Vacancies and Vacancy Clusters in Semiconductors

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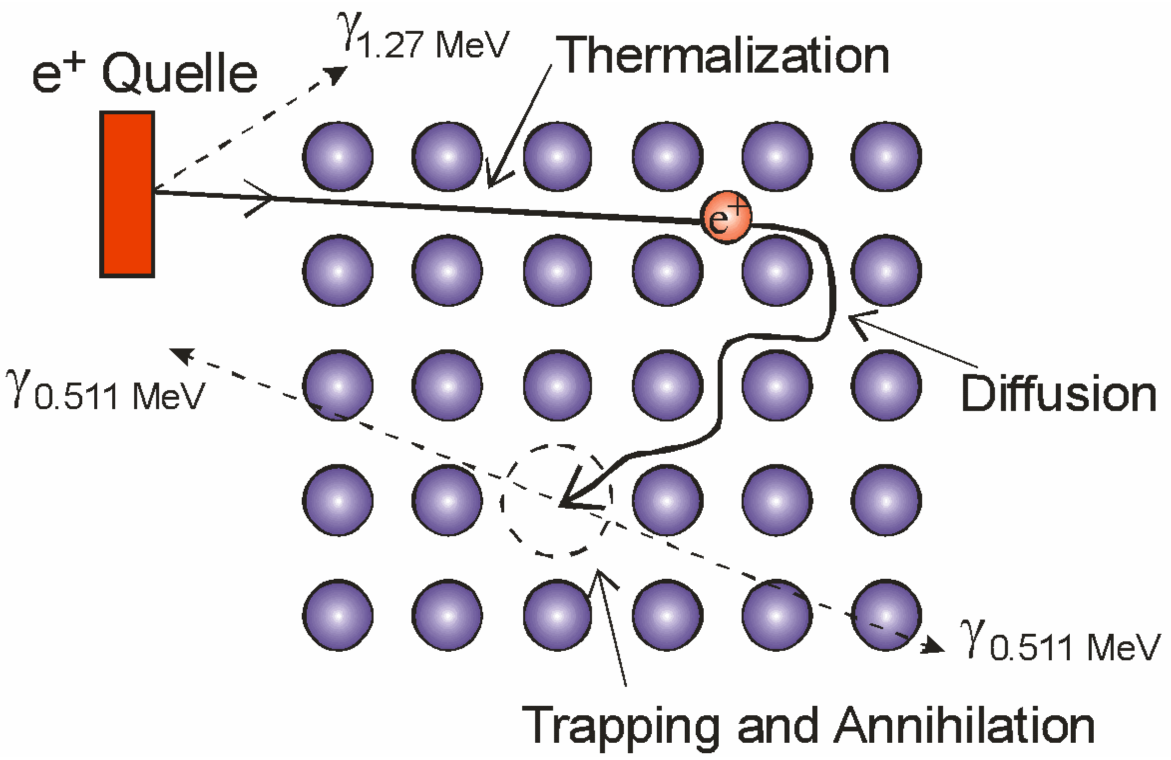
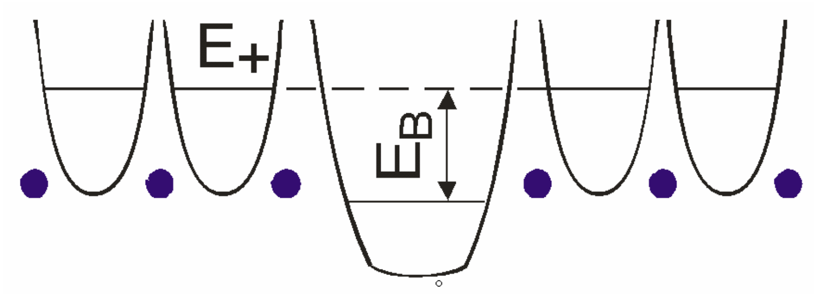
- Positron trapping by charged vacancies
- Shallow positron traps
- Vacancy clusters
- Examples

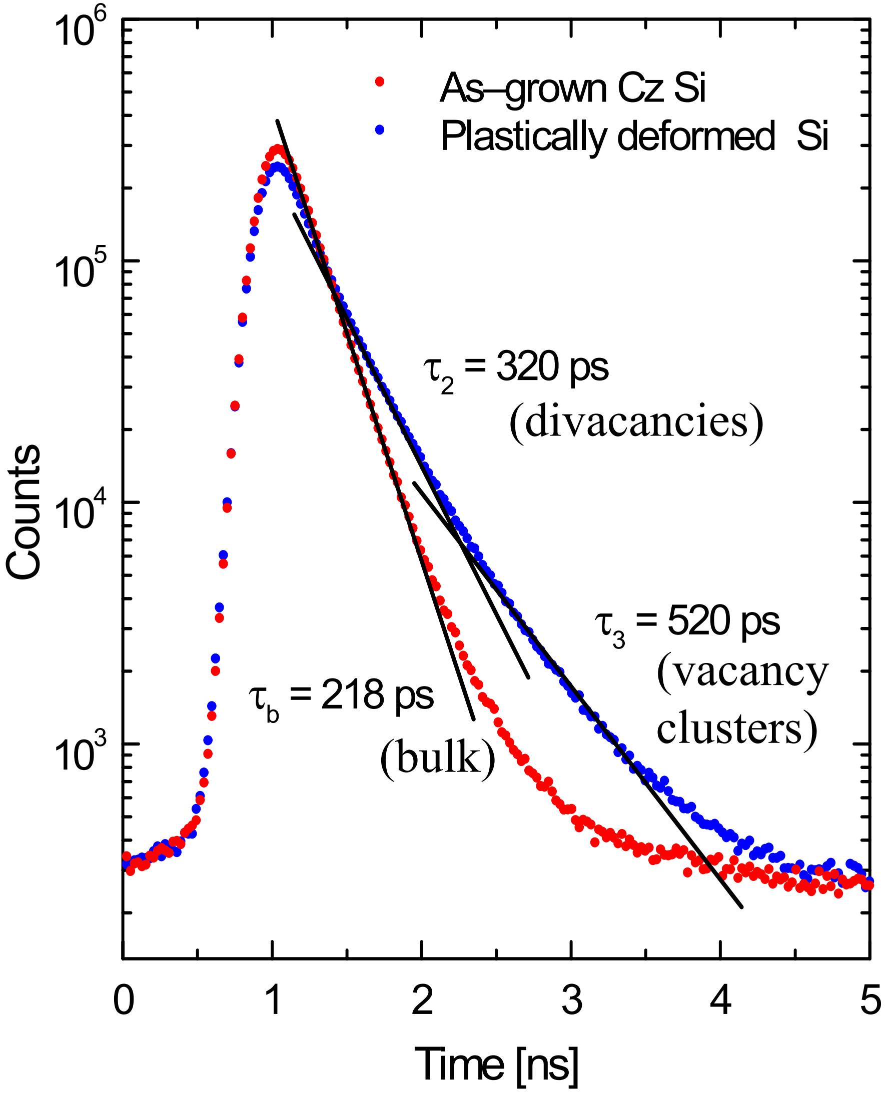
The positron lifetime spectroscopy





- positron wave-function can be localized in the attractive potential of a defect
- annihilation parameters change in the localized state
- e.g. positron lifetime increases in a vacancy
- lifetime is measured as time difference between 1.27 and 0.51 MeV quanta
- defect identification and quantification possible

Positron lifetime spectroscopy



- positron lifetime spectra consist of exponential decay components
- positron trapping in open-volume defects leads to long-lived components
- longer lifetime due to lower electron density
- analysis by non-linear fitting: lifetimes τ_i and intensities I_i

positron lifetime spectrum:

