

2. Thermodynamics of native point defects in GaAs

The totality of point defects in a crystal comprise those existing in a perfectly chemically pure crystal, so called intrinsic defects, and those associated with some foreign atoms. The latter are termed “dopants” if they are deliberately added or “impurities” if they were introduced unintentionally. There are six principal intrinsic point defects in GaAs: vacancies on both sublattices (V_{Ga} and V_{As}), Ga and As interstitials (Ga_i and As_i) and antisites (Ga_{As} and As_{Ga}). In framework of this work, the term “native defects” is related to the point defects being in thermodynamical equilibrium with a host crystal and not introduced intentionally, e.g. by crystal deformation or irradiation. This definition comprises intrinsic defects, foreign atoms as well as their complexes. The equilibrium concentration of point defects in binary compound semiconductors such as GaAs is a complicated function depending of temperature, Fermi-level position and of the activity of either one of the constituents (gallium or arsenic), i.e. of crystal stoichiometry. In the following sections, some aspects important for this thesis concerning native defect formation are briefly reviewed.

2.1 GaAs system at melting point

Gallium arsenide crystallizes in the zincblendstructure at about 1513 K. The lattice constant is 0.5653 nm at 300 K (Brozel and Stillman 1996). As for any compound, there is a certain thermodynamically allowed region of homogeneity for $\text{Ga}_{1-x}\text{As}_x$. This is shown on

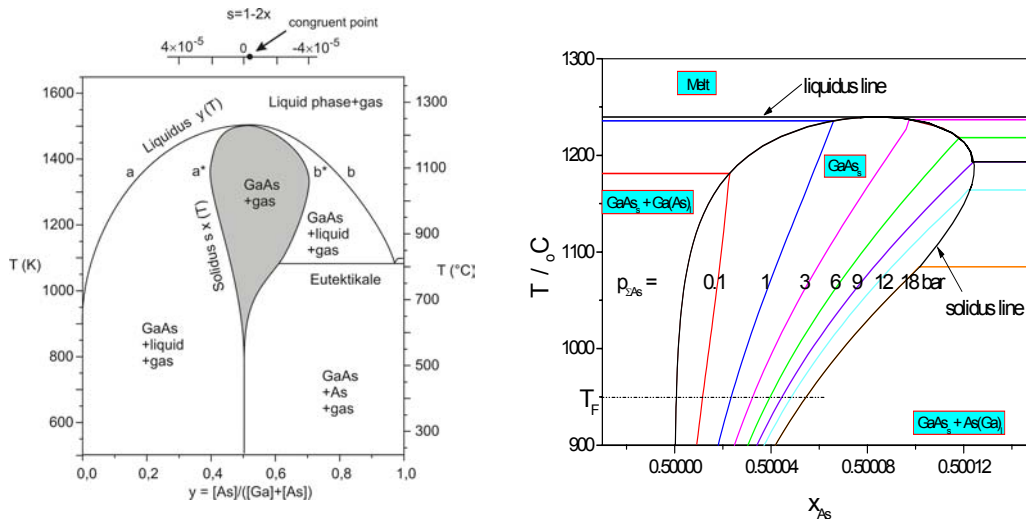


Fig. 2.1: Binary phase diagram of Ga-As-System. Data are taken from Refs. (Wenzl et al. 1991; Wenzl et al. 1994) (left) and (Jurisch and Wenzl 2002) (right)

