Identification of Defects in GaAs:Te after Cu in-diffusion by Positron annihilation

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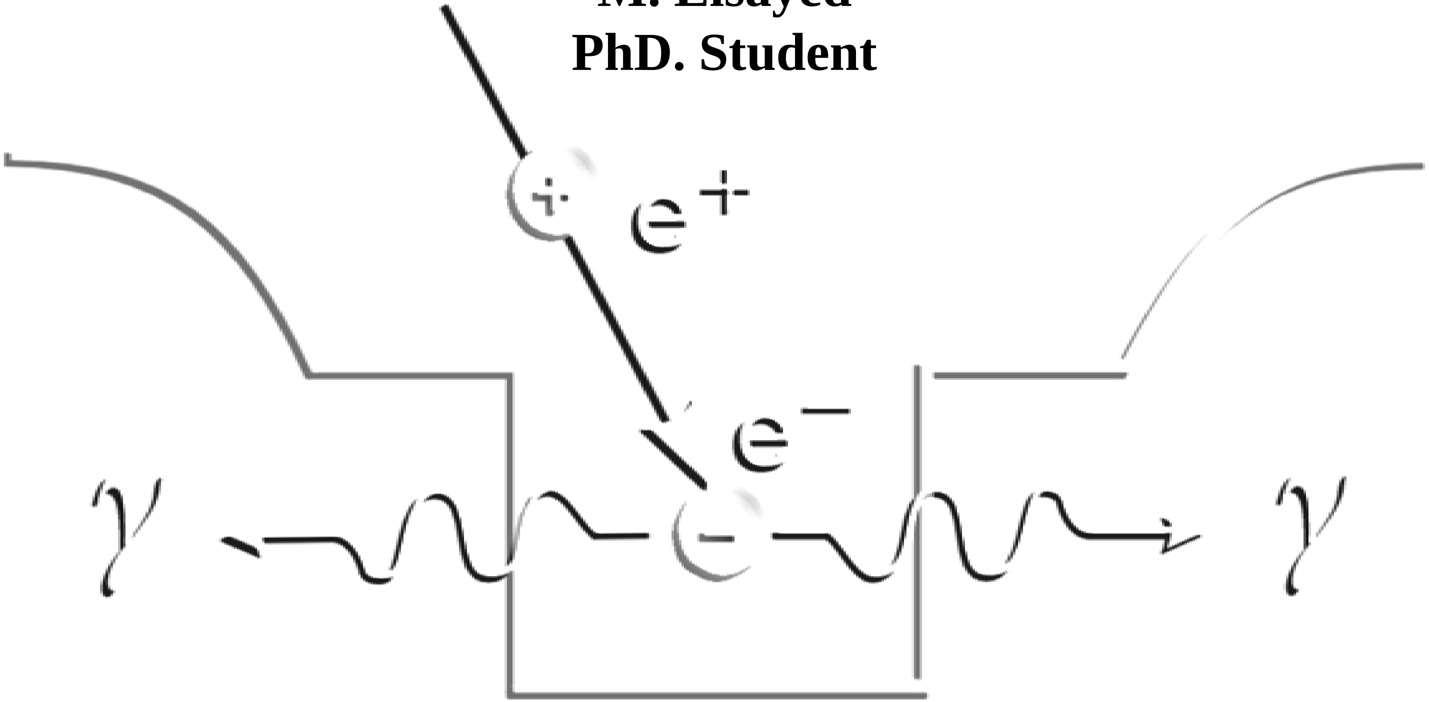

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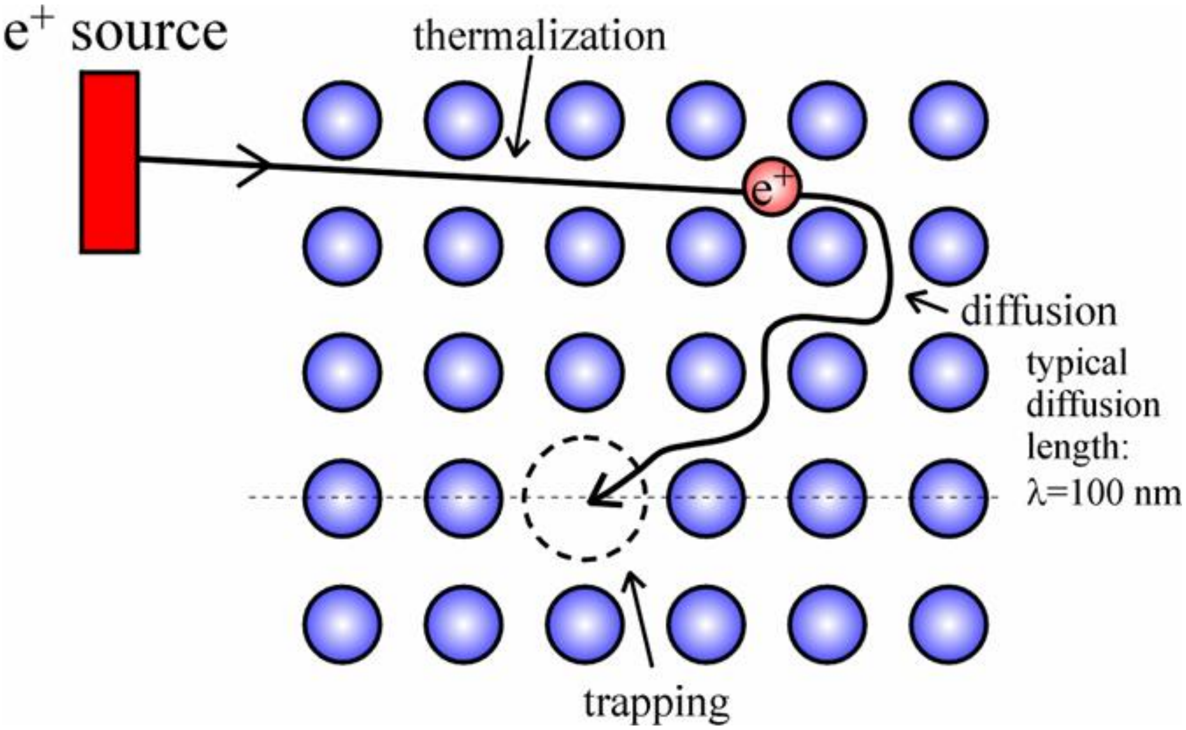
Outlines

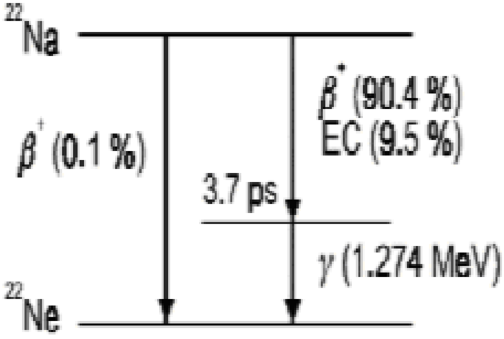
- ☐ Introduction to PAS
- ☐ Vacancies in Semiconductors and shallow positron traps
- ☐ Diffusion mechanisms and experimental methods for measuring depth profile
- ☐ Observation of vacancies during Cu diffusion in GaAs:Te
- ☐ Conclusion

