Revealing thermodynamic properties of vacancies in compound semiconductors by positron annihilation - Ga vacancies in n-doped GaAs

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Introduction

- Occurence of defects determined by thermodynamic properties → formation enthalpy, charge state
- PAS failed to reveal such properties for vacancies in semiconductors although succesful for metals
- Example: V_{Ga} in GaAs

→ Formation enthalpy and charge state not exactly known

V_{Ga}^{3-} (theory)	V_{Ga}^{2-} (diffusion experiments)
e.g. *S.B. Zhang, J.E. Northrup, PRL* ***67****, 2339 (1991)*	*H. Bracht et al., Solid State Communications* ***112****, 301 (1999)*

- Present work: establishing way to study thermodynamic properties of vacancies in compound semiconductors by PAS

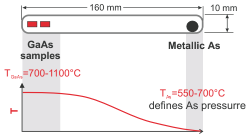
↓

1. Experiments resulting in thermodynamically well defined state
2. Exact identification and quantification of the vacancies studied
3. Correct modelling by appropriate theory

Experimental

Samples: LEC-grown GaAs:Te (Te is only donor as Te_{As})

1. Annealing:



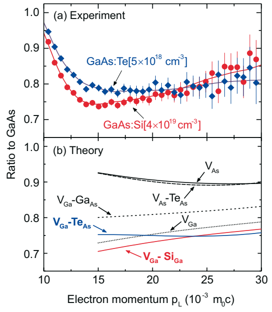
Control two degrees of freedom (T and p_{As})

→ Indispensable to establish thermodynamic defined defect concentrations in a binary compound (Gibb´s phase rule), annealing alone is not sufficient!

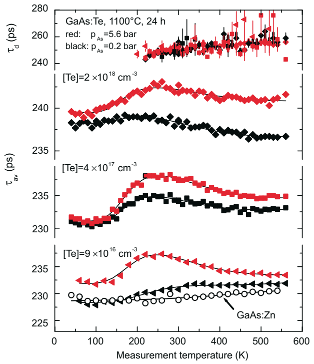
2. Quenching: 40 K/s in water to RT

3. PAS: Lifetime spectroscopy (fast-fast system, FWHM=250 ps), Doppler coincidence spectroscopy (Ge-Ge system, 1.03 keV)

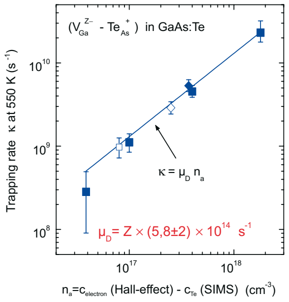
V_{Ga}-Te_{As} complexes



Microscopic **identification** of V_{Ga}-Te_{As}
Gebauer et al., PRB ***60****, 1464 (1999)*

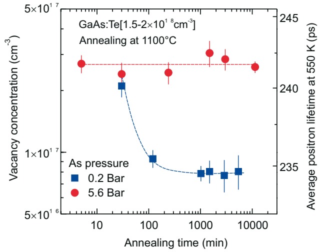


Detection of V_{Ga}-Te_{As} in annealed GaAs:Te



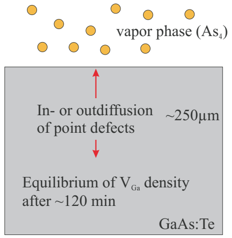
Exact determination of the trapping coefficent
→ **reliable quantification** of vacancies

Annealing



- Stationary state after ~120 min, depends only on p_{As}
- Vacancy concentrations can be reversible adjusted

→ Annealing results in equilibrium



vapor phase (As_4)

In- or outdiffusion of point defects ~250µm

Equilibrium of V_{Ga} density after ~120 min

GaAs:Te

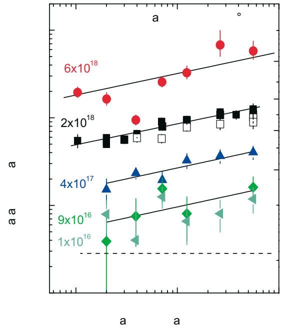
diffusion length:
$L=2\,(D_V t)^{1/2} \rightarrow D_V=2.5\times10^{-8}$ cm^2 s^{-1}

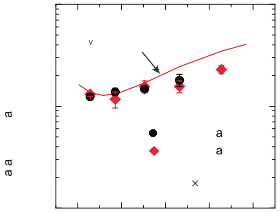
$D(V_{Ga}) > 1.5\times10^{-8}$ cm^2 s^{-1}
T. Y. Tan et al., Crit. Rev. Sol. State Mater. Sci. ***17****, 47 (1991)*

→ Equilibrium established by diffusion of isolated V_{Ga}

→ Complexes form only after cooling

Influence of stoichiometry, doping and temperature





- vacancy concentration [V] increases with p_{As} → V_{Ga} is equilibrium vacancy in n-GaAs
- characteristic power-law dependence $[V] \sim p_{As}^{\,n}$ with $n=1/4$ (all solid lines)
- incorporation reaction: $1/4\ As_4\,(gas) \leftrightarrow As_{As} + V_{Ga}$

→ $[V_{Ga}] = K\times p_{As}^{1/4}$, confirmed by experiment!

- Negative temperature dependence of the V_{Ga} concentration
- predicted by Fermi-level-effect model
  T. Y. Tan et al., Appl. Phys. A ***56****, 249 (1993)*

→ present results are the first direct experimental evidence for such effect

Fermi-level-effect model

Equilibrium concentration of charged V_{Ga}

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

with

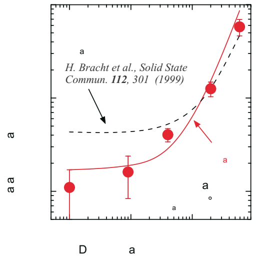
$B_{As} = 135\,T^{5/2}$ [atm] (gas constant for As_4)

$G_V = g^f_{V_{Ga}} - \left(z\,E_F - \sum_{i=1}^{Z} E_{a,i}\right)$ (enthalpy of formation)

$g^f_{V_{Ga}} = h^f_{V_{Ga}} - s^f_{V_{Ga}}$ (free enthalpy of formation for V_{Ga}^{0})

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

E_F (Fermi level)



Known properties of V_{Ga}

Activation enthalpy of Ga self-diffusion

$G_A = 3.7$ eV *H. Bracht et al., APL* ***74****, 49 (1999)*

Migration enthalpy of V_{Ga}

$G_M = 1.8$ eV *I. Lahiri et al., APL* ***69****, 239 (1996)*

→ **$G_V = G_A - G_M = 1.9$ eV**

→ **Properties of V_{Ga}**

$h^f_{V_{Ga}} = 3{,}5\ eV$ (enthalpy of formation for V_{Ga}^{0})

$s^f_{V_{Ga}} \sim 10\ k_B$ (entropy of formation for V_{Ga}^{0})

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

$E_{a,i}$ (ionization level of V_{Ga}^{3-}):
0/- .... $0{,}13 \times E_{Gap}$
-/2- .... $0{,}35 \times E_{Gap}$
2-/3- .... $0{,}49 \times E_{Gap}$

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