5. Vacancy formation in semi-insulating and silicon-doped GaAs under equilibrium conditions

5.1 Experimental

At temperatures lower than 1240° C (melting-point), the GaAs system consists of two phases – solid and gas – and has according to Gibbs' phase rule two degrees of freedom. In other words, it is necessary to fix two independent parameters, in order to adjust certain equilibrium state of the samples. The most convenient way is to choose sample temperature and the ambient gas pressure. At elevated temperatures, the gas phase consists predominantly of the arsenic tetramer As_4 and the partial vapor pressure of gallium can be neglected (Arthur 1967). The defect concentrations at equilibrium will then be a function of the sample temperature and the arsenic ambient vapor pressure. Holding the sample temperature fixed and varying the arsenic pressure, one can change the chemical composition of the crystal. This makes it possible to investigate the formation of point defects as a function of crystal stoichiometry. However, direct measurements of defect concentrations at the high temperatures necessary for their formation are difficult. Therefore, one often tries to "freeze" the high-temperature defect configuration by quenching of an investigated crystal from high to low (room) temperatures. This method was also used in this work.

The studied samples were cut from the semi-insulating undoped and silicon doped LEC grown GaAs wafers (5×5×0.5 mm). The wafers were supplied by FCM (Freiberger Compound Materials GmbH). The resistivity of undoped material was about 10^6 – 10^7 Ωcm. The concentrations of Si and free electrons in GaAs:Si were equal to $1{,}2\times10^{19}$ cm^{-3} and 5×10^{18} cm^{-3} respectively. For the annealing, two identical samples with

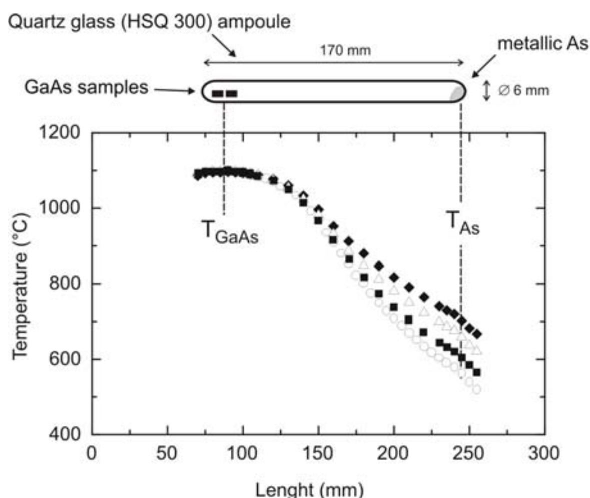

Fig. 5.1: *Temperature profile of the two-zone furnace used for the annealing of GaAs samples under different As pressures. Positions of the samples and As-source are shown by vertical lines.*

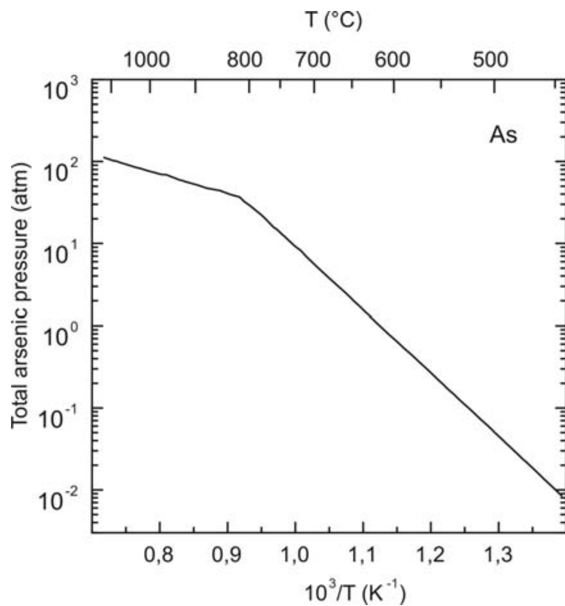

Fig. 5.2: *Vapor pressure of metallic As versus temperature (from Ref. (Gokcen 1989)). The sharp bend of the curve corresponds to the melting point of arsenic (817° C).*

a piece of metallic arsenic were sealed in the quartz ampoule and placed into a two-zone temperature furnace, as Fig. 5.1 shows. The arsenic vapor pressure is determined by the temperature at the coldest part of the ampoule and corresponds thus to the temperature of the metallic arsenic (T_{As} in Fig. 5.1) (Kröger 1964) providing the arsenic quantity is high enough to prevent its complete sublimation. The samples temperature was 1100° C for each annealing, whereas the temperature of As-source was varied over the range of 550° C – 740° C. Corresponding arsenic pressure values were determined with the help of the $p_{As}(T)$ dependence taken from Ref. (Gokcen 1989) (Fig. 5.2).

Since semi-insulating GaAs material was investigated, the purity of the annealing experiments was of special importance. The introduction of an electrically active impurity in concentration of 0.1 ppm (10^{15} cm^{-3}) changes immediately the conductivity type of GaAs from semi-insulating to semi-conducting by jump-like transition of the Fermi-level position, which in turn affects the formation of point defects (Tan et al. 1993; Hurle 1999). Copper is known as an often occurring impurity in the annealing experiments due to its ubiquity and high diffusive coefficient. In this connection, the high purity copper-free quartz ampoules HSQ300 (Heraeus Quarzglas GMBH&Co) have been used. The ampoules have been etched for 2 hours in nitrohydrochloric acid ($3HCl:1HNO_3$), rinsed three times with distilled water and two times with ethanol whereupon dried in air for 24 hours. The samples were etched in 2% of bromine methanol solution and bathed in methanol just before and after annealing. The etching time was about 5 min, which corresponded to the removing of ≈ 40 μm of the surface layer. Two identical samples with the piece of pure As (99,999%) were placed in the quartz ampoules, which were filled three times with argon and then they were sealed under a pressure of 10^{-3} Torr using a conventional gas-burner.

