Defect chemistry in GaAs studied by two-zone annealings under defined As vapor pressure

V. Bondarenko[1], **R. Krause-Rehberg**[1], **J. Gebauer**[2], **F. Redmann**[1]
[1] *Martin-Luther-University Halle-Wittenberg, Halle, Germany*
[2] *Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, CA 94720, USA*

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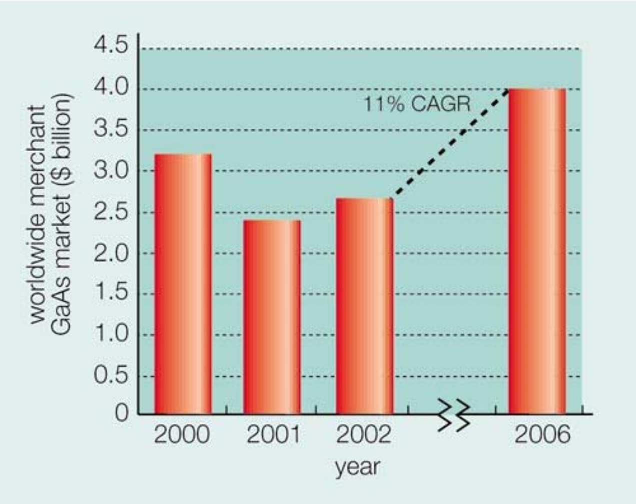
Outlook:

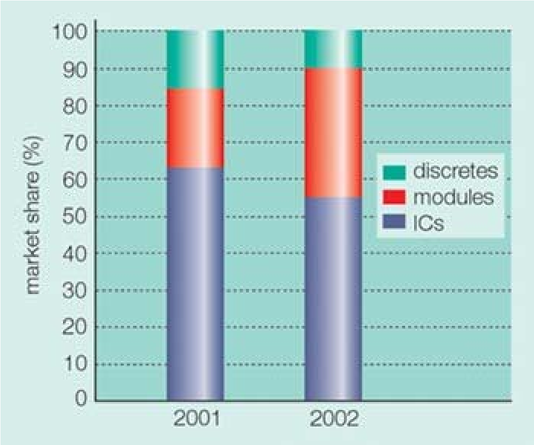
- Introduction
  - Thermodynamics of GaAs
  - Role of positron annihilation
- Experimental
- Results and discussion
  - Vacancy concentration as function of stoichiometry
  - Vacancy origin and charge state

Introduction

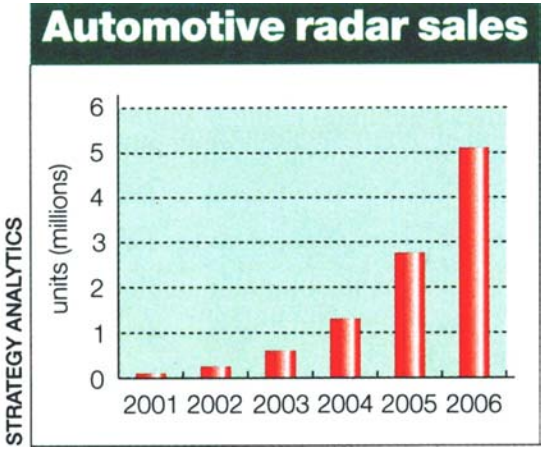
- GaAs Market continues growing
  - GaAs remains an important material for production of semiconductor devices
  - **Decrease** in GaAs ICs production is compensated by the **increase** in



- **PA (Power Amplifiers) modules for wireless local-area Networks**



- **MMIC for automotive radars**



- Detailed knowledge on native point defects formation is crucial in engeneering of electrical properties

Thermodynamics of GaAs

- Defects concentrations
  - Defect chemistry evaluate the **equilibrium** defect concentrations as function of doping, temperature and chemical potential (stoichiometry)

