# Experimental determination of the Gibbs free energy of formation of Ga vacancies in GaAs

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## Introduction

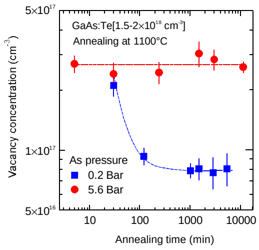
- Occurence of a defect in thermal equilibrium determined by the Gibbs free energy of formation $G_f = H_f - T\,S_f$ i.e.by formation enthalpy $H_f$ *and* formation entropy $S_f$ which are generally not well known
- $V_{Ga}$ in GaAs - diffusion studies so far only experimental approach to determine $G_f$
- rather discrepant (i.e. $H_f = 2$ or 4 eV [1,2]) and not in line with theory (i.e. $S_f = 33\,k_B$ from experiments [2] compared to $S_f = 7\,k_B$ [3]), diffusion suggest two minus charge [1] of $V_{Ga}$ compared to three minus charge expected from theory [3,4]
- This work: determination of $G_f$ employing a new experimental approach - high temperature annealing + direct investigation of the defects with positron annihilation

## Experimental

**Samples:** LEC-grown GaAs:Te, VB-grown GaAs:Si,Se,Sn

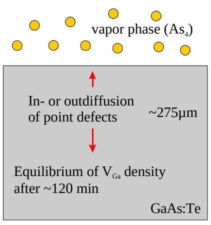
1. **Annealing to introduce equilibrium defect densities:** 2-zone furnace, control two degrees of freedom (sample temperature and As vapor pressure)
2. **Quenching:** 40 K/s in water to RT
3. **Detection of vacancies with positron annihilation:** Lifetime spectroscopy (fast-fast system, FWHM= 250 ps), Doppler coincidence spectroscopy (Ge-Ge system, 1.03 keV)

## Microscopic processes during annealing




- After annealing: $V_{Ga}$- donor complexes detected in all samples [5]
- Constant density after ~120 min, depends only on $p_{As}$ (and T)
- Vacancy concentrations are reversible

➜ Annealing yields equilibrium concentration of vacancies



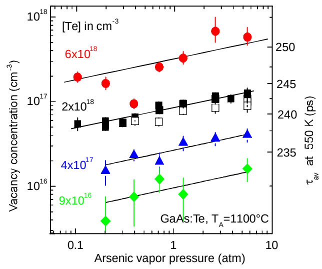

- Diffusion from/to surface required, diffusion length $L = 2\,(D_v t)^{1/2} \rightarrow D_v = 2.5\times10^{-8}$ cm² s⁻¹
- $D(V_{Ga}) > 1.5\times10^{-8}$ cm² s⁻¹ [6]

➜ Equilibrium established by diffusion of isolated $V_{Ga}$, complexes form after cooling

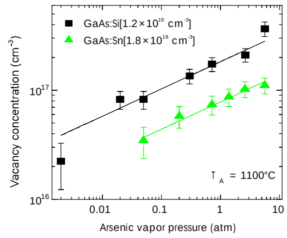
- At room temperature, all $V_{Ga}$ are bound by donors due to lack of other recombination centers (no $Ga_i$, dislocation density too low)

➜ Experiments probe density of $V_{Ga}$

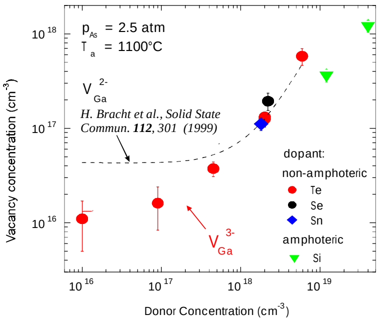
## Vacancy concentration in equilibrium



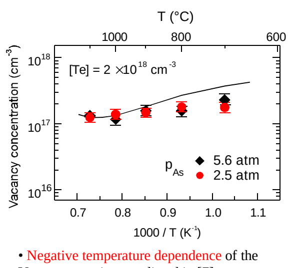

- vacancy concentration [V] increases with $p_{As}$
- characteristic power-law for all dopants: $[V] \sim p_{As}^{n}$ with $n = 1/4$ ( lines)
- explanation: equilibrium reaction $1/4\,As_4(gas) \leftrightarrow As_{As} + V_{Ga}$ i.e. $[V_{Ga}] = K \times p_{As}^{1/4}$




