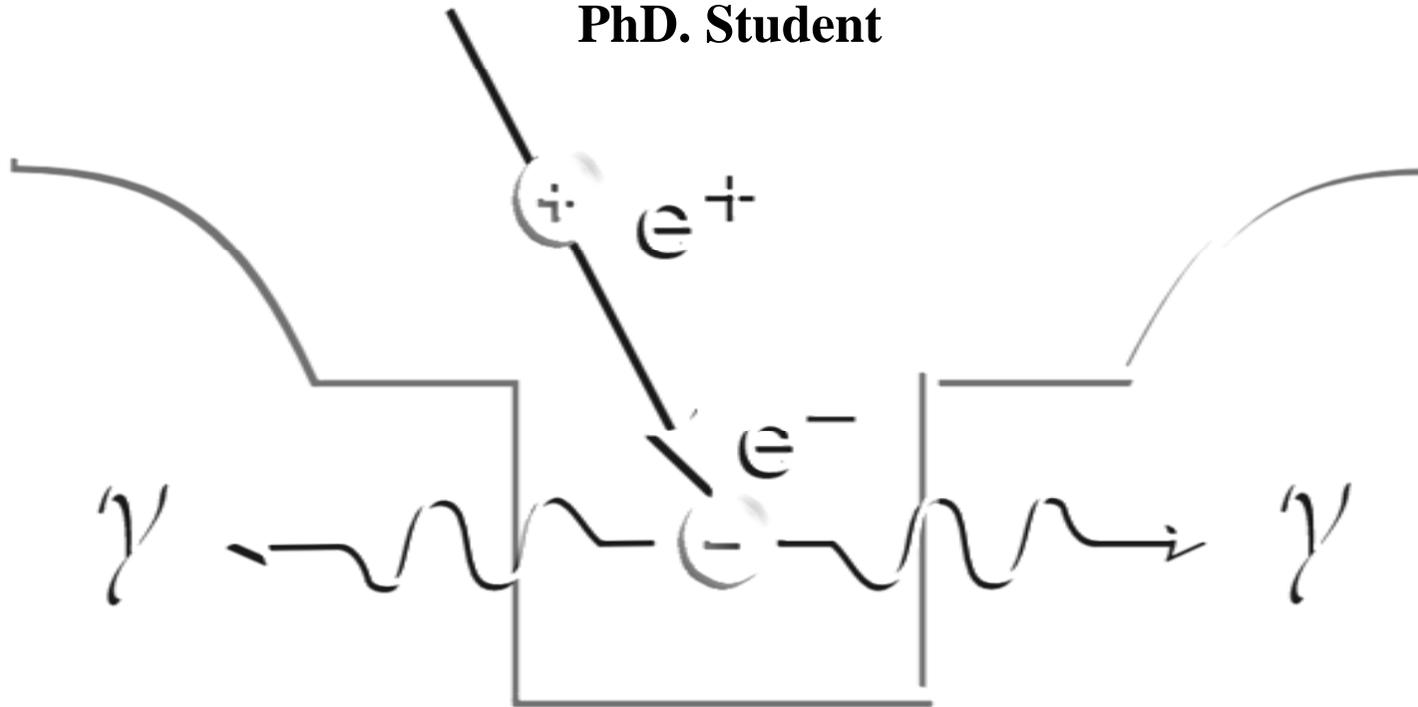


# Vacancy generation during Cu diffusion in GaAs

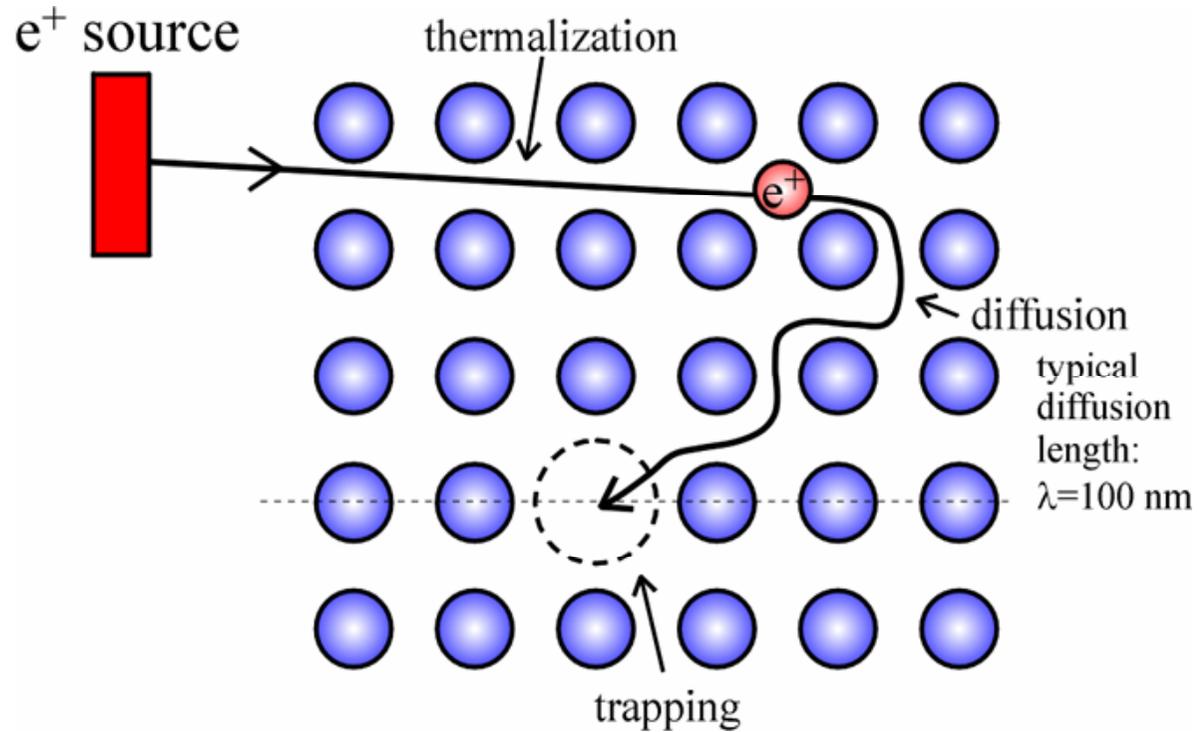
M. Elsayed  
PhD. Student



# Outlines

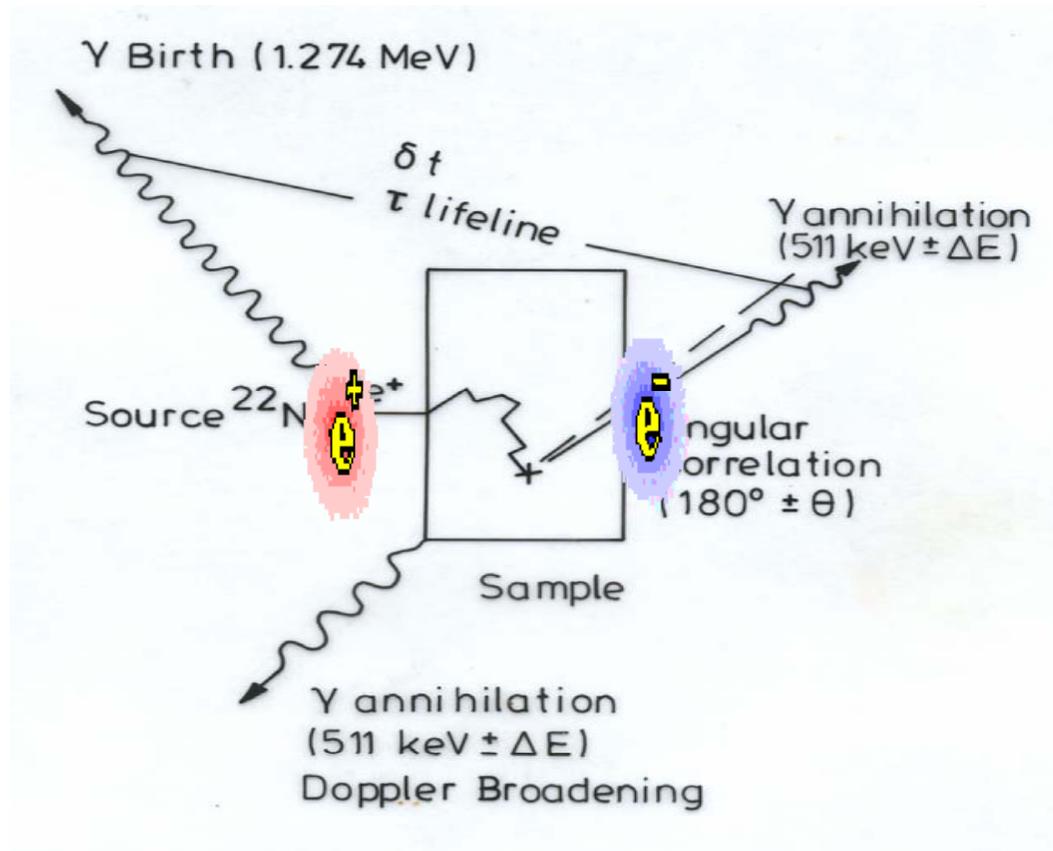
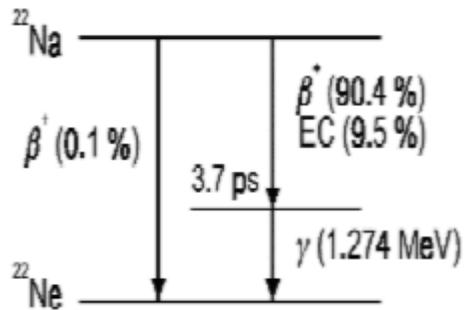
- Principles of PAS
- vacancy in Semiconductors and shallow positron traps