- Major achievments of thermodynamic analysis of GaAs
  - Demonstration of the key role of V_{As}^{+} for dopant solubility in GaAs and
  - of V_{Ga}^{m-} for annealing and diffusion of n-doped GaAs

D.T.J. Hurle, Journ. of Appl. Phys. 85 (1999)

  - prediction of negative T-dependence for V_{Ga} (Fermi-level effect)

T.Y.Tan et al, Appl. Phys. A 56 (1993)

- Role of Positron annihilation
  - Experimental proove of Fermi-level effect
  - Determination of formation enthalpy and entropy of the uncharged V_{Ga}

J. Gebauer et al.,
Physical Review B 67 (2003)

Thermodynamic model of undoped GaAs

- Native point-defects
  - six native defects formation is described by six thermodynamic mass-action law reactions:

$$\frac{1}{4}As_{4,vap} \leftrightarrow I_{As} \Rightarrow K_1(T) = \frac{[I_{As}]}{P_{As_4}^{1/4}}$$

$$Ga_{vap} \leftrightarrow I_{Ga} \Rightarrow K_2(T) = \frac{I_{Ga}}{P_{Ga}}$$

$$As_{As} \leftrightarrow I_{As} + V_{As} \Rightarrow K_3(T) = [I_{As}][V_{As}]$$

$$Ga_{Ga} \leftrightarrow I_{Ga} + V_{Ga} \Rightarrow K_4(T) = [I_{Ga}][V_{Ga}]$$

$$Ga_{Ga} + I_{As} \leftrightarrow As_{Ga} + I_{Ga} \Rightarrow K_5(T) = \frac{[As_{Ga}][I_{Ga}]}{[I_{As}]}$$

$$As_{As} + I_{Ga} \leftrightarrow Ga_{Ga} + I_{As} \Rightarrow K_6(T) = \frac{[Ga_{As}][I_{Ga}]}{[I_{Ga}]}$$

