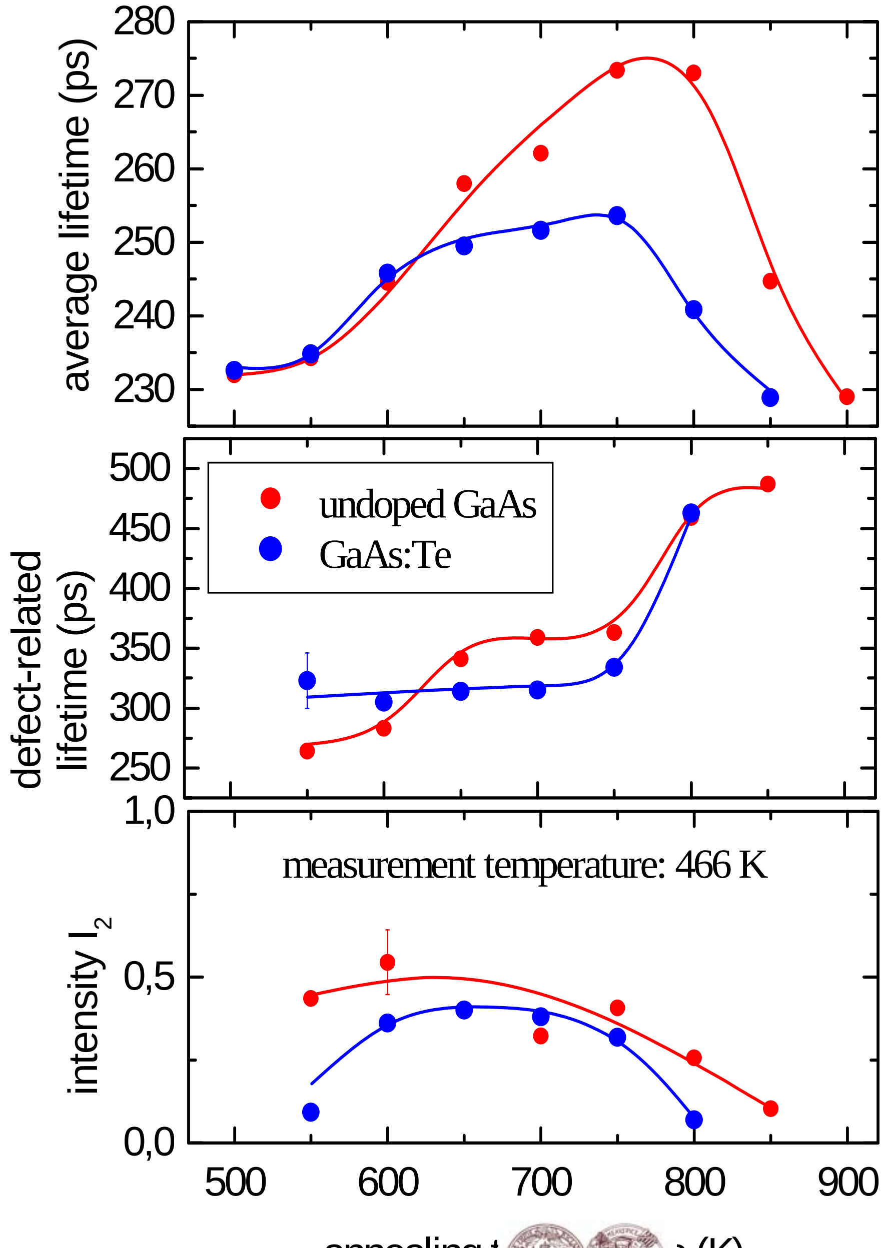
Diffusion of Cu in GaAs

- Positron experiment:
  - 30 nm Cu-layer deposited by evaporation
  - Annealing at 1100°C (under defined As-pressure) for Cu in-diffusion
  - Quenching to RT
  - then annealing with growing temperature
  - Positron lifetime measurement
- Cu is completely solved at 1100°C
- But it is oversaturated at RT
- Precipitation starts very slowly (slow diffusion)
- However: at elevated temperatures – diffusion becomes faster: out-diffusion process
- Result: formation of vacancy-type defects when out-diffusion starts
- Not compatible with current diffusion models