- Atomic diffusion mechanisms
- Observation of vacancies during Cu diffusion in GaAs
- Conclusion

# Principles of PAS

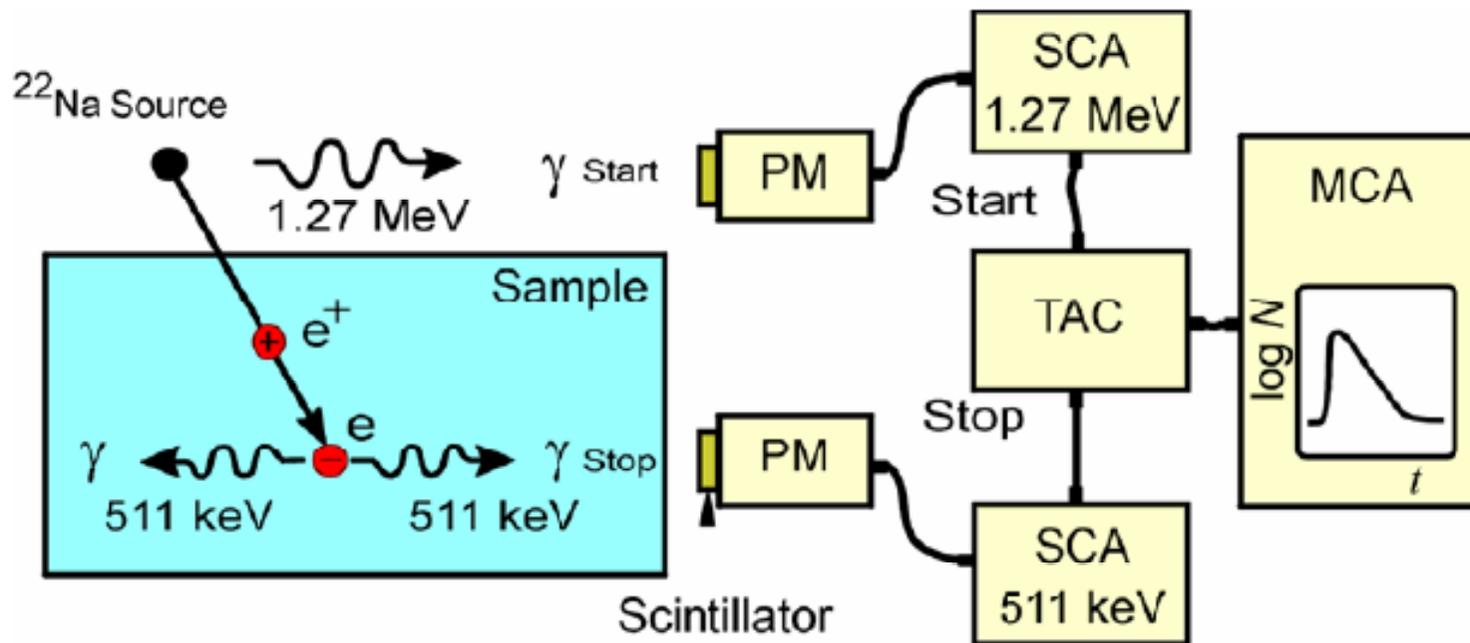


- **positrons:**
- thermalize
- diffuse
- being trapped
- **When trapped in vacancies:**  
Lifetime increases due to smaller electron density in open volume