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

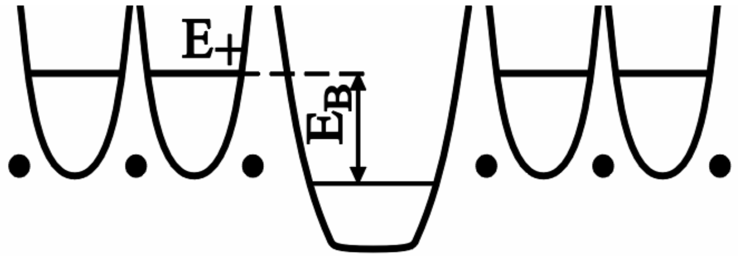
trapping coefficient

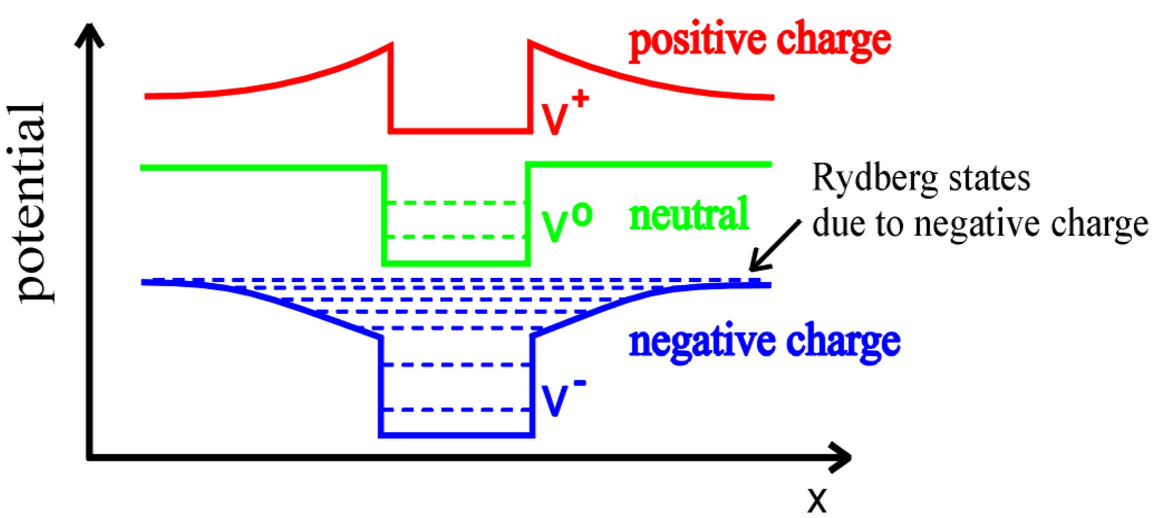
$$\boxed{\kappa_\mathrm{d} = \mu C_\mathrm{d}} = \frac{I_2}{I_1}\left(\frac{1}{\tau_\mathrm{b}} - \frac{1}{\tau_\mathrm{d}}\right)$$

trapping rate

defect concentration

Vacancies in a semiconductor may be charged

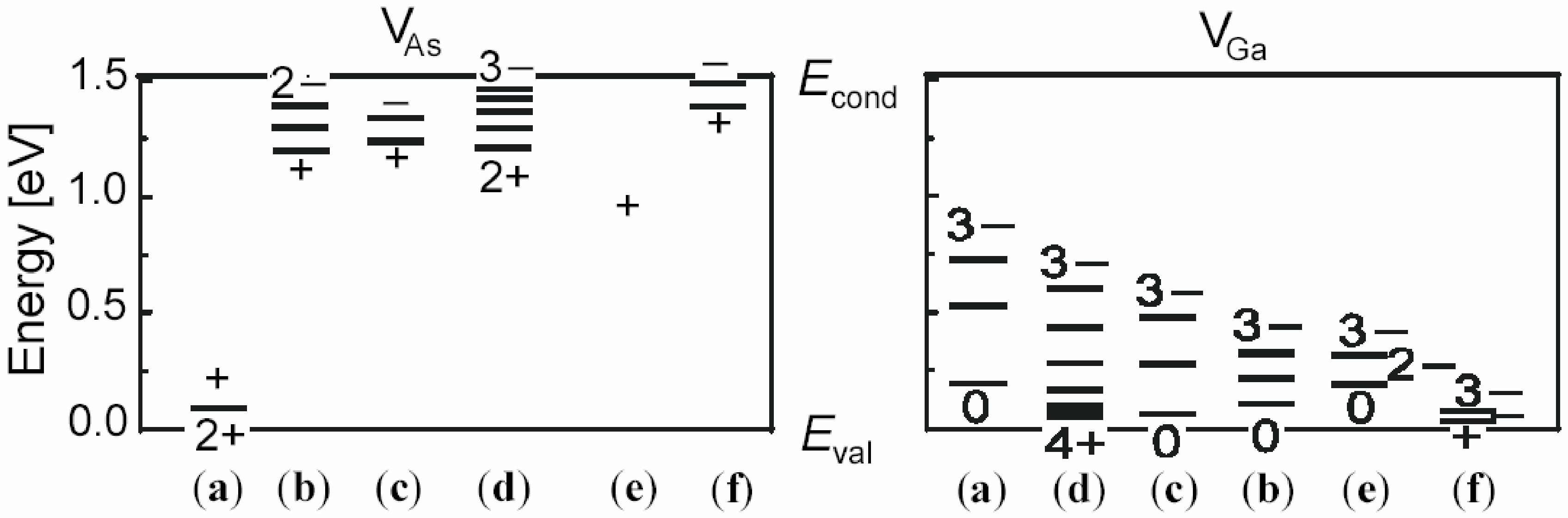




- in a metal: charge of a vacancy is effectively screened by free electrons
- they are not available in semiconductors
- thus, long-range Coulomb potential added
- positrons may be attracted or repelled
- trapping coefficient μ is function of charge state

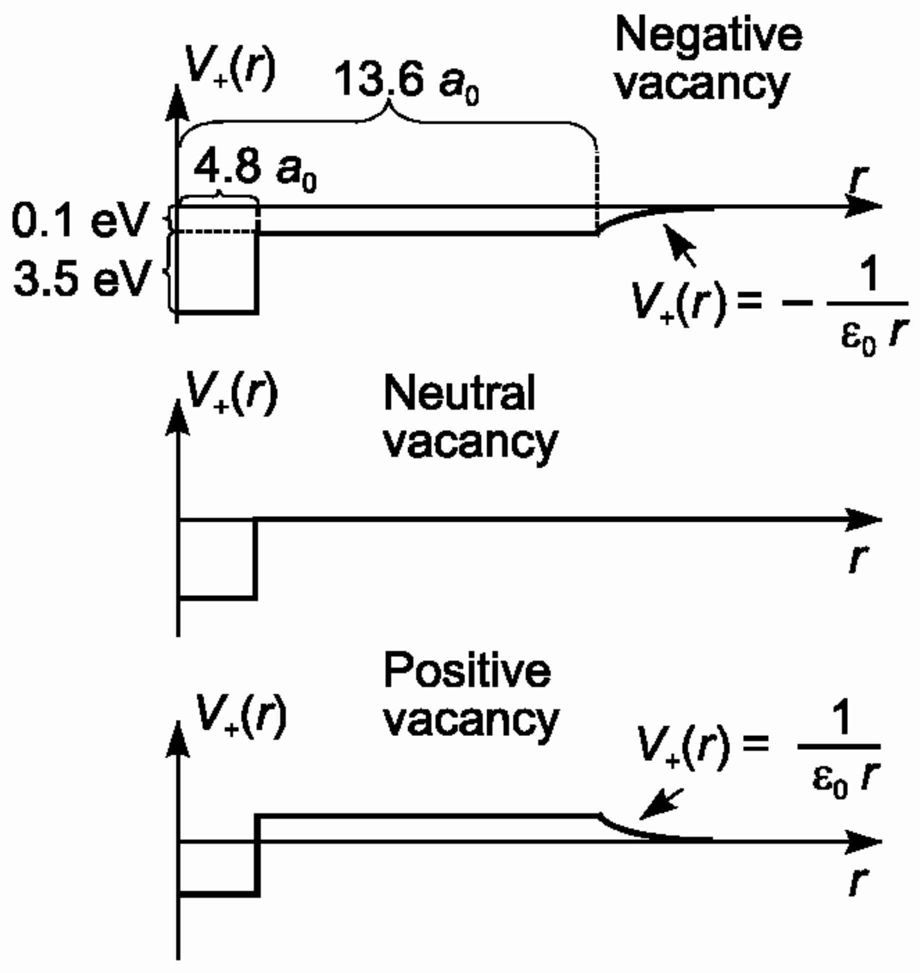
Theoretical calculation of vacancy levels in GaAs

- Theoretical description not simple
- relaxation of vacancy possible -> Jahn-Teller distortion / negative-U effect



Ionization levels of arsenic vacancies, gallium vacancies, and antisites according to theoretical calculations of (**a**) Baraff and Schlüter (1985a), (**b**) Puska (1989a), (**c**) Jansen and Sankey (1989), (**d**) Xu and Lindefelt (1990), (**e**) Zhang and Northrup (1991), and (**f**) Seong and Lewis (1995), (**g**) Zhang and Chadi (1990), (**h**) Pöykkö et al. (1997). E_{val} and E_{cond} are the edges of the valence and the conduction band, respectively.

