Defects in electron-irradiated GaAs studied by positron lifetime spectroscopy

A. Polity, F. Rudolf, C. Nagel, S. Eichler, and R. Krause-Rehberg
Fachbereich Physik der Martin-Luther-Universität Halle-Wittenberg, Experimentelle Physik III, Friedemann-Bach-Platz 6, D-06108 Halle/Saale, Germany

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A systematic study of electron-irradiation-induced defects in GaAs was carried out. The irradiation was performed at low temperature (4 K) with an incident energy of 2 MeV. Both, the defect formation and annealing behavior were studied in dependence on the fluence (10^{15}–10^{19} cm^{-2}) in undoped, n-, and p-doped GaAs. Temperature-dependent positron lifetime measurements were performed between 20 and 600 K. The thermal stability of defects was studied by annealing experiments in the temperature range of 90–600 K. A defect complex, which anneals in a main stage at 300 K, was found in all GaAs samples after electron irradiation. A possible candidate for this defect is a complex of a vacancy connected with an intrinsic defect. A second vancancylike defect was observed in n-type material after annealing at 550 K. This defect was assumed to be in the As sublattice. [S0163-1829(97)05915-8]

I. INTRODUCTION

Point defects strongly affect the optical and electrical behavior of GaAs. Therefore the knowledge of the physical properties of these defects is an essential requirement for device technology. Electrical and optical spectroscopy techniques detect various localized energy levels in the energy gap. However, the identification of the atomic structure of the defects is still a matter of discussion.

Positron annihilation spectroscopy, a well-established method to study vacancylike defects in solids, yields valuable information on the structure of the defects. During the last decade, it has found broad application for semiconductors.[1,2] The theoretical background of the interaction of positrons with matter is well understood now.[3] Positrons may be trapped in open-volume defects, resulting in characteristic changes of the annihilation parameters.[4] Because of their charge, positrons are also sensitive to different charge states of a vacancy in semiconductors and thus they represent a selective tool for their identification. The charge state of a defect is determined by the position of the Fermi level in the energy-band gap. Hall-effect experiments allow the determination of the Fermi-level position and therefore correlated investigations enable us to identify the vacancies within the given population of existing electrically active defects.

Electron-irradiation-induced defects in GaAs were extensively studied by various techniques characterizing their electrical and optical properties.[5] A few positron investigations of vacancylike defects in electron-irradiated n-type and semi-insulating GaAs have been carried out in the past.[6–10] These studies have clearly shown that irradiation by 0.5–3-MeV electrons produces monovacancy defects. In addition to vacancies, electron irradiation produces negative ions (negatively charged antisites) in GaAs crystals.[10] These negative ions act as shallow traps for positrons.[11]

In this paper we report on a systematic study by positron lifetime spectroscopy and Hall-effect measurements about defect formation and annealing behavior in dependence on the electron fluence (10^{15}–10^{19} electrons per cm^2) and on the conductivity type (n doped, p doped, and undoped) of GaAs crystals.

The paper is organized as follows. The material and experimental details are presented briefly in Sec. II. The method of positron annihilation for studying vacancy defects in semiconductors is described in Sec. III. In Sec. IV the obtained results are described and discussed. The presentation of the data and the discussion are divided in four parts. Part A is concerned with unirradiated material, part B with Te-doped, part C with Zn-doped, and part D with undoped GaAs. The annealing kinetics of compensated GaAs samples will be dealt with in part E of Sec. IV. Conclusions are drawn in Sec. V.

II. MATERIAL AND EXPERIMENTAL PROCEDURES

The GaAs samples of a size $6\times6\times0.5$ mm^3 were cut from crystals grown by the liquid-encapsulated Czochralski method. Undoped n-GaAs ($n=1\times10^{15}$ cm^{-3}), Te-doped n-GaAs [$n=(2–6)\times10^{17}$ cm^{-3}], and Zn-doped p-GaAs ($p=5\times10^{17}$ cm^{-3}) were used for the experiments. The net carrier concentrations of the as-grown samples were determined at room temperature.

Electron irradiations were performed at 4 K with the Van de Graaff accelerator in the Forschungszentrum Jülich. The incident energy of electrons was 2 MeV. Different fluences between 10^{15} and 10^{19} cm^{-2} were used for irradiation. The samples remained under liquid nitrogen (77 K) to prevent warming up and annealing. They were mounted into a cryoheater system that enabled measurements and annealings at temperatures between 90 and 600 K. The annealings were performed isochronally (15 min). After different annealing steps temperature-dependent measurements were also carried also out in a second cryoheater system in the range between 15 and 600 K.

The carrier concentration and mobility of irradiated samples were obtained by Hall-effect and conductivity measurements according to van der Pauw[12] at 300 K.

The positron lifetimes were measured using the conventional technique.[4] A fast-fast coincidence system having a time resolution full width at half maximum of 260 ps was used for the collection of a lifetime spectrum of 5×10^6 counts within 3 h. The positron source with an active size of 1×1 mm^2 was radioactive ^{22}NaCl (0.5 MBq) covered with two thin (1 mg/cm^2) Al foils and placed between a pair of identical samples (cut from the same wafer). The lifetime spectra were analyzed after source and background correction[13,14] in terms of the trapping model.[15,16]

The determined average positron lifetime is reliable, but the decomposition of the spectra is difficult in GaAs. This is due to positron trapping in shallow positron traps in as-grown GaAs. This effect is even intensified by irradiation-induced shallow traps (see also discussion in Sec. IV).

