Vacancy generation during Cu diffusion in GaAs

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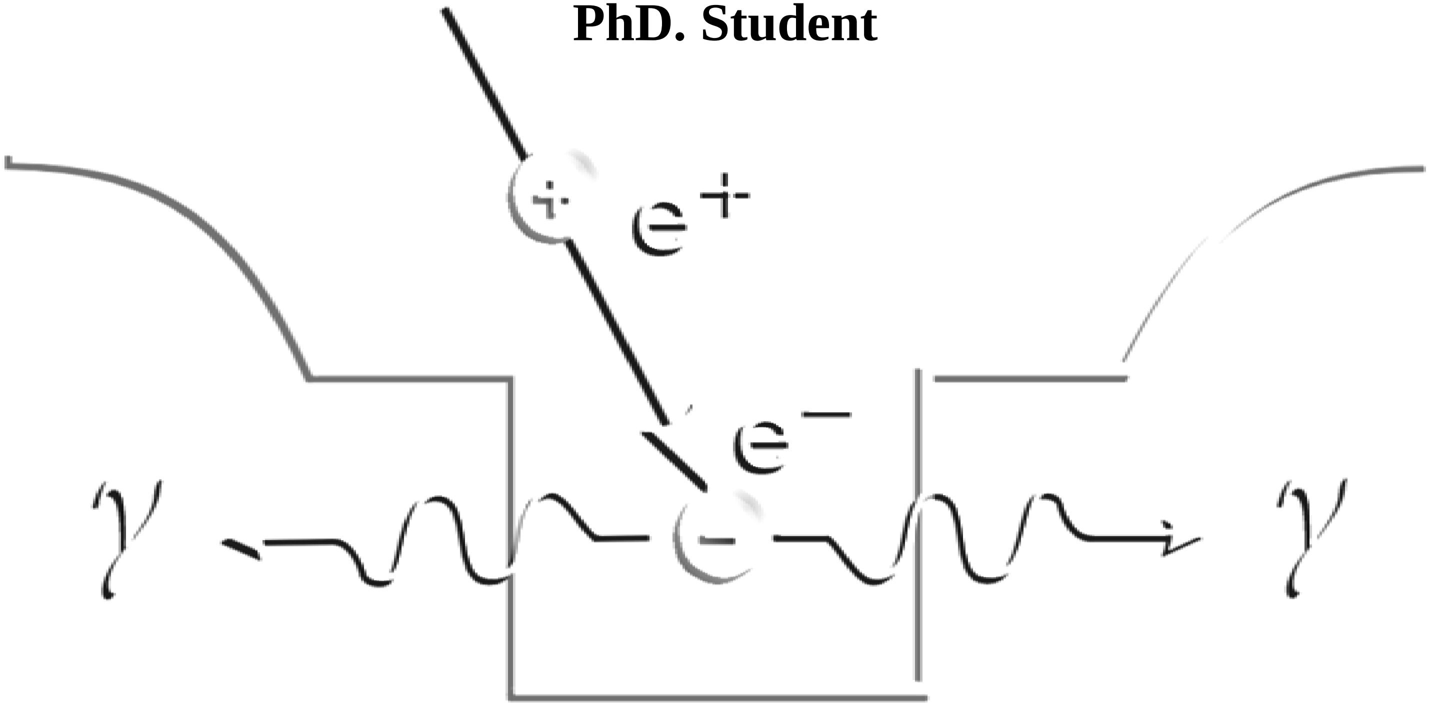

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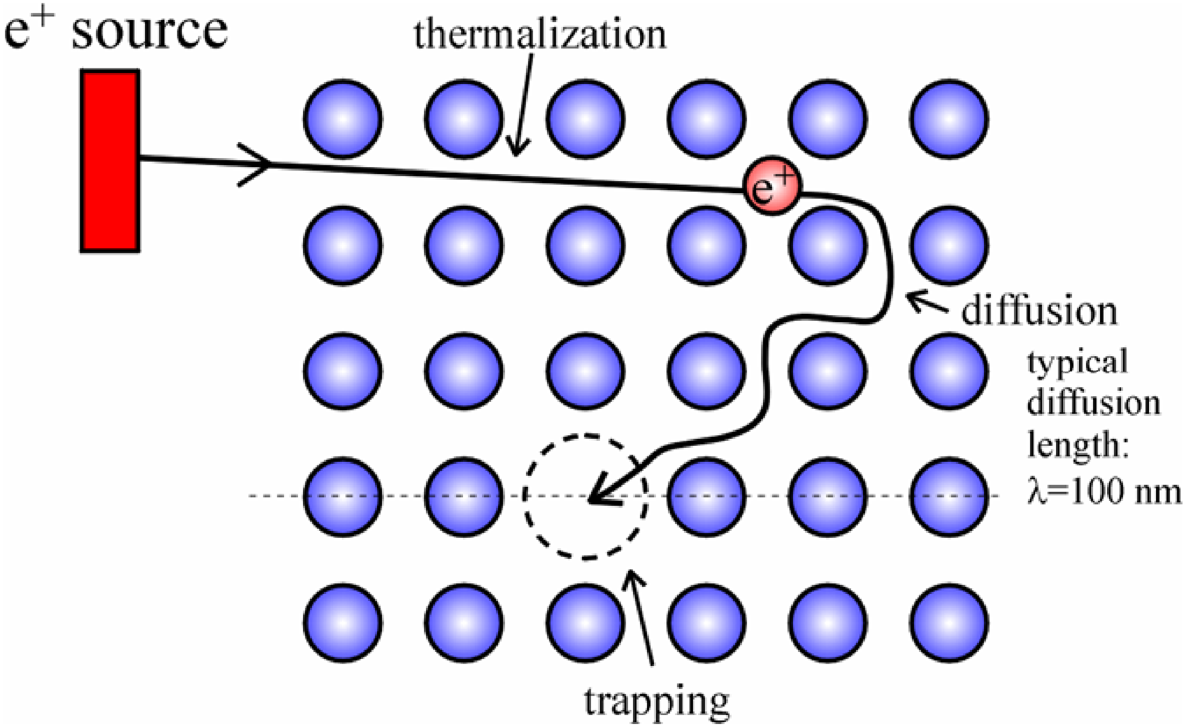
Outlines

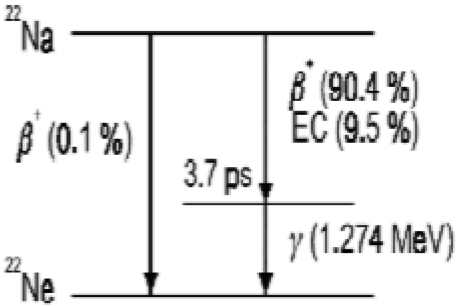
- Principles of PAS
- vacancy in Semiconductors and shallow positron traps
- Atomic diffusion mechanisms
- Observation of vacancies during Cu diffusion in GaAs
- Conclusion