Vacancies may be charged



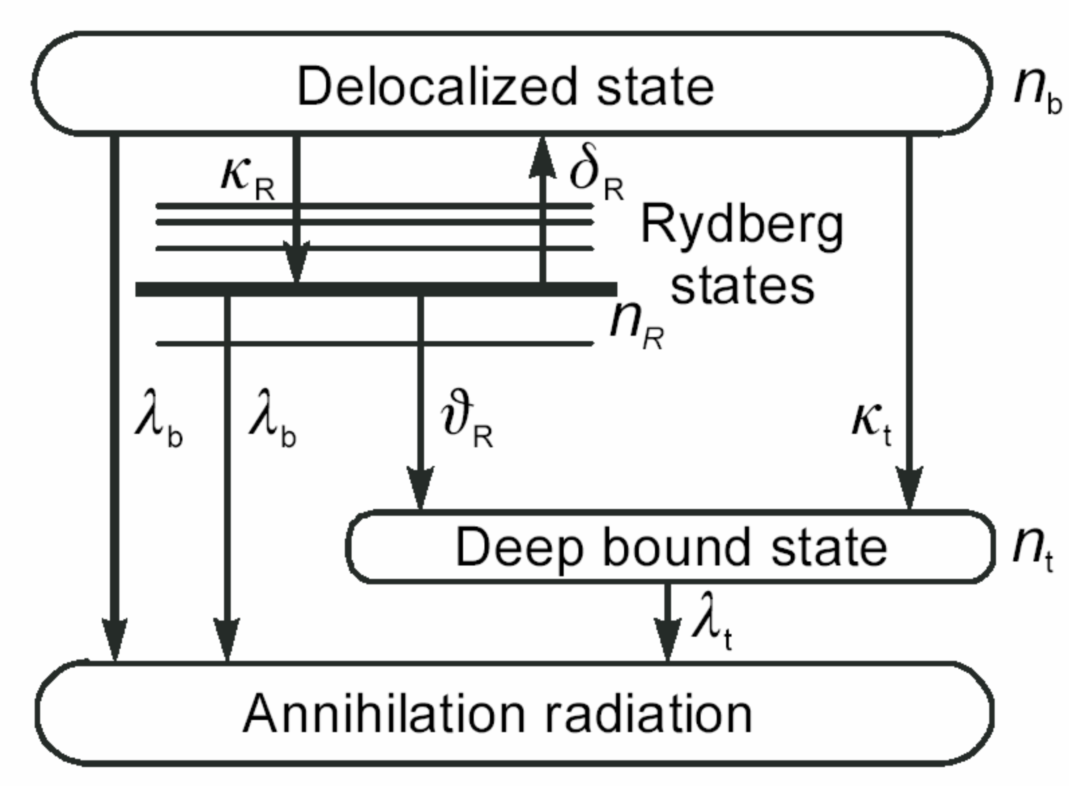
Puska et al. 1990

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

Positron trapping by negative vacancies



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

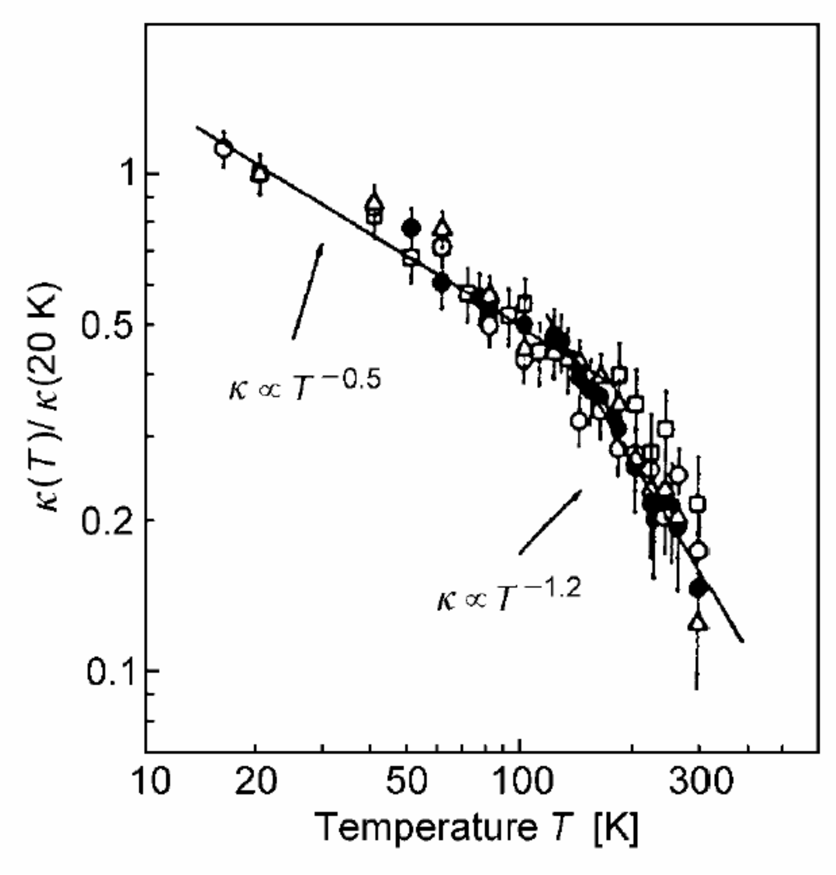
$$\delta_R = \frac{\kappa_R}{\rho_v}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{E_R}{k_B T}\right)$$

E_R binding energy of positron in Rydberg state

ρ_v vacancy density

Manninen, Nieminen, 1981

Negative vacancies show temperature-dependent positron trapping



positron trapping in negatively charged Ga vacancies in SI-GaAs

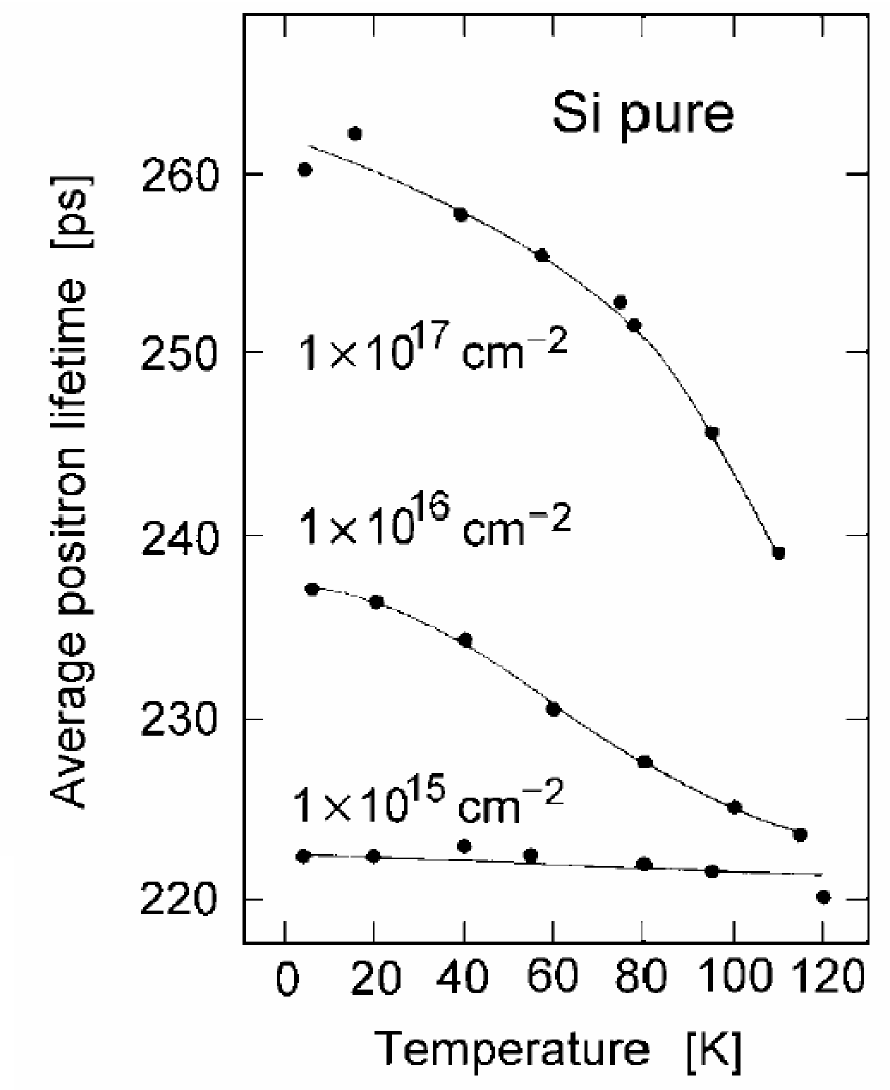
- temperature dependence of positron trapping is rather complex