$$[I_{As}] \propto P_{As_4}^{1/4}$$

$$[I_{Ga}] \propto P_{As_4}^{-1/4}$$

$$[V_{As}] \propto P_{As_4}^{-1/4}$$

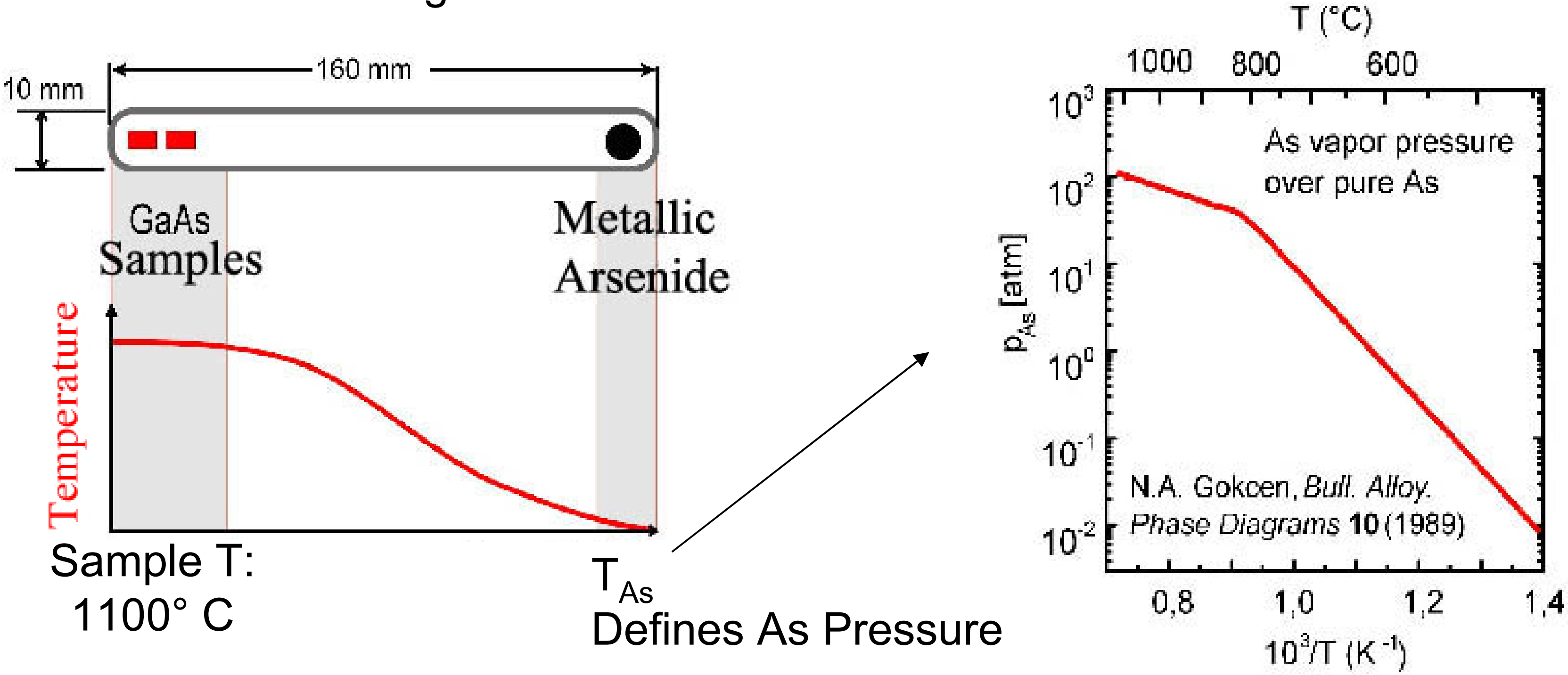
$$[V_{Ga}] \propto P_{As_4}^{1/4}$$

$$[As_{Ga}] \propto P_{As_4}^{1/2}$$

$$[Ga_{As}] \propto P_{As_4}^{-1/2}$$

Experimental

- Annealing in a two-Zone oven at 1100° C
  - High-purity quartz ampoule *([Cu] < 0.02 ppm)*
  - 2 hours heating



Sample T:
1100° C

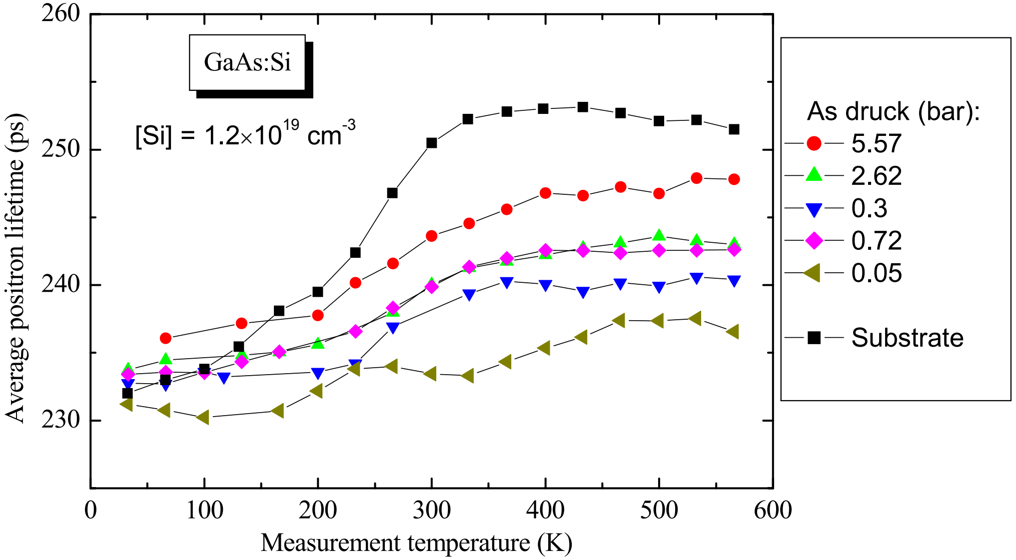
T_{As}
Defines As Pressure

N.A. Gokcen, *Bull. Alloy. Phase Diagrams* **10** (1989)