# Principles of PAS



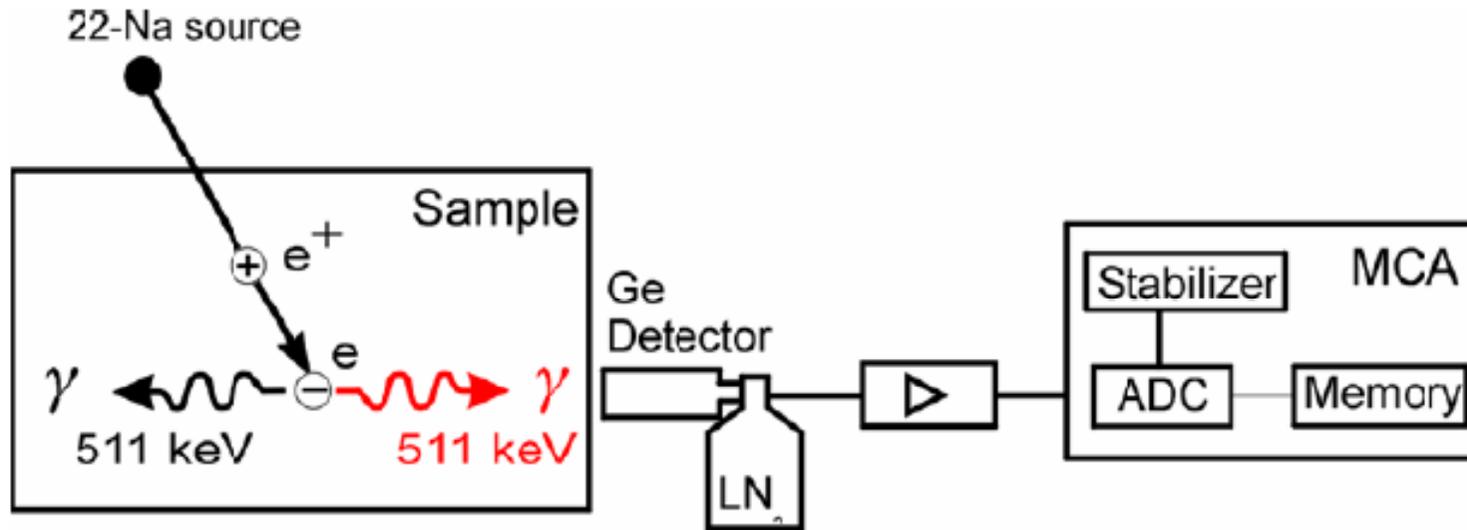
# Principles of PAS



- Positron lifetime is measured as time difference between  $1.27\text{ MeV}$  quantum and  $0.511\text{ MeV}$  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

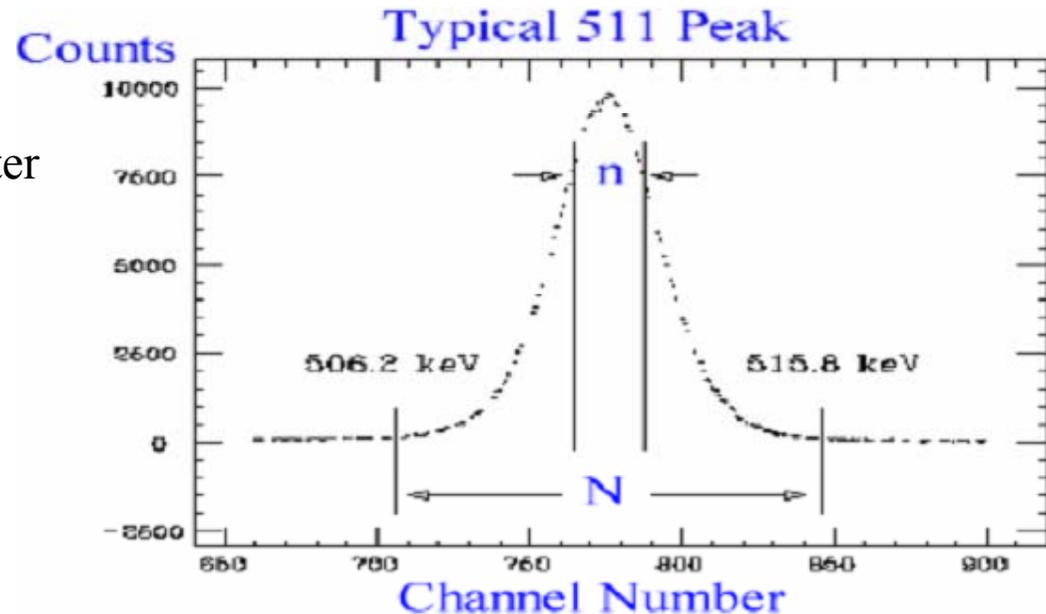


- electron momentum in propagation direction of 511 keV  $\gamma$ -ray leads to Doppler broadening of annihilation line
- can be detected by conventional energy-dispersive Ge detectors and standard electronics