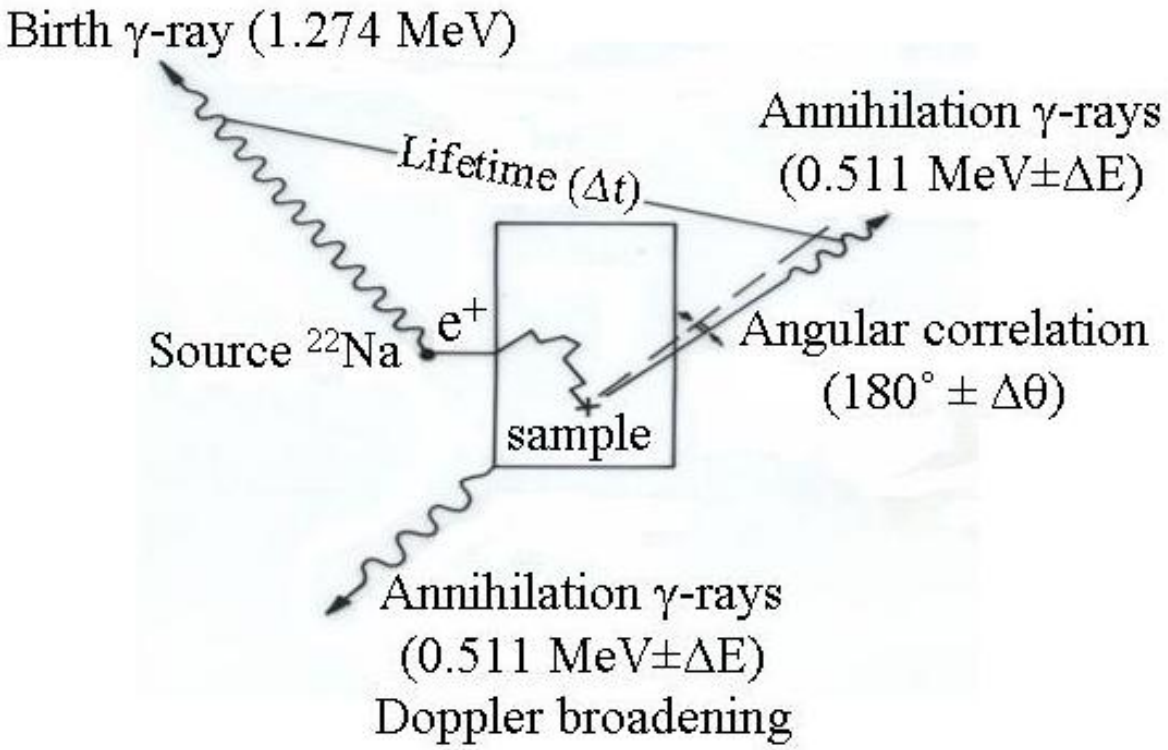
Introduction to PAS



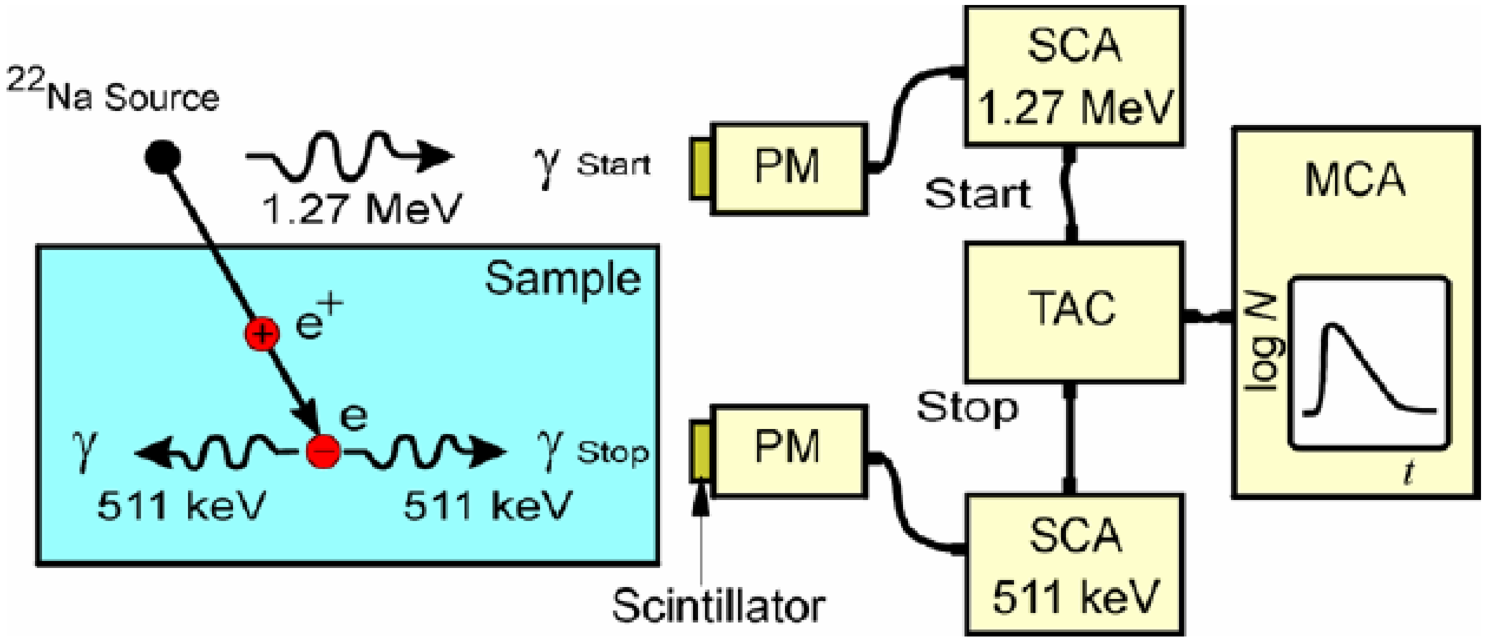
- **positrons:**
- thermalize
- diffuse
- being trapped
- **When trapped in vacancies:** Lifetime increases due to smaller electron density in open volume

Introduction to PAS





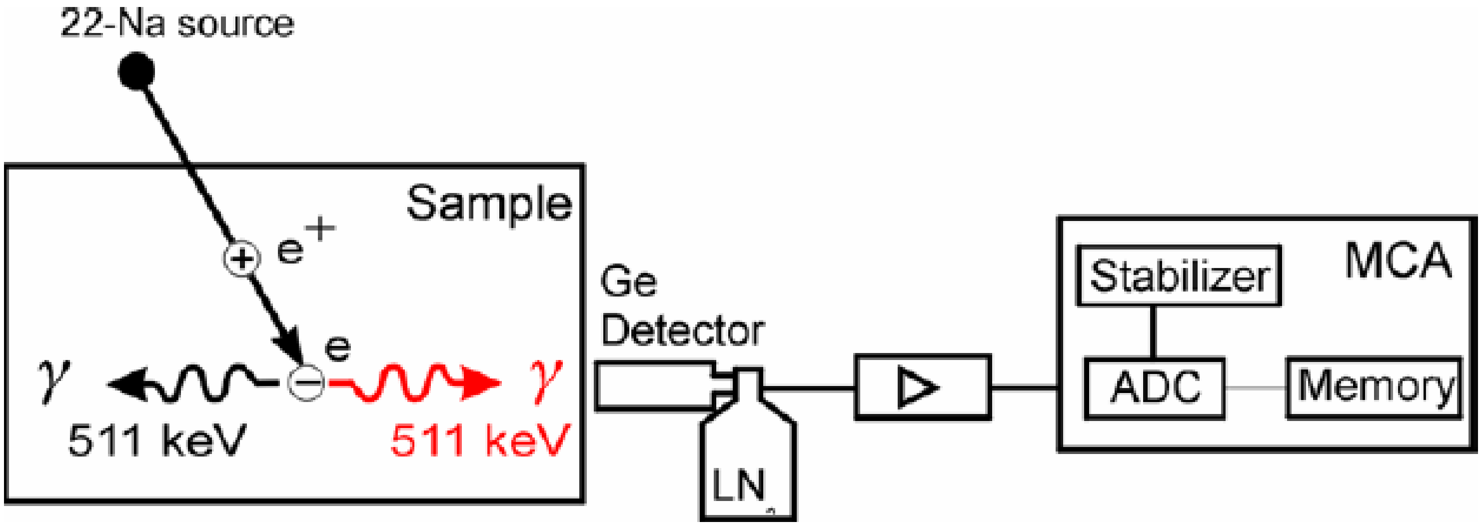
Introduction to PAS



- 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

Introduction to 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.

Introduction to PAS

Line Shape Parameters

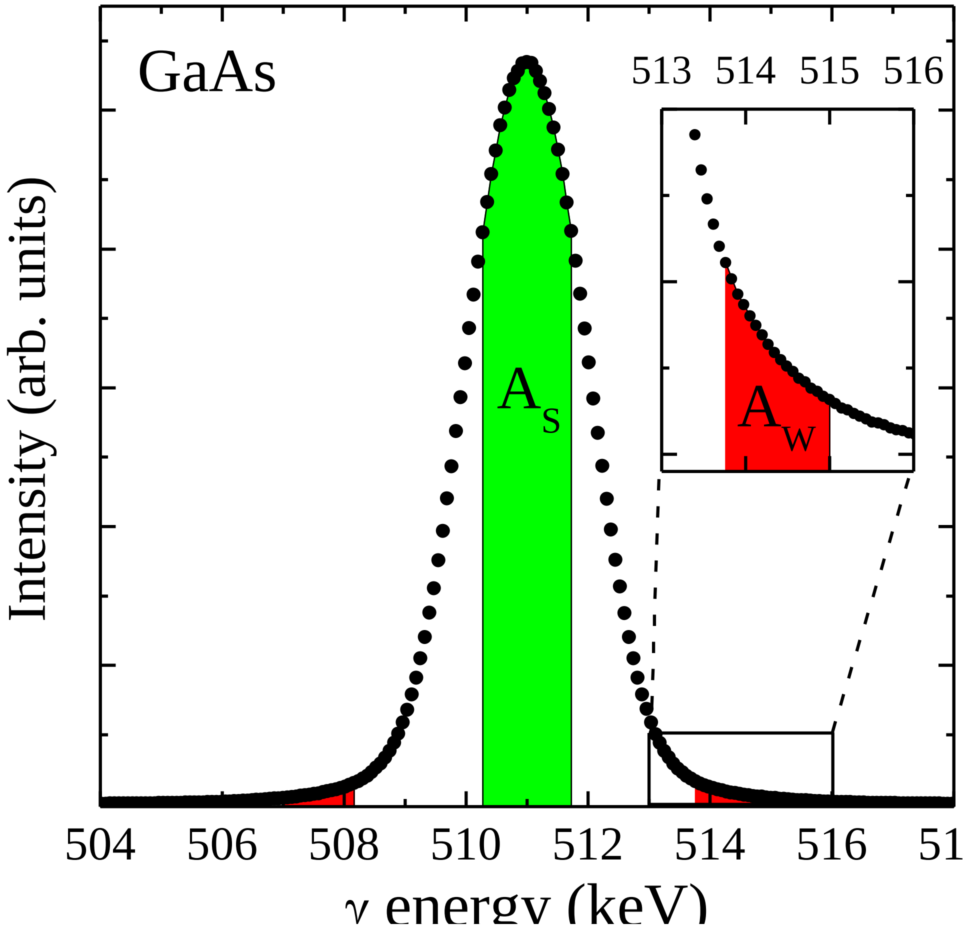
- Valance annihilation (Shape) parameter