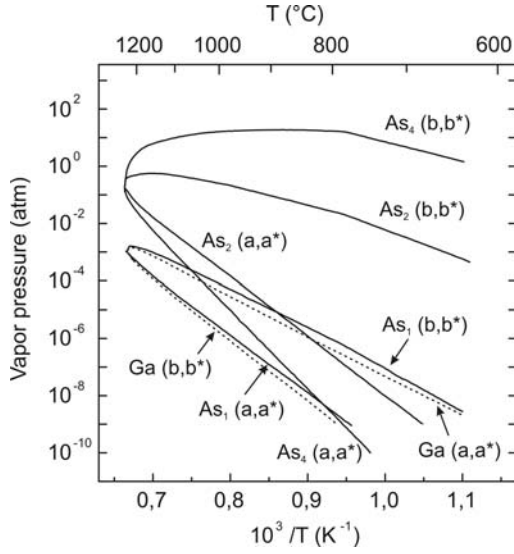


Fig. 2.2: Equilibrium pressures of As , As_2 , As_4 and Ga along the Ga-rich (a,a^*) and As-rich (b,b^*) phase boundary of GaAs. (From Ref. (Arthur 1967))

the binary phase diagram in fig. 2.1. The homogeneity region is represented by the shaded area within the solidus line a^*b^* . If concentration of one of the components (e.g., As) exceeds a value allowed by the solidus line b^* , the GaAs system consists of three phase – GaAs crystal, melt and gas. Inside the homogeneity region, GaAs crystal is in thermal equilibrium with its gas phase. Corresponding vapour pressures determined along the solidus line are shown in fig. 2.2. In case of the arsenic-rich melt, the As_4 -pressure dominates while the vapour pressure of gallium is negligibly small. The resulting pressure is then $\approx p_{As_4}$. On the gallium-rich side, As_2 is the dominating gas component. The Ga pressure becomes important only at low temperatures ($T < 800^\circ C$).

It is important to note that the exact shape of the GaAs phase diagram is unknown at present. This subject is still under investigations. According to the recent thermodynamic calculations of Jurisch and Wenzl, there is no crystallization at all possible on the Ga-rich side [Fig. 2.1 (right)]. This may explain the fact why gallium precipitates were never observed even in the crystals grown from a very Ga-rich melt (Kießling 2003). However, the Wenzl's hypothesis needs stronger experimental evidence. Anyway, it is commonly accepted that the congruent point, where the solidus and liquidus lines osculate, lies on the As-rich side of the phase diagram (Fig. 2.1). Therefore, growth from a stoichiometric melt always yields arsenic-rich material (Wenzl et al. 1991, Hurle 1999).

The deviation from stoichiometry s is realized through the formation of point defects on both sublattices. The deviation can be expressed as $s = 1 - 2x = s_1 - s_2$, where s_1 and s_2 are determined as:

$$\begin{aligned} 2s_1 &= [Ga_i] + [Ga_{As}] - [V_{Ga}] - [As_{Ga}] - [X_{Ga}] \quad \text{and} \\ 2s_2 &= [As_i] + [As_{Ga}] - [V_{As}] - [Ga_{As}] - [X_{As}] \end{aligned} \quad (2.1)$$

where X_{Ga} and X_{As} imply an arbitrary foreign atom on the As or Ga lattice site. The brackets denote defect concentration in atomic units. Thus, by measuring the stoichiome-

try deviation s , type and concentration of the dominating point defects can be determined. There are two direct methods for estimation of s :

- 1) the direct determination of the amounts of Ga and As atoms in a sample by electrochemical titration of one or both of the species;
- 2) the determination of the average mass of the unit cell in a sample by measuring its density (which is the mass per unit volume of crystal) and the cube of its lattice parameter (which is volume of the unit cell). The quotient of these two quantities is, therefore, the mass per unit cell. By subtracting from this the mass of an ideal unit cell (containing one Ga and one As atom), the excess mass per unit cell which is related to the deviation from stoichiometry is obtained.

Application of these two approaches to study GaAs crystals grown from Ga- and As-rich melt showed that deviations on the As sublattice dominate (Hurle 1999). Thus, under As-rich conditions, there are large concentrations of As_i and V_{Ga} grown into the crystals at the melting point. However, deviation from stoichiometry provides information only on dominating defects, which remain in a crystal after its cooling. Investigation of other point defects present at elevated temperatures with the help of these methods is impossible.