However, despite all the precautions a sample contamination with copper in the order of 10^{16} atoms/cm^3 occurred usually during the annealing (Section 5.3.2). Most probably, the source of copper atoms was the brass head of the gas-burner. Moreover, about 10^{15} copper atoms/cm^2 can be adsorbed from alcohol used for the sample and ampoule cleaning (Hall and Racette 1964). In order to reduce the level of contamination, a new sample preparation procedure was developed. A different burner with a head made of quartz glass (Herbert Arnold GmbH) was used. Only high-purity distilled water and no ethanol was used in the ampoule cleaning procedure. The SI GaAs samples were prepared and packed under "clean-room" conditions at FCM. Immediately after unpacking, they were sealed in the ampoules and annealed. As a result, the copper contamination was indeed reduced and amounted to 10^{14} atom/cm^3. This had a great influence on the quality of the experimental data and has helped significantly in the interpretation of the results. (Section 5.3.3)

5.2 Defects detected by PALS in annealed GaAs

5.2.1 Si-doped GaAs

Average positron lifetime curves versus measurement temperature for silicon doped GaAs in the as-grown state and after annealing under different As-pressures are presented in Fig. 5.3. The temperature dependent behavior of the average positron lifetime in as-grown and annealed samples is similar to that observed for GaAs:Si material studied in Section 4. At high temperatures, it is distinctly larger than that of bulk GaAs due to positron trapping into vacancy type defects. The decrease of the average positron lifetime with decreasing temperature is related to the positron trapping at negative ions that act as shallow positron traps at low temperatures having positron lifetime close to bulk value τ_b=230 ps (Saarinen et al. 1989). This means that at low temperatures, positrons are trapped by two kinds of defects, namely by vacancies and negative ions, whereas at high

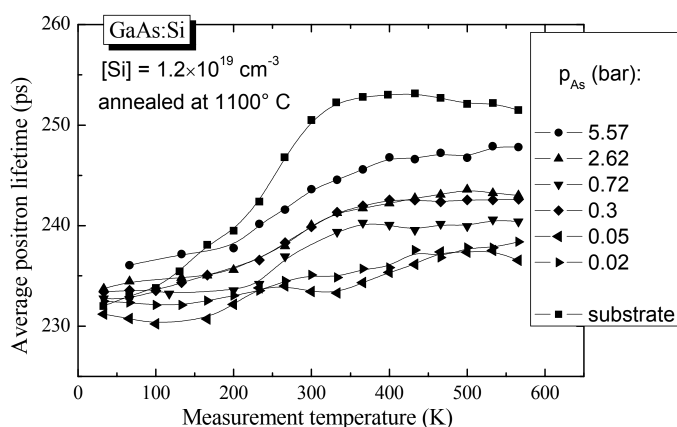

Fig. 5.3: *Average positron lifetime versus temperature obtained in GaAs:Si annealed at different arsenic pressures p_{As}. Lines are to guide the eye only.*

temperatures, the trapping by the negative ions is negligibly small.

The origin of the observed vacancy-type defects and the shallow traps in as-grown material is well known from the previous positron annihilation and scanning tunneling microscopy studies of GaAs:Si and has been discussed in detail in Section 4. The vacancies are related to Ga-vacancy–Si_{Ga}-donor complexes ($Si_{Ga}V_{Ga}$) with a defect-related lifetime of τ_v = 262±5 ps (Gebauer et al. 1997). A similar τ_{vac} was found in both as-grown and annealed samples. On this basis, vacancy defects in annealed GaAs:Si have been attributed to V_{Ga}-Si_{Ga} defect complexes, too. The negative ions observed at low temperatures correspond to silicon acceptors mentioned above and probably to the acceptor-type impurities (C_{As}, Cu_{Ga}) that might be unintentionally introduced during sample handling.

5.2.2 Undoped semi-insulating GaAs

No vacancy defects were observed in as-grown semi-insulating GaAs (Fig. 5.4). The average positron lifetime τ_{av} was close to τ_b at all temperatures of measurement. This observation itself represents an important result. In earlier positron annihilation studies of undoped SI GaAs, there were always some vacancy-like defects found (Saarinen et al. 1993; Chen et al. 1996; Kuisma et al. 1996). In the annealed samples, τ_{av} is strongly enhanced indicating positron trapping at vacancies. A defect-related lifetime of 293±10 ps was found. This value is distinctly larger than that for V_{Ga}-Si_{Ga} complex in GaAs:Si indicating a larger open volume of the vacancy, but still below the value calculated for a divacancy in GaAs (e.g., 332 ps in Ref. (Gebauer et al. 1999)). Thus, the observed vacancies should also be monovacancies. The decrease of the average positron lifetime toward low temperatures is due to the positron trapping at negative ions. The origin of the negative ions was attributed to the copper double acceptors, Cu_{Ga}^{2-}, as it is discussed in Section

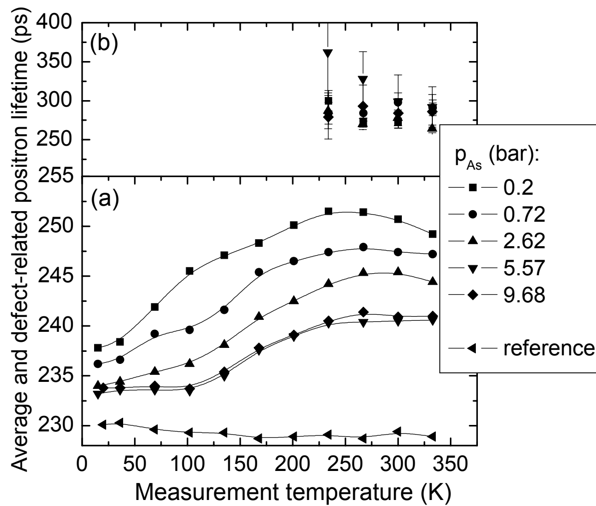

Fig. 5.4: *(a) Average and (b) defect-related positron lifetime versus temperature obtained in undoped semi-insulating GaAs annealed at different arsenic pressures, p_{As}. The not annealed material is denoted as reference. Lines are to guide the eye only.*

5.3.2.