III. POSITRON TRAPPING IN DEFECTS

Positrons are usually obtained by the β^+ decay of ^{22}Na sources. The lifetime of a single event is measured by detecting the time difference between the positron birth γ quantum (1.27 MeV) and the annihilation γ quanta (0.51 MeV). The lifetime spectrum consists of a sum of exponential decay components with the lifetimes τ_i and their intensities I_i. Positrons may annihilate from the delocalized ground state in the perfect lattice or from localized states formed at defects being able to trap positrons. If no trapping centers locate the positrons during their diffusion through the sample, a single exponential component will be observed for the lifetime spectrum, $\tau=\tau_b$ (b denotes bulk). In the case of the presence of one open-volume defect (e.g., vacancies) the positrons may be trapped there with the trapping rate κ. The lifetime spectrum consists of two components. The positron lifetime in the defect τ_d (d denotes defect) is larger than τ_b due to the decrease of the electron density in the defect compared to the bulk. From the experimentally obtained fitting parameters τ_1, τ_2, and I_2 (lifetimes and intensities), the positron trapping rate may be determined from the average positron lifetime ($\overline{\tau}=I_1\tau_1+I_2\tau_2$ with $\tau_2=\tau_d$). The positron trapping rate κ yields the defect concentration C_d, if the constant μ (trapping coefficient) could be obtained at least once by an independent method (e.g., Hall-effect measurements, infrared absorption, electron paramagnetic resonance):

$$C_d=\frac{\kappa}{\mu}=\frac{1}{\mu\tau_b}\,\frac{\overline{\tau}-\tau_b}{\tau_d-\overline{\tau}}. \tag{1}$$

The so-called trapping coefficient μ depends strongly on the defect type, defect charge, and possibly on temperature. For negative defects $\mu=(1\text{–}4)\times10^{15}$ s^{-1} at 300 K and $\mu=10^{16}\text{–}10^{17}$ s^{-1} at 20 K were found.[17,2] For neutral vacancies μ is assumed to be temperature independent and amounts to about $10^{14}\text{–}10^{15}$ s^{-1}.[18] For the determination of the vacancy concentration in GaAs we used the average value of $\mu=10^{15}$ s^{-1} (300 K).

A vacancy in a semiconductor is neutral or may carry a positive or negative charge, which gives rise to an additional Coulombic tail of the potential. Positively charged vacancies repel positrons. Positrons are trapped only in vacancy defects which are neutral or negatively charged. Thus the positron trapping may be affected by the position of the Fermi level.

The calculations for ideal vacancies and multivacancies in III–V semiconductors indicate that the positron lifetime responds to the extent of the open volume affecting the positron, and this open volume is more or less proportional to the unit-cell volume of the compound. The relaxation depending on the charge state of the vacancy and on the positions of ions around the defect affects the positron lifetime as well.[3] For Si and GaAs the outward breathing relaxation of 1% of the bond distance means an increase of ~3.5 ps in the positron lifetime.[19] It is possible that an isolated vacancy is not distinguishable from a larger complex containing a vacancy.

Additionally, so-called shallow positron traps are possible candidates for positron trapping. They are negatively charged non-open-volume defects (negative ions), able to locate positrons at low temperatures.[11,10] At higher temperatures (above 300 K) the thermal detrapping from the shallow potential becomes dominant and no significant influence on the positron trapping is detectable. The temperature dependence of this detrapping process was theoretically described by Manninen and Nieminen.[20] The ratio of the detrapping rate δ to the trapping rate κ_{ST} of shallow traps (ST denotes shallow trap) is given by

$$\frac{\delta}{\kappa_{\mathrm{ST}}}=\frac{1}{C_{\mathrm{ST}}}\left[\frac{m}{2\pi\hbar^2}\right]^{3/2}(k_BT)^{3/2}\exp\left[-\frac{E_b}{k_BT}\right]. \tag{2}$$

C_{ST} is the concentration of shallow traps and E_b the binding energy of the positron to the shallow trap. k_B is the Boltzmann constant, m the positron effective mass, and T the sample temperature. The positron lifetime in shallow traps is close to the lifetime in the bulk due to the small change of the electron density affecting the positron. Therefore only the temperature dependence of the positron lifetime as a result of competition between positron trapping in vacancies and in shallow traps proves the presence of these shallow positron traps.

IV. RESULTS AND DISCUSSION

In Sec. IV A the results of positron measurements in as-grown GaAs will be presented. The results of annealing behavior and of temperature-dependent measurements in electron-irradiated GaAs will be discussed with regard to the conductivity type and to the irradiation fluence. In Sec. IV B the experiments on GaAs:Te, in Sec. IV C on GaAs:Zn, and in Sec. IV D on undoped GaAs are presented and analyzed. In Sec. IV E the annealing kinetics of compensated GaAs samples is dealt with.

A. Unirradiated material

The positron lifetimes in as-grown GaAs and their temperature dependencies were determined before electron irradiation. The lifetime of 230 ps was measured in GaAs:Zn and was previously attributed to positron annihilation from the delocalized state in the bulk.[1] The positron lifetime for bulk material was also found in semi-insulating, undoped GaAs.[1,8] The increased average lifetime in undoped n-GaAs, 235 ps at 300 K, and Te-doped n-GaAs, 245 ps at 300 K, are due to positron trapping in native defects. The nature of these defects was discussed earlier.[8,9,21,22] In undoped GaAs the higher average lifetime is due to positron trapping in As vacancies. The positron lifetime in the defect was $\tau_d=290$ ps. The As vacancies are detectable in the n-type material due to their neutral or negative charge determined by the position of the Fermi level near the conduction-band edge (see Fig. 2). In Te-doped GaAs the positron trapping is due to compensating centers $Te_{As}V_{Ga}^{-}$ and the resolved lifetime in the defect is 255 ps. Temperature-dependent measurements show the presence of negative ions acting as shallow positron traps in n-type material. Corresponding to the earlier investigations these shallow traps are assigned to negatively charged Ga antisites.[21]

B. GaAs:Te

Prior to irradiation the samples were n type with a carrier concentration $n=6.1\times10^{17}$ cm^{-3}. The Fermi level was located above the conduction-band edge ($E_f=E_c+0.03$ eV). The average positron lifetime of $\overline{\tau}=244.9$ ps was measured and the positron lifetime in the defect was determined to be $\tau_d=255$ ps. The increased lifetime compared to the lifetime in perfect GaAs ($\tau_b=230$ ps) is due to the positron trapping in compensating centers, $Te_{As}V_{Ga}^{-}$, which are thermally stable at least up to $T_a=1075$ K.[21]

1. Annealing experiments of high-dose irradiated GaAs:Te

After electron irradiation with a fluence of $\Phi=10^{19}$ cm^{-2} an increased averaged positron lifetime of 248.4 ps was observed. Hence irradiation-induced defects were detected. The decomposition of the spectra yields a defect component of 262 ps. The location of the Fermi level after irradiation and after annealing at 300 K was determined by Hall-effect measurements to be $E_f=E_c-0.54$ eV. The carrier concentration decreased due to irradiation-induced acceptors and was determined to be $n=3.1\times10^{8}$ cm^{-3} ($\rho=1.8$ MΩ cm). We call this sample state ''compensated.'' If both donors and acceptors are distributed at random in the semiconductor one calls it a compensated semiconductor. At ideal compensation there would be equal numbers of donors and acceptors and consequently the carrier concentration is very low ($\rho\approx\infty$) and the Fermi level is in mid-band-gap position. For GaAs the compensation will be realized by deep-level defects (for instance, $EL2$) of high concentration which compensate the carriers and pin the Fermi level. Similar deep-level defects will also be induced by electron irradiation.