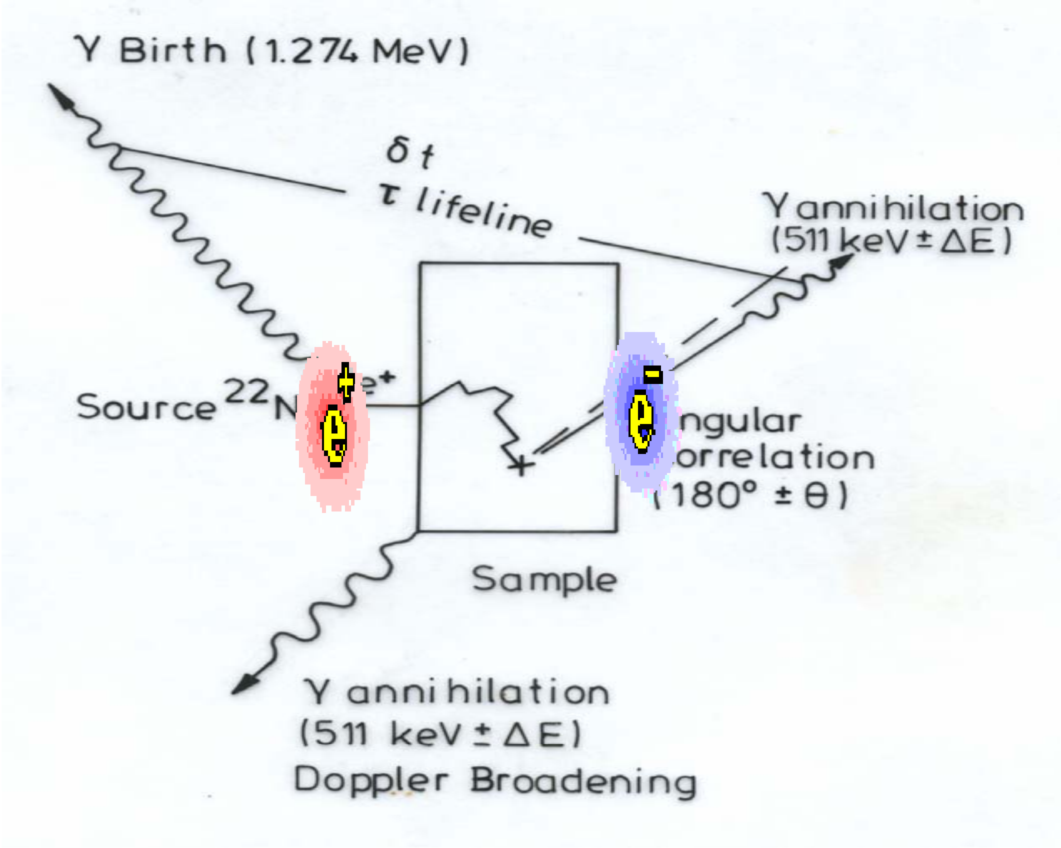
Principles of PAS



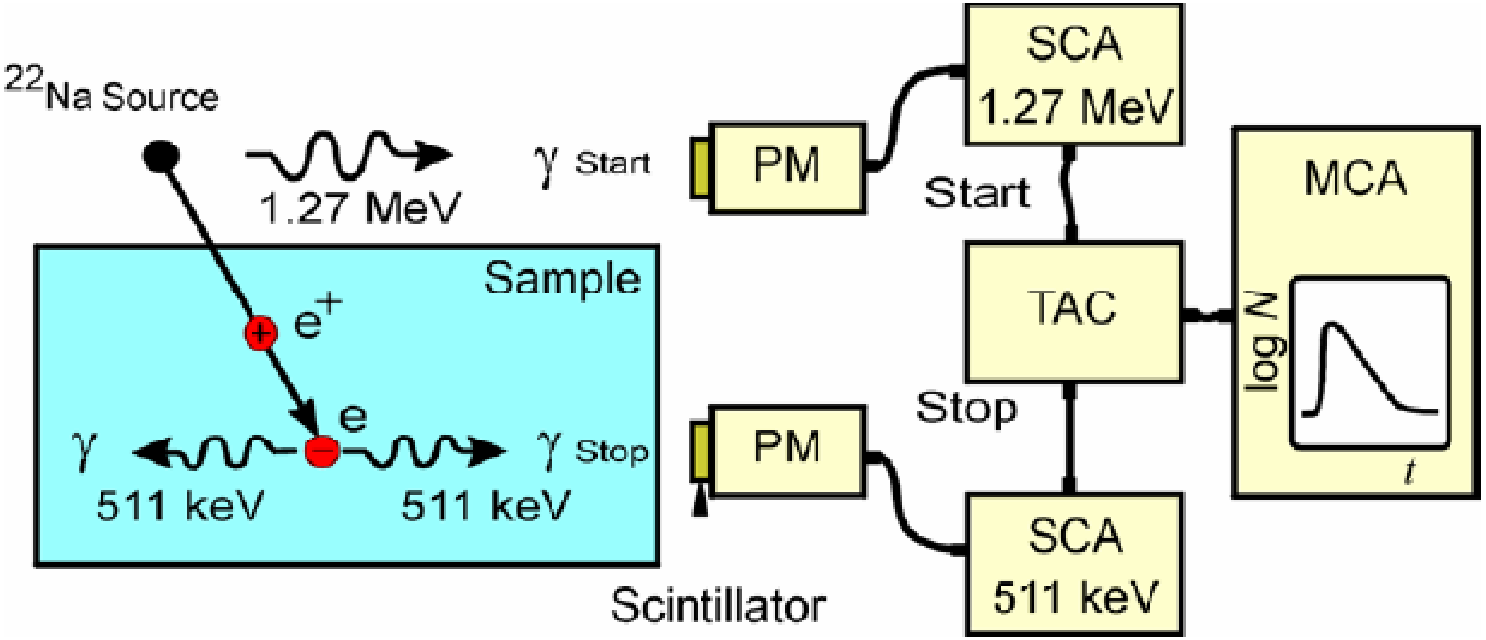
- **positrons:**
- thermalize
- diffuse
- being trapped
- **When trapped in vacancies:** Lifetime increases due to smaller electron density in open volume