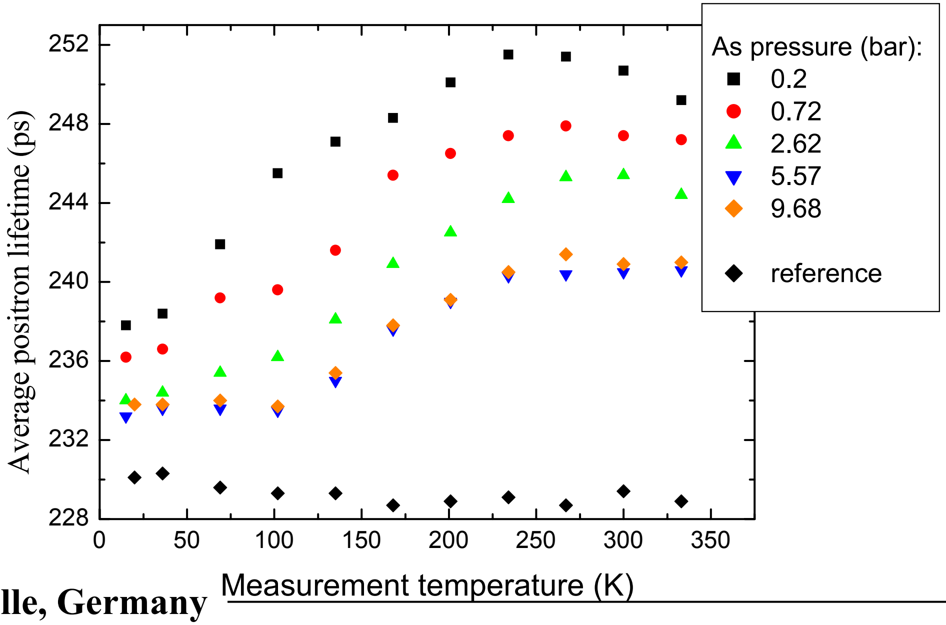
- Quenching into the water at room temperature
- PALS measurements at 20-600 K

Results: Positron lifetime spectroscopy

- Si-doped GaAs
  - Vacancy + shallow traps
  - τ_2 = 260±5 ps
  - $Si_{Ga}V_{Ga}$ defect complex
  - Si_{As} as shallow trap
  - $[Si_{Ga}V_{Ga}]$ increases with increasing p_{As}



- Semi-insulating GaAs
  - Vacancy + shallow traps
  - Origin unknown
  - τ_2 = 293±10 ps; I_2 = 40-70%
  - Reciprocal dependence [Vacancy] - p_{As}



Results: Hall-effect measurements (SI GaAs)

- Hall-measurements at room temperature
  - All SI samples became p-type
  - No correlation between P_{As} and [p]

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  - Neutral vacancy defect

P_{As}, bar	[p], cm^{-3}	μ, cm^2/Vs	ρ, Ωcm
0.2	7.28×10^{11}	333	2.57×10^{4}
0.7	4.74×10^{10}	191	6.87×10^{5}
2.6	1.42×10^{11}	176	2.47×10^{5}
5.6	7.18×10^{10}	203	4.27×10^{5}
9.7	5.35×10^{11}	407	2.86×10^{4}

- Temperature-dependent measurement
  - Acceptor level: $E_A = E_V + 0.48$ eV
  - Usually attributed to Cu_{Ga} acceptor