$$S = \frac{A_s}{A_o} = \int_{E_0 - E_s}^{E_0 + E_s} N_D dE$$

- Core annihilation (Wing) parameter

$$W = \frac{A_w}{A_o} = \int_{E_1}^{E_2} N_D dE$$

- 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

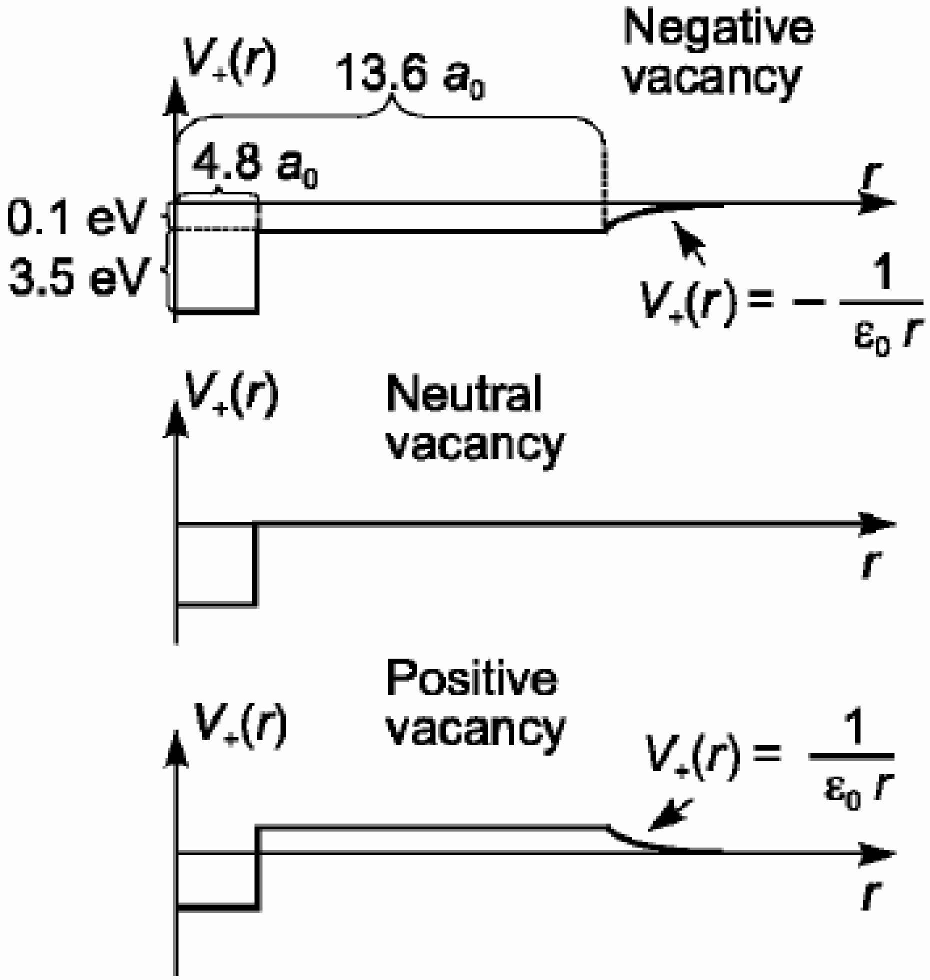


- CDBS

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

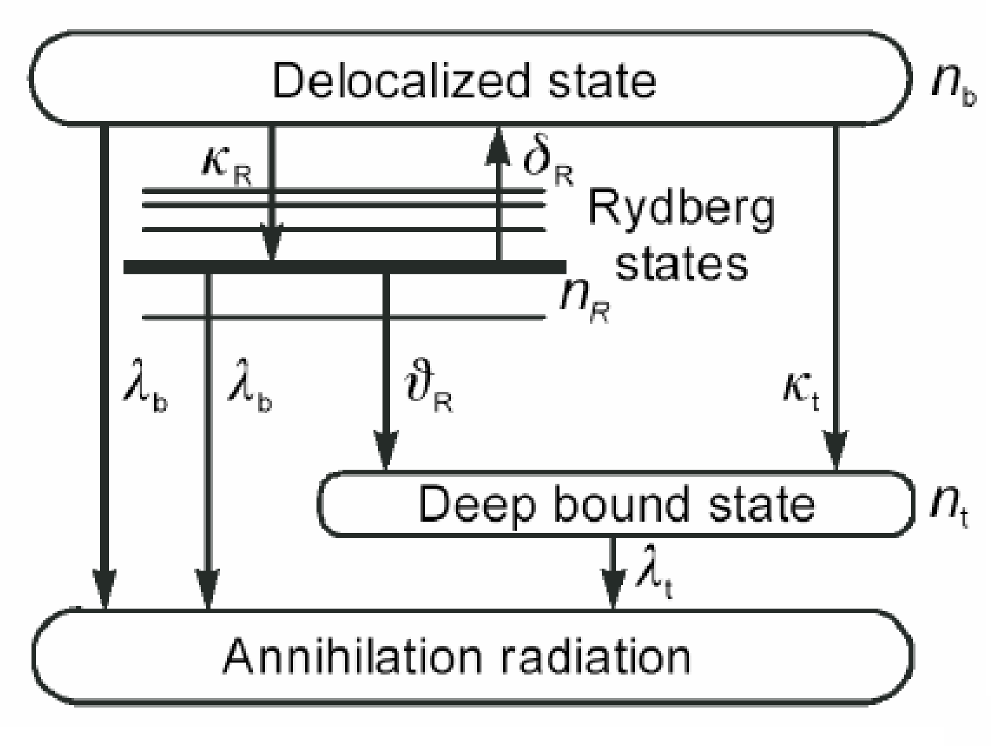
For a negative vacancy:

- 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

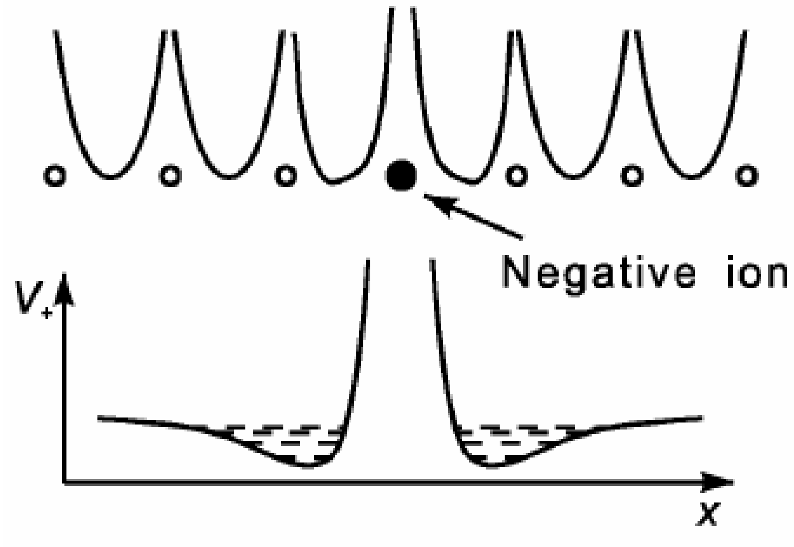


- trapping process can be described quantitatively by trapping model
- Coulomb potential leads to Rydberg states
- from there: positrons may reescape by thermal stimulation
- once in the deep state: positron is captured until annihilation
- detrapping is strongly temperature dependent

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

[1] Manninen, Nieminen, 1981

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:

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

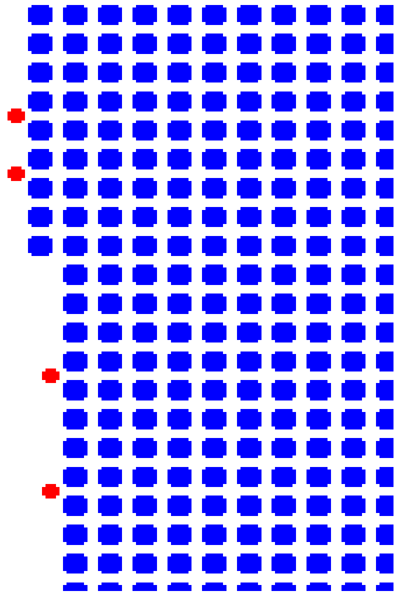
[2] Saarrinen et al., 1989

Diffusion mechanisms

1- Diffusion without involvement of native point defect

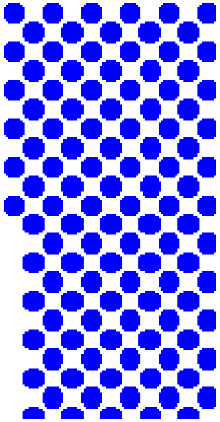
- Interstitially dissolved impurity atoms diffuse by jumping between interstitial sites