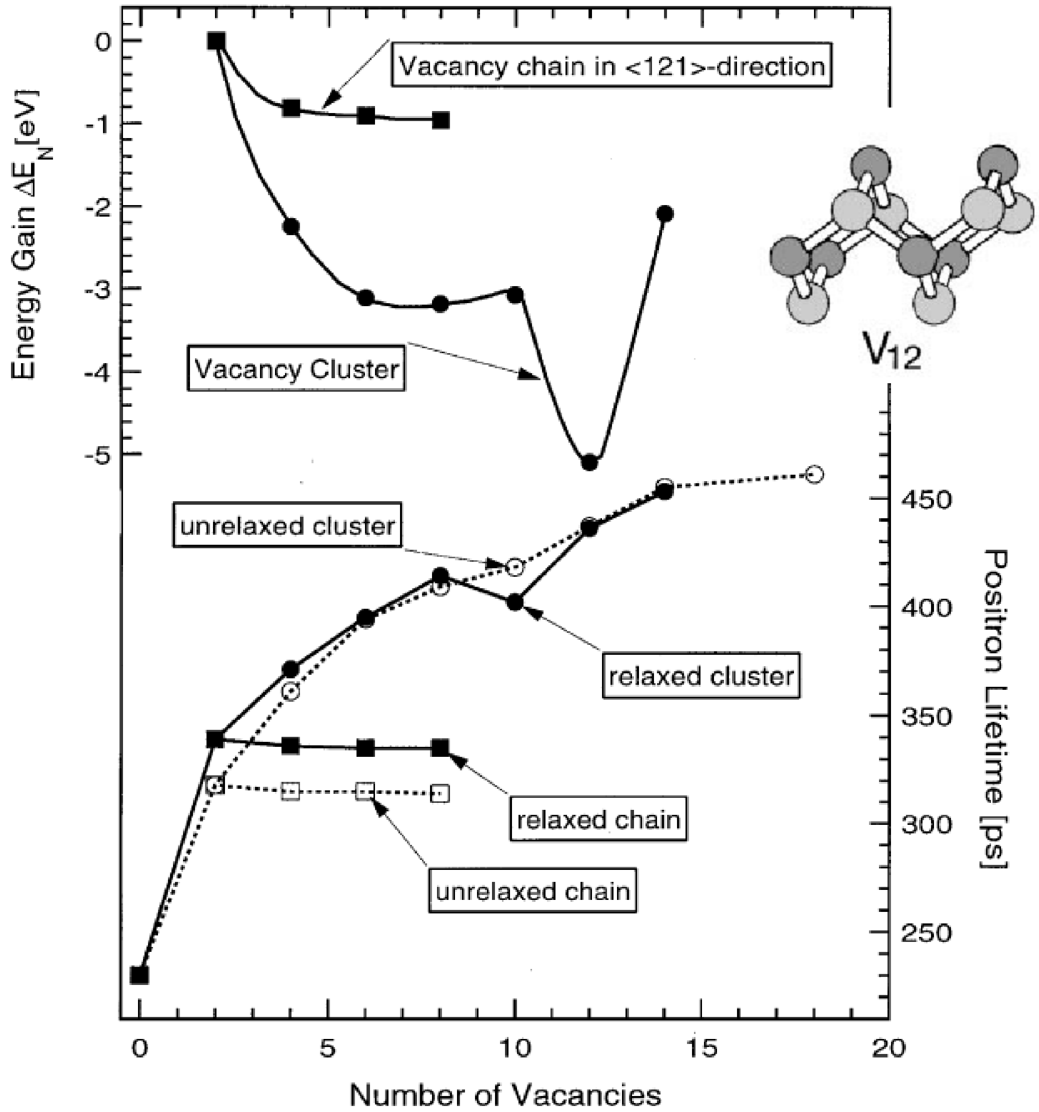
Determination of Defect Type

- Formation of these clusters is almost independent of doping / conduction type
- Identical behavior in undoped GaAs
- In beginning of defect formation: defect-related lifetime is about 250 ps – a monovacancy
- In course of annealing: lifetime growth to 320-350 ps corresponding to a divacancy
- at 800 K: $\tau_2 > 450$ ps: rather large vacancy clusters (n > 10)