# Principles of PAS

## Line Shape Parameters

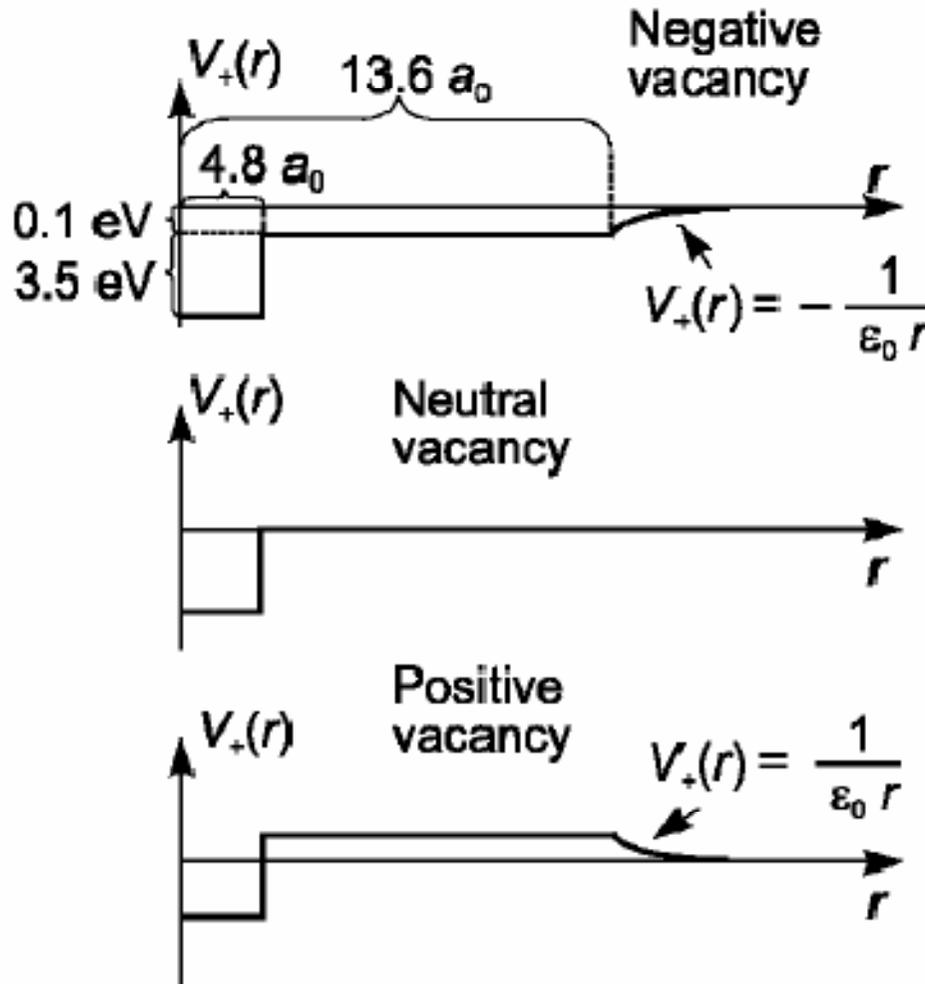
- Valance annihilation (Shape) parameter
- Core annihilation (Wing) parameter



- 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
- CDDBS
  - 2  $\gamma$ -detectors (germanium) simultaneously
  - better energy resolution and reduced background

# Vacancies in a semiconductor

Vacancies in a semiconductor may be charged



Puska et al. 1990

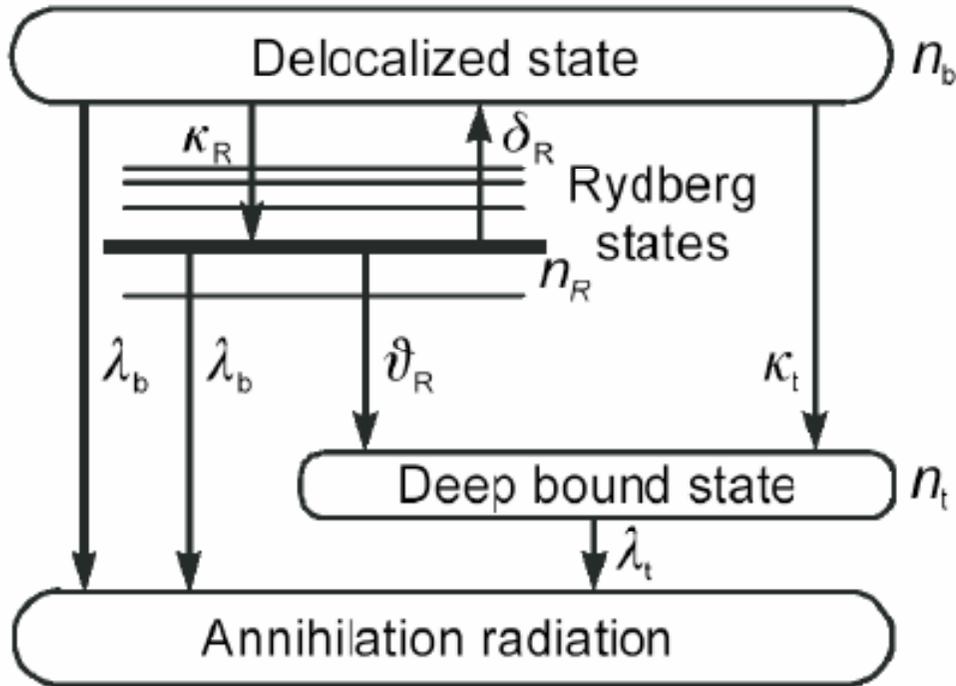
For a negative vacancy:

- 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



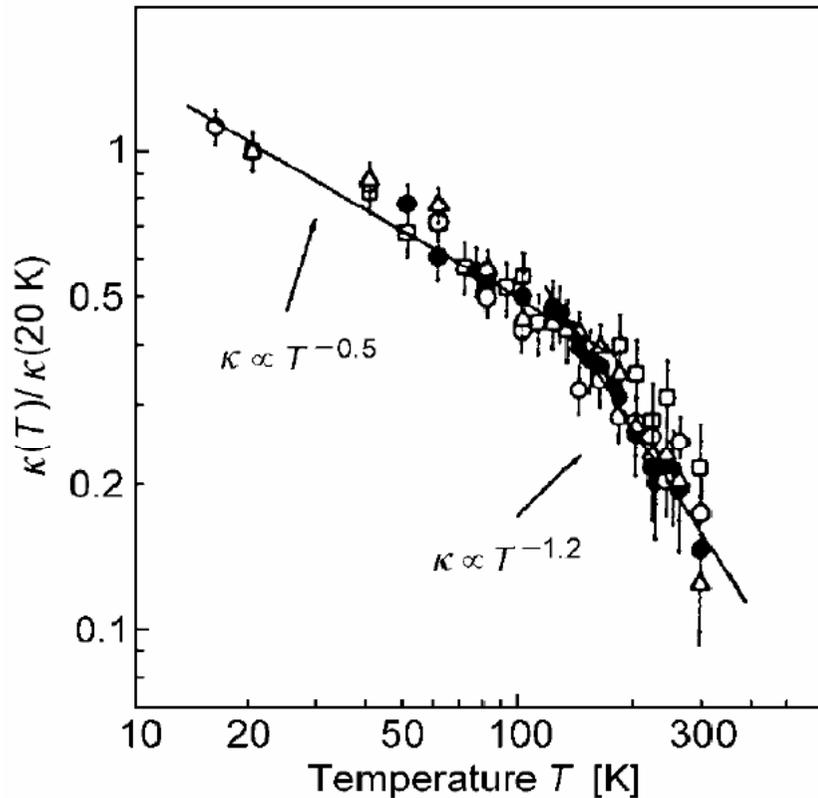
- trapping process can be described quantitatively by trapping model
- Coulomb potential leads to Rydberg states
- from there: positrons may reescape by thermal stimulation
- once in the deep state: positron is captured until annihilation
- detrapping is strongly temperature dependent