In contrast to the Si-doped GaAs (Fig. 5.3), the average positron lifetime in the annealed undoped GaAs decreases with the increasing arsenic vapor pressure during annealing. The maximal τ_{av} was observed after the annealing at 0.2 bar (Fig. 5.4), whereas GaAs:Si annealed at this pressure reveals almost no positron trapping. Since the average positron lifetime determines the magnitude of the positron trapping rate (Eq. 3.6) and thus the concentration of the vacancy-like defects (Eq. 3.4), the pressure dependence of τ_{av} reflects a relation between the concentration of the vacancy defects at 1100° C and the arsenic vapor pressure. The enhancement of the vacancy concentration towards higher arsenic pressures in n-type GaAs had also been observed in previous positron annihilation studies (Gebauer 2000; Gebauer et al. 2003) and attributed to the formation of complexes containing gallium vacancies. This is consistent with the results obtained in this work for the annealed GaAs:Si. The reduction of the vacancy concentration by an increase of the arsenic pressure observed in SI GaAs represents an important result that was not reported before. Therefore, the following discussion concentrates mostly on the defects observed in the annealed SI GaAs.

5.2.3 Reproducibility of results for annealed SI GaAs

While the results of positron annihilation measurements in annealed GaAs:Si were found to be in good accordance with the previous annealing studies of n-type GaAs (Gebauer 2000) and hence may be considered as well-reproducible, the pressure dependence of the vacancy-related signal observed in semi-insulating GaAs should be subjected, as a qualitatively new result, to a reproducibility test. During the two year investigation of SI GaAs, several sample series were prepared and annealed under similar conditions. Subsequently, the temperature dependent positron annihilation measurements were performed. In contrast to silicon-doped GaAs, rather bad reproducibility of the positron annihilation results was found. The $\tau_{av}(T)$ curves obtained for three measurement series are shown in Fig. 5.5. As can be seen, both absolute values of the average positron lifetime and also its arsenic pressure dependence demonstrate very big fluctuations from one set of samples to another. However, it is important to note that the tendency of the highest τ_{av} at the lowest p_{As}, is preserved for each annealing series.

There are several reasons for the observed irreproducibility:

1) Uncertainties of the arsenic pressure. The temperature profile in the two-zone oven (Fig. 5.1) has a plateau only in the high-temperature region (at T_{GaAs} = 1100° C), whereas it demonstrates a rather big gradient in the low-temperature zone, at T_{As}. Therefore, small variations in the position of the arsenic source, i.e. in the ampoule length, have a relatively big effect on its temperature and hence on the whole pressure in the ampoule. Thus, the typical temperature error amounting to 10 K corresponds to $\Delta p_{As} \approx 0.5$ bar (Fig. 5.2).

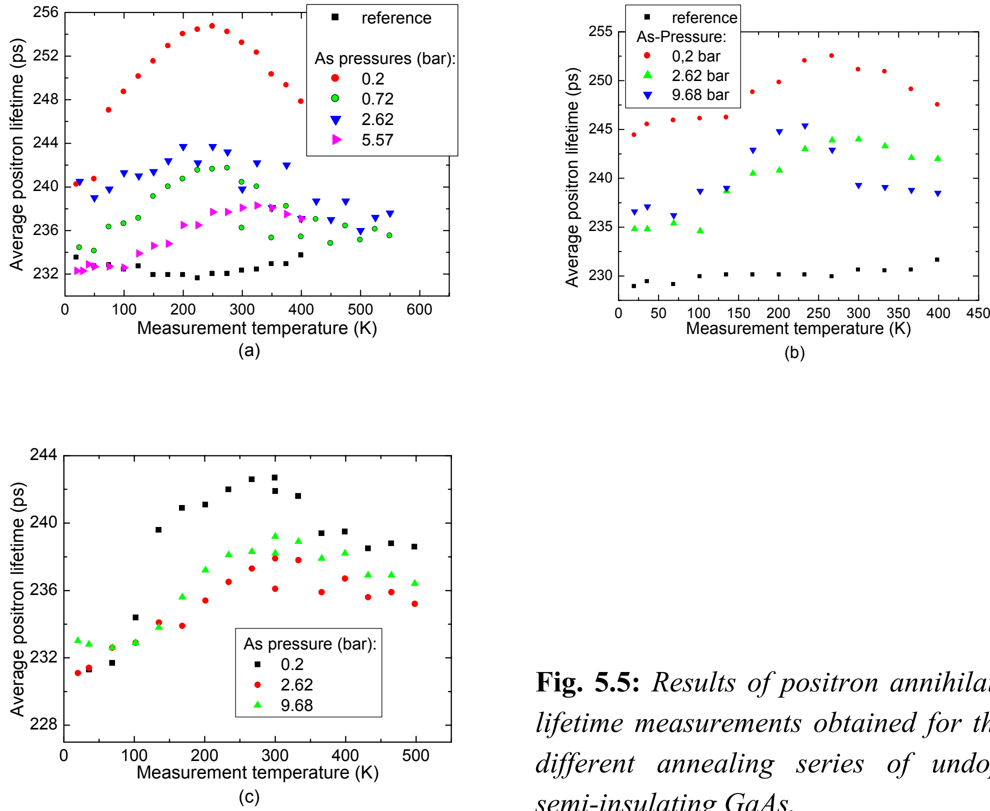

Fig. 5.5: *Results of positron annihilation lifetime measurements obtained for three different annealing series of undoped semi-insulating GaAs.*

2) Uncertainties of the quenching rate. After each annealing, the ampoules were quenched into the water at room temperature to preserve the high temperature defect configuration. Even though the cooling was done as quickly as possible, it is rather improbable that the quenching rate at each quenching was the same.

3) Uncertainties of the position of the Fermi-level. In annealed samples, the Fermi-level was found to be in the lower part of the band-gap (Sect. 5.3, Table 5.1). Its exact position may have a big influence on the concentrations of point defects.