Figure 1 shows the results of the isochronal (15 min) annealing experiments of Te-doped GaAs after electron irradiation with a fluence of $\Phi=10^{19}$ cm^{-2}. A second sample with a lower Te content (as-grown state: $n=2.2\times10^{17}$ cm^{-3}, $\overline{\tau}=242.1$ ps, $\tau_d=255$ ps; irradiated state: $\overline{\tau}=248.1$ ps, $\tau_d=262$ ps, $E_f=E_c-0.52$ eV) was included to show the influence of the doping concentration. For all figures of this paper it holds that the lines are only guides for the eye if not otherwise marked. The samples were annealed in the temperature range between 90 and 550 K. For both samples a wide annealing stage between 90 and 550 K was observed. The positron lifetime of the bulk of 230 ps was measured after this treatment. No significant difference in the annealing behavior was detected for different doping concentrations. Therefore we assume that the defect introduction rate is independent of the Te concentration. Because the compensating centers are thermally stable up to 1075 K in nonirradiated samples, we conclude that the increase of the positron lifetime after irradiation and decrease after annealing is due to irradiation-induced vacancylike defects. The positron lifetime in the defect of $\tau_d=(262\pm5)$ ps is a typical value for a monovacancy in GaAs. The lifetime of the isolated Ga vacancy was experimentally found to be 260 ps (Refs. 1 and 10) and the theoretically calculated value was 263 ps.[19] For isolated As vacancies 257 and 295 ps in the neutral and negatively charged state were determined.[1,23]

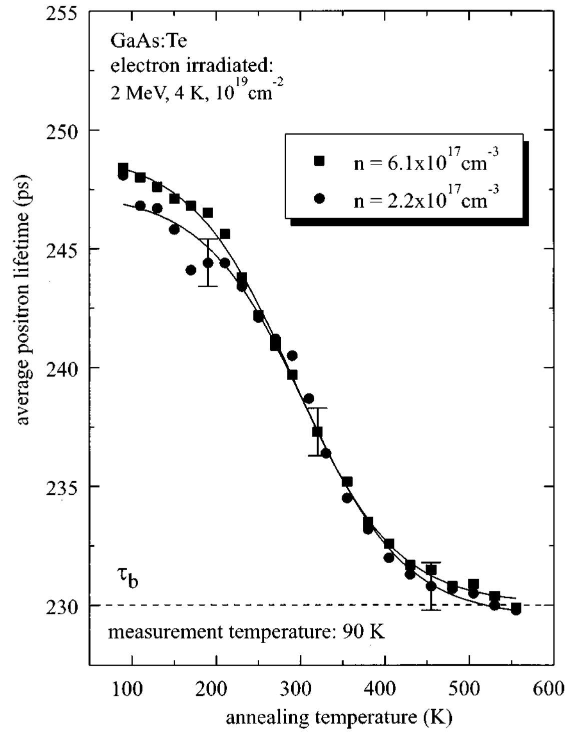

FIG. 1. Average positron lifetime is shown as a function of the annealing temperature in electron-irradiated GaAs:Te ($\Phi=10^{19}$ cm^{-2}).

The positron trapping depends on the charge state of the trapping center (vacancy), i.e., it depends on the location of the Fermi level. To illustrate the main idea, the results of a theoretical calculation of ionization levels of vacancies in GaAs (Ref. 24) are schematically drawn in Fig. 2.

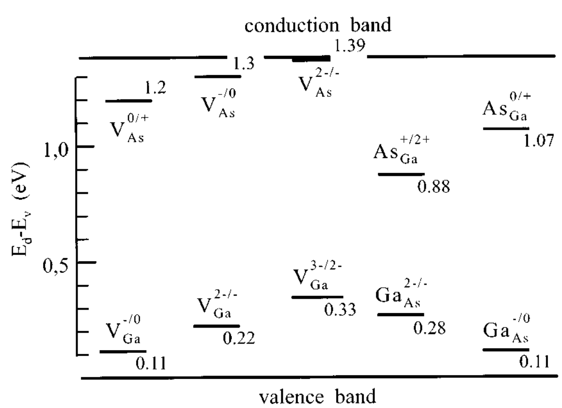

FIG. 2. Calculated ionization levels of vacancies and antisites of GaAs are presented. The energy levels E_d are related to the upper valence-band edge E_v. The values given in eV were taken from Ref. 24.

The ionization levels of the Ga vacancy are located in the lower half of the band gap. According to the calculations, the Ga vacancies are always negatively charged or at least neutral. Thus the positrons should always be sensitive to Ga vacancies in GaAs, independent of the location of the Fermi level, whenever the vacancy concentration exceeds the sensitivity limit of the method. The ionization levels of the As vacancies are located in the upper half of the band gap and the vacancies may exist in all possible charge states. Positive As vacancies are expected in the case of semi-insulating or p-type samples (Fermi level in midgap position or lower). They are neutral for slightly doped n-type samples (Fermi level is in the upper half of the band gap) and they should be found in the negative charge state, when the sample is strongly n type (Fermi level is close to or within the conduction band).

The relaxation around the vacancy which may lead to a shift of the ionization levels was not taken into account in the calculation. Such an effect was observed for the As vacancy in GaAs, where the $V^{0/-}$ level was predicted to be 220 meV below the conduction-band edge[24] and was found at about 30 meV.[8,23] Also for the ionization level $V_{\mathrm{P}}^{0/-}$ in GaP a discrepancy between the obtained value of about $E_c - E_d = 250$ meV (Ref. 25) and the predicted value of 410 meV (Ref. 24) was determined. Furthermore, no experimental evidence was found for the existence of the ionization level of the P vacancy, $V_{\mathrm{P}}^{-/2-}$, inside the band gap.[25] But the relative positions of calculated ionization levels are correct and detectable by measurements.