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

Manninen, Nieminen, 1981

# Vacancies in a semiconductor

## Negative vacancies show temperature-dependent positron trapping



- dependence of positron trapping on temperature is rather complex

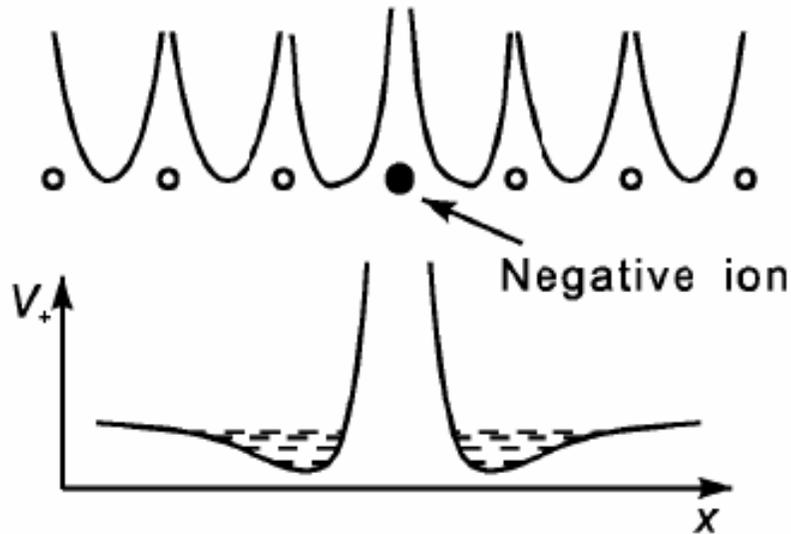
$$\kappa = \frac{\mathcal{G}_R \rho_V \kappa_{R_o} T^{-1/2}}{\mathcal{G}_R \rho_V + \kappa_{R_o} \left( \frac{m^* k_B}{2\pi\hbar^2} \right)^{3/2} T \exp\left( -\frac{E_R}{k_B T} \right)}$$

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

positron trapping in negatively charged Ga vacancies in SI-GaAs

Le Berre et al., 1995

## Shallow positron traps



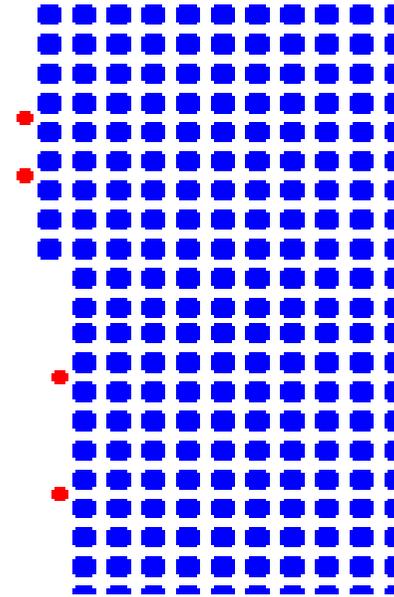
- at low T: negatively charged defects without open volume may trap positrons and trapping is based on the capture of positron in Rydberg states
- “shallow” refer to small positron binding energy
- acceptor-type impurities, negative antisite defects
- annihilation parameters close to bulk parameters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

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

# 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

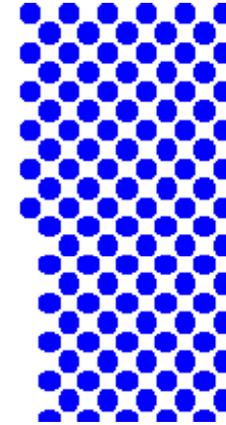


# Atomic diffusion mechanisms

## 2. Simple Vacancy Exchange & Interstitialcy Mechanisms

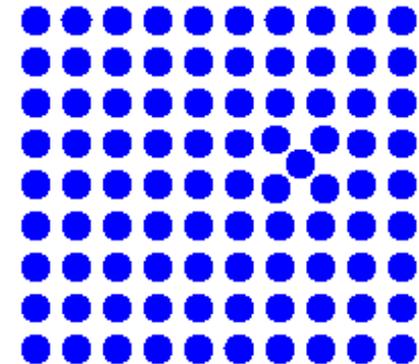
- In a simple vacancy exchange mechanism, substitutional atom jumps into a neighbor vacancy on the lattice

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



- 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

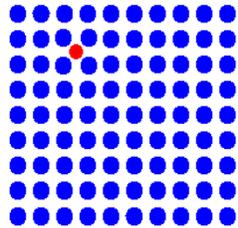
$$D_s^I \propto C_I^{\text{eq}}$$



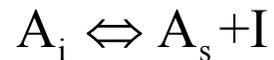
# Atomic diffusion mechanisms

## 3- Interstitial- Substitutional Mechanism

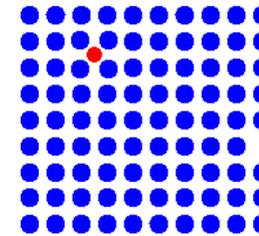
### 3.1- Kick-out mechanism



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



### 3.2- Frank Turnbull mechanism



- is qualitatively different from vacancy exchange mechanism

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



## 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
- $C > C^{\text{eq}}$  induced by optical excitation or particle irradiation