Obviously, the first two reasons are of a minor significance. They can lead to insignificant fluctuations but they are unable to explain the big discrepancies observed in Fig. 5.5. The third argument seems to be the most important one. Before the annealing, the Fermi-level in SI GaAs samples is pinned by deep EL2 donors in the middle of the band-gap. The annealing at 1100° C with subsequent quenching destroys the EL2 centers (Hurle 1999). In this state, the position of the Fermi-level is not fixed any more but determined by the ratio between the concentrations of donors and acceptors present in a crystal. Since SI GaAs is usually intentionally doped by carbon atoms, which form C_{As}-acceptors (Section 6.2), the acceptor concentration dominates and the Fermi-level moves from the mid-gap position towards the valence band. The position of E_F becomes then very sensitive to the number of acceptor-like defects, which in its turn is defined by the purity conditions of the annealing experiments. The initial carbon content in as-grown SI

GaAs amounts normally to 10^{14}-10^{15} cm^{-3} (Korb et al. 1999), whereas the concentration of impurity atoms introduced unintentionally during the sample handling may exceed this value by one order of magnitude. The chemical analysis of the annealed samples showed concentrations of copper atoms, [Cu] ≈ 10^{16} cm^{-3}, i.e. an enhanced value with respect to the as-grown sample having [Cu] ≈ 10^{13} cm^{-3}. Cu in GaAs is known to be sited on the gallium sublattice, Cu_{Ga}, forming an acceptor-like level at 0.5 eV above the valence band (Tin et al. 1987; Kuriyama et al. 1994; Leon et al. 1995) (for more detailed discussion of the Cu-contamination see Section 5.3.2). In such a way, uncontrolled contamination in the range of 1 ppm only, being the source of the dominating acceptor-like impurities, represents the main factor determining the electronic properties of annealed SI GaAs samples. This was not the case in the investigations of n-type GaAs mentioned above, where the Fermi-level position was expelled into the conduction band by high (up to 10^{19} cm^{-3}) concentrations of Te_{As}-donors, and where contamination with impurities in the order of 10^{16} cm^{-3} did not play significant role.

It turned out, that the electronic properties of a crystal (i.e. Fermi-level position) have a profound effect on the formation of vacancy-like defects in GaAs. The following two examples demonstrate this fact. Three $\tau_{av}(T)$ curves shown in Fig. 5.6 represent the results obtained for three SI GaAs samples, which were prepared and annealed under very similar conditions. The arsenic pressure was equal to 0.2 bar, the annealing time was 2 hours for each annealing. However, the PALS results for one of the samples (▲,Fig. 5.6) were found to be quite different from those obtained for the other two specimens. Hall-Effect measurements showed that all the samples became p-type, whereas the hole concentrations were practically equal in the samples demonstrating similar $\tau_{av}(T)$ dependence ([p] ≈ 2×10^{12} cm^{-3}) and two orders of magnitude lower ([p] ≈ 4×10^{10} cm^{-3}) in the third sample. Obviously, the vacancy concentration is a function of chemical potential (i.e. crystal composition), which can be controlled by maintaining the arsenic vapour pressure, and it depends also on the Fermi level position. This was also confirmed by the results of

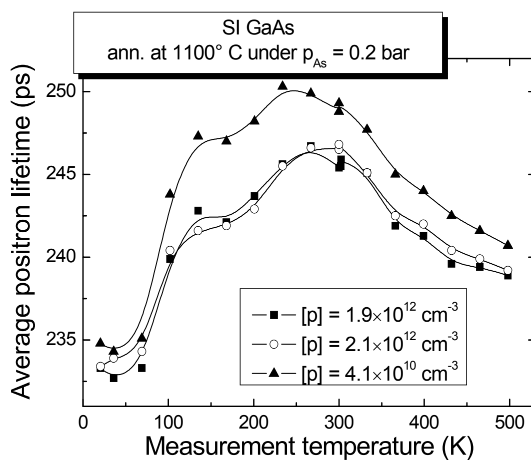

Fig. 5.6: *Average positron lifetime as a function of measurement temperature in three SI GaAs samples prepared under identical conditions and annealed for 2 hours at 1100° C under arsenic pressure of 0.2 bar. Hole concentrations are indicated.*

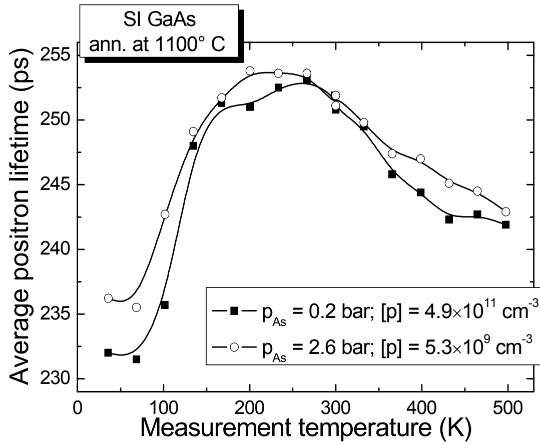

Fig. 5.7: *Average positron lifetime as a function of measurement temperature in two SI GaAs samples annealed for 2 hours at 1100° C at 0.2 and 2.6 bar. Hole concentrations corresponding to each samples are indicated.*

the lifetime measurements performed on two GaAs samples annealed under different arsenic pressures – 0.2 and 2.6 bar (Fig. 5.7). Surprisingly, both the samples demonstrated very similar values of τ_{av}. It should be that the concentrations of the vacancy-like defects in these samples have been nearly the same. However, electrical measurements revealed hole concentrations, which differed by two orders of magnitude, 4.9×10^{11} cm^{-3} and 5.3×10^{9} cm^{-3} for crystals annealed at 0.2 and 2.6 bar, respectively. The difference in the free charge carrier concentrations reflects the different positions of the Fermi-level, E_F, in these samples, which obviously has an effect on the vacancy concentration. Note that the different hole densities cannot be directly related to the numbers of the vacancy-like defects, since the concentration change in the region of 10^{9} - 10^{11} cm^{-3} is well under the sensitivity limit of positron annihilation.