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



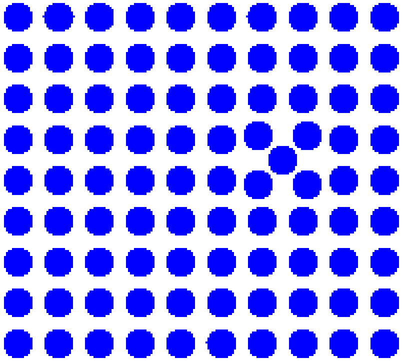
Diffusion mechanisms

2. Simple Vacancy Exchange & Interstitialcy Mechanisms



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

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



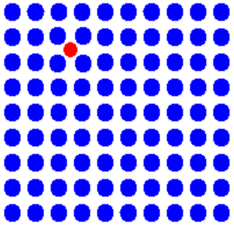
- In interstitialcy Mechanism (interstitial), the substitutional atom is first replaced by a self-interstitial and pushed into an interstitial position, it pushes out one of the neighbor atom in the lattice

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

Diffusion mechanisms

3- Interstitial- Substitutional Mechanism

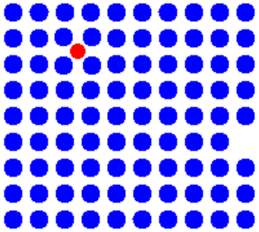
3.1- Kick-out mechanism



- 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

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

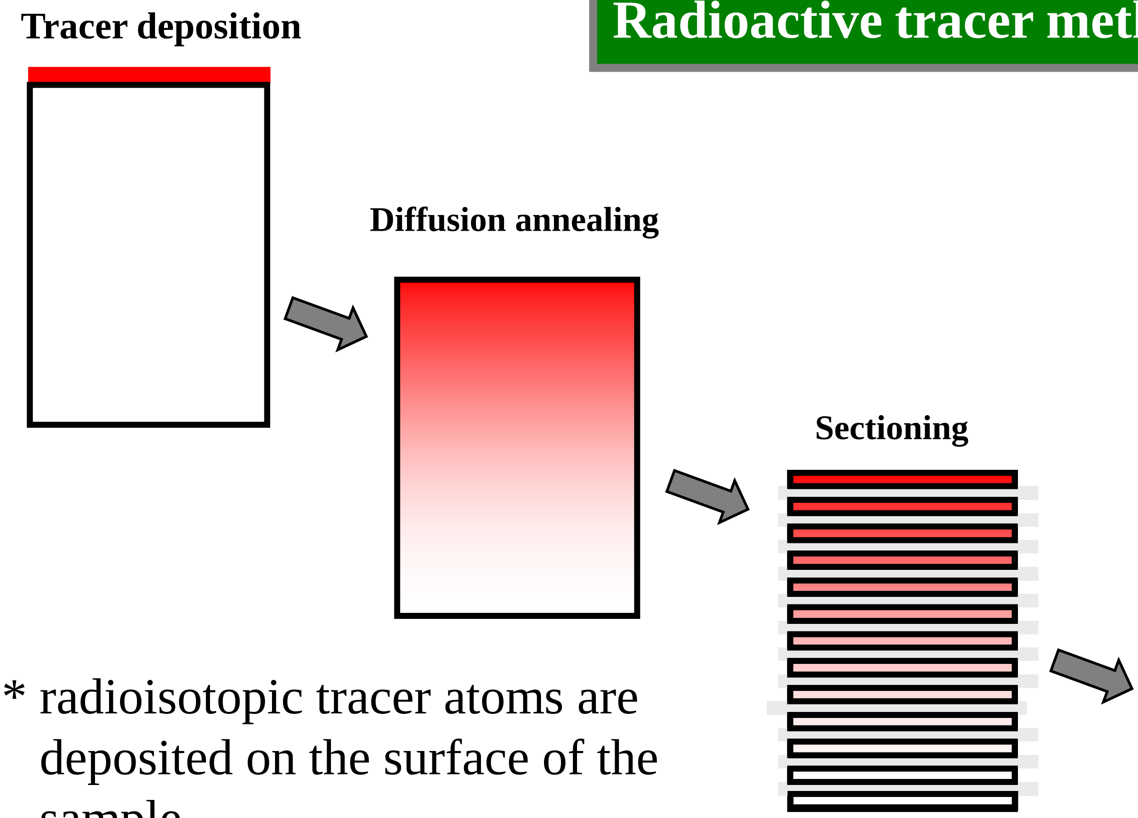
$$A_i + V \Leftrightarrow A_s$$

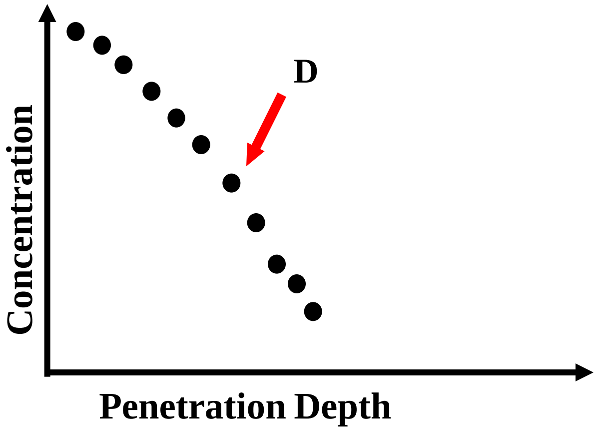
4- Recombination-Enhanced diffusion

- 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

Diffusion profile measurement

Radioactive tracer method





* radioisotopic tracer atoms are deposited on the surface of the sample

* isothermal diffusion is performed for a given time t

* thin layers are removed from the sample either mechanically or chemically

* concentration of the element is determined then the diffusivity can be determined

Diffusion profile measurement

SIMS

The sample is bombardment by high energy ions. The sputtered material is mass analyzed to determine the composition of the substrate

Advantages:

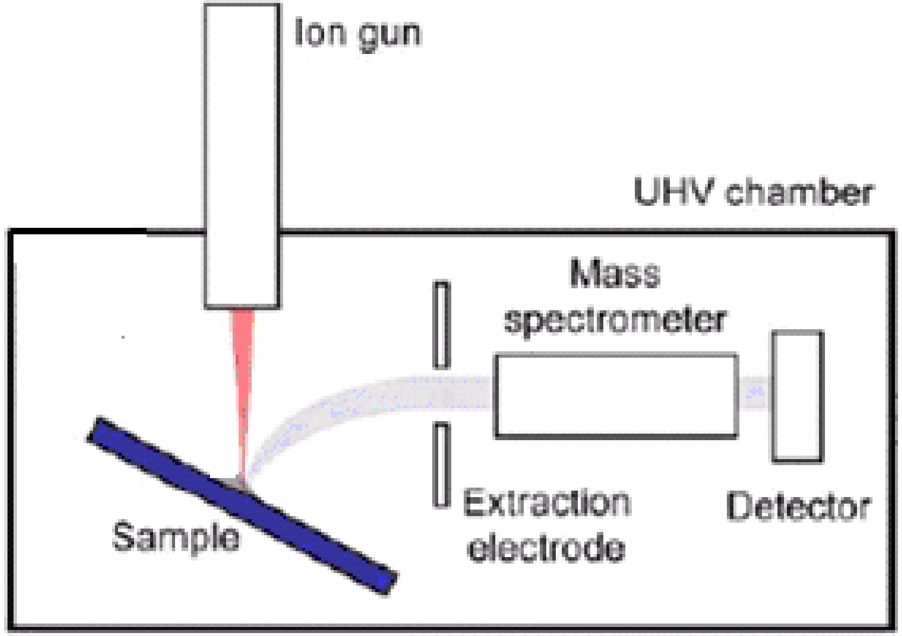
* Detection all elements.

* Identify elements to very low concentration

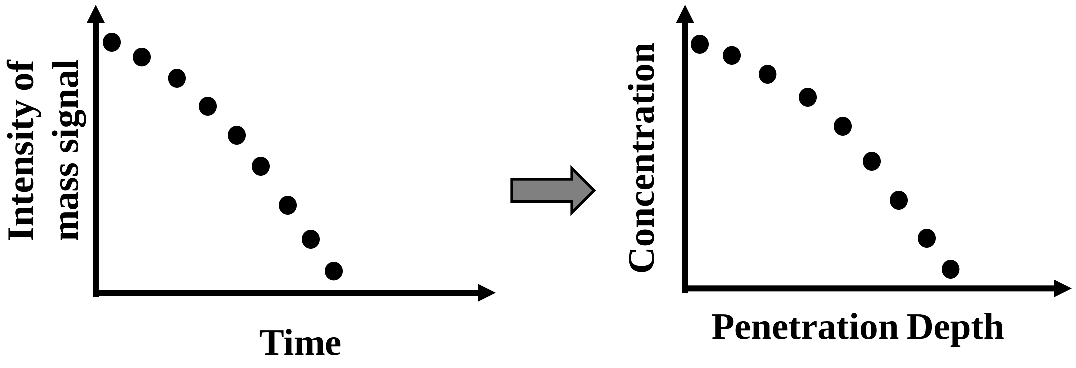
Drawbacks:

* destructive technique.