After electron irradiation both GaAs:Te samples are compensated and the Fermi level is in a midgap position. Therefore the observed annealing stage cannot be caused by As vacancies but by Ga vacancies or neutral or negatively charged complexes containing vacancies of either sublattice linked with the Te dopant or with an intrinsic point defect. This annealing stage is known in electron-irradiated GaAs and has been discussed in terms of recovery of isolated Ga monovacancies.[6,9,26] The annealing studies of p-type and undoped GaAs after electron irradiation described in Secs. IV C and IV D support this identification of the defect.

2. Temperature-dependent measurements after high-dose electron irradiation

Temperature-dependent measurements were performed after different annealing steps. Figure 3 shows the results of these positron-lifetime measurements, i.e., the average positron lifetime in as-grown and electron-irradiated (annealed at 320 and 580 K) GaAs:Te. For as-grown GaAs:Te the positron lifetime depends on the sample temperature due to two competitive processes, positron trapping in shallow traps and in compensating centers.[22] At low temperatures the detrapping of positrons from shallow traps ($\mathrm{Ga}_{\mathrm{As}}^{2-}$, $\tau_d = 230$ ps) is lower and leads to a decrease of the positron lifetime with decreasing temperature. At temperatures above 200 K the positron trapping in the negatively charged vacancy defect ($\mathrm{Te}_{\mathrm{As}}V_{\mathrm{Ga}}^{-}$, $\tau_d = 255$ ps) dominates the annihilation behavior and leads to a decrease of the positron lifetime with increasing temperature. Consequently, one observes a maximum in the temperature-dependent average positron lifetime. This behavior of the positron lifetime in GaAs:Te has been extensively investigated earlier.[21,22]

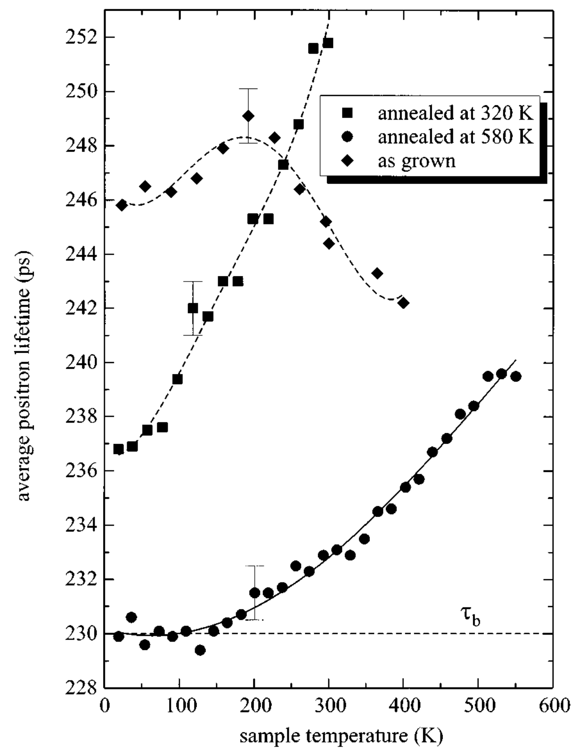

FIG. 3. Average positron lifetime is shown as a function of sample temperature in as-grown and in electron-irradiated ($\Phi = 10^{19}$ cm^{-2}) GaAs:Te after different annealing steps. The fitted curve (solid line) corresponding to the two-defect trapping model with detrapping from one defect is drawn for the sample annealed at 580 K. The positron binding energy to shallow traps $E_b = (65 \pm 8)$ meV and the trapping rate in shallow traps $\kappa_{\mathrm{ST}} = (7.6 \pm 2.4) \times 10^{11}$ s^{-1} were determined as parameters from the fit.

After electron irradiation and annealing at 320 K the temperature dependence of the positron lifetime is different from that of the as-grown sample (see Fig. 3). The average positron lifetime is lower and the decrease is weaker at low temperatures for the as-grown sample. It may be concluded that the concentration of shallow positron traps increases due to irradiation. Irradiation induces besides vacancies also other charged defects such as interstitials and antisites. The tetrahedral interstital configurations $\mathrm{Ga}_i\mathrm{As}_4$, $\mathrm{Ga}_i\mathrm{Ga}_4$, $\mathrm{As}_i\mathrm{As}_4$, and $\mathrm{As}_i\mathrm{Ga}_4$ are positively charged independent of the location of Fermi level and therefore these defects are no positron traps.[27,28] $\mathrm{As}_{\mathrm{Ga}}$ antisites are neutral or positively charged in compensated samples and only the $\mathrm{Ga}_{\mathrm{As}}$ antisites carry a negative charge and may act as shallow traps (see Fig. 2).[10] The increase of the average positron lifetime (at least above 200 K) is caused by the presence of the irradiation-induced vacancy defect, which has not yet completely annealed at 320 K (see Fig. 1). The positron lifetime in defect was determined to be (262 ± 5) ps.

The observed temperature dependence of the average positron lifetime is thus a result of competitive positron trapping in irradiation-induced vacancy defects and in native and irradiation-induced shallow traps. The negative temperature dependence at temperatures above 200 K caused by the compensating centers in the as-grown sample is superimposed by irradiation-induced defects.

Assuming the average defect introduction rate per electron of 1 cm^{-1},[5] the concentration of shallow traps is about 10^{19} cm^{-3}. Provided that the trapping coefficient amounts to $\mu_{ST}=10^{15}$–10^{16} s^{-1},[10] an estimation of the according trapping rate results in $\kappa_{ST}=2\times10^{11}$–$2\times10^{12}$ s^{-1}.

Compared to the positron lifetime after annealing at 320 K, the positron lifetime after annealing at 580 K is lower within the whole temperature range (see Fig. 3). At a sample temperature of 500 K the average lifetime reaches the value for the as-grown sample (≈240 ps). Figure 1 shows that the irradiation-induced vacancy defect is completely annealed at 550 K. Therefore the observed temperature dependence of the positron lifetime is due to simultaneous positron trapping in native defects (compensating centers: $Te_{As}V_{Ga}^{-}$) and in shallow positron traps. The thermal stability up to 1075 K of these compensating centers has already been mentioned above.