Principles of PAS





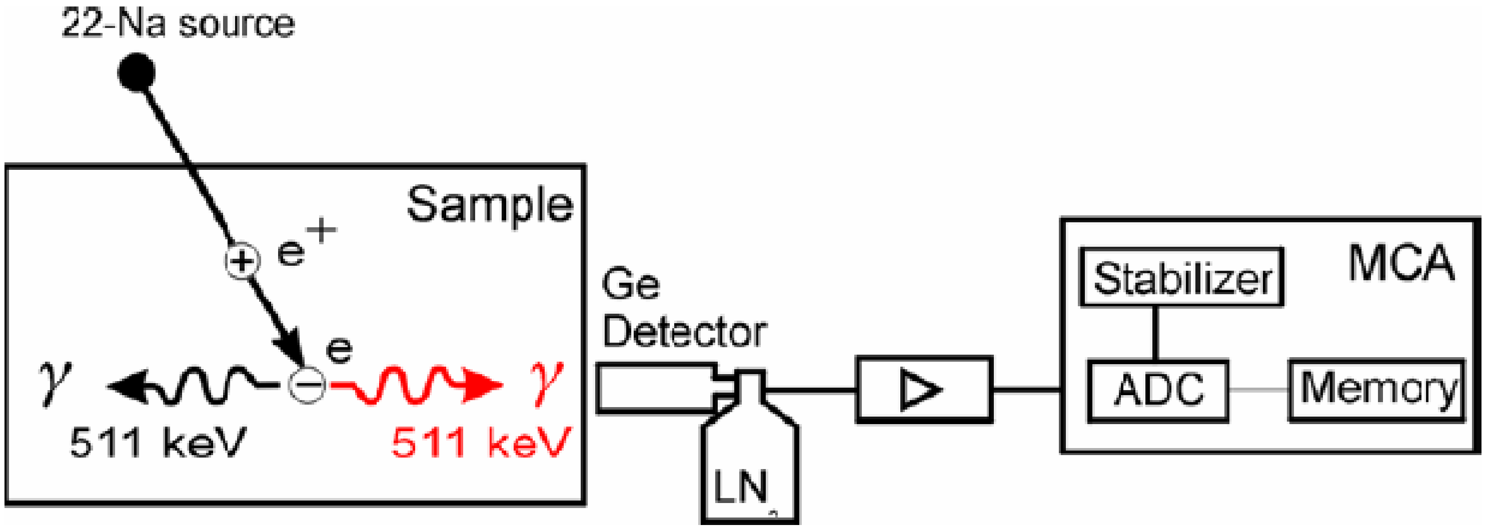
Principles of PAS



- Positron lifetime is measured as time difference between 1.27 MeV quantum and 0.511 MeV quantum
- PM=photomultiplier, SCA=single channel analyzer (constant fraction type), TAC=time to amplitude converter, MCA= multi channel analyzer

Principles of PAS

Measurement of Doppler Broadening

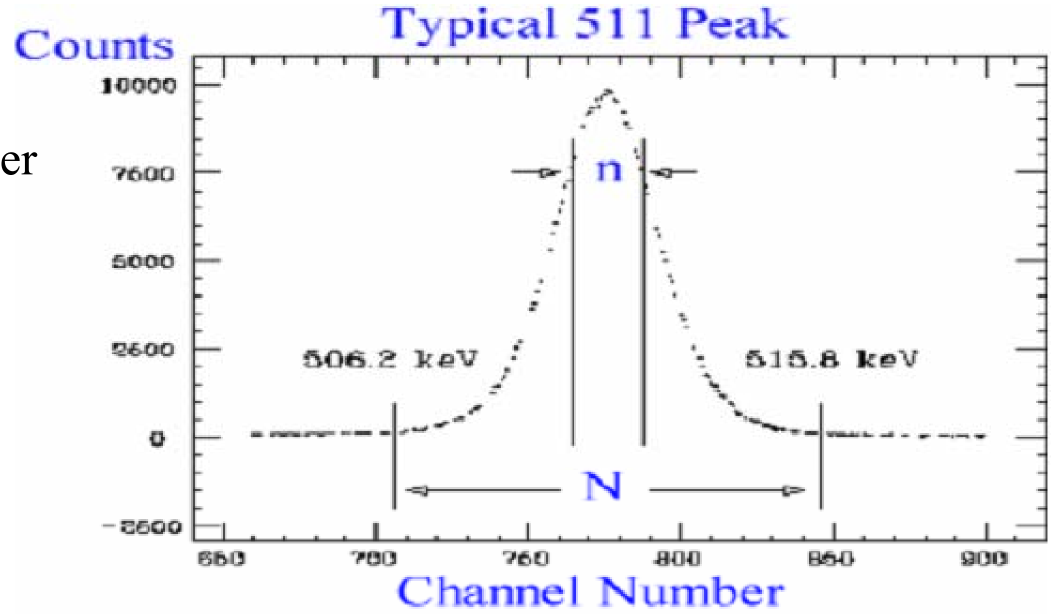


- electron momentum in propagation direction of 511 keV γ-ray leads to Doppler broadening of annihilation line
- can be detected by conventional energy-dispersive Ge detectors and standard electronics

Principles of PAS

Line Shape Parameters

- Valance annihilation (Shape) parameter
- Core annihilation (Wing) parameter

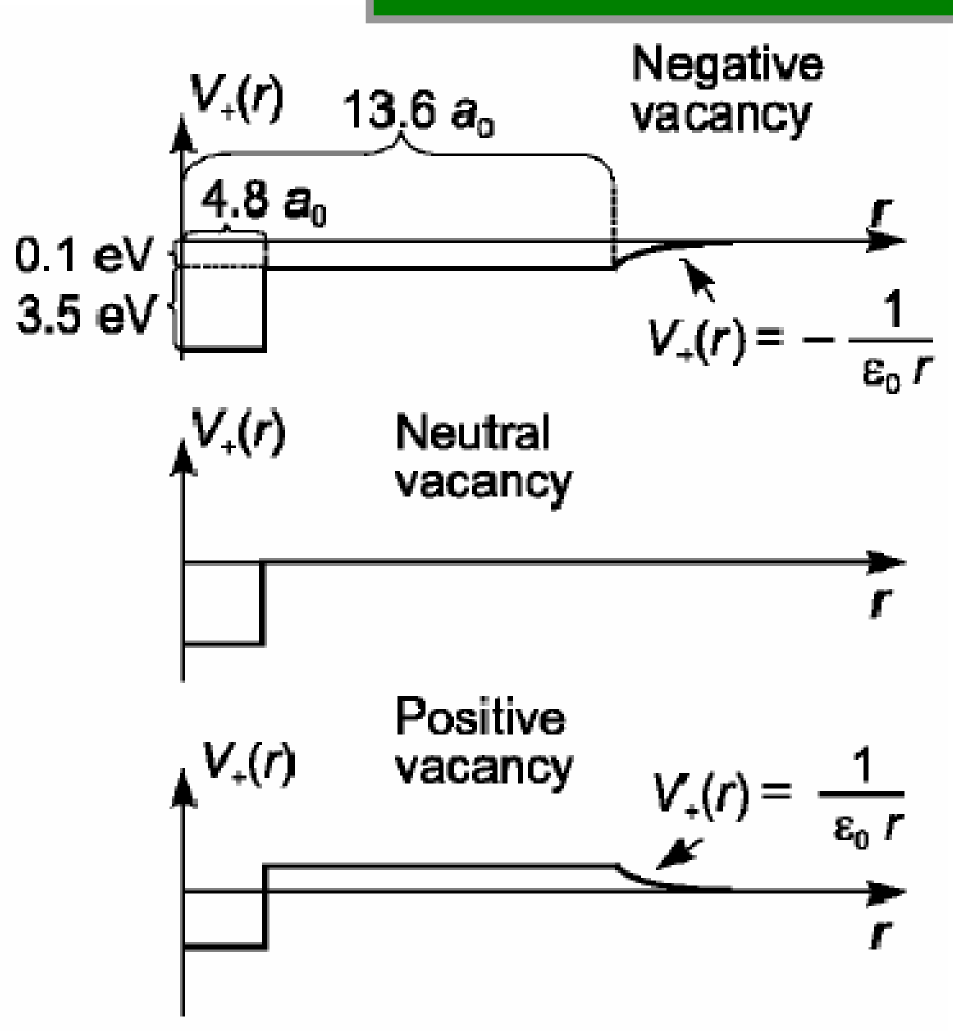


- Both S and W are sensitive to the concentration and defect type
- W is sensitive to chemical surrounding of the annihilation site, due to high momentum of core electrons participating in annihilation