$$\kappa = \frac{\vartheta_{\mathrm{R}}\rho_{\mathrm{v}}\kappa_{\mathrm{R0}}T^{-1/2}}{\vartheta_{\mathrm{R}}\rho_{\mathrm{v}} + \kappa_{\mathrm{R0}}\left(\frac{m^* k_{\mathrm{B}}}{2\pi\hbar^2}\right)^{3/2} T \exp\left(-\frac{E_{\mathrm{R}}}{k_{\mathrm{B}}T}\right)}$$

- low temperature: $\sim T^{-0.5}$ due to diffusion limitation in Rydberg states
- higher T: stronger temperature dependence due to thermal detrapping from Rydberg state

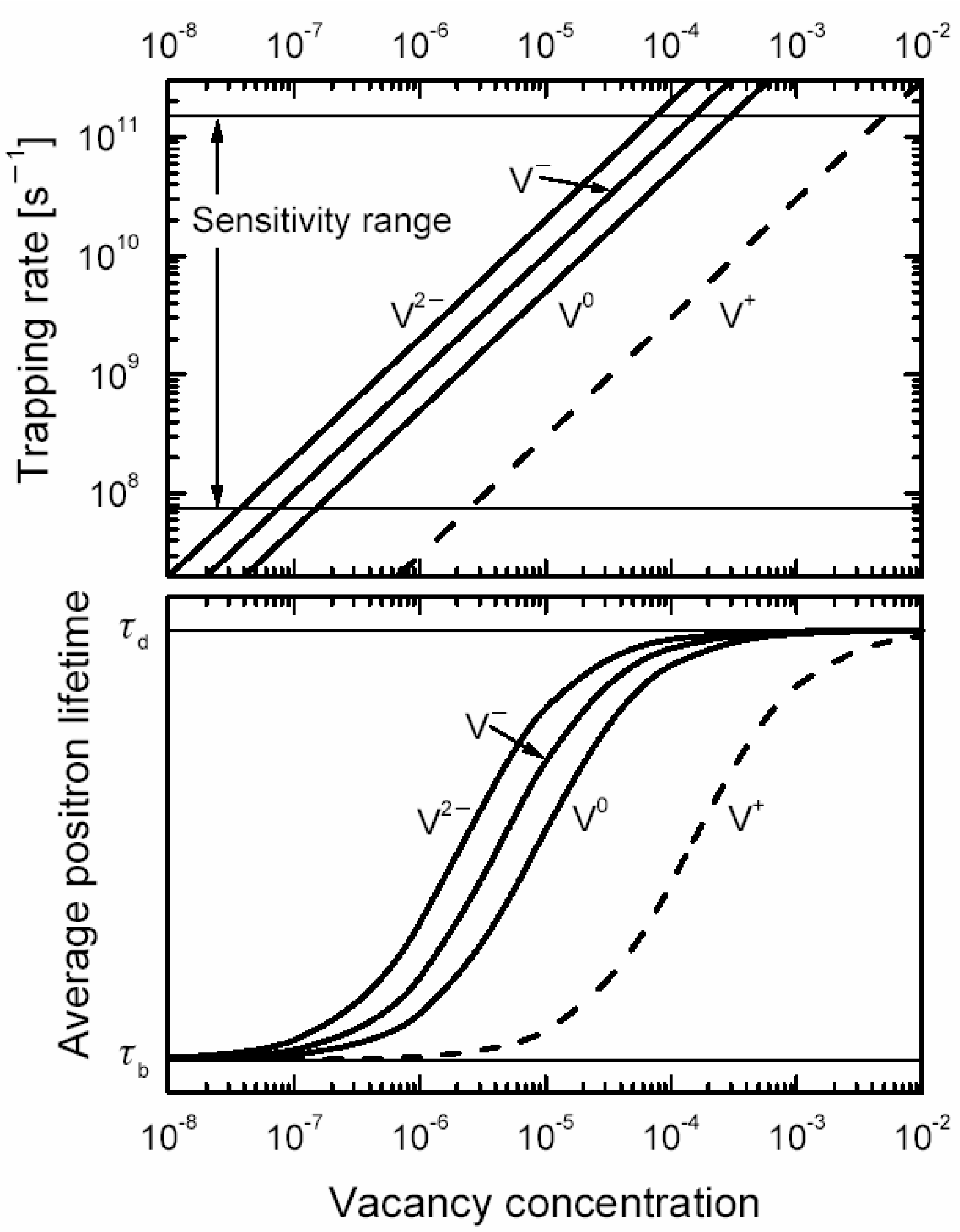
Le Berre et al., 1995

Temperature-dependent positron trapping



- temperature dependence of positron trapping can be used to determine the charge state of vacancies
- trapping to positive vacancies possible at elevated T
- however: has never been observed
- example: Positron trapping in e-irradiated Si
- trapping by negatively charged divacancies

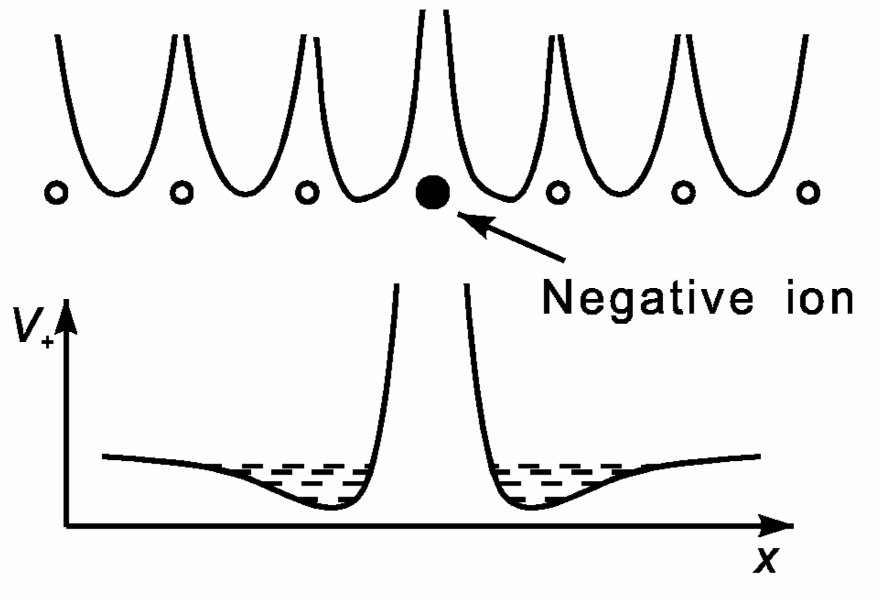
(Mäkinen et al. 1989)



Sensitivity limits of PAS for vacancy detection

- **lower sensitivity limit** e.g. for negatively charged divacancies in Si starts at about 10^{15} cm^{-3}
- **upper limit**: saturated positron trapping
- defect identification still possible
- only lower limit for defect density can be given