A fit applied to the temperature-dependent average positron lifetime according to the positron trapping model shows the effectiveness of shallow traps up to 550 K, if their concentration is high. The fitting procedure requires the temperature independence of the trapping rate of the vacancy defect in this case. On condition that negative ions trap no positrons due to strong detrapping at the highest temperature (550 K), this rate was determined. The decrease in the average lifetime with decreasing temperature is described by the trapping model considering detrapping in shallow traps. There are three unknown parameters: the trapping rate for the shallow traps κ_{ST}, the binding energy E_b of positrons to the shallow traps, and the concentration of shallow traps C_{ST} [see Eq. (2)]. The fit yields $E_b=(65\pm8)$ meV and $\kappa_{ST}=(7.6\pm2.4)\times10^{11}$ s^{-1}. The estimated trapping rate presents a lower limit because the compensating centers are negatively charged, but a temperature-independent trapping rate was assumed in the fit. At low temperatures the measured positron lifetime is equivalent to the positron lifetime in the bulk ($\tau_b=230$ ps). The negative ions are the dominating trapping centers there.

3. Annealing experiments on GaAs:Te after low-dose irradiation

Figure 4 shows the annealing behavior of GaAs:Te samples electron irradiated with doses of 10^{15}, 10^{16}, 10^{17}, and 10^{19} cm^{-2}. After irradiation with fluences up to 10^{17} cm^{-2} the samples are only partially compensated, the location of the Fermi level is above $E_c-0.11$ eV (see Table I). Therefore As vacancies are in principle detectable in the negative or neutral charge state (see Fig. 2).

The annealing behavior of noncompensated samples differs from compensated GaAs:Te. An annealing stage was observed, which is followed by a range of constant average positron lifetime. Finally an increase of the positron lifetime was detected (see Fig. 4).

The results of the GaAs:Te sample irradiated with $\Phi=10^{15}$ cm^{-2} are discussed first. After irradiation, an increased positron lifetime of 251 ps was measured and can be attributed to irradiation-induced vacancy defects. The annealing stage at 200 K may be due to the annealing of these defects. Possible candidates are As vacancies or acceptorlike defects according to the annealing behavior of compensated material after 10^{19} cm^{-2} irradiation (see Sec. IV B 1). This means that below $T_a=250$ K two vacancylike positron trapping centers are present, the compensating centers and irradiation-induced vacancylike defects. Assuming the average defect introduction rate of 1 cm^{-1},[5] the trapping coefficient for irradiation-induced defects at 90 K are estimated to be $\mu\approx1\times10^{17}$ s^{-1}. However, this value is underestimated because shallow traps are neglected. This positron trapping coefficient agrees with values determined earlier for negatively charged vacancy defects.[2]

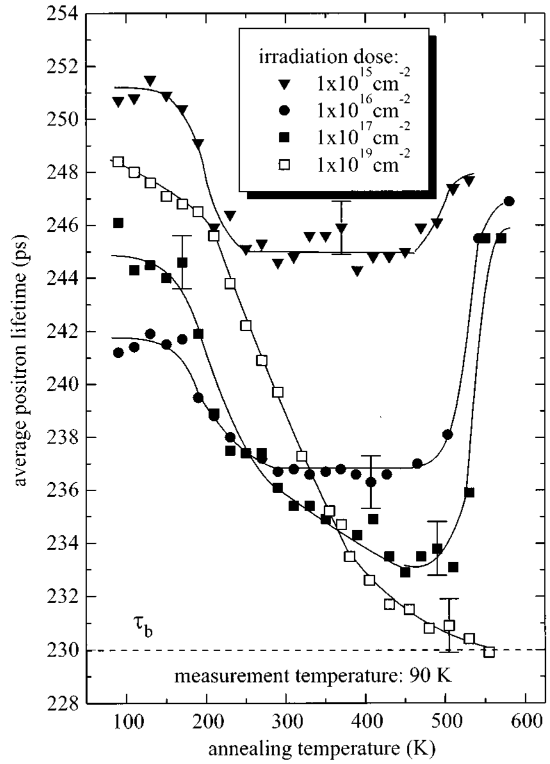

FIG. 4. Average positron lifetime is represented as a function of annealing temperature in GaAs:Te after electron irradiation with different fluences ($\Phi=10^{15}$–10^{19} cm^{-2}).

A plateau of the annealing curve was detected for annealing temperatures ⩾250 K. The average positron lifetime in the range between 250 and 450 K is equal to the lifetime before the irradiation, $\overline{\tau}=245$ ps, and the positron trapping is dominated by the compensating centers. For higher fluences, the plateau level of the lifetime decreases due to increasing concentration of shallow positron traps.

For annealing temperatures above 450 K, the positron lifetime increases again. This behavior is more distinct after

TABLE I. Fluence, carrier concentration, and location of Fermi level of as-grown and electron-irradiated GaAs:Te are tabulated. Negative values mean that Fermi level is located in the conduction band.

Fluence Φ (cm^{-2})	Carrier concentration n (cm^{-3})	Fermi level E_c-E_f (eV)
As-grown	6.1×10^{17}	−0.03
10^{15}	3.7×10^{17}	−0.01
10^{16}	2.2×10^{16}	+0.07
10^{17}	5.6×10^{15}	+0.11
10^{19}	3.1×10^{8}	+0.54

irradiation with higher fluences but not detectable after compensating irradiation. This effect is discussed in the following.

After irradiation with fluence of $\Phi=10^{16}$ cm^{-2}, the average positron lifetime of 242 ps was measured for GaAs:Te. This value is lower compared to the positron lifetime of the as-grown sample. However, the annealing behavior is similar to that of the sample irradiated with $\Phi=10^{15}$ cm^{-2} (see Fig. 4), but the positron lifetime is lower within the whole annealing range. Therefore this irradiation induces also a vacancy defect which anneals above 200 K. The sample is only partially compensated (see Table I). Thus the isolated As vacancy and an acceptorlike vacancy defect are possible trapping centers. The measured positron lifetime is constant for $T_a \geqslant 250$ K. In the plateau range, the compensating centers, $\mathrm{Te_{As}}V_{\mathrm{Ga}}^{-}$, which are stable up to 1075 K, are the dominating vacancy defects. The decreased positron lifetime compared to the as-grown sample is due to the irradiation-induced shallow traps, which act at the measurement temperature (see also Sec. IV B 4).