- CDBS
  2 γ-detectors (germanium) simultaneously
  better energy resolution and reduced background

Vacancies in a semiconductor

Vacancies in a semiconductor may be charged



Puska et al. 1990

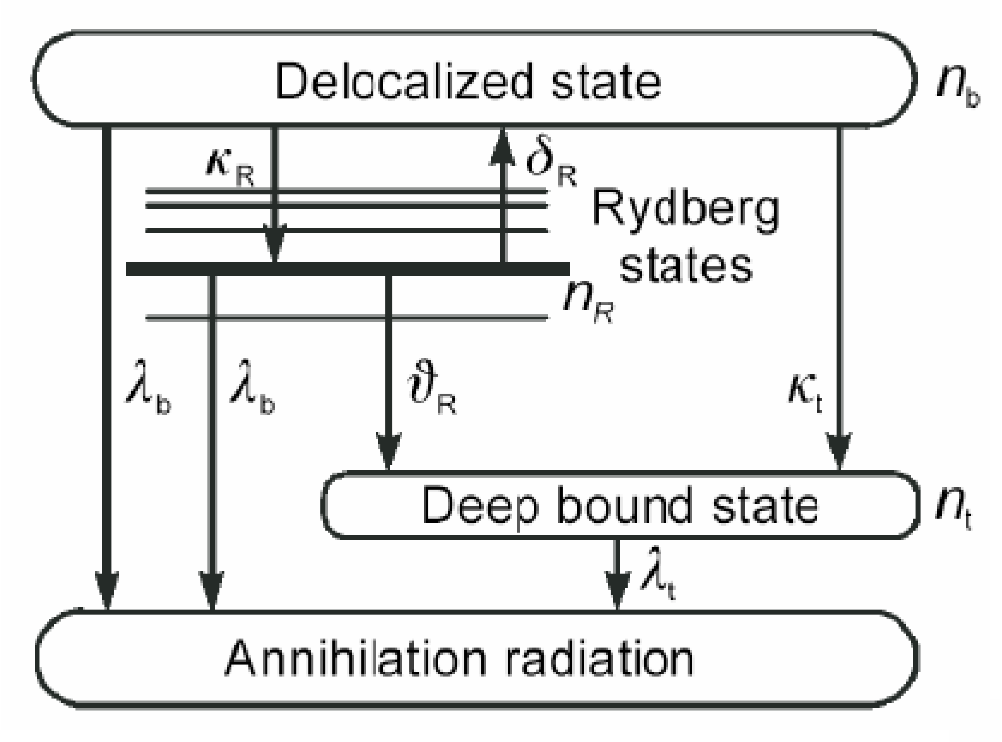
For a negative vacancy:

- Coulomb potential is rather extended but weak
- it supports trapping only at low temperatures
- at higher temperatures: detrapping dominates and vacancy behaves like a vacancy in a metal or a neutral vacancy

Positive vacancies repel positrons

Vacancies in a semiconductor

Positron trapping by negative vacancies



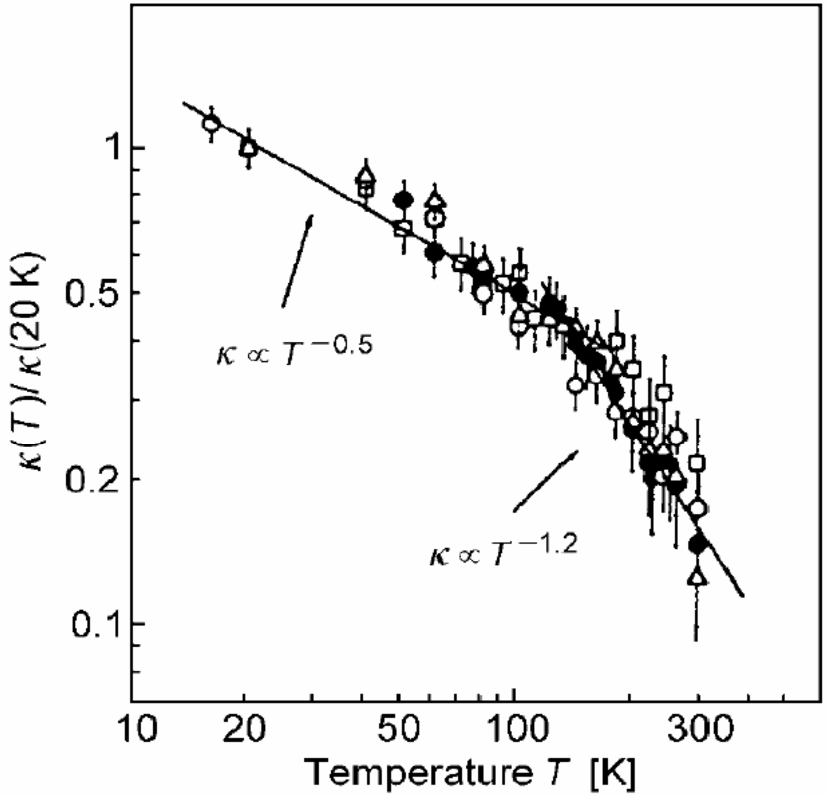
- trapping process can be described quantitatively by trapping model
- Coulomb potential leads to Rydberg states
- from there: positrons may reescape by thermal stimulation
- once in the deep state: positron is captured until annihilation
- detrapping is strongly temperature dependent

$$\delta_R = \frac{K_R}{\rho_V}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{E_R}{k_B T}\right)$$

Manninen, Nieminen, 1981

Vacancies in a semiconductor

Negative vacancies show temperature-dependent positron trapping



positron trapping in negatively charged Ga vacancies in SI-GaAs

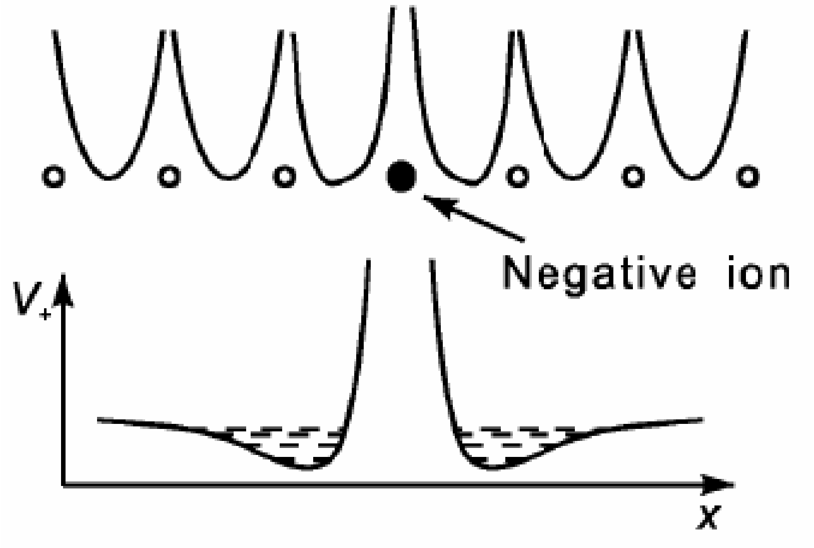
Le Berre et al., 1995

- dependence of positron trapping on temperature is rather complex

$$\kappa = \frac{\vartheta_{\mathrm{R}} \rho_V \kappa_{R_o} T^{-1/2}}{\vartheta_{\mathrm{R}} \rho_V + \kappa_{R_o} \left(\frac{m^* k_B}{2\pi\hbar^2} \right)^{3/2} T \ \exp\left(-\frac{E_R}{k_B T} \right)}$$