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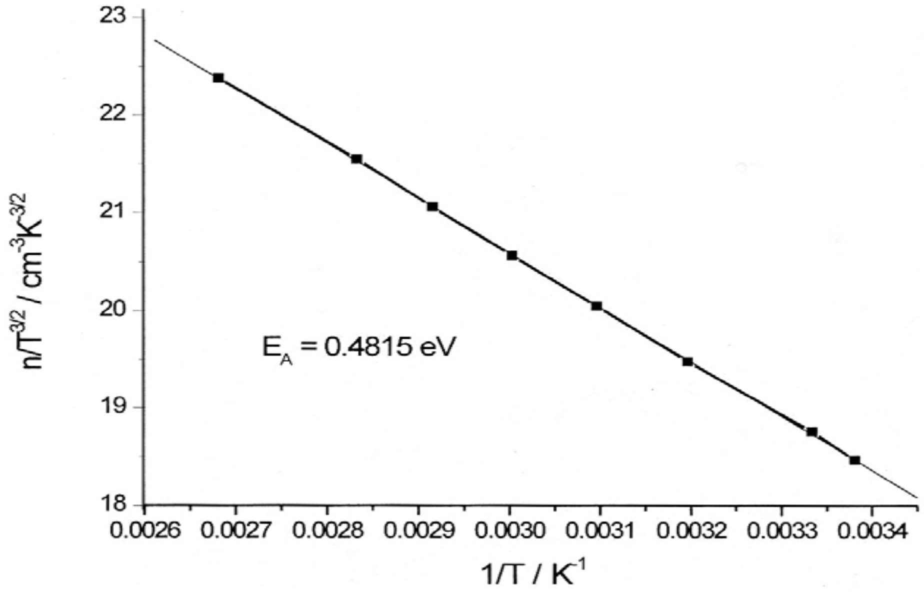
  - Act as positron shallow trap defects



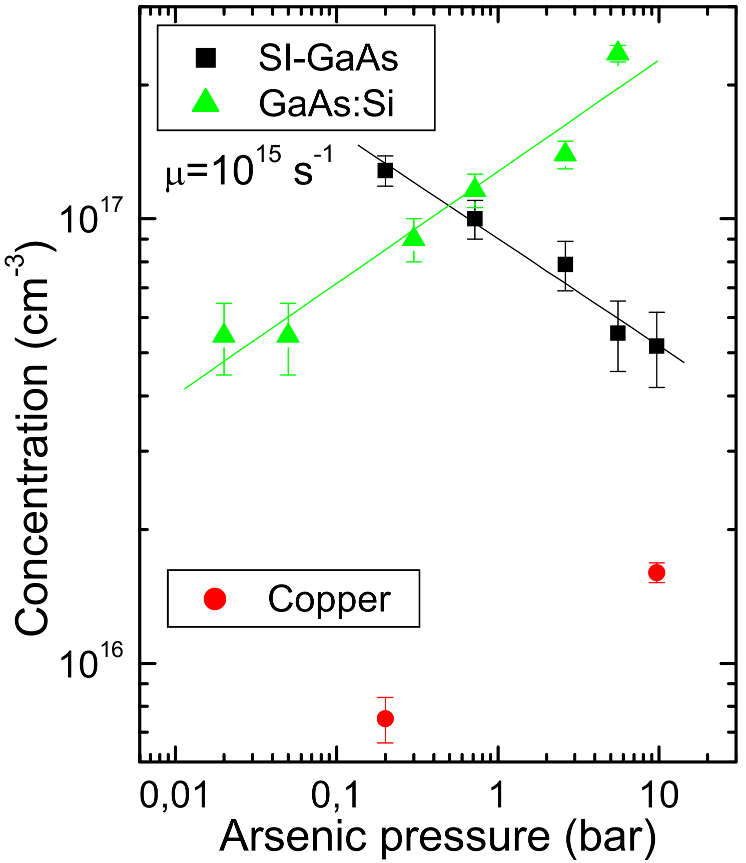
Discussion: evidence of V_{As} in annealed SI GaAs