There are always some point defects existing in a crystal at thermodynamical equilibrium, which contribute to minimization of the Gibbs free energy. In elemental semiconductor such as Si, the equilibrium concentration of an individual point defect depends on temperature and the position of the Fermi level. For compound semiconductor, the situation is more difficult since the equilibrium concentrations depend additionally on the crystal stoichiometry (Eq. 2.1). This means that defect concentrations, crystal composition and ambient vapour pressure are in thermodynamical equilibrium and thus depend on each other. In addition, many of the point defects may exist in more than one charge state and interact strongly through their influence on the Fermi energy. Thus, dopant solubility can be strongly influenced by charged native point defects grown into the crystal and conversely, doping markedly affects charged native point defect populations.

2.2 Defects chemistry in GaAs

Defect chemistry represents a chemical approach to the problems dealing with imperfections in crystalline solids. This method considers the generation of defects, interaction between them and between defects and ambient as chemical reactions based on the assumption that the crystal is in an equilibrium state (Kröger 1964). Six intrinsic point defects in GaAs can be described by the following six thermodynamic reactions (Hurle 1999):



$$0 = V_{As}^0 + V_{Ga}^0 \quad (2.4)$$

$$Ga_{Ga} = Ga_i^0 + V_{Ga}^0 \quad (2.5)$$

$$As_i^0 + V_{Ga}^0 = As_{Ga}^0 \quad (2.6)$$

$$Ga_i^0 + V_{As}^0 = Ga_{As}^0 \quad (2.7)$$

where the superscript (0) indicates the neutral state. Only one of the reactions involves the external phase (Eq. 2.2). The external phase may be liquid or vapor. To avoid writing different equations for the two cases, the activity of the external phase is expressed in terms of the partial pressure of arsenic dimers which would be in equilibrium either with the vapor or with a liquid which was in equilibrium with that vapor. The arsenic tetramer is chosen, since it is the dominating species in arsenic vapor (Fig. 2.2). Having expressed a condition of equilibrium of one component with the external phase, equilibrium with respect to the other component (Ga) is defined as:

$$p_{Ga} p_{As_4}^{1/4} = \exp(-g^f / kT) \quad (2.8)$$

where p_{Ga} is the partial pressure of gallium monomers and g^f is the free energy of formation of GaAs from gaseous gallium monomer and arsenic tetramers at one atmosphere total pressure and temperature T . Substituting (2.2) into (2.3), one obtains the following reaction for V_{As} formation:

$$As_{As} = V_{As}^0 + 1/4 As_4(\nu) \quad (2.9)$$

From (2.4) and (2.9), a similar reaction for the Ga vacancy may be deduced:

$$1/4 As_4(\nu) = V_{Ga}^0 + As_{As} \quad (2.10)$$

Concentrations of vacancies in their neutral states are determined by mass-action law:

$$[V_{Ga}^0] = K_{V_{Ga}}(T) p_{As_4}^{1/4} \quad (2.11)$$

$$[V_{As}^0] = K_{V_{As}}(T) p_{As_4}^{-1/4} \quad (2.12)$$

where $K_{V_{Ga}}$ and $K_{V_{As}}$ are mass-action constants of formation of gallium and arsenic vacancies, respectively. According to (2.11) and (2.12), the density of V_{Ga} should increase and of V_{As} decrease with increasing arsenic pressure.

In case of charged vacancies, their ionization reactions and corresponding concentrations are given by the following reactions:

Arsenic vacancy

$$V_{As}^0 = V_{As}^+ + e^- \quad (2.13)$$

$$[V_{As}^+] = [V_{As}^0](N_C / n) \exp(-E_{V_{As}} / k_B T) \quad (2.14)$$

$$V_{As}^0 = V_{As}^- + h^+ \quad (2.15)$$

$$[V_{As}^-] = [V_{As}^0](n / N_C) \exp(-E_{V_{As}} / k_B T) \quad (2.16)$$

Gallium vacancy

$$V_{Ga}^0 = V_{Ga}^{q-} + qh^+ \quad (2.17)$$

$$[V_{Ga}^{q-}] = [V_{Ga}^0](n / N_C)^q \exp\left\{\left(qE_g - \sum_q E_{V_{Ga}^{q-}}\right) / k_B T\right\} \quad (2.18)$$

where $q=1,2,3$, $E_g(T)$ is the energy gap. $E_{V_{As}}$ is the ionization energy of the arsenic vacancy and $E_{V_{Ga}^{q-}}$ is the ionization energy of the q charge state of the gallium vacancy. n is the free electron concentration, N_C is the effective density of conduction-band states and k_B is Boltzmann's constant.