## Observation of vacancies during Cu diffusion in GaAs

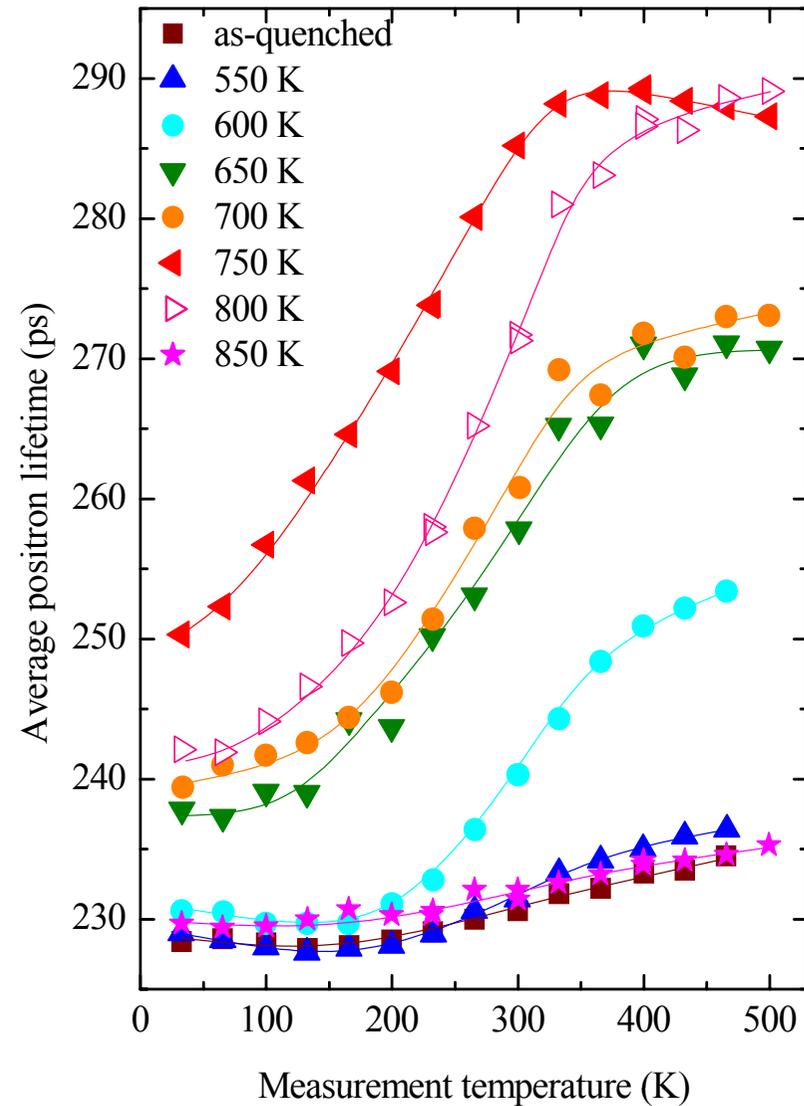
- Copper is an unintentional impurity in most semiconductors
- Cu diffuses rapidly already at low temperatures
- GaAs: diffusion coefficient  $D = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at  $500^\circ\text{C}$  [1]
- Cu diffuses very fast by interstitial diffusion (kick-out process) [2]
- The solubility between  $2 \times 10^{16} \text{ cm}^{-3}$  ( $500^\circ\text{C}$ ) and  $7 \times 10^{18} \text{ cm}^{-3}$  ( $1100^\circ\text{C}$ ) [1]
- $\text{Cu}_{\text{Ga}}$  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  $1100^\circ\text{C}$  under different  $P_{\text{As}}$  (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.

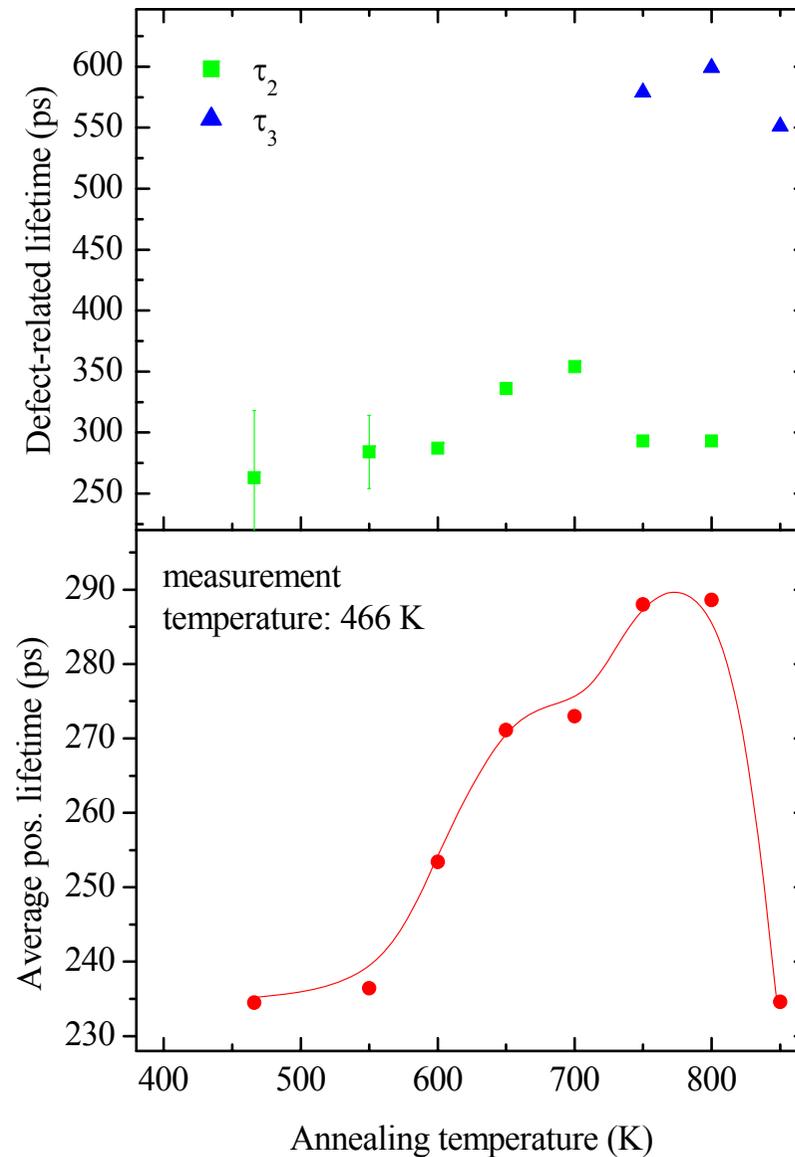
# GaAs:Cu

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



# GaAs:Cu

- $\tau_d$  is much higher than that for monovacancies (250-260 ps)
- from  $\tau_d$  open volume increases during annealing
- this explained by trapping of positron at small microvoids.
- $\tau_3$  reach the value of 600 ps corresponding to vacancy clusters with  $n > 10$  [3].