The existence of an interrelation between the Fermi-level and the concentration of vacancies was predicted by Tan in Ref. (Tan et al. 1993) for n-type GaAs. It was shown that in highly n-doped crystals, the concentration of gallium vacancies, $[V_{Ga}]$, does not increase with increasing temperature, T, as one would expect according to $[V_{Ga}] \sim \exp(-E/k_BT)$, where E is the formation energy and and k_B is the Boltzmann constant, but remains constant or even decreases slightly. This phenomenon, called Fermi-level effect,

Table 5.1 – *Results of the room-temperature Hall measurements on the undoped SI GaAs samples annealed at defined As-pressure. The sample series corresponds to that shown in Fig. 5.4*

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}

was confirmed experimentally by J. Gebauer in a positron annihilation study of GaAs:Te (Gebauer et al. 2003). The results presented in this subsection demonstrated that the Fermi-level has a certain effect on the vacancy formation also in p-type GaAs. Obviously, the influence of the location of E_F may be compared with that of the chemical potential, i.e. p_{As} (Fig. 5.6 and Fig. 5.7). In principle, the vacancy concentration must be then treated as a function of p_{As} and E_F, i.e. $[V] = f(p_{As}, E_F)$. However, control over the Fermi level in annealed SI samples is hardly possible, first of all due to its high sensitivity to the concentration of impurities unintentionally introduced during sample handling. Obviously, the contamination level in the samples, the results of which are presented in Fig. 5.4, was nearly constant, since their electrical properties were found to be very similar (Table 5.1). This enables the analysis of the vacancy concentration as a function of p_{As} only, given in the next section.

5.3 Defect identification in annealed n-type and SI GaAs

5.3.1 Identification of vacancies

This subsection discusses the dependence of vacancy-like defects concentration on arsenic ambient pressure in the undoped and silicon-doped GaAs samples. The concentrations were calculated from the data of decomposition of positron lifetimes spectra via the Eq. 3.4 at 300 K and 500 K for undoped and silicon doped samples, respectively. At these temperatures the spectra were found to have only two components, i.e. no positron trapping into shallow traps was observed. The C_{vac} vs p_{As} plot, presented in Fig. 5.8, reveals an opposite behavior of the concentrations of the vacancy-like defects with increasing As pressure for undoped and silicon doped GaAs. This difference points to a different origin of the vacancies observed in these two kinds of samples. According to the mass-action law reactions (2.11) and (2.12):

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

where K_{VGa} and K_{VAS} are the mass action constants for the gallium and arsenic vacancy at a certain temperature and p_{As} is the ambient arsenic vapor pressure.

It follows that $[V_{Ga}]$ should increase and $[V_{As}]$ decrease with arsenic pressure as a power of +1/4 and -1/4, respectively. The fit to the experimental data (solid lines in Fig. 5.8) have indeed yielded an exponent close to 0.25 for GaAs:Si and -0.25 for SI GaAs.

Based on these results, the origin of vacancy-type defects in silicon doped GaAs was attributed to V_{Ga}, whereas in annealed SI GaAs formation of V_{As} was assumed. While this assignment in the case of GaAs:Si is in agreement with the interpretation of the positron lifetime data given earlier (see Section 5.2.1), the observation of As vacancies is more surprising than expected. The point is that according to theoretical calculations, the

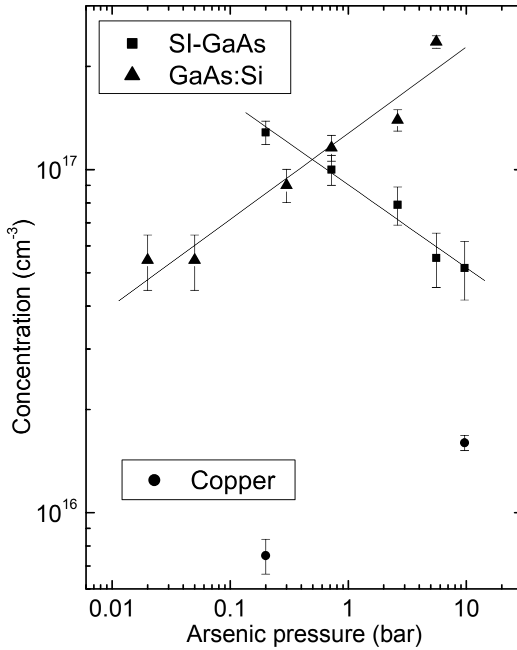

Fig. 5.8: *Vacancy-defects concentrations in annealed GaAs:Si and SI GaAs extracted from the positron lifetime data presented in fig. 5.3 and 5.4. Solid lines represent power law fit to data corresponding data point. Full circles present the concentration of copper impurities obtained with the help of titration measurements.*

ionization levels of V_{As} are in the upper part of the energy gap, close to the conduction band (Baraff and Schlüter 1985; Puska 1989; Xu 1990) (Fig. 2.5). The theoretical expectations were supported by a few positron studies, where observation of V_{As} in n-type (Saarinen et al. 1991; Ambigapathy et al. 1994) or in *photoexcited* semi-insulating material (Peng et al. 1994; Kuisma et al. 1996) were reported. There had been two defect-related lifetimes found, 295 ps and 257 ps, which were attributed to neutral and negative charge states of the arsenic vacancy (Saarinen et al. 1991). The value of 295 ps is in good agreement with the defect-related lifetime, τ_v = 293±10 ps, found in this study for annealed SI GaAs, supporting thereby the identification of the observed vacancy defect as V_{As}. However, earlier investigations revealed the ionization levels of V_{As} at E_C – 140 meV (Saarinen et al. 1991) for +/0 and E_C – 30 meV (Saarinen et al. 1991) and E_C – 60 meV (Kuisma et al. 1996) for 0/- transitions, respectively, which were in good qualitative agreement with theoretical calculations mentioned above. Consequently, arsenic vacancies should be positive (and thus not detectable with positrons) in semi-insulating or in p-type GaAs, where the position of Fermi level is in the middle or in the lower part of the band gap. The Hall-effect measurements of the samples investigated in this study (Table 5.1) have shown that all annealed samples became slightly p-type with [p]=10^{11}-10^{12} cm^{-3} that corresponds to the position of Fermi level at 0.4-0.5 eV above the valence band. It is worth to note, that this is the first time vacancy-like defects were observed with positrons in as-grown *p-type* GaAs. These results can be explained by the formation of V_{As}-X defect complex, where the X represents another at least one time negatively charged defect that compensates the positive charge of the arsenic vacancy. The possibilities for X to be a native or impurity-kind defect are discussed in the following.