2.3 Tan model and Fermi-level effect

The considerations presented in the previous subsection give a qualitative description of vacancy formation. However, they cannot be applied quantitatively if the mass-action constants are unknown. Tan et. al. tried to evaluate the concentrations of equilibrium point defects explicitly (Tan et al. 1993; Tan 1994). According to Tan's model, concentrations of neutral arsenic and gallium vacancies are determined by:

$$[V_{As}^0] = \left(B_{As_4} / p_{As_4}\right)^{1/4} \exp\{-[g^f(V_{As}^0) - \delta g_{As}] / k_B T\} \quad (2.19)$$

$$[V_{Ga}^0] = \left(p_{As_4} / B_{As_4}\right)^{1/4} \exp\{-[g^f(V_{Ga}^0) + \delta g_{As}] / k_B T\} \quad (2.20)$$

$g^f(V_{As}^0)$ and $g^f(V_{Ga}^0)$ are the free energies of formation of neutral arsenic and gallium vacancies, respectively. δg_{As} is the difference:

$$\delta g_{As} = g_{As}(GaAs) - g_{As}(As_4) \quad (2.21)$$

$g_{As}(GaAs)$ is the free energy of bonding of an arsenic atom in the crystal and $g_{As}(As_4)$ is that of bonding of an arsenic atom in the tetramer molecule. $B_{As_4} = (2\pi m_{As_4} / h^2)^{3/2} (kT)^{5/2}$ is the gas constant assuming As_4 can be described as an ideal gas. m_{As_4} is the mass of the As_4 molecule and h – Planck's constant.

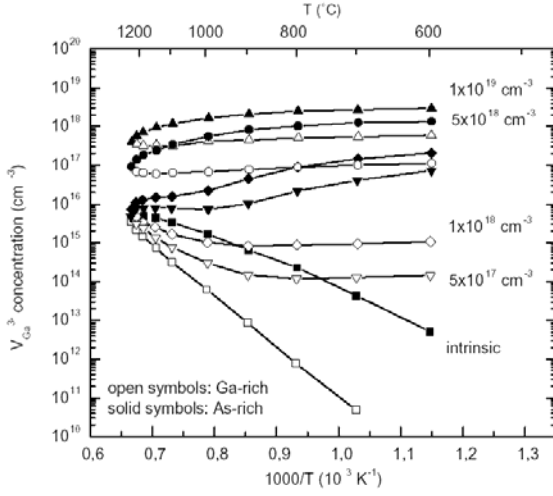


Fig. 2.3: Equilibrium concentrations of V_{Ga}^{3-} in n-type GaAs calculated as a function of temperature for different concentrations of donor atoms, i.e. for different positions of the Fermi level .

Concentrations of the charged defects in Tan's model are determined similarly to the Eq. 2.18

$$[V_{Ga}^{z-}] = [V_{Ga}^0] \exp\left(\left[zE_f - \sum_{m=1}^z E_{am}\right]\right) \quad (2.22)$$

E_F is the Fermi energy, z is the charge and E_{am} are the ionisation energies of the Ga vacancy measured from the valence band. As can be seen from Eq. (2.22), the concentration of the charged vacancies increases with the Fermi-level position moving towards the conduction band edge. The physical reason is the energy difference $E_F - E_a$ gained by a whole system (GaAs crystal) in a process of electron transition to the acceptor level E_a , i.e. formation of an additional acceptor. The dependence of the concentration of a charged point defect in a semiconductor on the charge carrier concentration (i.e. Fermi level position) is called the *Fermi-level effect*.