Negative ions act as shallow positron traps

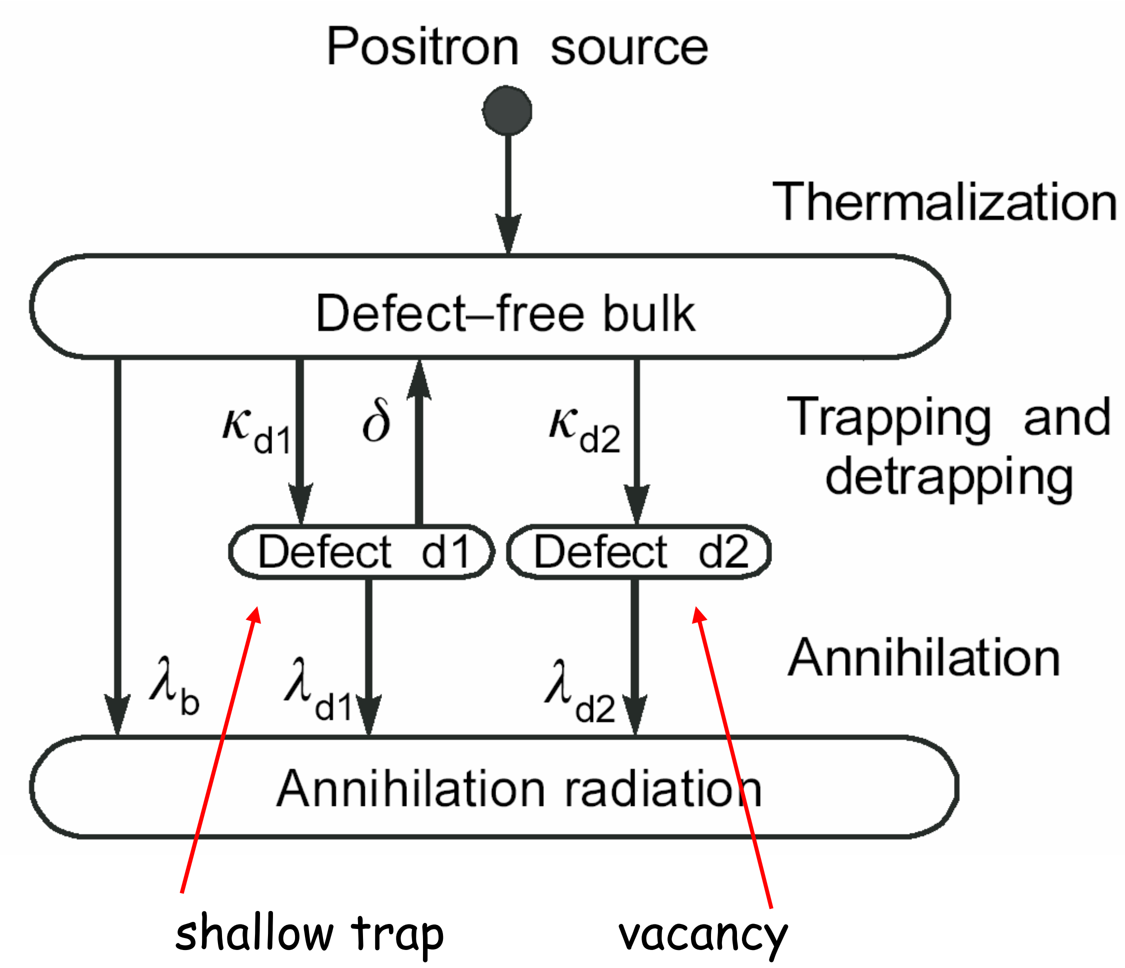


- at low T: negatively charged defects without open volume may trap positrons
- "shallow" due to small positron binding energy
- annihilation parameters close to bulk parameters
- acceptor-type impurities, dopants, negative antisite defects
- thermally stimulated detrapping can be described by:

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

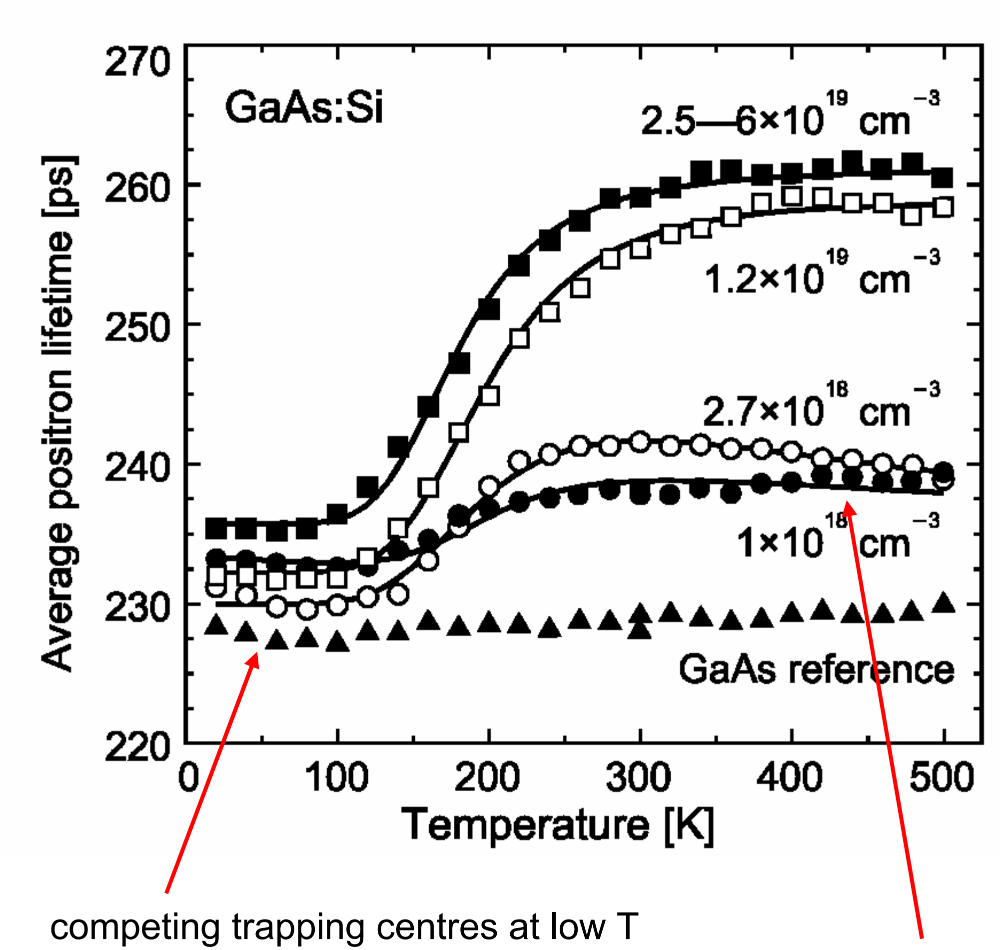
Saarinen et al., 1989

Shallow positron traps



- positron trapping model gets more complex
- however: trapping at shallow traps can be avoided at high temperatures

Effect of shallow positron traps



- temperature dependence is characterized by competing trapping by vacancies and shallow traps
- in GaAs:Si we observe V_{Ga}-Si_{Ga} complexes at high temperatures
- and Si_{Ga}^{-} donors at low T in addition (shallow traps)

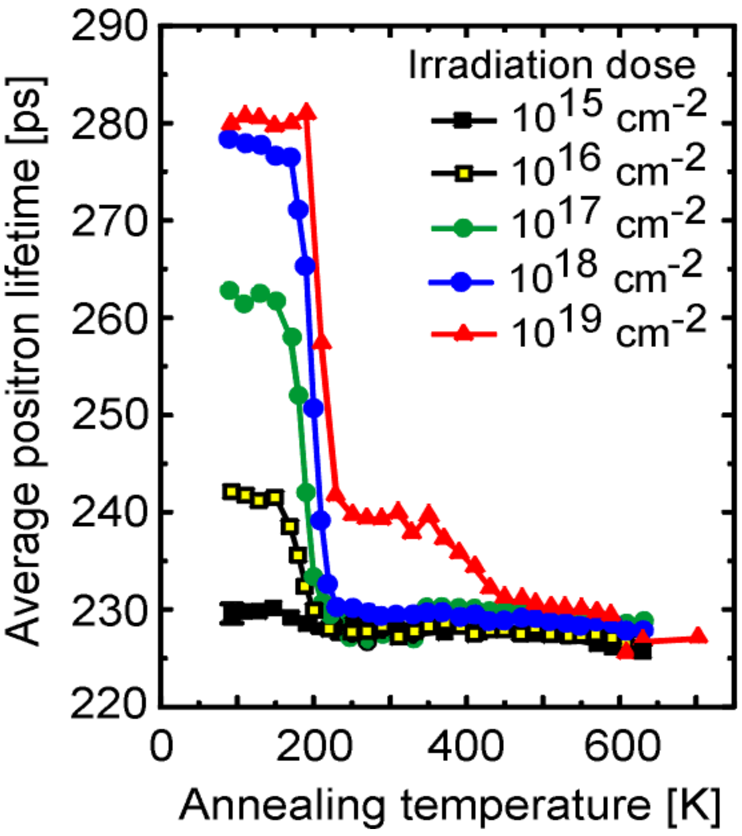
competing trapping centres at low T
shallow positron traps (Si_{Ga}^{-})