As far as the investigated crystals were cut from undoped semi-insulating commercially available wafers, the concentration of the residual impurities in the samples was extremely small – below 10^{15} cm^{-3} – and thus not able to explain the occurrence of 10^{17} cm^{-3} (s. Fig. 5.8) vacancy-complexes. Other impurity sources are an uncontrolled contamination that might happen during the samples preparation. Copper is a good candidate for such kind of contaminations, because of its high diffusion coefficient and high solubility in GaAs (Tin et al. 1987; Kuriyama et al. 1994; Leon et al. 1995). Cu atoms are incorporated on the Ga sublattice as double acceptors Cu_{Ga}^{2-} (Leon et al. 1995), which can form electrically active complexes with positively charged arsenic vacancies due to their Coulomb attraction. Different structures of such complexes have been proposed in the literature: $Cu_{Ga}V_{As}$ (Tin et al. 1987; Kuriyama et al. 1994), $V_{As}Cu_{Ga}V_{As}$ (Tin et al. 1987).

The chemical analysis of the annealed SI GaAs samples has indeed shown a distinct increase of their Cu content (full circles in Fig. 5.8) after annealing. However, the Cu concentration was about 10^{16} cm^{-3} only; that is one order of magnitude lower than the measured number of vacancies. Independent of the concentration arguments, there exists another possibility to check whether the As vacancy is neighbored by a Cu atom. The high momentum part of the Doppler broadening of 511 keV annihilation line carries information on the chemical surrounding of positron trapping centers (Section 3.3). This method was found to be successful in identification of donor-V_{Ga} complexes in n-type GaAs (Gebauer et al. 1999; Gebauer 2000; Gebauer et al. 2001). Results of Doppler broadening measurements normalized to the data obtained for as-grown SI GaAs reference sample are shown in Fig. 5.9. In the upper part of the figure the ratio curve of anni-

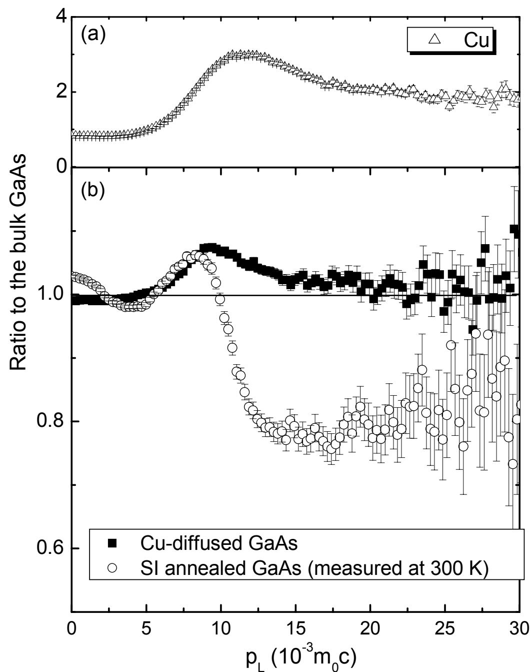

Fig. 5.9: *Normalized annihilation momentum distribution measured at room temperature in a) pure Cu; b) SI GaAs annealed at p_{As} = 0.2 bar (○) and in SI GaAs after Cu in-diffusion experiment (■)*

hilation momentum distribution obtained in pure copper is shown. In Fig. 5.9 (b), two kind of samples are compared – SI GaAs annealed at p_{As} = 0.2 bar (○) and GaAs crystal after copper in-diffusion (■). In the latter, the formation of the vacancy clusters neighbored by copper precipitates was observed (Krause-Rehberg et al. 1999; Bondarenko et al. 2001). In the case of the positron annihilation with electrons of copper, the intensity in the high momentum region of Doppler peak, (10-20)×10^{-3} m_0c, is higher than in bulk GaAs [ratio is larger than 1, Fig. 5.9 (a)]. Thus, the presence of Cu atoms in the immediate vicinity of a positron trap can be seen as such characteristic increase of the intensity of the electron-positron momentum distribution like it was observed for Cu-diffused GaAs. In annealed GaAs in contrast, no sign of Cu in the neighborhood of detected vacancies was observed [Fig. 5.9 (b), (○)]. This result provides us with additional support for the assumption that copper is not responsible for the observed vacancy-like defect complex in annealed semi-insulating GaAs.

There were no other foreign atoms with a concentration about that of V_{As} found. Thus, we can exclude impurities from the possible candidates for the defect X. The observed V_{As}-like defect must be related to a native defect-complex. The exact nature of this complex is impossible to determine from results of positron annihilation alone.