- low temperature: ~ $T^{-1/2}$ due to limitation of diffusion in Rydberg states
- higher T: stronger temperature dependence due to thermal detrapping from Rydberg state

Shallow positron traps



- at low T: negatively charged defects without open volume may trap positrons and trapping is based on the capture of positron in Rydberg states
- "shallow" refer to small positron binding energy
- acceptor-type impurities, negative antisite defects
- annihilation parameters close to bulk parameters
- thermally stimulated detrapping can be described by:

$$\delta = \frac{\kappa}{\rho_{\mathrm{st}}} \left(\frac{m^* k_B T}{2\pi\hbar^2} \right)^{3/2} \exp\left(-\frac{E_{\mathrm{st}}}{k_B T} \right)$$

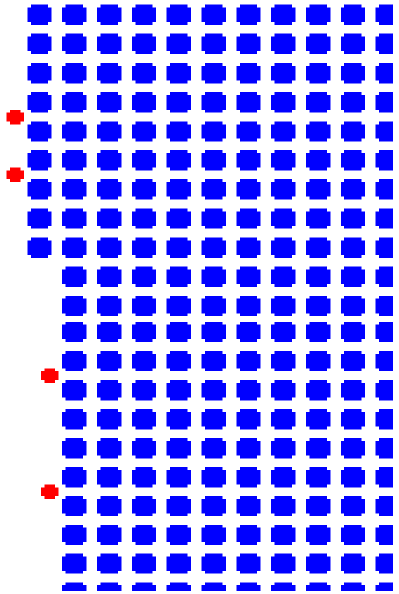
Saarrinen et al., 1989

Atomic diffusion mechanisms

1- Diffusion without involvement of native point defect

- Interstitially dissolved impurity atoms diffuse by jumping between interstitial sites

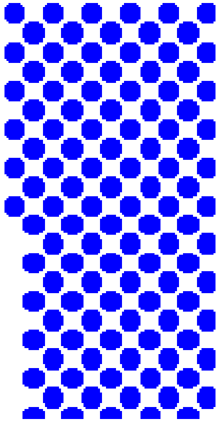
- Examples: diffusion of Li, Fe and Cu in Si. Also Oxygen diffuse among interstitial sites with so low diffusivity



Atomic diffusion mechanisms

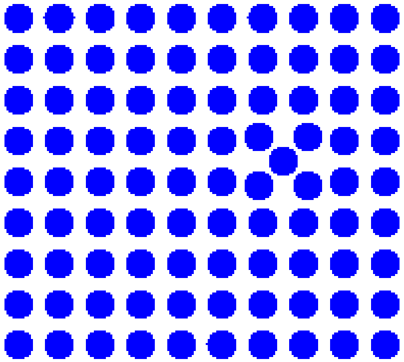
2. Simple Vacancy Exchange & Interstitialcy Mechanisms

- In a simple vacancy exchange mechanism, substitutional atom jumps into a neighbor vacancy on the lattice



$$D_s^v \propto C_v^{eq}$$

- In interstitialcy Mechanism (interstitial), the substitutional atom is first replaced by a self-interstitial and pushed into an interstitial position, it pushes out one of the neighbor atom in the lattice

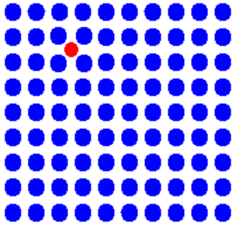


$$D_s^I \propto C_I^{eq}$$

Atomic diffusion mechanisms

3- Interstitial- Substitutional Mechanism

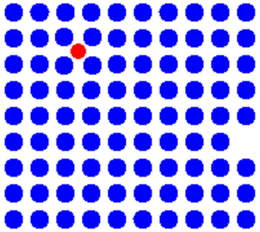
3.1- Kick-out mechanism



- closely related to interstitialcy diffusion mechanism
- foreign atom (interstitial) remains for many steps

$$A_i \Leftrightarrow A_s + I$$

3.2- Frank Turnbull mechanism



- is qualitatively different from vacancy exchange mechanism

$$D_s^v \propto 1/C_v^{eq}$$

$$A_i + V \Leftrightarrow A_s$$

4- Recombination-Enhanced diffusion

- Thermally activated diffusion of defects may be enhanced by the transfer of energy associated with the recombination of electrons and holes into the vibrational modes of defects and their surrounding
- $C > C^{eq}$ induced by optical excitation or particle irradiation

Observation of vacancies during Cu diffusion in GaAs

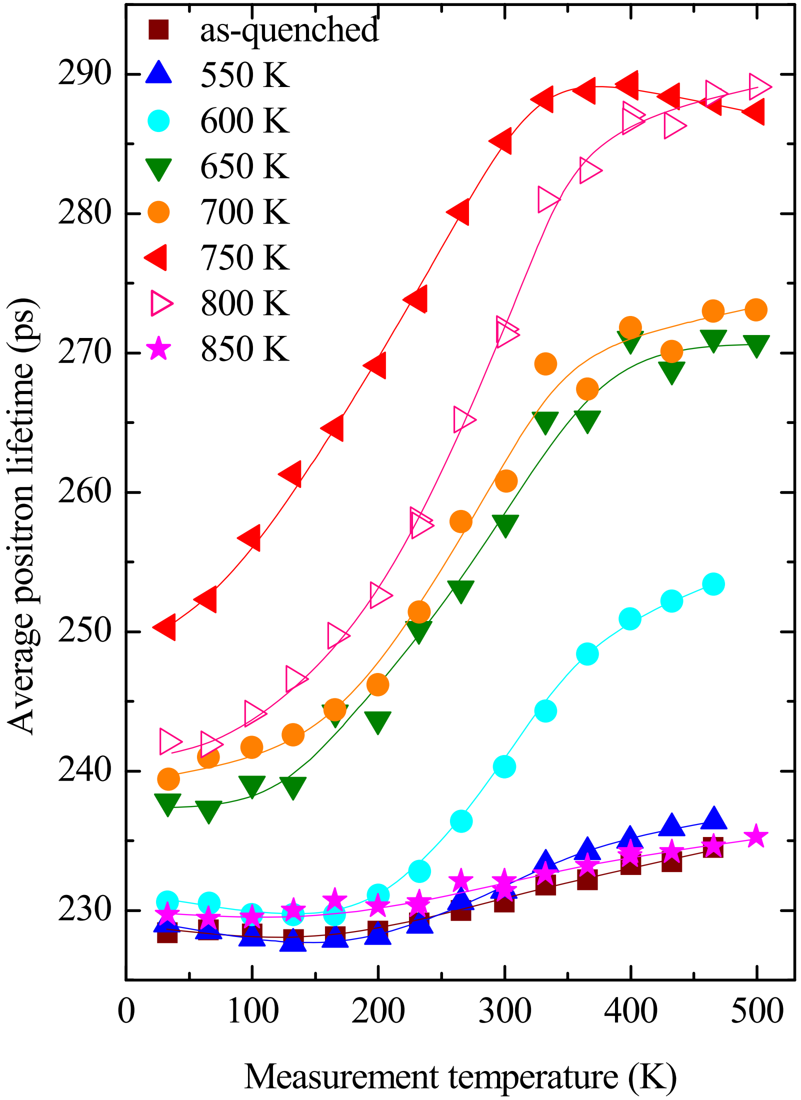
- Copper is an unintentional impurity in most semiconductors
- Cu diffuses rapidly already at low temperatures
- GaAs: diffusion coefficient $D = 1.1\times10^{-5}$ cm^2 s^{-1} at 500°C [1]
- Cu diffuses very fast by interstitial diffusion (kick-out process) [2]
- The solubility between 2×10^{16} cm^{-3} (500°C) and 7×10^{18} cm^{-3} (1100°C) [1]
- Cu_{Ga} is a double acceptor
- work: comprehensive positron annihilation study of GaAs after Cu in-diffusion
- Experimental: 0.5 mm samples covered by 30 nm Cu, annealed at 1100 ^{o}C under different P_{As} (0.2-9.68 bar), quenched in RT water and subject to isochronal annealing