For annealing temperature $T_a \geqslant 500$ K, the average positron lifetime increases. The decomposed lifetime in the defect was determined to be 275 ps. This value is typical for a monovacancy in GaAs.[19] The increase of the positron lifetime after annealing was also observed in electron-irradiated ($E=0.5$–1.5 MeV, $T_{\mathrm{irr}}=90$ K) highly n-doped GaAs:Si and GaAs:Sn (Ref. 26) and was attributed there to a shift of the Fermi level due to the recombination of As vacancies and As interstitials, i.e., due to annealing of defects in the As sublattice. Furthermore, in electron-irradiated ($E=1.5$ MeV, $T_{\mathrm{irr}}=20$ K) Te- and Si-doped GaAs a steep increase of the positron lifetime after annealing between 500 and 550 K was measured.[29] This was explained by the removal of compensating defects which reveals irradiation-induced As vacancies. Here, no annealing of As vacancies was presumed up to 550 K.

However, our experimental data are in contrast to this interpretation. No change of the Fermi-level location after annealing at 550 K results from the Hall-effect measurements in our GaAs:Te samples. The values of carrier concentration determined after 550-K annealing correspond within the error limit to the values after 300-K annealing. We conclude that a structural change of a defect complex may be observed. Furthermore, the annealing of a complex $\mathrm{As_{Ga}}$-X at 450 K in electron-irradiated ($E=2.2$ MeV, $T_{\mathrm{irr}}=4$ K, $\Phi=2.2\times10^{17}$ cm^{-2}) GaAs:Te ($n=2\times10^{17}$ cm^{-3}) was detected by magnetic circular dichroism of the optical absorption (MCDA).[30] Wietzke, Koschnick, and Spaeth[31] identified this complex in electron-irradiated ($E=2$ MeV, $T_{\mathrm{irr}}=4.2$ K, $\Phi=1\times10^{17}$ cm^{-2}) GaAs:Te ($n=3.4\times10^{17}$ cm^{-3}) as $\mathrm{As_{Ga}}$-V_{As} with an ionization level of $E_v+1.2$ eV $(2+/+)$ by optical detection of electron nuclear double resonance (ODENDOR). However, this defect complex is not detectable by positrons.

The connection supposed between the increase of the average positron lifetime and the annealing stage at 450 K observed by MCDA and ODENDOR in electron-irradiated n-type GaAs will be the topic of future investigations.

In summary one can say that for noncompensated n-GaAs after electron irradiation and annealing at about 550 K an increased positron lifetime was measured. There are different interpretations in the literature. Our positron measurements were correlated with Hall-effect investigations and no Fermi-level shift in this annealing range was detected. Therefore we conclude the increase of positron lifetime is due to a structural change of defect complexes. At the same annealing temperature a disappearance of $\mathrm{As_{Ga}}V_{\mathrm{As}}$ complex was observed by optical methods. We assume a connection between the two effects and we will study this behavior in more detail in future.

The annealing behavior of the sample irradiated with $\Phi=1\times10^{17}$ cm^{-2} shows clearly a transition to the annealing behavior of compensated samples, without consideration of the increasing lifetime above 550 K. The sample was partially compensated due to the irradiation, the Fermi level is located 0.11 eV below the conduction band (see Table I). The first annealing stage is due to the annealing of irradiation-induced vacancies. For temperatures above 150 K a gradual decrease of lifetime was detected, i.e., no plateau was found. This is due to the higher electron fluence and therefore to the introduction of a higher concentration of vacancy defects, which dominate the positron trapping in compensating centers. Additionally, shallow traps were produced and lower the positron lifetime. Thus induced vacancy defects in GaAs:Te irradiated with $\Phi=10^{15}$–10^{16} cm^{-2} were dominated by the ingrowing compensating centers after annealing at 250 K. From the similarity of the annealing behavior (see Fig. 4) it was concluded that the same defect anneals in all samples.

After annealing at 550 K the positron lifetime increases for samples after noncompensating irradiation and the positron lifetime in the defect is 275 ps. The cause of this behavior is still under discussion (see above).

4. Dose dependence

Figure 5 shows the average positron lifetime measured at 90 K versus the irradiation fluence after different annealing stages. An increase of the defect concentration with increasing fluence was expected in principle. After annealing at 90, 250, and 320 K the highest positron lifetime was measured after irradiation with $\Phi=10^{15}$ cm^{-2}. Then a distinct decrease was observed and for $\Phi\geqslant10^{16}$ cm^{-2} a positive slope of the lifetime curve was detected. This dependence of the positron lifetime on the fluence has also been detected for n-type GaAs:Te earlier.[9] Irradiation induces simultaneously several types of defects detectable by positrons: vacancies, vacancy complexes, and antisites.[32] Antisites may carry a negative charge and act as shallow positron traps. Vacancylike defects increase the average positron lifetime, but shallow traps decrease it. The superposition of these two effects leads to the curves of Fig. 5. However, the complete explanation for this behavior is rather difficult and not yet understood.

After annealing at 450 K the irradiation-induced vacancy defect is recovered (see Fig. 4) and the positron trapping in irradiation-induced defects is dominated by trapping in shallow traps. Additionally, the samples contain ingrowing compensating centers which also give rise to a vacancy signal. This is visible for low irradiation fluences ($\Phi=10^{15}$ cm^{-2}). $\overline{\tau}$ decreases with increasing fluence by an increasing concentration of irradiation-induced shallow traps. The number of compensating centers is unchanged, but their vacancy signal is completely covered.