- p_{As} concentration dependence
  - Concentrations were determined at RT with $\mu = 10^{15}\ s^{-1}$
  - Different slopes for GaAs:Si and SI GaAs

⇓

  - Different vacancy sublattices

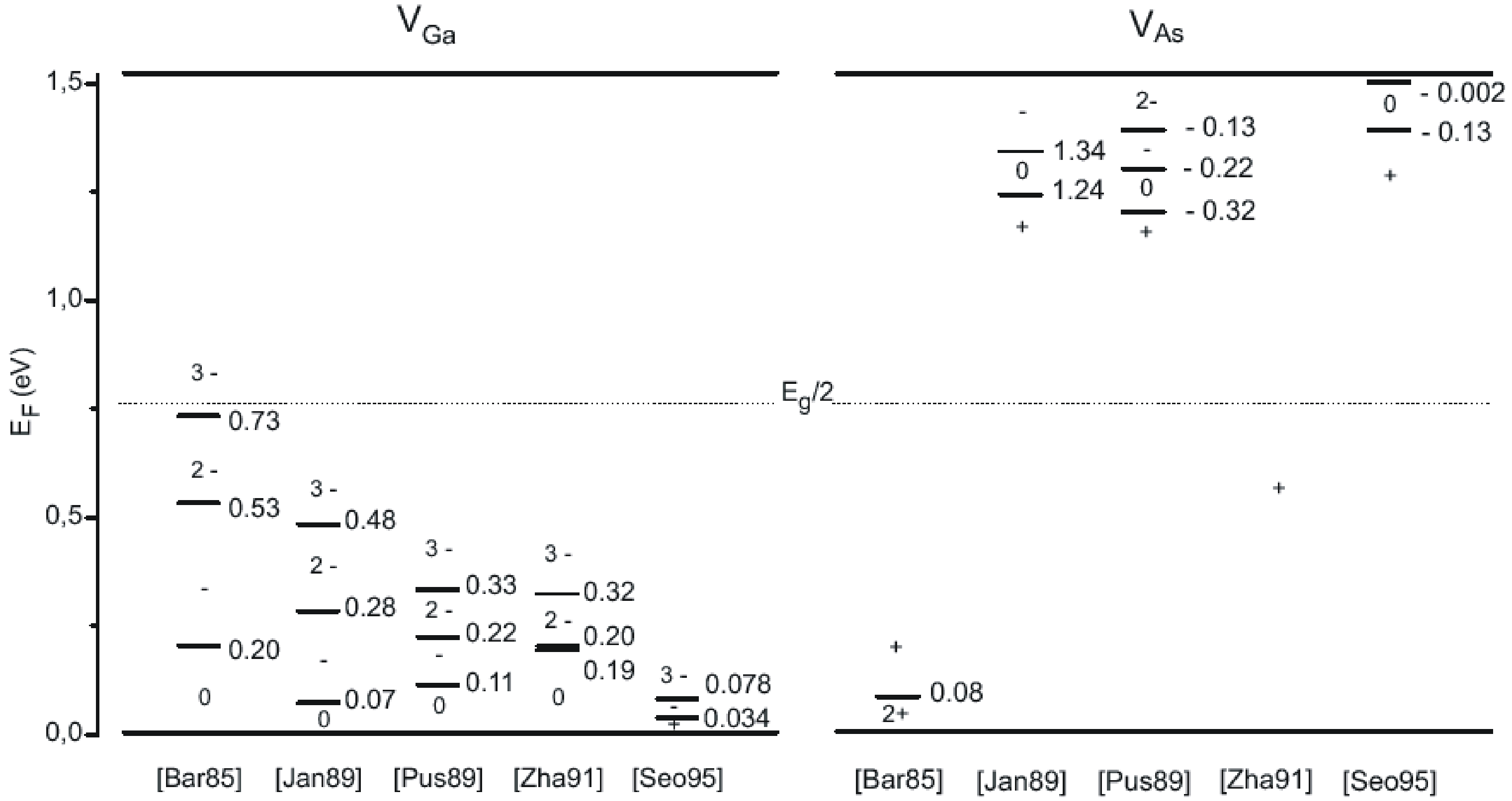
- Thermodynamic reactions
  - V_{Ga}:
    $1/4\ As_4^{gas} \leftrightarrow As_{As} + V_{Ga}$
    $[V_{Ga}] = K_{VGa} \times p_{As}^{1/4}$
  - V_{As}:
    $As_{As} \leftrightarrow V_{As} + 1/4 As_4^{gas}$
    $[V_{As}] = K_{VAs} \times p_{As}^{-1/4}$