5.3.2 Identification of shallow traps in undoped annealed GaAs

The conversion of electrical conductivity from semi-insulating to p-type in annealed GaAs samples is connected with the decrease of the number of EL2 donors and increase of the acceptor-like ion concentration after annealing (Section 5.2.3). The acceptors rep-

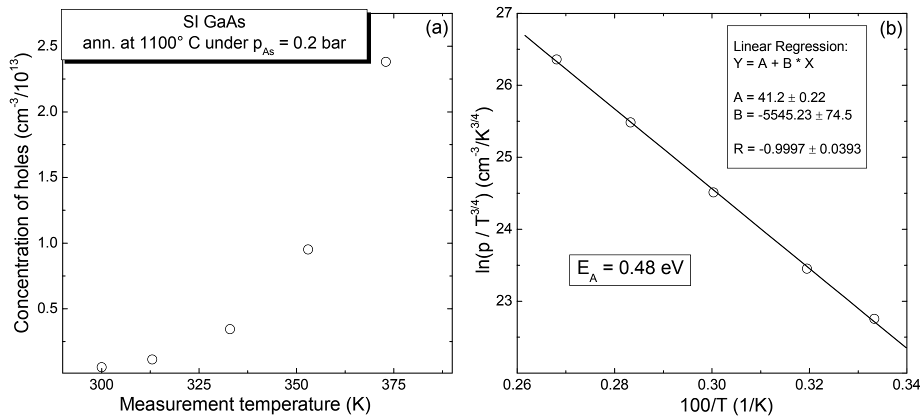

Fig. 5.10: *Results of the temperature-dependent Hall-effect measurements on SI GaAs annealed at 1100° C under 0.2 bar of arsenic vapour pressure. Solid line represent a fit to experimental data. By the fit, the activation energy of 0.48 eV above the valence band was determined (see text).*

resent positron shallow trap defects and are seen in lifetime measurements as a decrease of the average positron lifetime at low temperatures (Fig. 5.4). However, they cannot be directly identified by PALS because the positron lifetime related to them is close to the bulk value. In this subsection, this question is addressed by determination of the acceptor ionization level with the help of temperature-dependent Hall-effect measurements (TDH) and by the observation of changes of the annihilation momentum distribution by the coincidence Doppler broadening spectroscopy.

Fig. 5.10 (a) shows the temperature dependence of the hole concentration, p, in the SI GaAs annealed at p_{As} = 0.2 bar. The dependence $\ln\left(p\cdot T^{-3/4}\right)\left(1/T\right)$ represents a straight line [Fig. 5.10 (b)], which slope corresponds to the activation energy of the acceptor defect. The energy E_A = 0.48 eV above the valence band was found. In the literature, this energy level is attributed to the Cu_{Ga} acceptor (Tin et al. 1987; Leon et al. 1995). As was mentioned in the previous subsection, copper is a frequently occurring contaminant in annealing studies due to its ubiquity and high diffusion coefficient, D = 1.1×10^{-5} cm^2s^{-1} at 500° C (Hall and Racette 1964). The chemical analysis of the samples annealed at 0.2 and 9.7 bar revealed a distinct enhancement of the copper content (Fig. 5.8). On this basis, the observed shallow trap defects were attributed to negative copper ions.

Additional support for this assumption comes from the results of the coincidence Doppler broadening (CDB) investigation (Fig. 5.11). The curve consisting of the open symbols represents the measurement of the annealed GaAs samples performed at 20 K. At this temperature, negative ions are dominating positron trapping centers, as can be seen from lifetime measurements (Fig. 5.4) – τ_{av}(20 K) is close to τ_b value. Thus, the observed annihilation momentum distribution corresponds to annihilation of positrons with the electrons of acceptor-like atoms. Note the difference to the CDB measurement performed on the same sample at the temperature of 300 K corresponding to positron trapping into vacancies (Fig. 5.9). The second curve in Fig. 5.11 (■) is the same one shown in

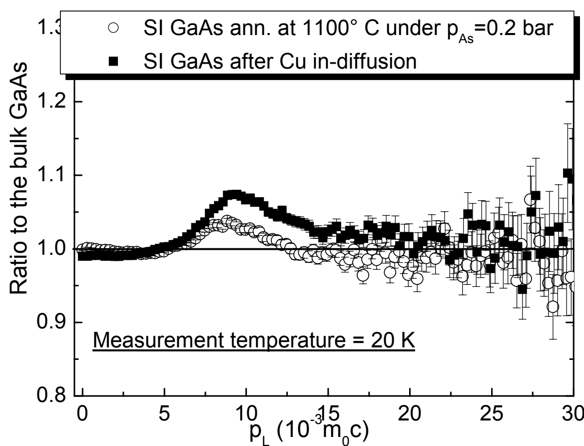

Fig. 5.11: *Normalized annihilation momentum distribution in (■) SI GaAs after Cu in-diffusion (Bondarenko et al. 2001) and (○) in annealed in this work SI GaAs. The temperature of measurement was 20 K.*

Fig. 5.9 and corresponds to annihilation of positrons with the electrons of Cu atoms. As can be seen, annihilation momentum distribution in the annealed SI GaAs measured at 20 K demonstrates the intensity increase characteristic for the presence of copper atoms in the neighborhood of the annihilation site. Hence, the assignment of shallow trap defects to copper acceptors is justified.

5.3.3 Charge state of the V_{As} complex

The presence of high concentrations of shallow positron traps, identified in the previous subsection as Cu_{Ga}-acceptors, hampers the investigations of vacancy-like defects in the annealed GaAs. Firstly, copper atoms being an uncontrolled impurity influence the reproducibility of the annealing experiments (Section 5.2.3). Secondly, lifetime measurements were found to be affected by positron trapping into shallow positron traps already at temperatures slightly below 300 K (Fig. 5.4). This makes the quantitative analysis of the low-temperature spectra extremely difficult. At the same time, the low-temperature region is the most important, since it corresponds to the highest sensitivity of positron annihilation to open-volume defects (Section 3.2). In order to get rid of copper contamination, a new copper-free annealing procedure was applied (Section 5.1). According to chemical analysis of the samples prepared and annealed under high-purity conditions, it was possible to decrease the number of Cu impurities by two orders of magnitude, from 10^{16} cm^{-3} to 10^{14} cm^{-3}.