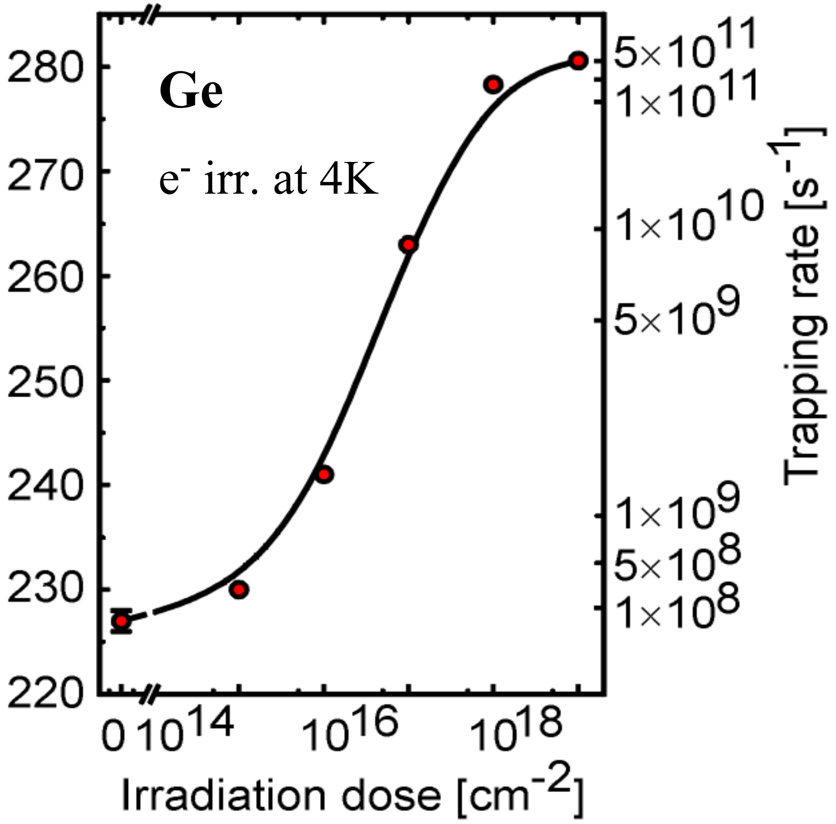
trapping by vacancies
at elevated temperatures (V_{Ga}-Si_{Ga})

J. Gebauer et al. 1997

Defects in electron-irradiated Ge

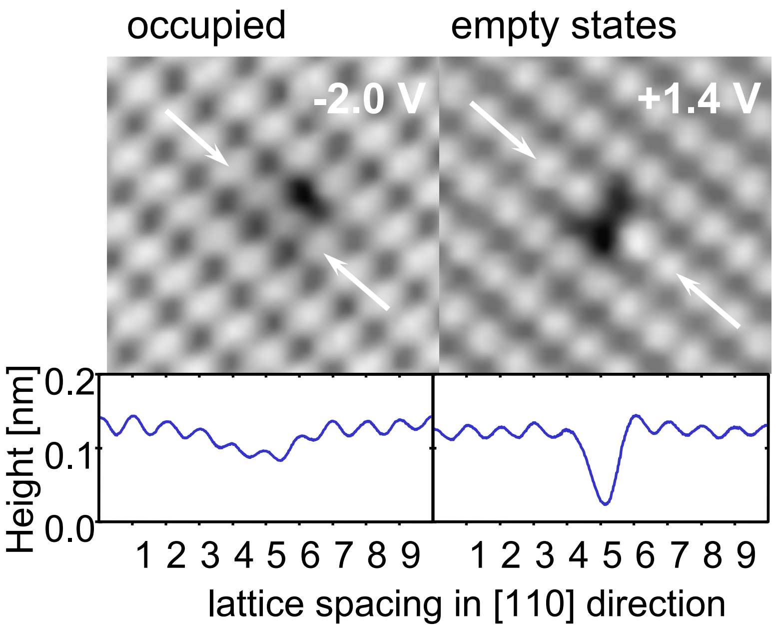
- Electron irradiation (2 MeV) induces Frenkel pairs (vacancy - interstitial pairs)
- steep annealing stage at 200 K
- at high irradiation dose: divacancies are formed (thermally more stable)

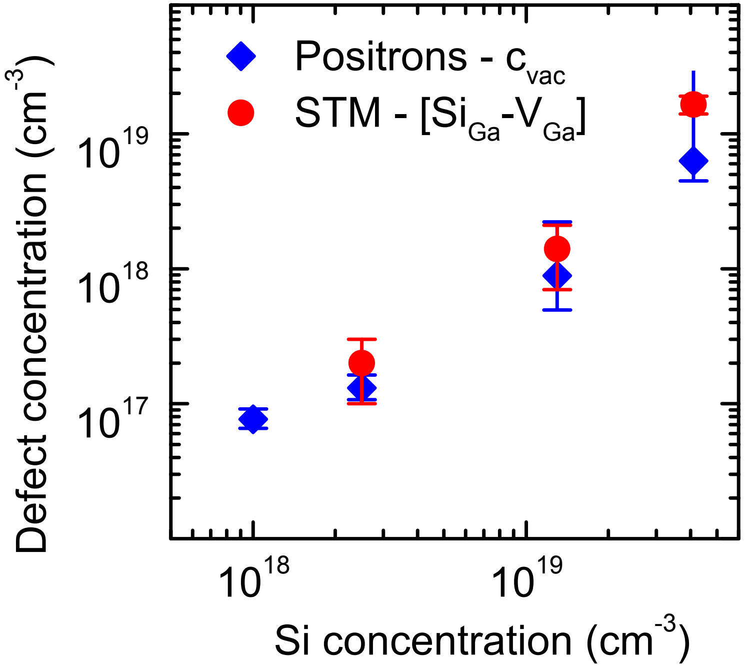




(Polity et al., 1997)