- Fit: $\ln[V] = n \times \ln(p_{As})$
  - GaAs:Si: $n = 0.25 \pm 0.03$
  - SI GaAs: $n = -0.24 \pm 0.02$

Discussion: charge state of V_{As}

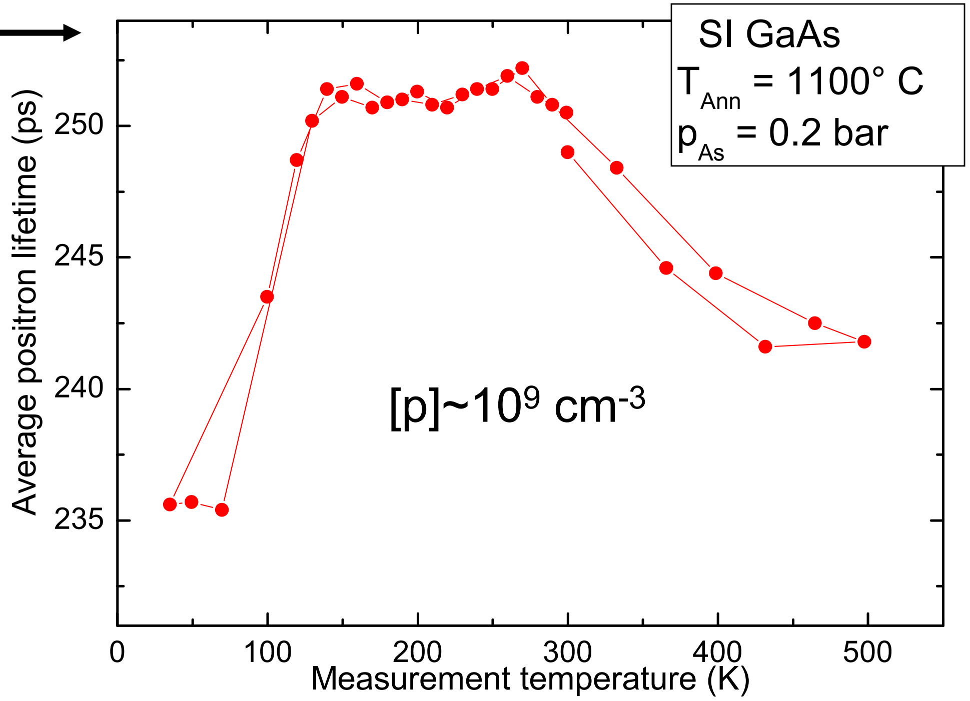
- Theoretical calculations for an arsenic vacancy
  - ionisation energies are lying in the upper part of the band gap
  - V_{As} are positive in SI or p-type GaAs



Discussion: charge state of V_{As}-defect

- Hall measurements
  - Showed no correlations with V_{As} concentrations and hence
  - imply they are in the neutral charge state

- Positron lifetime spectroscopy
  - Strong supression of uncontrolled contamination by advanced annealing procedure yielded →
  - The plateau at 120 – 300 K is a clear sign of neutral vacancy
  - The plateau is not seen in case of higher concentration of shallow traps