* Depth resolution is limited by sputter process which depends on the range of beam diameter.

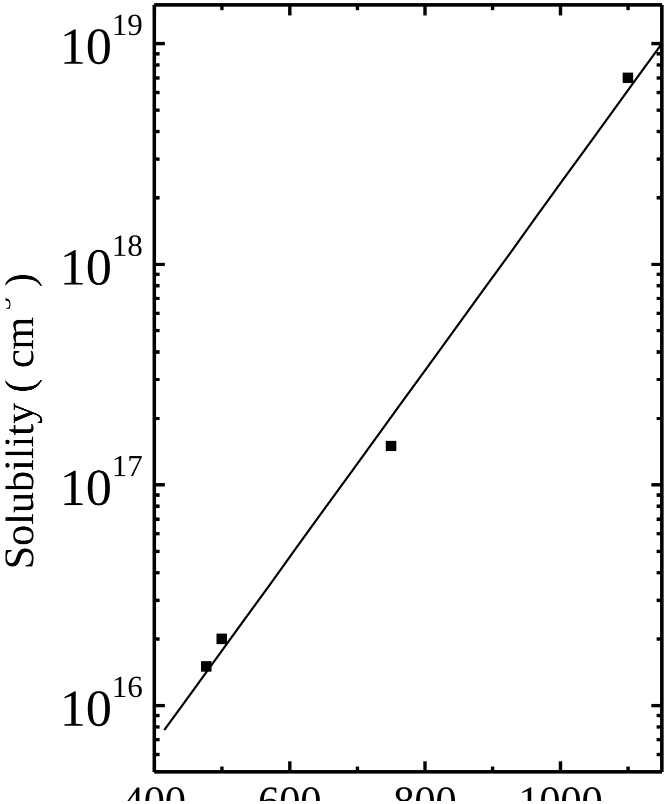


The depth profile is obtained by recording the sequential SIMS spectra as the surface is gradually eroded away by the incident ion beam.



Observation of vacancies during Cu diffusion in GaAs:Te

- 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 [3]
- Cu diffuses very fast by interstitial diffusion (kick-out process) [4]
- The solubility between 2×10^{16} cm^{-3} (500 °C) and 7×10^{18} cm^{-3} (1100 °C) [5]
- Cu_{Ga} is a double acceptor



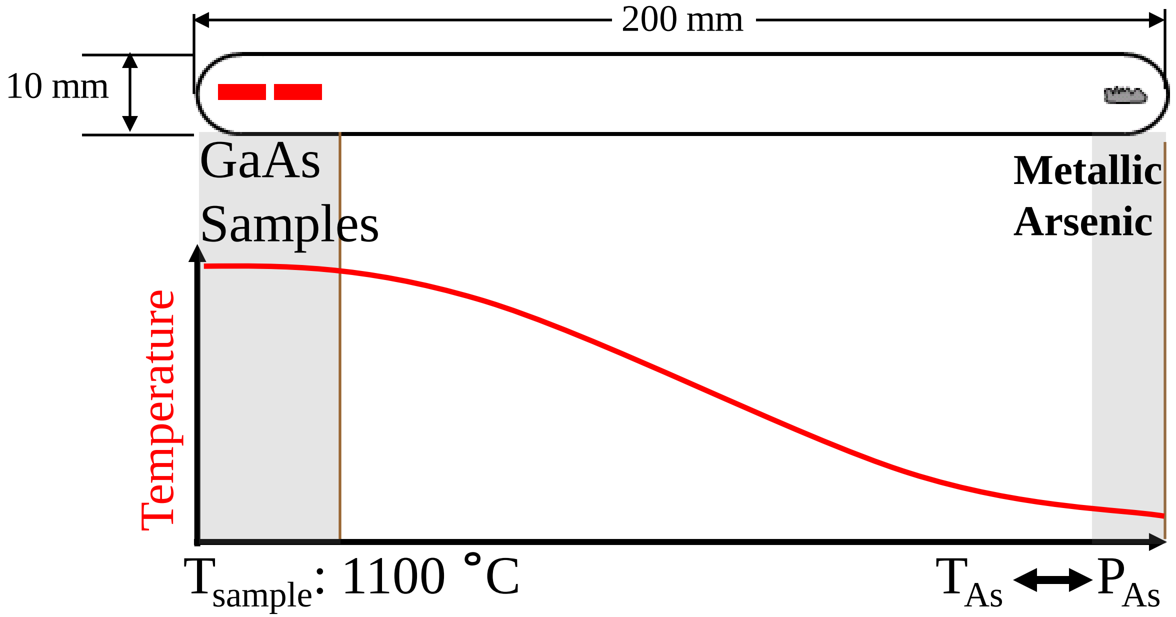
[3] R.N. Hall and J.H. Racette, J. Appl. Phys. 35 (1964) 379.

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

[5] M. Elsayed et al., J. Appl. Physics 104 (2008) 103526

Te doped GaAs:Cu

Diffusion procedure

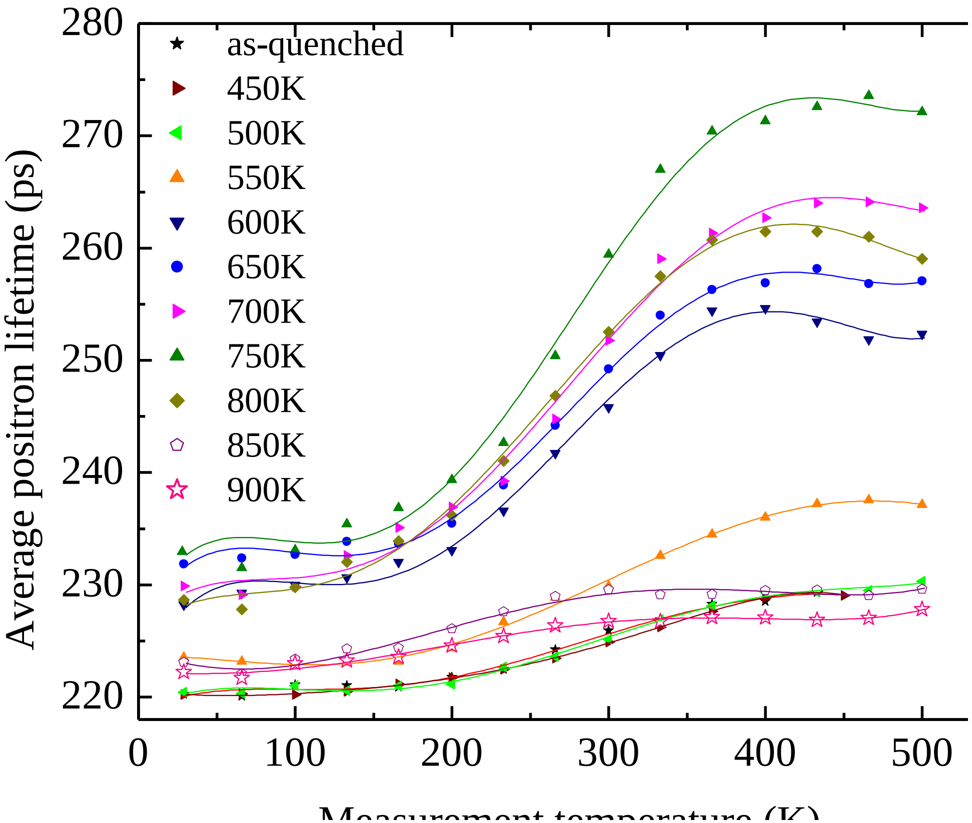


* two-zone-furnace: Control of sample temperature and As partial pressure
* Experimental: 0.55 mm samples covered by 35 nm Cu, annealed at 1100 °C under different P_{As} (0.2-10 bar), quenched in RT water and subject to isochronal annealing up to 900 K.

* work: comprehensive positron annihilation study of GaAs after Cu in-diffusion

Te doped GaAs:Cu

- annealed at 1100 °C under 10 bar P_{As}
- as-quenched shows $\tau_{av} = \tau_b = 228$ ps in the high temperature region.
- decrease of τ_{av} at low T shallow positron traps (Cu_{Ga}).
- up to 750 K, τ_{av} increase strongly to 275 ps- detected vacancy must be lager than V_{Ga}.
- annealing > 800 K, the vacancy signal disappear.