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}**

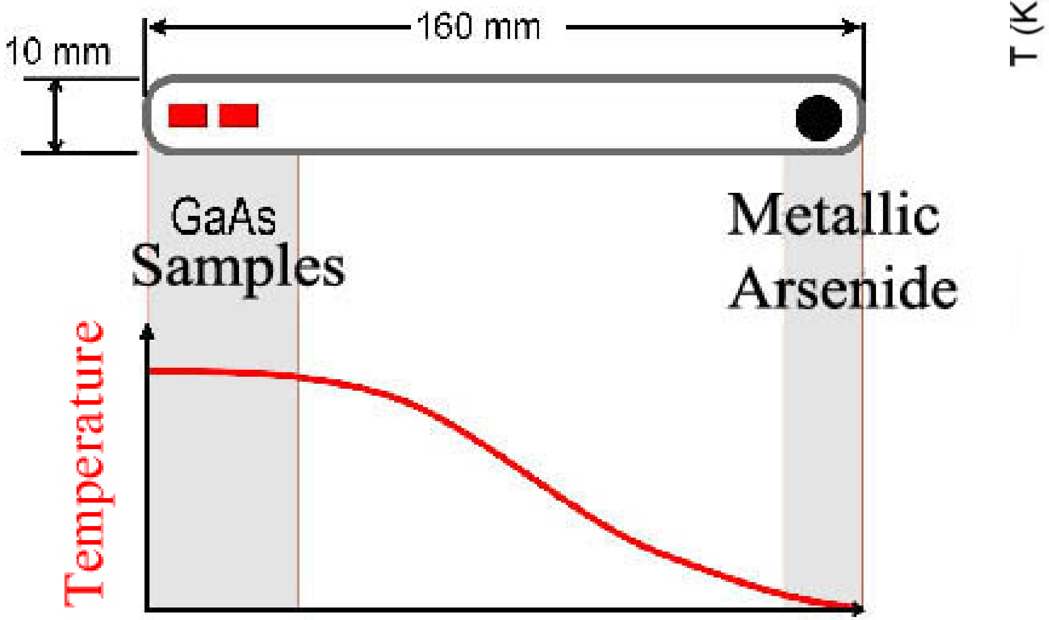
- Quantification → Agreement

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

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

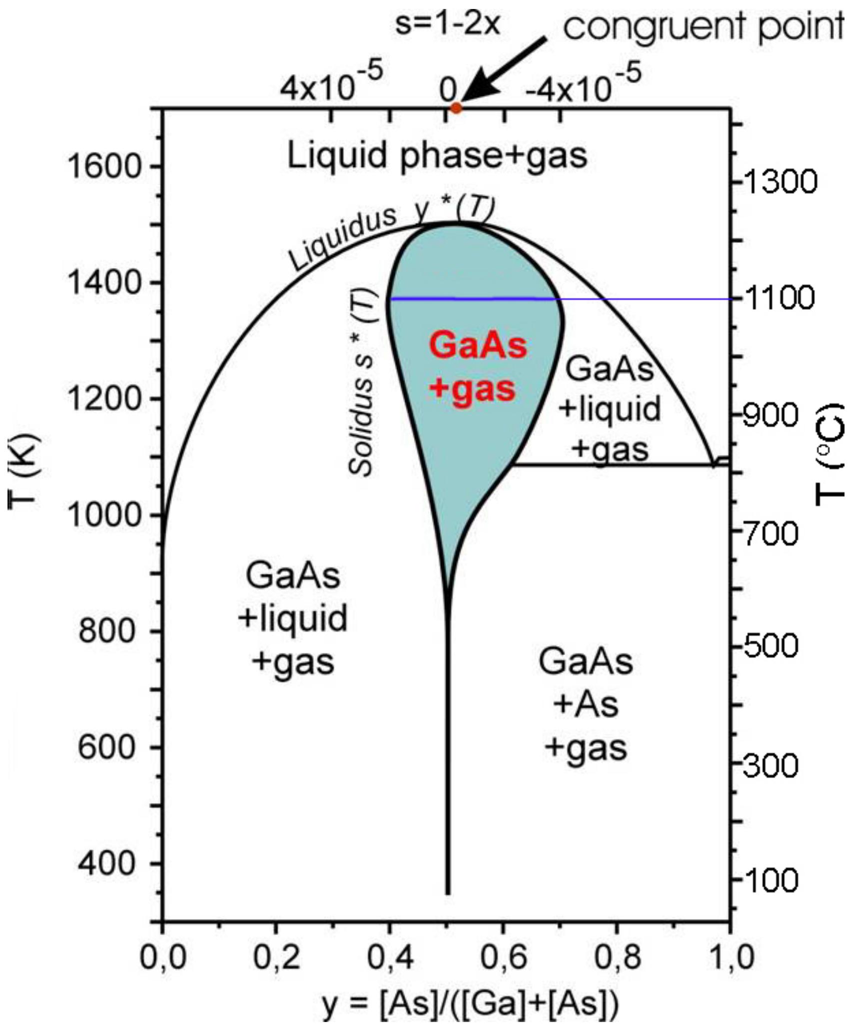
GaAs: annealing under defined As-partial pressure

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



T_{sample}: 1100° C

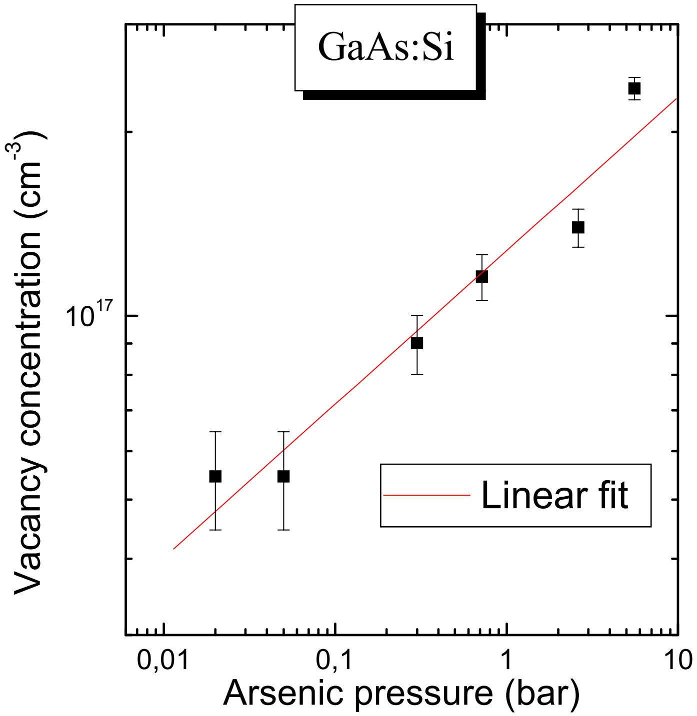
T_{As}: determines As-partial pressure



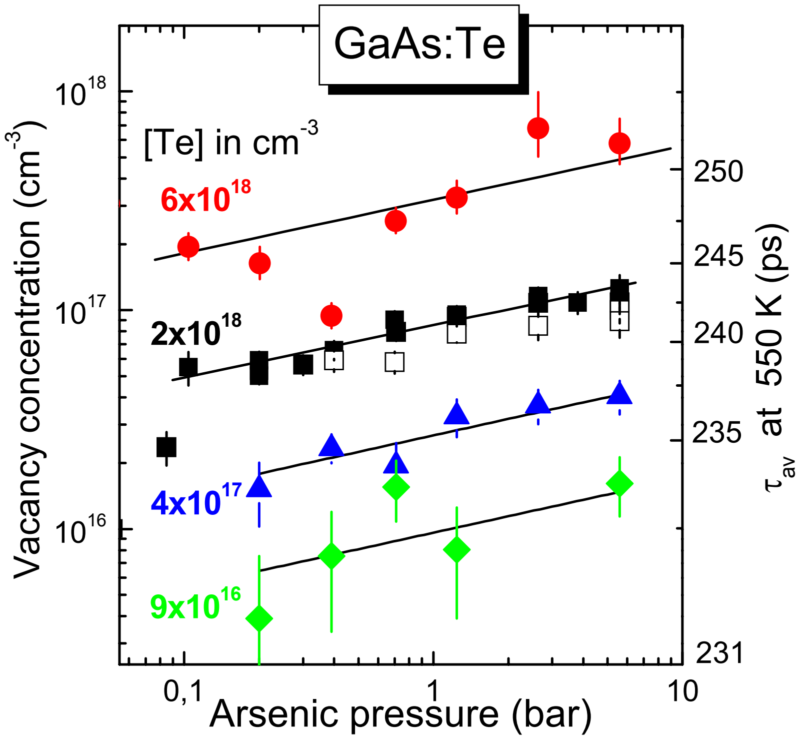
H. Wenzl et al., J. Cryst. Growth **109**, 191 (1991).