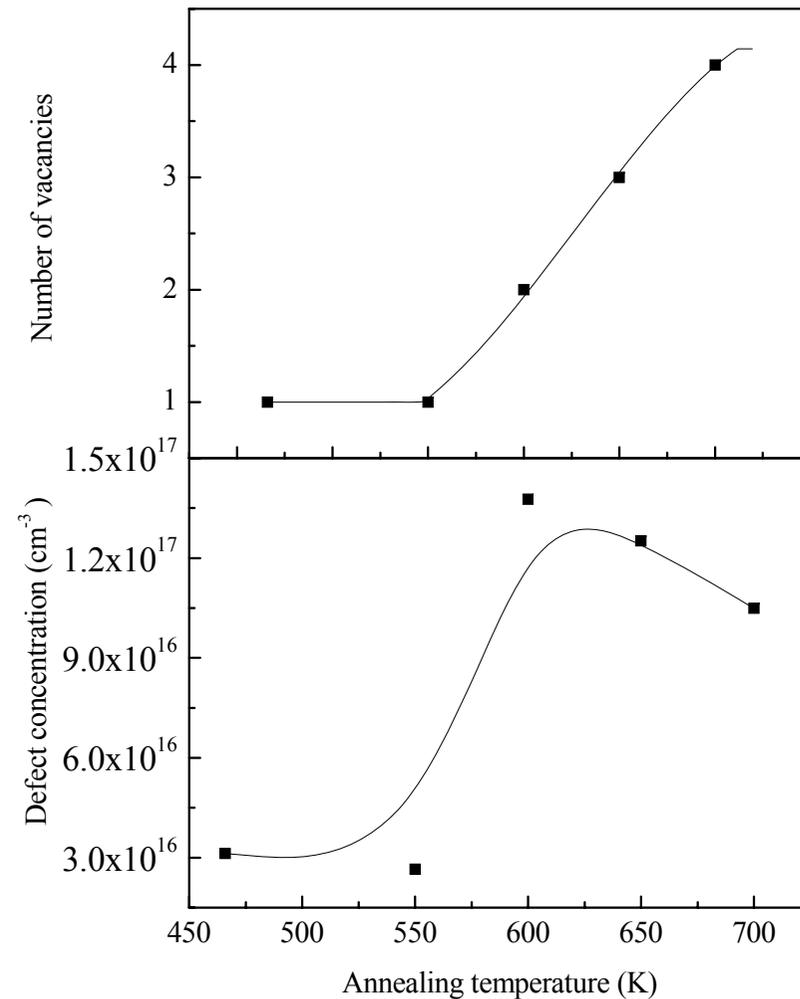
[3] T.E.M. Staab et. el. Physica B 273-274 (1999) 501.

# GaAs:Cu

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

$\mu = 10^{15} \text{ s}^{-1}$  at RT

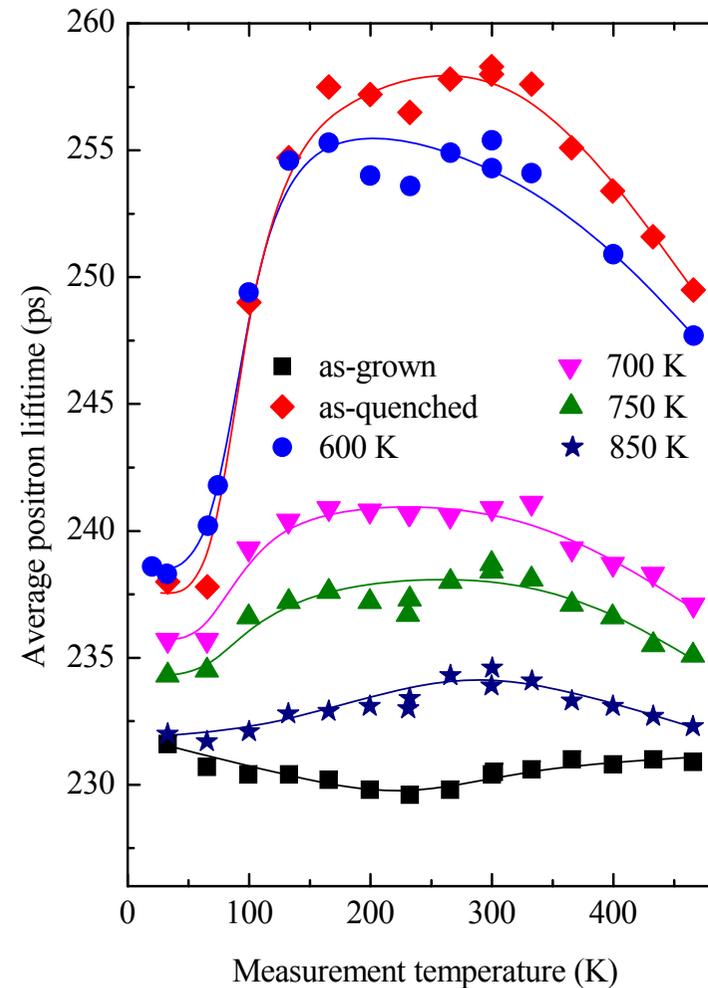
**n** increase from 1 at 466 K  
up to 4 vacancies at 700 K [3]



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

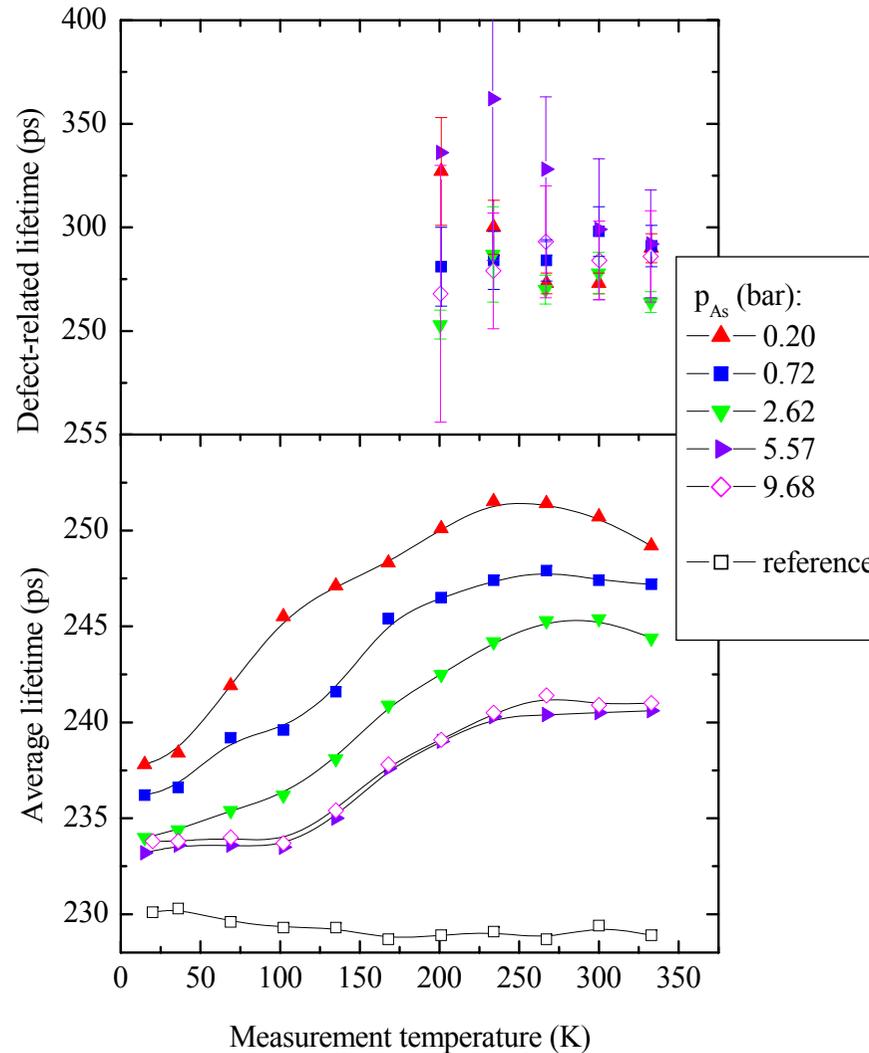
# GaAs:Cu

- SI GaAs sample was not treated with Cu and annealed at 1100 °C under 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  $\tau_{av}$  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