Assuming V_{Ga} as the only acceptor, Tan et al. calculated the density of gallium vacancies in n-type GaAs (Tan et al. 1991). The As pressures corresponded to those depicted in fig. 2.2. The Gibbs free energies in Eqs. (2.19,2.20) did not include entropy terms, i.e. they were set equal to the corresponding formation enthalpies h^f . The values $h_{V_{Ga}^0}^f = 2.59 eV$ (van Vechten 1975) and $\delta h_{As} = -0.69 eV$ were used. The data for V_{Ga} ionization energies were taken from Ref. (Baraff and Schlüter 1985). The results of the calculations performed for different free electron densities in n-GaAs are presented in fig. 2.3. In intrinsic material, the concentration of Ga vacancies increases with increasing temperature. However, the temperature dependence was found to be dramatically weakened by doping. At high doping level, E_F can be very close to the conduction band at all temperatures. This may result in temperature independence or even a small *negative temperature dependence* of equilibrium concentrations of V_{Ga}^{3-} (Tan 1994). The first experimental evidence of this effect was given by Gebauer et al. in a recent positron annihilation study of Te-doped GaAs (Gebauer et al. 2003). In their analysis, the formation en-

thalpy $h_{V_{Ga}^0}^f$ as well as the formation entropy $s_{V_{Ga}^0}^f$ was considered. The values $h_{V_{Ga}^0}^f = (3.2 \pm 0.5) eV$ and $s_{V_{Ga}^0}^f = (9.6 \pm 1) k_B$ were determined.

2.4 Quantum mechanical calculations

The calculations given in the previous subsection sensitively depend on the knowledge of defect formation and ionization energies. Experimental determination of these properties is usually possible only for a constrained number of defects. The charge state, formation energy E_D and equilibrium concentration C_D of a certain defect may also be obtained with the help of theoretical models based on quantum mechanical calculations. In equilibrium, C_D is given as:

$$C_D = N_s \exp[-E_D(\mu_e, \Delta\mu) / k_B T] \quad (2.23)$$

with $N_s = 2.2 \times 10^{22} \text{ cm}^{-3}$ being the density of lattice sites for one of the sublattices. E_D is a function of μ_e and $\Delta\mu$. μ_e is the electrons chemical potential, i.e. Fermi energy. $\Delta\mu$ is the difference between chemical potentials of Ga(As) in GaAs and in pure Ga(As) elements. In other words, $\Delta\mu$ reflects the stoichiometry deviation. As can be seen from Eq. (2.23), the defect with the lowest binding energy should have the highest equilibrium concentration. Since defect formation energies are usually not exactly known, the accuracy of such kind calculation is often insufficient. Thus, already small numerical uncertainties in the binding energy can affect the calculated defect density by orders of magnitude (Jansen and Sankey 1989). However, a quantum mechanical approach can be used for qualitative predictions of the type of dominating defects.