[1] R.N. Hall and J.H. Racette, J. Appl. Phys. 35 (1964) 379.

[2] F.C. Frank and D. Turnball, Phys. Rev. 104 (1956) 617.

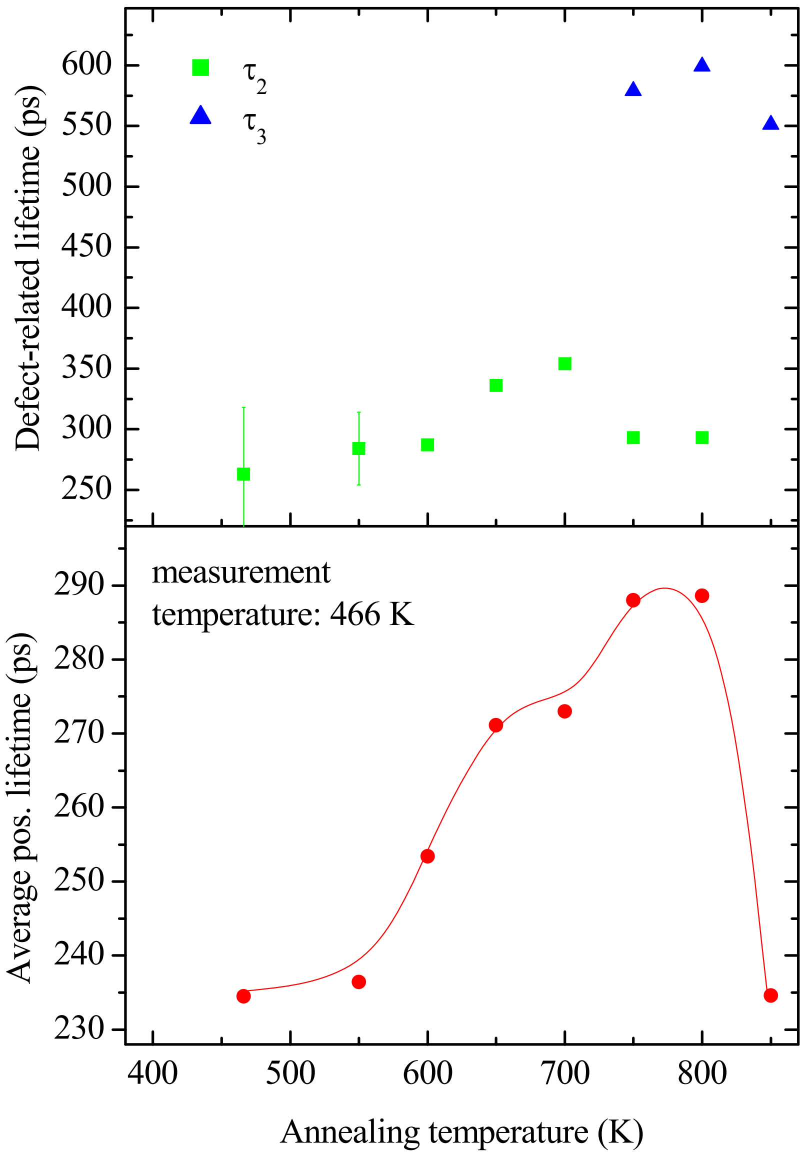
GaAs:Cu

- as-quenched and for annealing up to 550 K almost no change in $\tau_{av.}$
- Up to 800 K, τ_{av} increase strongly to 290 ps- detected vacancy must be lager than $V_{Ga.}$
- Decrease of τ_{av} at low T, shallow positron traps (Cu_{Ga}).
- annealing > 800 K, the vacancy signal disappear.



GaAs:Cu

- τ_d is much higher than that for monovacancies (250-260 ps)
- from τ_d open volume increases during annealing
- this explained by trapping of positron at small microvoids.
- τ_3 reach the value of 600 ps corresponding to vacancy clusters with n > 10 [3].



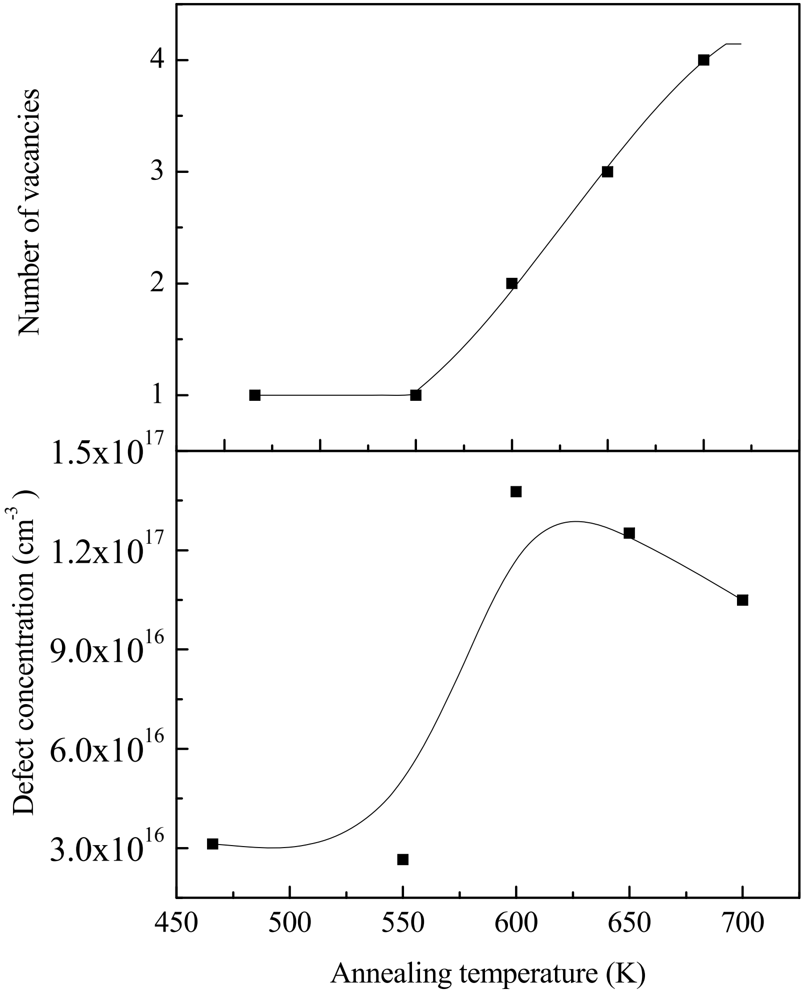
[3] T.E.M. Staab et. el. Physica B 273-274 (1999) 501.