Also the PALS results, shown in Fig. 5.12, were found to be qualitatively quite different from those obtained previously (Fig. 5.4). The average positron lifetime increases as the temperature decreases from 500 K to 300 K showing a plateau at T = 150-300 K and decreases rapidly at T<150. The presence of a plateau of such a kind has not been reported in previous positron studies of GaAs and is hence of a special interest. According to the theoretical calculations, the temperature independent positron trapping is expected for the neutral vacancy (Section 3.2.1). Hence, it is reasonable to suggest that at

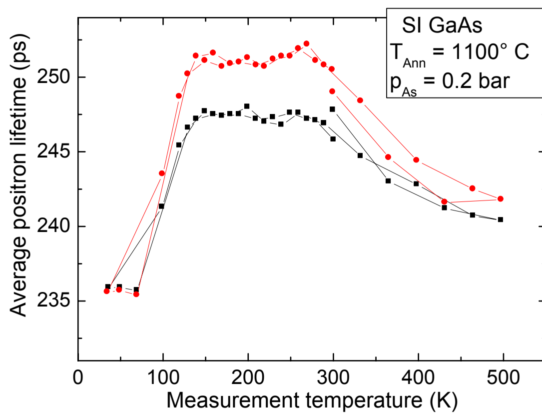

Fig. 5.12: *Average positron lifetime vs measurement temperature in SI GaAs after high-purity annealing at 1100° C at p_{As} = 0.2 bar.*

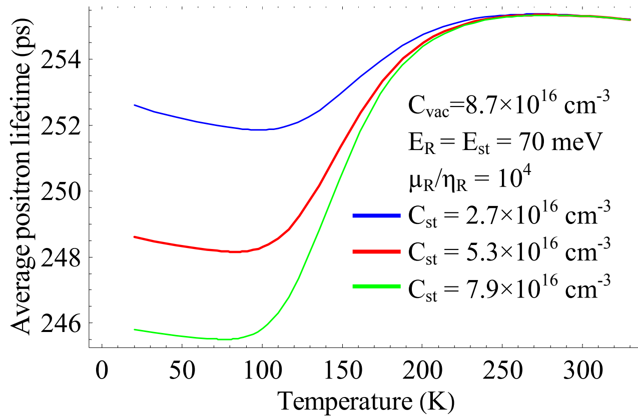

Fig. 5.13: *Results of the simulation of the average positron lifetime as a function of temperature for different concentrations of shallow trap defects C_{st}. The model used is described in section 3.2.2. Model parameters are denoted.*

150-300 K the dominating trapping center is a neutral vacancy complex. Obviously, the plateau was not observed by previous measurements (Fig. 5.4) due to high shallow trap (Cu_{Ga}) concentrations, which caused the continuous decrease of the positron average lifetime at temperature less than 300 K.

Shallow positron traps, however, can not explain the rapid drop of τ_{av} observed in Fig. 5.12 as temperature lowers from 150 K to 120. Taking into account the decreased concentrations of acceptor-like impurities, the decrease of τ_{av} is simply too abrupt to be imposed by a competitive positron trapping into vacancy and shallow trap defects. Even much higher acceptors concentration could not cause such a steep decrease of τ_{av}. This is demonstrated in Fig. 5.13 by modeling of the $\tau_{av}(T)$ for different concentrations of shallow traps. The model used is described in Section 3.2.2. As can be seen, the presence of shallow positron traps with concentration as high as 8×10^{16} cm^{-3} can reduce τ_{av} by 10 ps over the temperature decrease of 150 K. This is clearly far from the observed dynamics of $\tau_{av}(T)$ – decrease of 15 ps in 30 K.

Most probably, there is a temperature driven +/0 charge transition of the detected vacancy-complex. When the temperature falls below 150 K, the Fermi-level crosses the defect ionization energy level evoking the change of the defect charge state from neutral to positive. Since positrons are repelled by positively charged defects, most of them will annihilate in the crystal bulk or will be trapped and annihilate at shallow traps resulting in the observed quick decrease of $\tau_{av}(T)$. The neutral charge state of the V_{As} complex is in agreement with the results of the Hall-effect measurements (Table 5.1), according to which the hole concentrations do not correlate with the concentrations of the vacancy defects.

5.3.4 Gibbs free energy of V_{As} formation

Having identified the origin of the detected vacancy as V_{As} (Section 5.3.1) and determined its charge state (previous section) it is possible to obtain the formation energy of arsenic vacancies by analyzing the pressure dependence of their concentration. According to the thermodynamic model of defects in GaAs (Section 2.3), the concentration of neutral arsenic vacancies is defined by Eq. 2.19:

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

where H_f and S_f are the formation enthalpy and entropy, respectively. B_{As_4} is the gas pressure constant determined as (Tan 1994)

$$B_{As_4} = (2\pi m_{As_4} / h^2)^{3/2} (kT)^{5/2} = 131.5 \quad T^{5/2}$$

The difference $H_f - TS_f$ represents Gibbs free formation energy, G_f, which one can find from a fit to experimental data according to 2.19 for T equal T_{ann} = 1100° C and using G_f as the only fitting parameter. The fit yielded G_f = *3.94* eV (fig. 5.14).

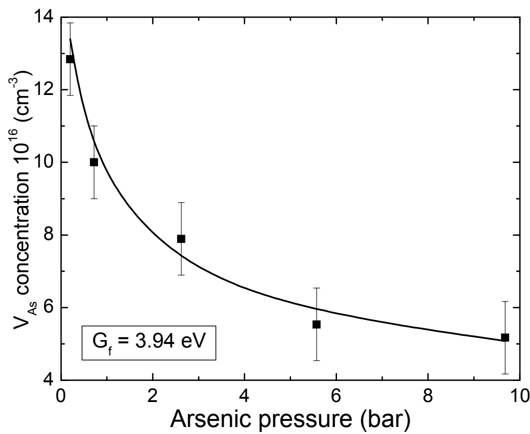

Fig. 5.14: *Concentration of As vacancies at 1100° C in SI GaAs as a function of arsenic vapour pressure. Fit to experimental data (solid line) yielded the value of 3.94 eV for Gibbs' free energy of formation of* V_{As}