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:

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

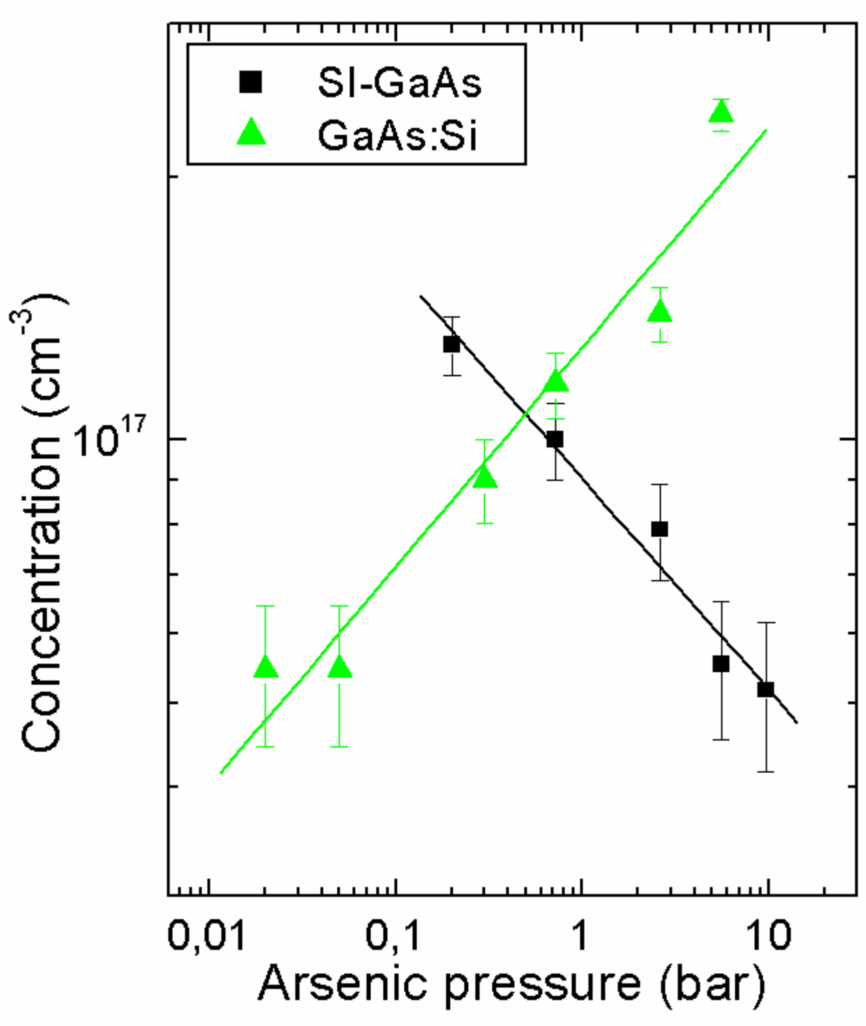
Mass action law:

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

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

$\rightarrow n = 1/4$

Comparison of doped and undoped GaAs



Thermodynamic reaction:

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

Mass action law:

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

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

$\rightarrow n = -1/4$

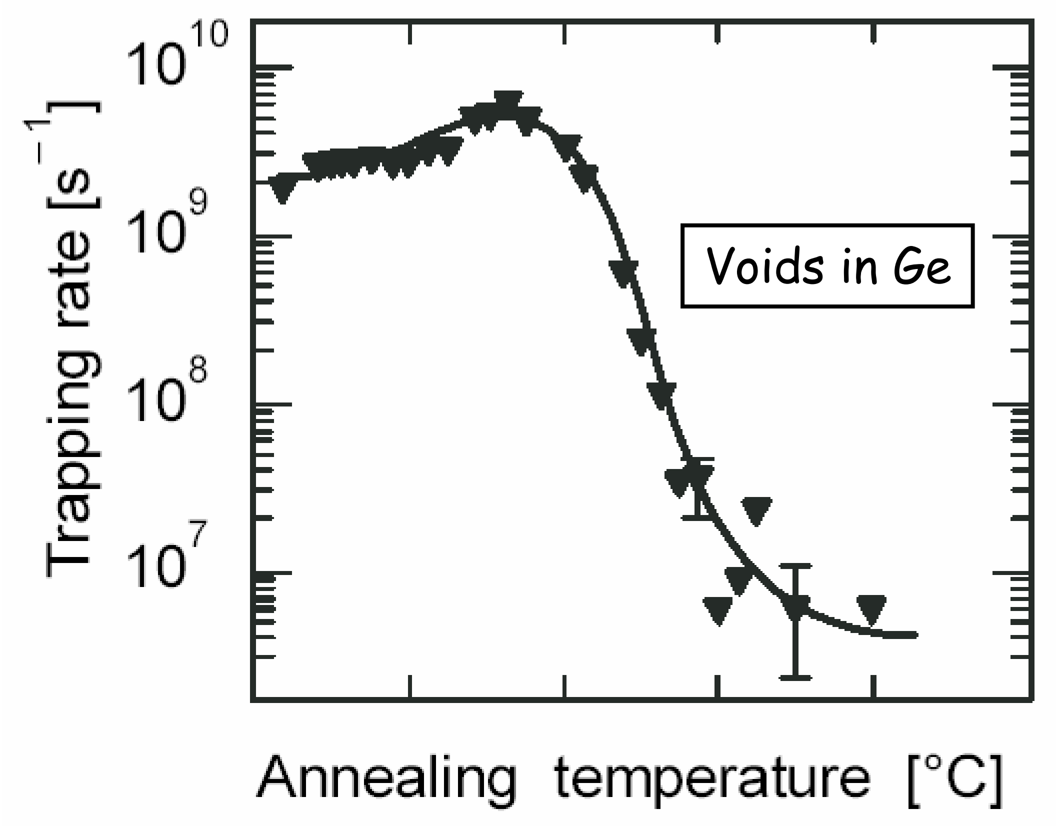
↓

As vacancy

Bondarenko et al., 2003

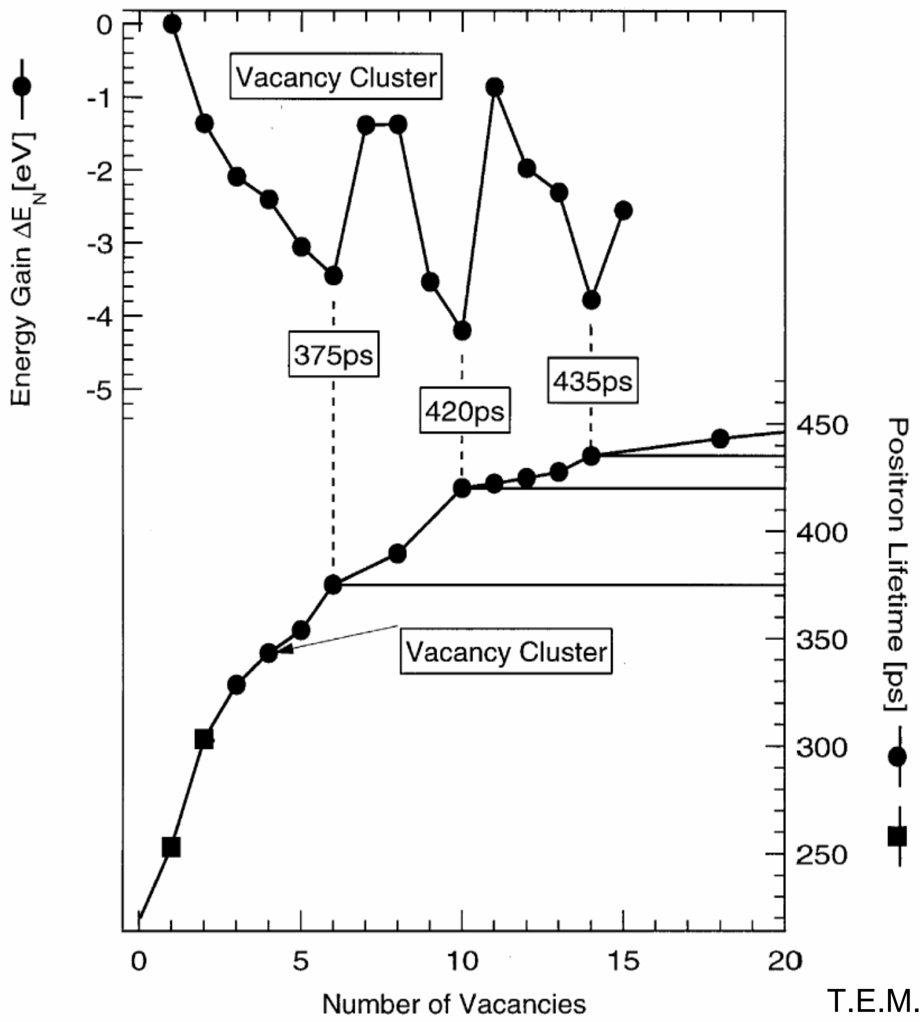
Vacancy clusters in semiconductors

- vacancy clusters were observed after 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



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

- 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

Conclusions

- Positrons are a unique tool for characterization of vacancy-type defects in semiconductors
- Positrons are sensitive for charge state of vacancies
- negative non-open volume defects act as shallow positron trap (only at low temperatures)
- vacancy clusters can easily be observed by positron lifetime spectroscopy (appear after irradiation and plastic deformation)

This presentation can be found as pdf-file on our Website:
http://positron.physik.uni-halle.de

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