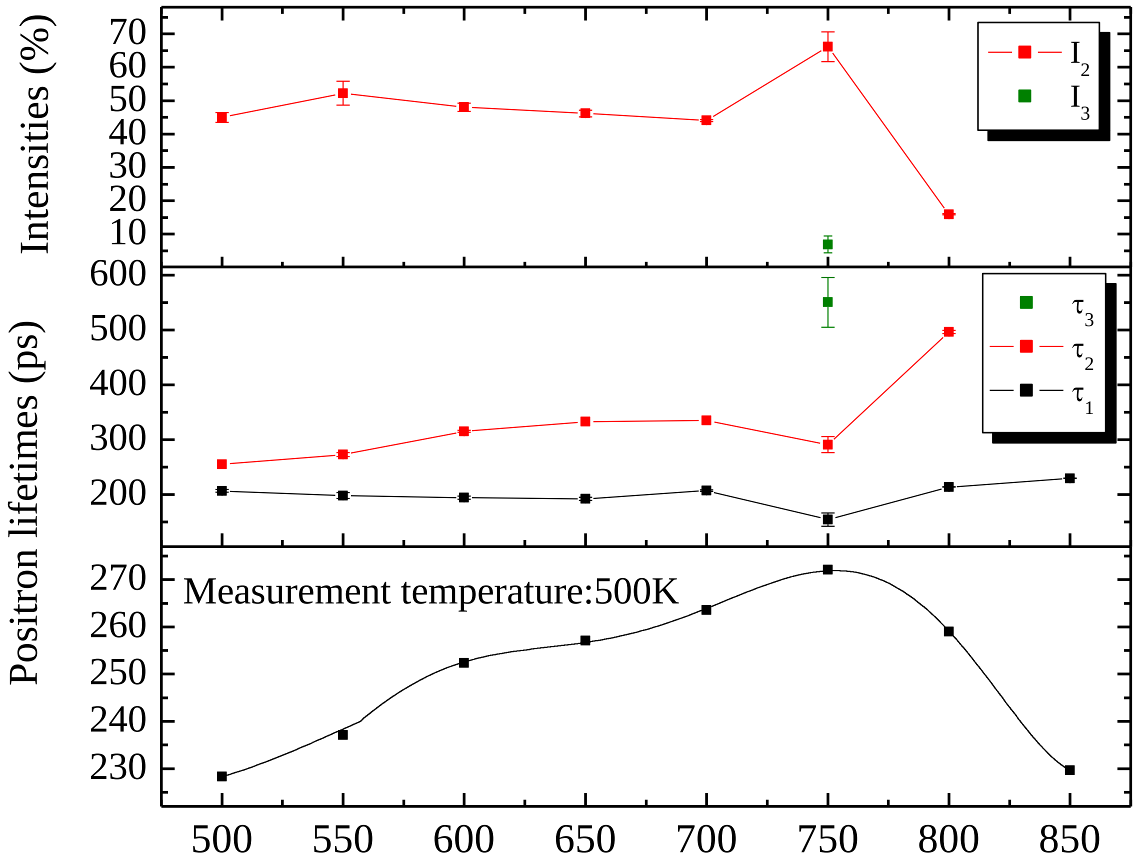
Te doped GaAs:Cu

- τ_d is much higher than that for monovacancies (250-290 ps)

- τ_d shows the increase of open volume during annealing

- this is explained by trapping of positron at small microvoids.

- τ_3 reach the value of 600 ps corresponding to vacancy clusters with n ~ 50.



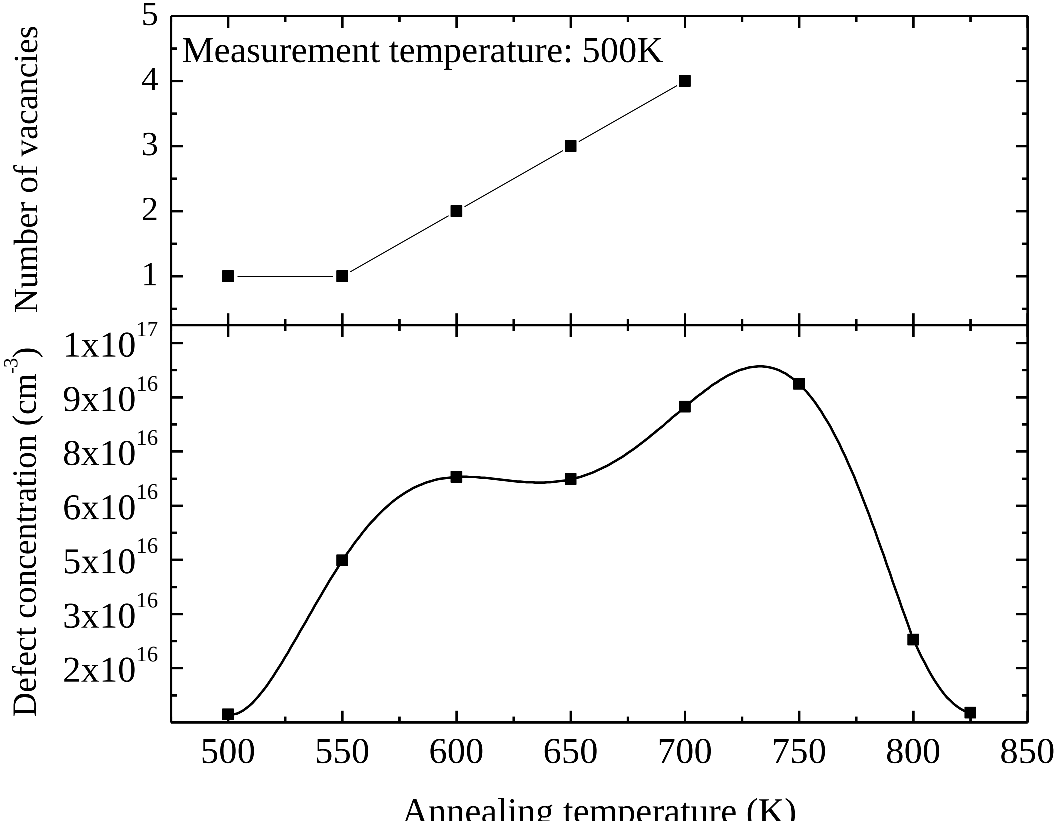
Te doped GaAs:Cu

$$\kappa_d = \mu \, C = \frac{1}{\tau_\mathrm{b}} \left(\frac{\tau_\mathrm{av} - \tau_\mathrm{b}}{\tau_\mathrm{d} - \tau_\mathrm{av}} \right)$$

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

n increases from 1 at 500 K up to 4 vacancies at 700 K [6]

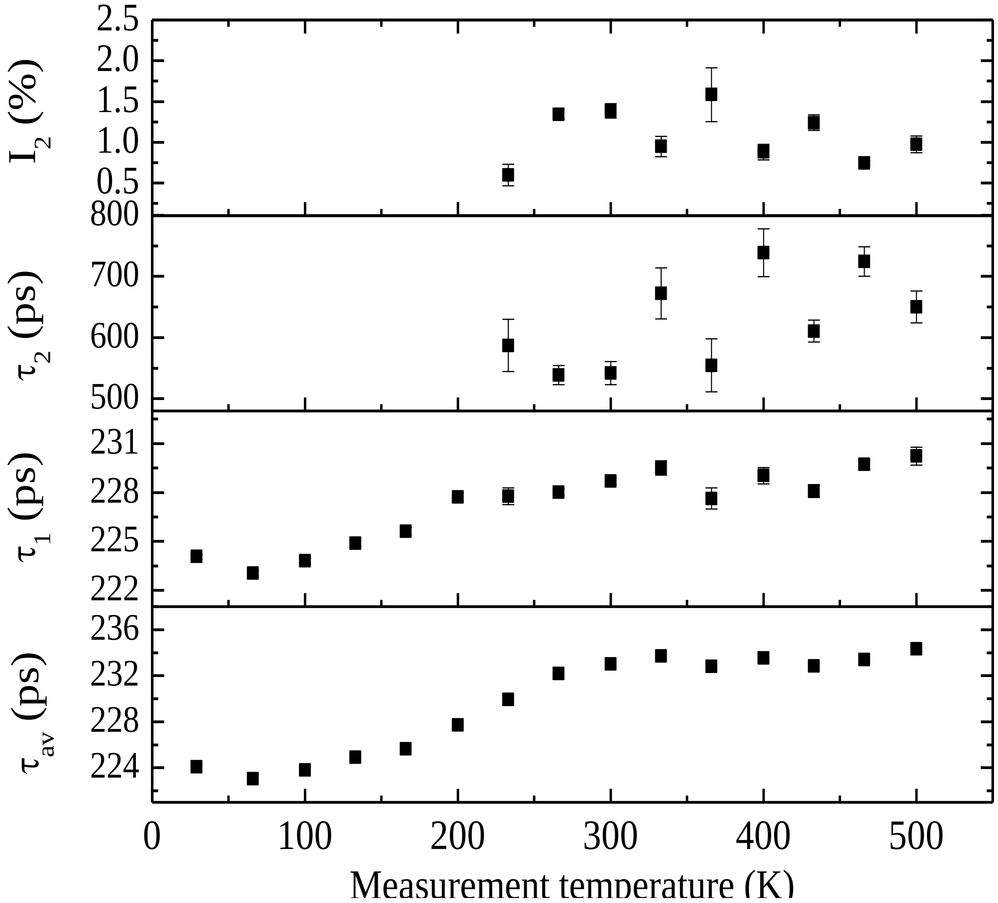
n ~ 50 vacancies at 750 K theoretically.