## Determination of the formation enthalpy




- $V_{Ga}$ concentration increases with doping - Fermi level effect
- Lines: Fit to data from GaAs:Te, data are only compatible with 3- charge of $V_{Ga}$
- Vacancy concentration in GaAs:Si is lower, most probable due to the existence of additional $Si_{As}^{-}$ acceptors




- Negative temperature dependence of the $V_{Ga}$ concentration, predicted in [7]

**Equilibrium concentration of $V_{Ga}^{z-}$**

$$[V_{Ga}^{z-}] = \left(\frac{p_{As}}{B_{As}}\right)^{1/4} \exp\left(-\frac{G_f}{k_B T}\right) \qquad [6,7]$$

where

$$G_f = H_f - s^f_{V_{Ga}} = h^f_{V_{Ga}} - \left(z\,E_F - \sum_{i=1}^{Z} E_{a,i}\right) - s^f_{V_{Ga}}$$

**(Gibbs free energy of formation of $V_{Ga}^{z-}$)**

| | |
|---|---|
| $H_f$ | (formation enthalpy of $V_{Ga}^{z-}$) |
| $h^f_{V_{Ga}}$ | (formation enthalpy of $V_{Ga}^{0}$) |
| $s^f_{V_{Ga}}$ | (formation entropy of $V_{Ga}$) |
| $B_{As} = 135\,T^{5/2}$ [atm] | (gas constant for $As_4$) |
| $E_{a,i}$ | (ionization level of $V_{Ga}$) |
| $E_F$ | (Fermi level) |

- fit to data (solid lines) with $H_f = 1.9$ eV for intrinsic GaAs, difference between activation enthalpy of Ga self-diffusion (3.7 eV, [8]) and migration enthalpy of $V_{Ga}$ (1.8 eV [9])

$h^f_{V_{Ga}}$ = **(3.2±0.2) eV** (enthalpy of formation of $V_{Ga}^{0}$)

$s^f_{V_{Ga}}$ = **(9.6±1) $k_B$** (entropy of formation of $V_{Ga}^{0}$)

$V_{Ga}$ has **3 minus** charge state in n-GaAs

$E_{a,i}$ (ionization level of $V_{Ga}^{3-}$)

- 0/- .... 0.13 × $E_{Gap}$
- -/2- .... 0.35 × $E_{Gap}$
- 2-/3- .... 0.49 × $E_{Gap}$

- Exact values for $E_a$ can not be obtained because only the sum over the single values is relevant. Uncertainty for $\Sigma E_{a,i}$ is 0.3 eV at 1100°C

## Discussion

- Only available theory where entropy is considered: $G_f = 3.6$ eV - 3 $E_F$ - 7.3 $k_B$ [3]

➜ good agreement with our experimental result

- previous experiments:

a) $H_f = 4$ eV and $s^f = 32.9\,k_B$ from diffusion in AlGaAs/GaAs structures [2]

b) $V_{Ga}$ only twofold negative from diffusion in isotopically controlled GaAs layers[1]

- Both (a) and (b) in discrepancy to our results - most likely explanations that amphotericity of Si and formation of $V_{Ga}$-donor-complexes was not considered

## Literature


[1] H. Bracht et al., Solid State Commun. **112**, 301 (1999)
[2] J. Rouviere et al., Phys. Rev. Lett. **68**, 2798 (1992)
[3] M. Bockstedte and M. Scheffler, Z. Phys. Chem. **200**, 195 (1997)
[4] e.g. G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985)
[5] J. Gebauer et al., Phys. Rev. B **60**, 1464 (1999)
[6] T.Y. Tan et al., Crit. Rev. Sol State Mat. Sci. **17**, 47 (1991)
[7] T.Y. Tan et al., Appl. Phys. A **56**, 249 (1993)
[8] H. Bracht et al., Appl. Phys. Lett. **74**, 49 (1999)
[9] I. Lahiri et al., Appl. Phys. Lett. **69**, 269 (1996)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