GaAs:Cu

$$K_d = \mu\, C = \frac{1}{\tau_b}\left(\frac{\tau_{av} - \tau_b}{\tau_d - \tau_{av}}\right)$$

μ= 10^{15} s^{-1} at RT

n increase from 1 at 466 K
up to 4 vacancies at 700 K [3]

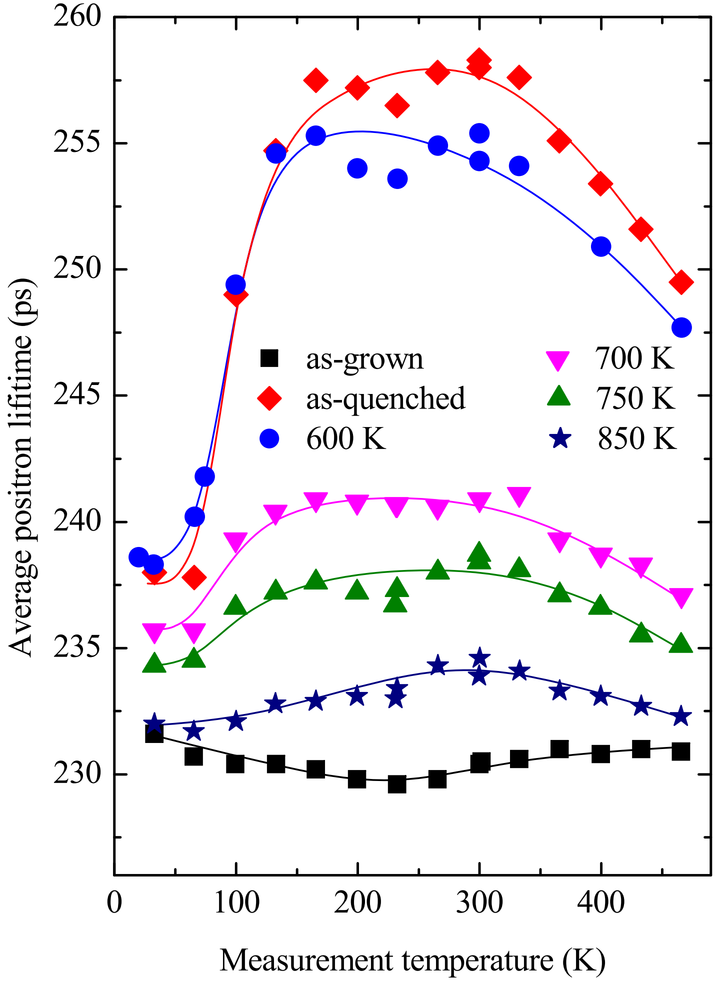


[3] T.E.M. Staab et. el. Physica B 273-274 (1999) 501.

GaAs:Cu

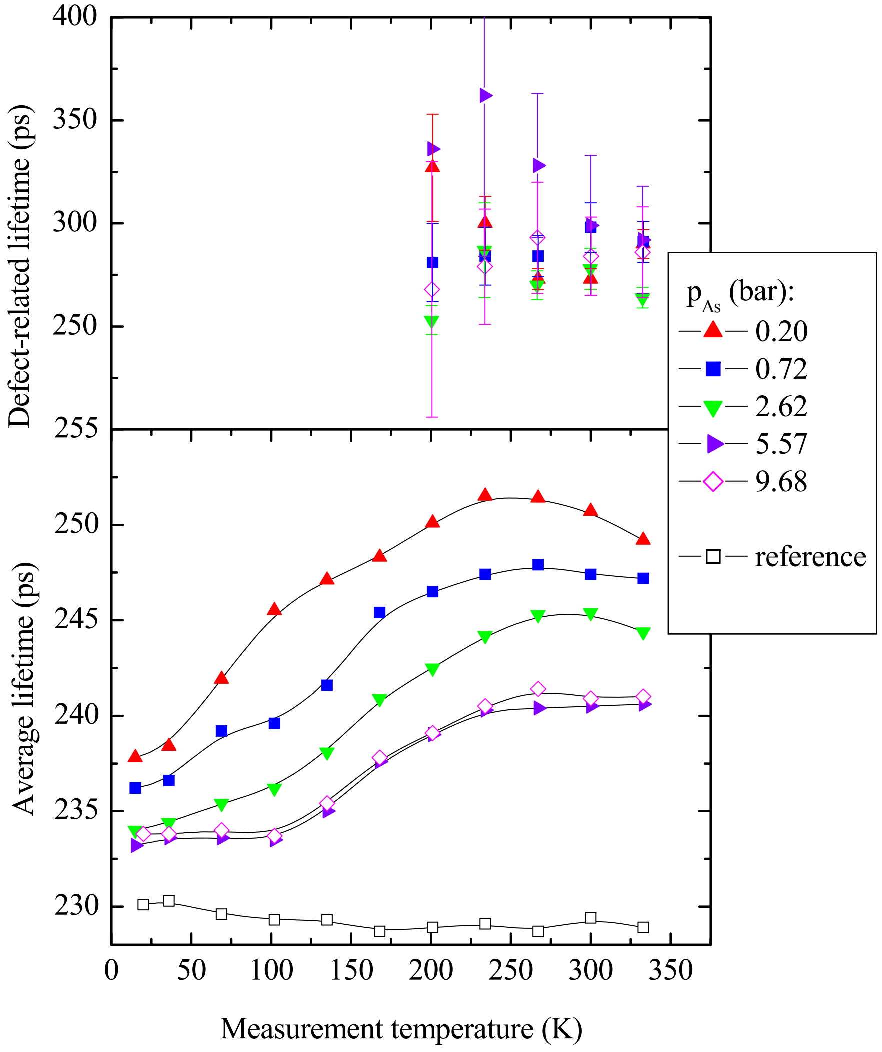
- SI GaAs sample was not treated with Cu and annealed at 1100 ^{o}Cunder 0.2 bar P_{As}