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

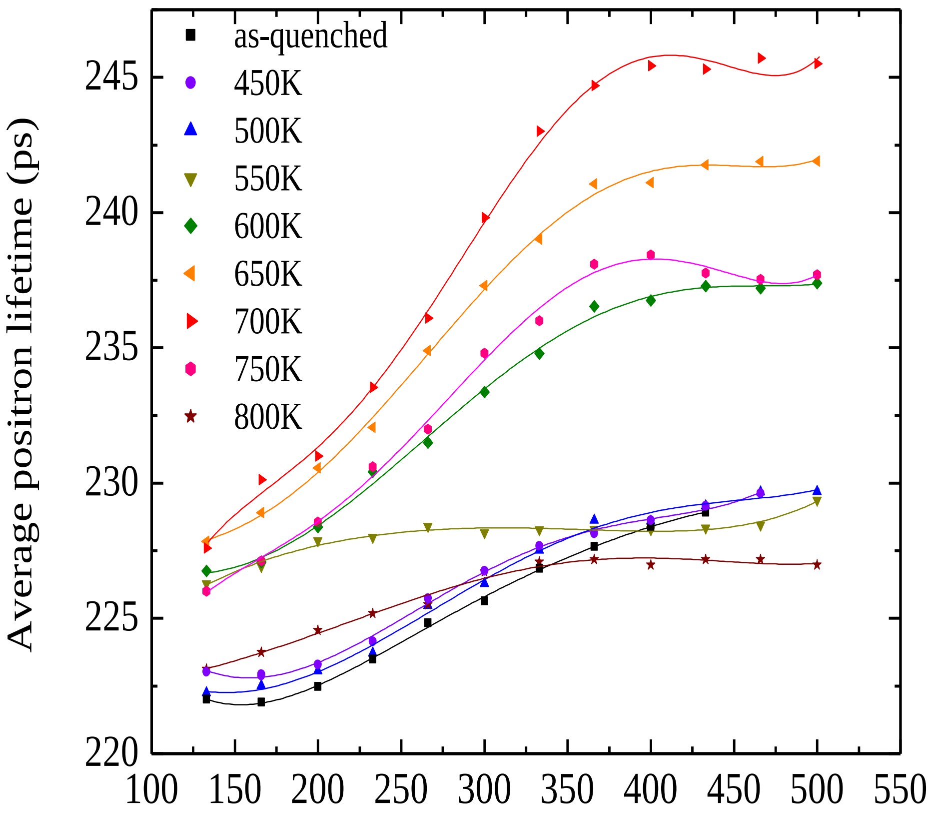
Te doped GaAs:Cu

- Cu diffused GaAs:Te sample was annealed at 1100 °C under 10 bar P_{As}. annealed up to 825K.
- τ_{av} ~ 232 ps
- $\tau_1 > \tau_b$
- τ_d ~ 750 ps. (I_d =1 %)
- at T>825K, the vacancies grow forming larger clusters. L_D> the distance between the clusters.



Te doped GaAs:Cu

- annealed at 1100 °C under 0.2 bar P_{As}
- as-quenched shows $\tau_{av} = \tau_b = 228$ ps in the high temperature region.
- decrease of τ_{av} at low T, shallow positron traps (Cu_{Ga}^{2-}).
- up to 700 K, τ_{av} increases to 246 ps.
- annealing > 800 K, the vacancy signal disappear.
- a larger quantity of excess arsenic should support the formation of vacancy cluster, i.e. As atoms to go into interstitial sites more easy.



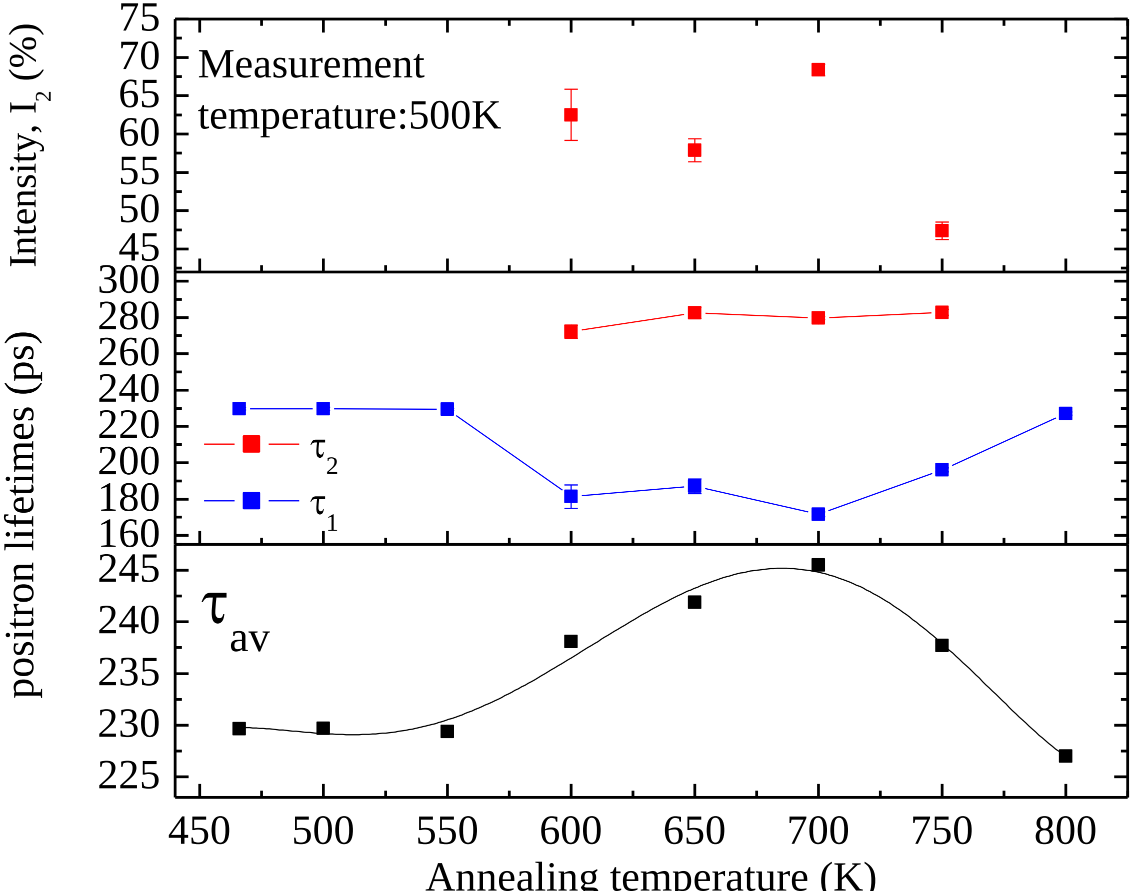
Te doped GaAs:Cu

- τ_d is higher than that for monovacancies (250-260 ps)

$\tau_d \sim 280$ ps.

- V_{Ga}-V_{As} → 330 ps
- **n**=1 vacancy
- [V]= 5-8 x10^{16} cm^{-3}
- Theoretical calculation

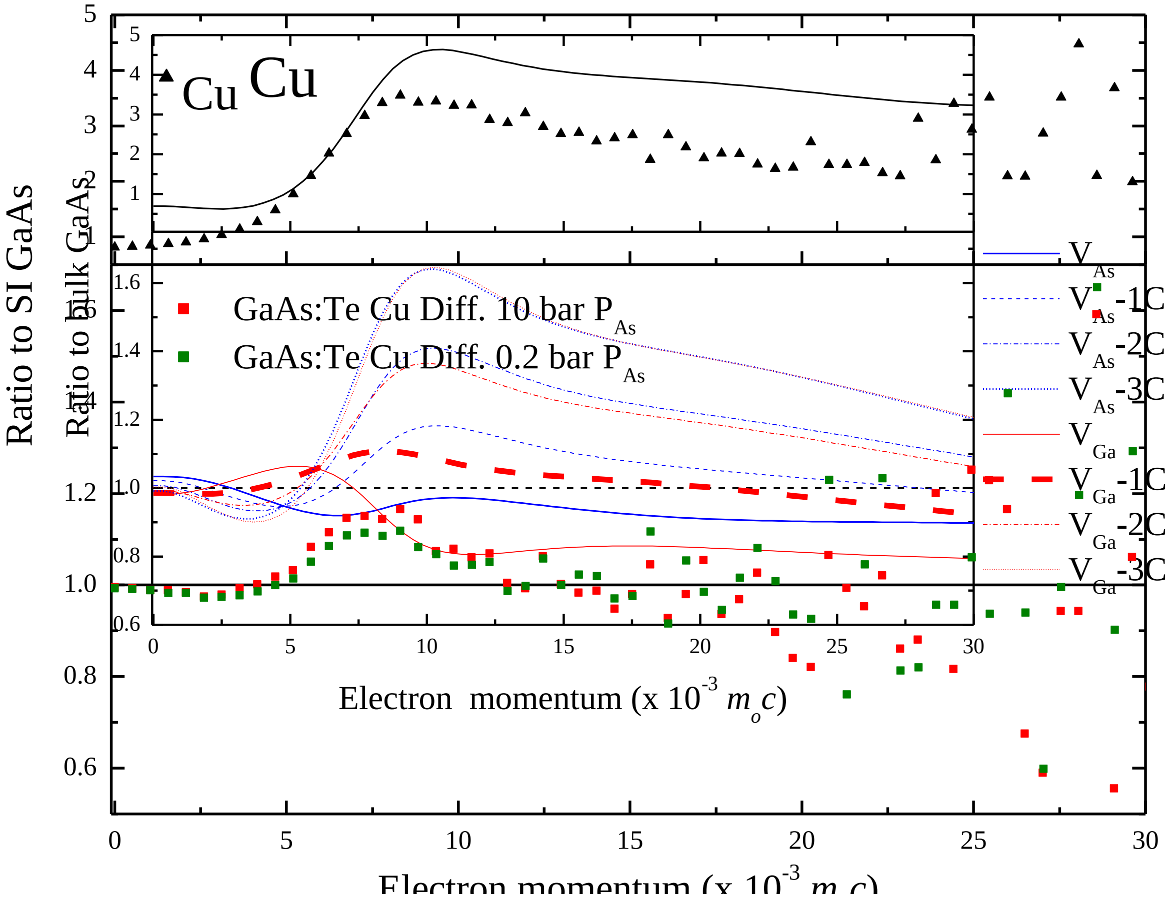
Vacancy	Lifetime (ps)
V_{Ga}	267
V_{Ga}-Cu_{Ga}	275
V_{Ga}-$2Cu_{Ga}$	283
V_{Ga}-$3Cu_{Ga}$	291