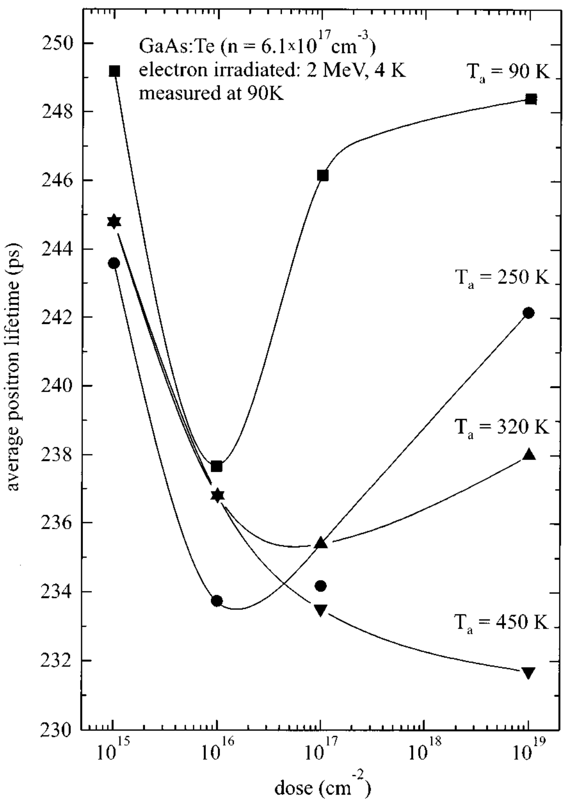

FIG. 5. Average positron lifetime is shown as a function of electron fluence in GaAs:Te after different annealing steps.

Figure 5 also illustrates that the positron lifetime decreases with increasing annealing temperature for compensating irradiation ($\Phi = 10^{19}$ cm^{-2}).

The dose dependencies show clearly that the interaction between the generation and annealing of vacancy defects and shallow positron traps is complicated. The calculation of trapping rates or defect concentrations from the average positron lifetime measured at low temperatures is therefore very difficult and often impossible.

5. Summary

It was shown in Sec. IV B that a vacancylike irradiation-induced defect anneals above 200 K. For the compensated sample ($\Phi = 10^{19}$ cm^{-2}) one can exclude the annealing of isolated As monovacancies due to the localization of the Fermi level in midgap position. In this case, the As vacancies are positively charged and therefore undetectable by positrons. After low-dose irradiation the samples were still of n-type conductivity, so that evidence of As vacancies is possible. But from the shape of the annealing curves one can conclude the annealing of the same vacancylike defect. Therefore the annealing is attributed to the disappearance of a defect which contains a vacancy and which is neutral or negatively charged for the compensated state of the sample. The vacancy could be associated with an intrinsic defect (As_{Ga}, Ga_{As}, As_i, Ga_i) or with the dopant (Te). The second possibility is the annealing of isolated Ga vacancies.

At the annealing temperature of 550 K an additional defect was detected for n-type samples, but not for the compensated sample. No Fermi-level shift was observed by Hall-effect measurements in this annealing range. Therefore we conclude that the increase of positron lifetime is due to a structural change of defect complexes connected with a change of the charge state of these complexes or of the vacancy involved.

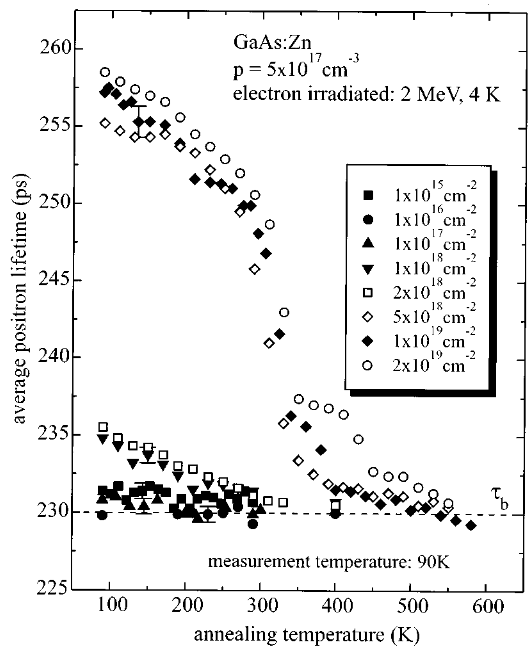

FIG. 6. Average positron lifetime is represented as a function of the annealing temperature in GaAs:Zn irradiated with different electron fluences.

A fit corresponding to the two-defect trapping model with detrapping from one defect[21] yields for the compensated sample after the 580-K annealing step a positron binding energy to shallow traps of $E_b = (65 \pm 8)$ meV and a trapping rate in shallow traps of $\kappa_{ST} = (7.6 \pm 2.4) \times 10^{11}$ s^{-1}.

C. GaAs:Zn

Prior to irradiation, the samples were p type with a carrier concentration of $p = 5 \times 10^{17}$ cm^{-3}. The Fermi level was located near the valence-band edge $E_f = E_v + 0.08$ eV due to the Zn dopant with an acceptor level of $E_A - E_v = 0.33$ eV. Thus the Fermi level is located below the lowest ionization level of the Ga vacancy (see Fig. 2) and the Ga vacancies should be neutral. They must be detectable by positrons in any case.[24] The As vacancies are positively charged and are undetectable for all GaAs:Zn samples under investigation. The average positron lifetime was determined to be 230 ps. This value agrees with the positron lifetime in the bulk. Thus the concentration of Ga vacancies is below the sensitivity limit of positrons (some 10^{15} cm^{-3}).

1. Annealing experiments

Figure 6 shows results of the annealing experiments (isochronally for 15 min) of p-type GaAs:Zn after electron irradiation with fluences of $\Phi = 10^{15}$–2×10^{19} cm^{-2}. The samples were annealed in the temperature range between 90 and 580 K. No change of the average positron lifetime was observed after irradiation up to the fluence of $\Phi = 10^{17}$ cm^{-2}. $\overline{\tau}$ weakly

TABLE II. Fluence, carrier concentration, and location of the Fermi level for as-grown and electron-irradiated GaAs:Zn are tabulated.

Fluence Φ (cm^{-2})	Carrier concentration p (cm^{-3})	Fermi level $E_f - E_v$ (eV)
As-grown	5.0×10^{17}	0.068
1×10^{15}	5.5×10^{16}	0.125
1×10^{16}	9.2×10^{16}	0.112
1×10^{17}	2.1×10^{17}	0.091
1×10^{18}	2.4×10^{16}	0.147
2×10^{18}	3.8×10^{14}	0.254
5×10^{18}	7.8×10^{10}	0.474
1×10^{19}	1.4×10^{9}	0.578
2×10^{19}	4.5×10^{8}	0.607

increases for fluences of 10^{18} and 2×10^{18} cm^{-2} and a distinct change of the average positron lifetime and the positron lifetime in the defect of 265 ps were observed after irradiation with $\Phi\geqslant5\times10^{18}$ cm^{-2}. A main annealing stage was found for these samples between 200 and 500 K.