- As-quenched sample shows a higher $\tau_{av.}$
- In contrary, GaAs samples after Cu in-diffusion, almost no change of τ_{av} in the as-quenched state



GaAs:Cu

- Vacancy + shallow traps
- [V] and P_{As} exhibit reciprocal dependence
- $\tau_d = 293 \pm 10$ ps
- $\tau_d = 254$ and 262 ps in Te and Si doped GaAs
- $\tau_d = 330$ ps for V_{Ga}-V_{As}



GaAs:Cu

- P_{As} vacancy concentration dependence
  - concentration were determined at RT with $\mu = 10^{15}\ s^{-1}$
  - different slopes for GaAs:Si and SI GaAs
  - different vacancy sublattices
- Thermodynamic reactions

V_{Ga}:

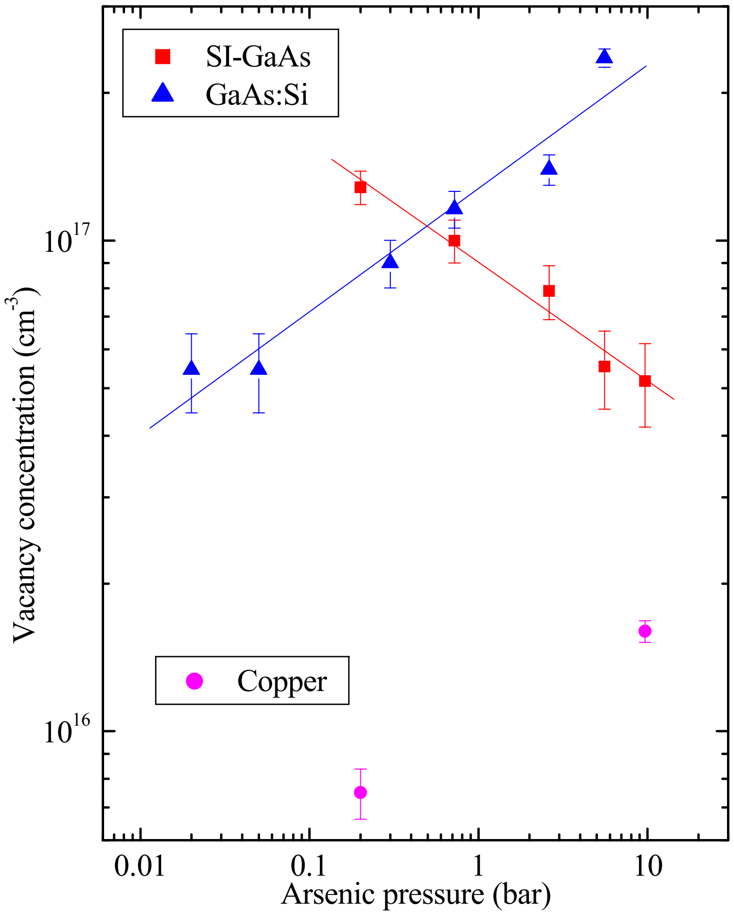
$$1/4As_4^{gas} \leftrightarrow As_{As} + V_{Ga}$$

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

V_{As}:

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

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

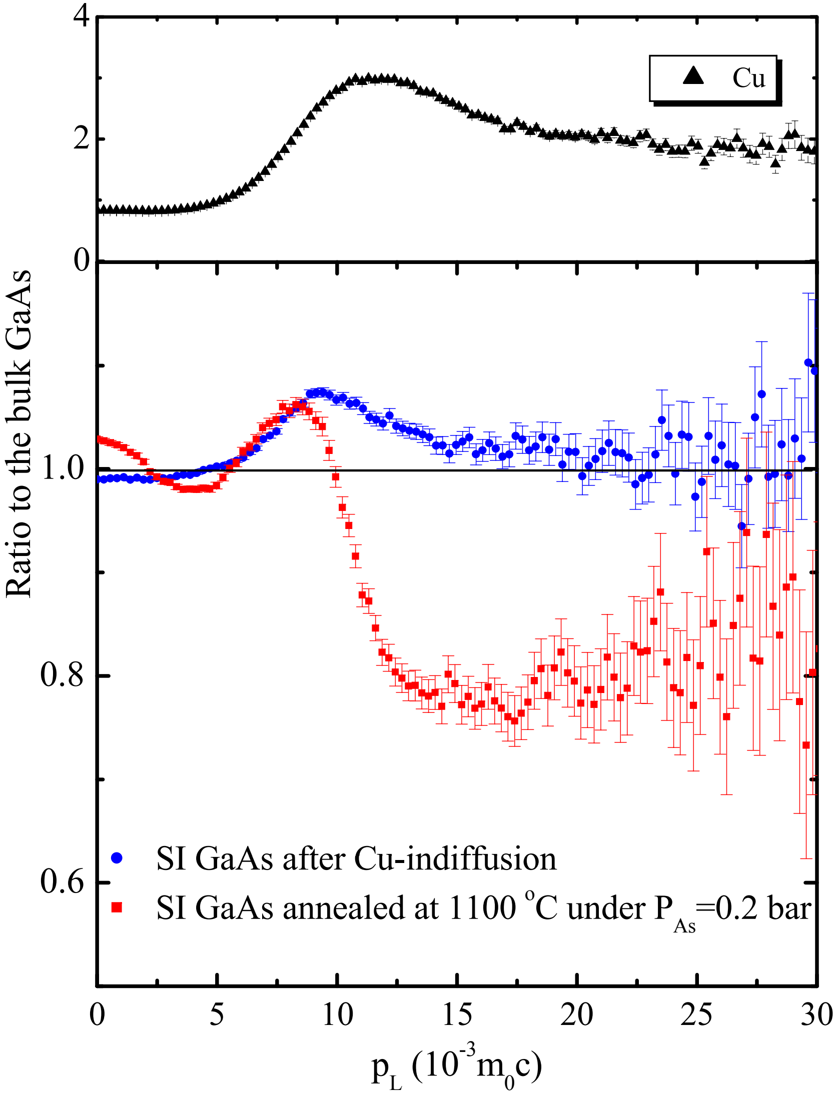


Fit: $\ln[V] = n x \ln(P_{As})$

- GaAs:Si n= 0.25 ± 0.03
- SI GaAs n= -0.24 ± 0.02

GaAs:Cu

- for e^+ annihilation with Cu core e^-, the ratio of high momentum part > 1 and presence of Cu in neighbor of e^+ trap seen as such characteristic increase in intensity of e^- e^+ momentum distribution
- no sign of Cu in vicinity of the detected vacancies in annealed GaAs
- Cu is not constitute of the defect complex
- V_{As}-like defect should be related to a native defect-complex



Conclusions

- Positron annihilation is a sensitive tool for investigation of vacancy-like defects and their charge states in semiconductors
- Vacancy-like defect and shallow traps were observed
- from the thermodynamics, defect complex contains V_{As}
- V_{As} is positively charged, vacancy complex containing an As vacancy was assumed
- CDBS, Cu is not a constituent of the defect complex
- vacancy complex represents a native defect complex but the structure can not be exactly recognized from e^+ annihilation parameters alone

Vielen Dank fuer Ihre Aufmerksamkeit