Discussion: formation energy of V_{As}

- Concentration of neutral V_{As}

$$[V_{As}^{0}] = K_{VAs} / p_{As_4}^{1/4} = (B_{As_4} / p_{As_4})^{1/4} \exp[-(H_f - TS_f)/kT]$$

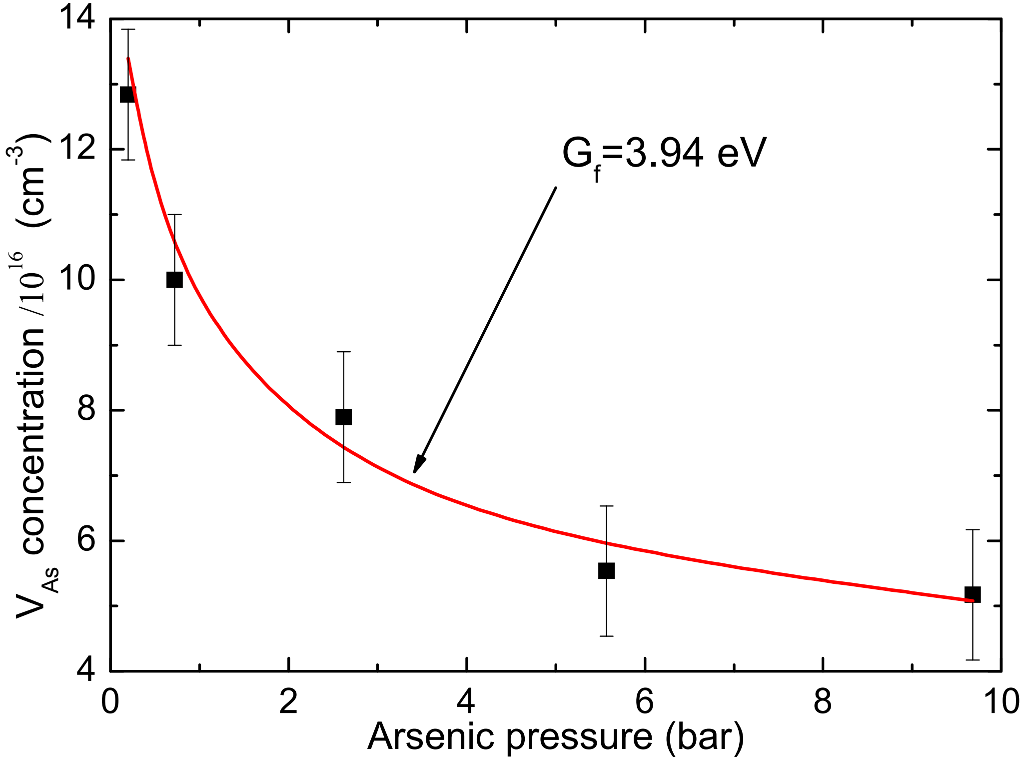
  - B_{As4} – gas pressure constant $B_{As_4} = (2\pi m_{As_4} / h^2)^{3/2} (kT)^{5/2} = 131.5 T^{5/2}$
  - $G_f = H_f - TS_f$ Gibbs formation energy

- Fitting to the concentrations

  - G_f as only fitting parameter

$$\Downarrow$$

  - $G_f = 3.94 \pm 0.003$ eV



Summary

- Positron annihilation + annealing experiments
  - Formation of monovacancy-like defects at 1100° C in SI GaAs
  - τ_2 = 293 ± 10 ps
  - Shallow traps
- Hall-measurements
  - Vacancy-like defect is neutral
  - Cu_{Ga} acceptor-like impurity, acting as the positron shallow traps
    $E_A = E_V + 0.48$ eV
- Pressure dependence
  - Arsenic vacancy V_{As} is observed
  - Gibbs free energy of formation of the V_{As} was obtained:
    $G_f = 3.94 \pm 0.003$ eV