Fig. 2.4 represents the formation energy of intrinsic point defects in GaAs as a

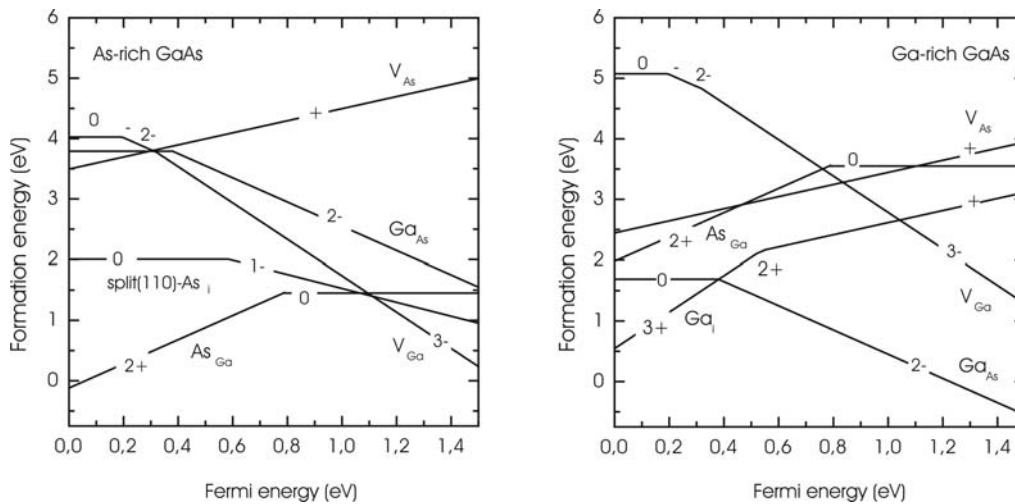


Fig. 2.4: Formation energy of intrinsic defects in As-rich (left) and Ga-rich (right) GaAs as a function of Fermi energy.

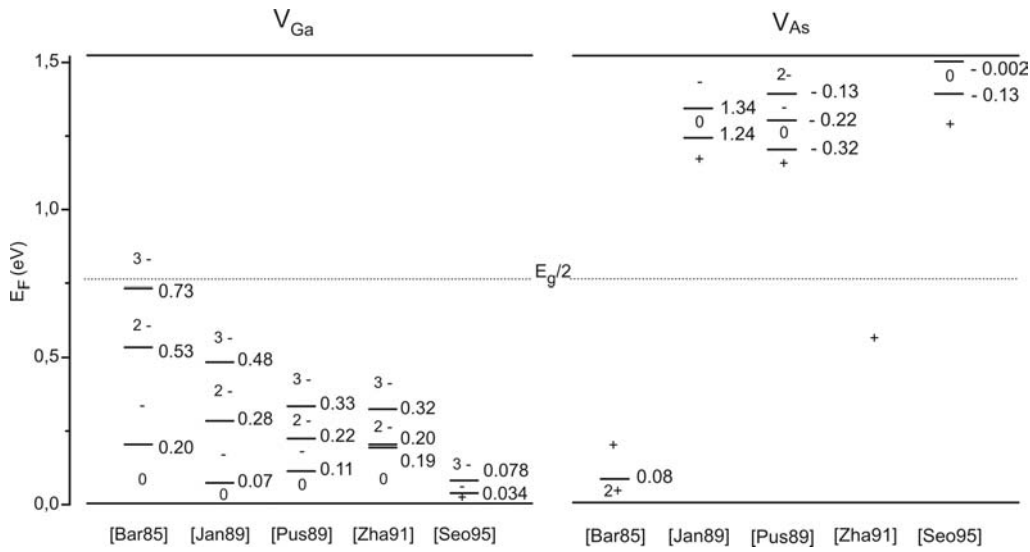


Fig. 2.5: Calculated ionization levels of Ga (left) and As (right) vacancies. Positive numbers designate values measured from the valence band, negative – from conduction band.

function of Fermi energy (from Refs. (Zhang and Northrup 1991; Northrup and Zhang 1993; Landman et al. 1997)). In As-rich, p-type and semi-insulating GaAs, the arsenic antisite As_{Ga} has the smallest formation energy. This is in accordance with the well-known fact that the EL2-centers govern properties of semi-insulating GaAs (Brozel and Stillman 1996). In n-conducting As-rich GaAs, triply negative gallium vacancy has the minimal formation energy. Gallium interstitials Ga_i should dominate in Ga-rich p-type GaAs and gallium antisites Ga_{As} – in SI and n-GaAs. Similar results were obtained in several other theoretical works (Baraff and Schlüter 1985; Jansen and Sankey 1989; Seong and Lewis 1995). According to them, gallium vacancies V_{Ga} should appear in As-rich n-doped GaAs. The formation energy of As-interstitials is according to (Landman et al. 1997) comparable with the formation of V_{Ga} or As_{Ga} in As-rich material. This is in agreement with the results of mass per unit cell measurements, according to which As_i is the dominating defect in As-rich GaAs (Section 2.1).