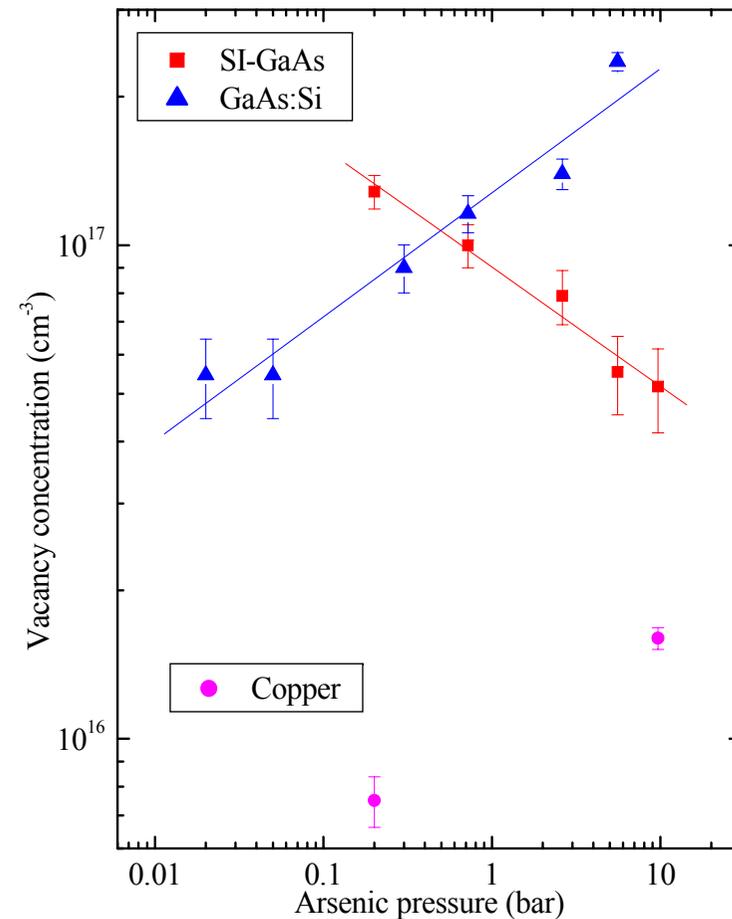
- $P_{As}$  vacancy concentration dependence
  - concentration were determined at RT with  $\mu = 10^{15} \text{ s}^{-1}$
  - different slopes for GaAs:Si and SI GaAs
  - different vacancy sublattices
- Thermodynamic reactions



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



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



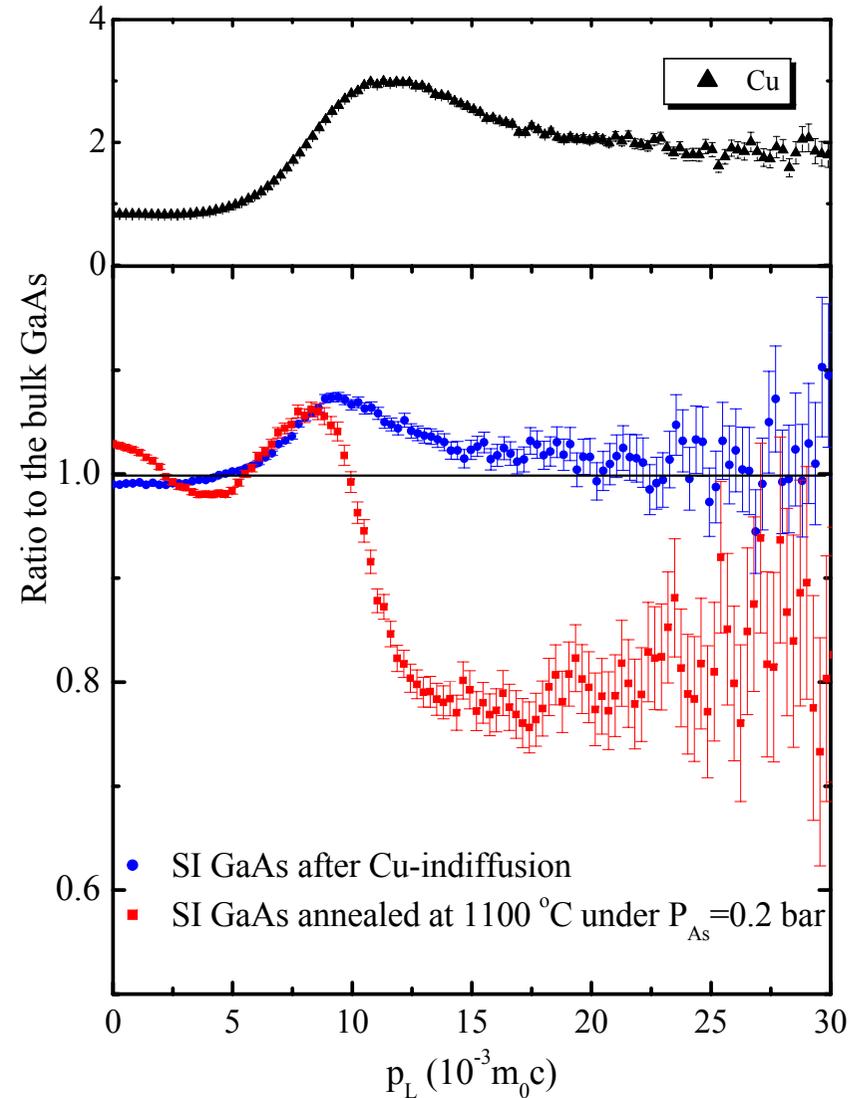
$$\text{Fit: } \ln[V] = n \times \ln(P_{As})$$

$$\text{- GaAs:Si } n = 0.25 \pm 0.03$$

$$\text{- SI GaAs } n = -0.24 \pm 0.02$$

# 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