Voids in GaAs

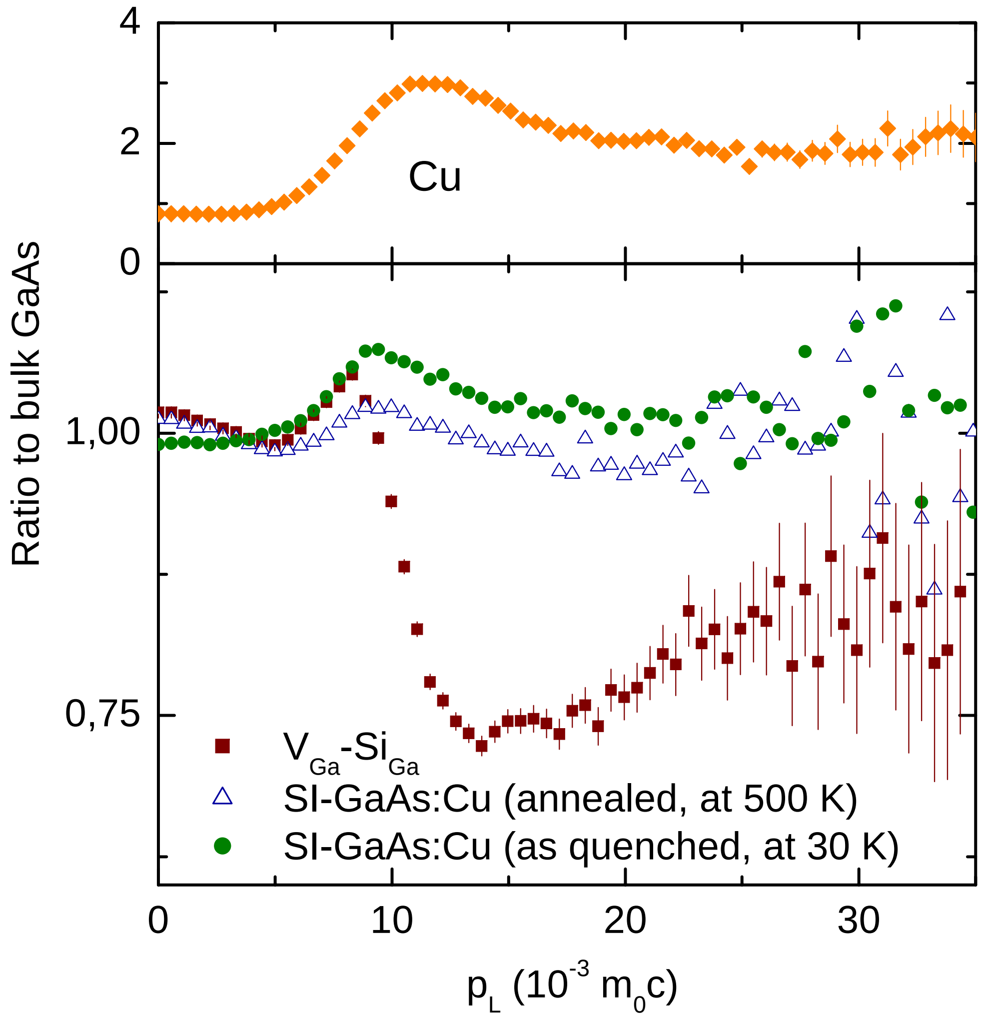
- Molecular-dynamic cluster calculations give energy gain compared to sum of monovacancies
- Relaxation was taken into account
- Energetically favored: 12 vacancies
- Positron lifetime was calculated
- stable 12-atom cluster exhibit positrc lifetime of about 450 ps
- Found in experiment



TEM Staab et al., Physica B 273-274 (1999) 501-504

Coincidence-Doppler Spectroscopy at GaAs:Cu

- In high-momentum region (>10^{-2} m_0c) annihilation with Core-electrons dominate
- Electron momentum distribution of core electrons almost not changed compared to individual atoms
- Relatively easy to calculate
- In example: the detected vacancies have Cu atoms in closest vicinity
- Vacancies are obviously stabilized by Cu



V. Bondarenko, K. Petters, R. Krause-Rehberg, J. Gebauer, H.S. Leipner, Physica B 308-310 (2001)792-795

Conclusions

- Positrons are a useful tool
  - For characterization of vacancy-type defects in crystalline solids
  - Unique for mono-vacancies
  - Very sensitive for vacancy clusters for n < 10 (below TEM sensitivity)
  - Sensitivity limit for monovacancies $\approx 10^{15}$ /ccm

R. Krause-Rehberg, H.S. Leipner
„Positron Annihilation in Semiconductors“
Springer-Verlag, 1999