The arsenic vacancy V_{As} has a formation energy much higher than that of V_{Ga} in n-type Ga- and As-rich GaAs. Consequently, occurrence of V_{As} is rather improbable in n-GaAs. However in p-conducting material, where the Fermi level is positioned in the lower half of the band gap, formation of V_{As} can be energetically more favourable compared to V_{Ga} .

Knowledge about the defect ionisation levels is very important for the interpretation of PALS-results. The positron being a positively charged particle feels the charge of the defects. The direct consequence is that positively charged defects can not be detected by positrons. Unfortunately, ionisation levels of vacancies in GaAs are not well-known experimentally. In principle, they can be determined with the help of quantum mechanical calculations. Fig. 2.5 presents ionisation levels of Ga- and As-vacancy obtained in differ-

ent theoretical works. According to the calculations, the gallium vacancy has ionisation levels in the lower half of the band gap and thus, it is in n-type and SI GaAs triply negative charged. The arsenic vacancy should be positive in p-conducting and semi-insulating material. According to some calculations, V_{As} has ionisation levels near the conduction band (Refs. (Jansen and Sankey 1989; Puska 1989; Seong and Lewis 1995)). Thus, both V_{Ga} and V_{As} must be detectable in n-GaAs. However, calculated ionisation levels demonstrate rather big quantitative differences. Therefore, only qualitative conclusions may be drawn from them, whereas direct comparison with experimental data seems to be questionable.

2.5 Electrical compensation in n-type GaAs

GaAs having electron conductivity type can be produced by means of doping with the atoms of group IV (Si, Ge, Sn) or group VI (S, Se, Te) of the Periodic Table. The elements of the group VI can be incorporated exclusively on the As sublattice forming shallow donors. The atoms of the IV group demonstrate in contrary amphoteric behavior: they behave as shallow donors when incorporated on Ga site and as shallow acceptors – on the As site.

N-doped GaAs is always partially electrically compensated. This means that the free electron density is smaller than the number of introduced dopants. The compensation in GaAs doped with the atoms of the IV group can to some extent be explained by simultaneous formation of donors and acceptors due to the amphoteric dopants incorporation. However, measurements of carrier mobility demonstrated the compensation effect occurring also in S-, Se- or Te- doped material. The degree of compensation N_D/N_A was found to be ~ 0.25 at moderate doping levels regardless of the dopant kind.

Hurle in Ref. (Hurle 1977) supposed that the compensating species was the donor atom complexed with its nearest gallium vacancy to form an acceptor. Positron annihilation studies of Te- and Si-doped GaAs have rather clearly demonstrated the existence of $Te_{As}V_{Ga}$ (Krause-Rehberg et al. 1995; Gebauer et al. 1999) and $Si_{Ga}V_{Ga}$ complexes (Laine et al. 1996; Gebauer et al. 1997). Vacancy-like defects were found also in GaAs doped with S, Ge and Sn atoms (Gebauer 2000). The complexes were found to be negatively charged. However, there is still a lack of knowledge on their exact charge state (e.g., $-1e$ or $-2e$). Nowadays, donor-gallium vacancy complexes are commonly accepted as compensating centers in all kinds of n-GaAs.

Compared to point-like imperfections, influence of large-scale defects on electrical properties of GaAs is much less investigated. Thus, it was found that the distribution of carrier concentration across silicon-doped GaAs wafer showed structures corresponding to the arrangement of dislocations (Börner 2002). This might be due to the decreased concentration of $Si_{Ga}V_{Ga}$ complexes in dislocation-rich regions of a GaAs wafer, as was proposed in the recent photoluminescence study of GaAs:Si (Baeumler et al. 2002).

However, photoluminescence spectroscopy could provide only qualitative information on defect concentrations. In contrary, the method of positron annihilation used in this work is suitable for quantitative analysis of the distribution of $\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$ complexes.