Te doped GaAs:Cu

- for e$^+$ annihilation with Cu core e$^-$, the ratio > 1
- presence of Cu in neighbor of e$^+$ trap seen as such characteristic increase in intensity of e$^-$ e$^+$ momentum distribution.
- sign of Cu in vicinity of the detected vacancies in annealed GaAs:Te
- Theoretically:

experimental curves correspond to V$_{Ga}$-1Cu.



Te doped GaAs:Cu

Shallow traps concentration

One defect type

$$\kappa_{d1} = \frac{1}{\tau_b}\frac{\tau_{av}-\tau_b}{\tau_{d1}-\tau_{av}}$$

two types of defect

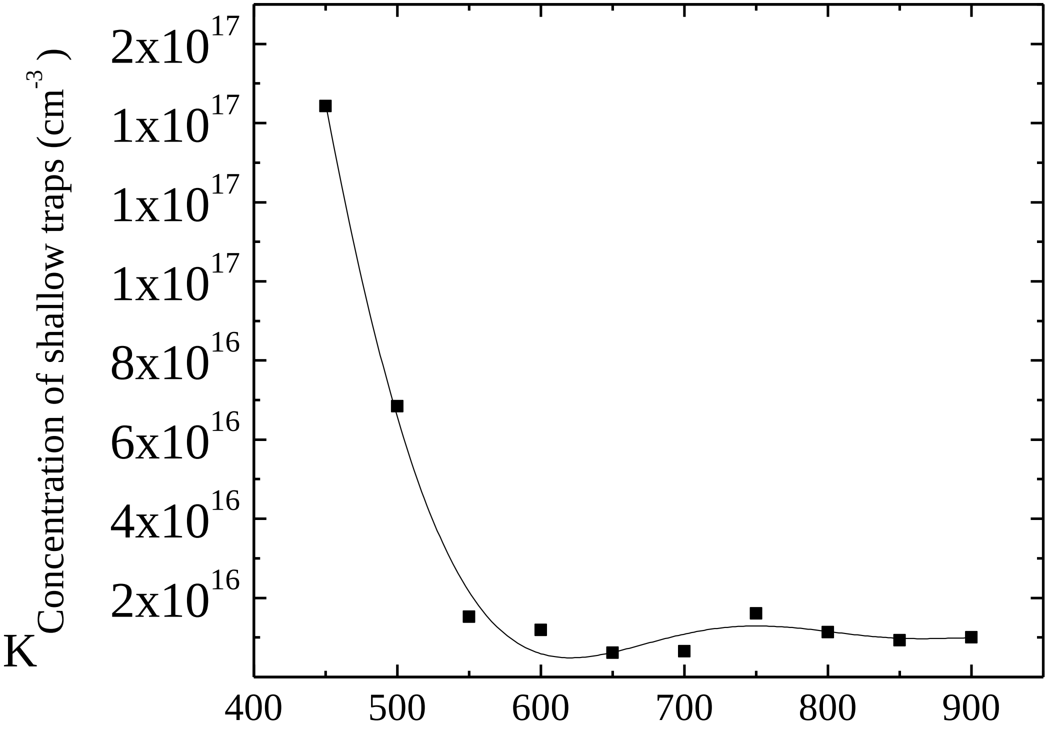
$$\kappa_{d1} = \frac{K_{d2}(\tau_{d2}-\tau_{av})+1-\tau_{av}\lambda_b}{(\tau_{av}-\tau_{d1})}$$

$\tau_{d1}= \tau_{st}$=220 ps & τ_b= 228 ps

κ_{d2} calculated from the analysis of the spectra at T= 500K.

$$\kappa_d = \mu C_d$$

C_{St} calculated at T= 29 K



μ=5x10^{16} s^{-1} at 20 K [7]

Hall measurement (2.24x10^{17}cm^{-3}) for as-quenched sample. This gives μ=3.22x10^{16} s^{-1}.

[7] R. Krause-Rehberg and H.S. Leipner, (Springer, Berlin, 1999).

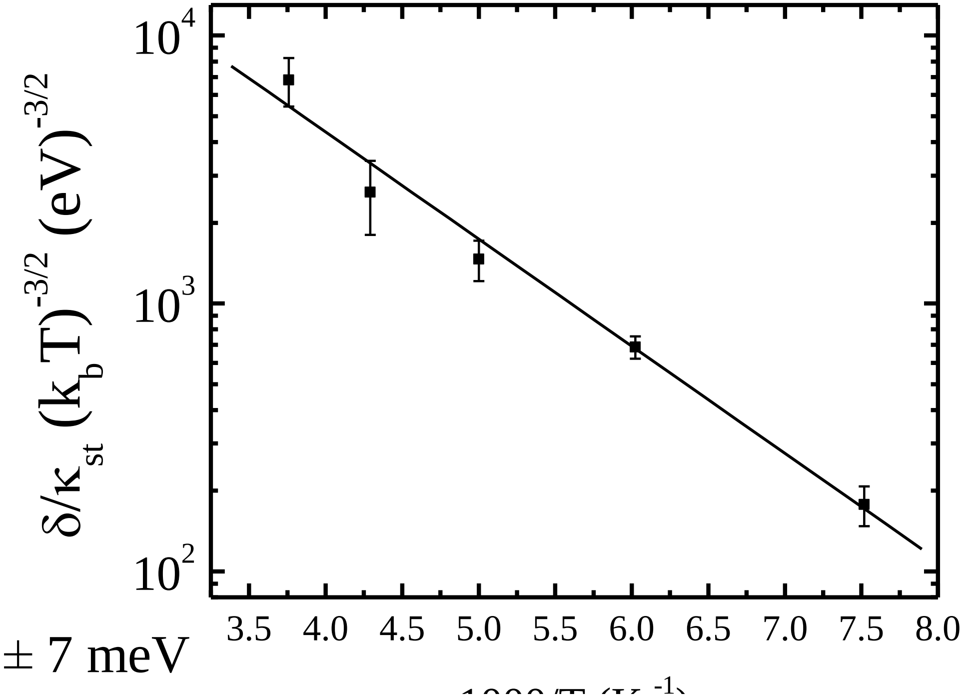
Te doped GaAs:Cu

e^+ binding energy to Shallow traps

$$\frac{\delta}{\kappa_{st}} = \frac{1}{C_{st}}\left[\frac{m^*}{2\pi\hbar}\right]^{3/2}\left(k_B T\right)^{3/2}\exp\left[\frac{E_b}{k_B T}\right]$$

$$\frac{\delta}{\kappa_{st}} = \left[\frac{I_2}{I_2\kappa_v - I_2\left(\lambda_b - \lambda_2\right)} - \frac{1}{\kappa_{st}}\right]\left(\lambda_{st} - \lambda_2\right)$$

$\tau_2=\lambda_2^{-1}$ lifetime of the longest component has intensity I_2. $\lambda_b= \tau_b^{-1}=$ (228 ps)$^{-1}$. $\lambda_{st}= \tau_{st}^{-1}=$ (220 ps)$^{-1}$



The slope yields a binding energy of 79.4 ± 7 meV

$$E_b = \frac{13.6\text{ eV}}{\varepsilon^2}\left[\frac{m^*}{m_e}\right]\frac{1}{n^2},$$

Calculated E_b= 81.7 meV

[2] Saarinen et al., 1989

Conclusions

- Vacancy-like defects and shallow traps were observed.
- The average lifetime increases with increasing the annealing temperature.
- Vacancy clusters grow up to a size of more than 50 vacancies in the sample annealed under 10 bar of P_{As}
- Sample annealed under 0.2 bar of P_{As} shows vacancy-like defect of lifetime in the monovacancy region.
- CDBS showed the presence of copper in the vicinity of the detected vacancy-like defects. Theoretical calculation of the momentum distribution showed that V_{Ga} decorated with one Cu atoms.
- Shallow trap concentration was calculated using positron trapping model. The calculated value agrees with that measured using Hall-effect.
- e^+ binding energy of E_b= 79.4 meV to shallow traps was estimated.

Vielen Dank fuer Ihre Aufmerksamkeit