Table II summarizes the results of the Hall-effect measurements performed on differently irradiated GaAs:Zn samples after the 300-K annealing step. A Fermi-level shift due to the irradiation-induced carrier compensation was observed. Up to the fluence of 2×10^{18} cm^{-2} the samples are still of p-type conductivity and only partially compensated (see Table II). The carrier concentration is low for $\Phi=5\times10^{18}$ cm^{-2}, and the shift of the Fermi level is distinct, E_f reaches a near-midgap position for $\Phi=2\times10^{19}$ cm^{-2}. Because of this shift a positron trapping center was ionized and the trapping rate increased. This is indicated by the increased average positron lifetime.

Assuming an average introduction rate for Ga vacancies by electron irradiation in GaAs of 1 cm^{-1} we expected an increase of positron lifetime for $\Phi>10^{16}$ cm^{-2}. Because Ga vacancies act as positron trapping centers in p-type and in semi-insulating material and the average positron lifetime is constant up to $\Phi=10^{17}$ cm^{-2}, the behavior of average positron lifetime in dependence on Φ is surprising. There are two possible explanations.

(i) At first, the irradiation-induced defects are isolated Ga vacancies. For irradiation fluences $\Phi\leqslant2\times10^{18}$ cm^{-2}, the Ga vacancies could be neutral and due to simultaneously induced shallow positron traps either no or a weak increase of average positron lifetime was measured. Assuming an average introduction rate for defects by electron irradiation in GaAs of 1 cm^{-1} and a trapping coefficient of 10^{16} s^{-1} for shallow traps at the measurement temperature of 90 K (Ref. 2) an estimation of the trapping coefficient of the vacancy defect according to the two-defect trapping model is possible.[15,16] The calculation provides $\mu=3.5\times10^{14}$ s^{-1} for the sample irradiated with $\Phi=10^{17}$ cm^{-2} and $\mu=1.6\times10^{15}$ s^{-1} for irradiation with $\Phi=2\times10^{18}$ cm^{-2}. These values are reasonable for neutral defects at low temperatures.[25,3,2] For irradiation fluences $\Phi\geqslant5\times10^{18}$ cm^{-2}, the Ga vacancies are negatively charged due to the shift of the Fermi level caused by the irradiation-induced compensation of carriers. The estimation of the trapping coefficient of the vacancy defect gives a value of $\mu=2.3\times10^{16}$ s^{-1} under the same conditions. This is in agreement with determined values for negatively charged vacancies at low temperatures.[2] However, from the calculated energy levels[24] follow that the shallow traps have the 0/$-$ ionization level at the same position of the Fermi level as the Ga vacancies at $E_f-E_v=0.11$ eV. This means, if neutral Ga vacancies are present, the antisites ($\mathrm{Ga_{As}}$) are also neutral and should not act as shallow traps. The dependence of the positron lifetime on the irradiation fluence up to $\Phi=2\times10^{18}$ cm^{-2} cannot be explained in this way. Slow-positron beam investigations are planned to prove the presence of shallow traps in p-type GaAs after noncompensating irradiation.

To sum up, the isolated Ga vacancy and its transition from the neutral to the negative charge state can only be responsible for the measured positron-lifetime dependence on the irradiation dose and for the annealing stage at about 300 K, when the ionization levels of $V_{\mathrm{Ga}}^{-/0}$ and $\mathrm{Ga}_{\mathrm{As}}^{-/0}$ differ distinctly. The calculations of Puska[24] yield no difference between the energy positions of these ionization levels. It was also earlier assumed that the isolated Ga vacancy anneals below 100 K.[5]

(ii) The second possibility to explain the positron-lifetime behavior in electron-irradiated GaAs:Zn is an irradiation-induced defect complex containing a vacancy. This vacancy-like defect has to have a +/0 ionization level in the lower half of the band gap and is the dominating trapping center for positrons after compensating irradiation in GaAs:Zn. For partially compensating irradiation, the Fermi level was shifted through the band gap into midgap direction (see Table II) and the vacancylike defect becomes neutral. Consequently, the average positron lifetime increases. The samples irradiated with fluences $\Phi\geqslant5\times10^{18}$ cm^{-2} are nearly compensated and the vacancylike defect complex is detectable by positrons. Hence the variation of $\overline{\tau}$ with the carrier concentration p and consequently with the location of Fermi level E_f is due to the change of the trapping coefficient μ and/or of the vacancy-defect concentration C. In this case, μ changes distinctly due to the +/0 transition with increasing Fermi level ($\mu_+\ll\mu_0$). Assuming an ionization level of this defect at the energy E_d within the band gap the positron trapping rate may be written as $\kappa=[f\mu_0+(1-f)\mu_+]C \approx f\mu_0 C$, where f is the Fermi-distribution function: $f=\{1+g\exp[(E_d-E_f)/(k_BT)]\}^{-1}$. g is the degree of degeneracy of the level. The average positron lifetime was fitted with these expressions to the experimental data using E_d and $\mu_0 C$ as parameters for the fit ($\tau_d=265$ ps, $\tau_b=230$ ps, $g=2$). The fit provides the ionization level of the detected vacancy-type defect to be $E_d-E_v=(0.355\pm0.020)$ eV.

Additionally, the annealing of a V_{Ga}-X complex was found by the magnetic circular dichroism of the optical absorption at about 300 K.[33] Optically detected magnetic resonance (ODMR) studies[34] showed that this MCDA spectrum correlates with the electron paramagnetic resonance (EPR) spectra[35] that were attributed to V_{Ga}^{2-}. However, the constituent X of the complex is not known. The connection of this complex with a Ga vacancy was earlier concluded from positron annihilation measurements,[9] where an annealing stage detected at about 300 K was attributed to isolated Ga vacancies.

In summary, an irradiation-induced defect complex connected with a vacancy may explain the positron results without further assumptions. This irradiation-induced defect an-

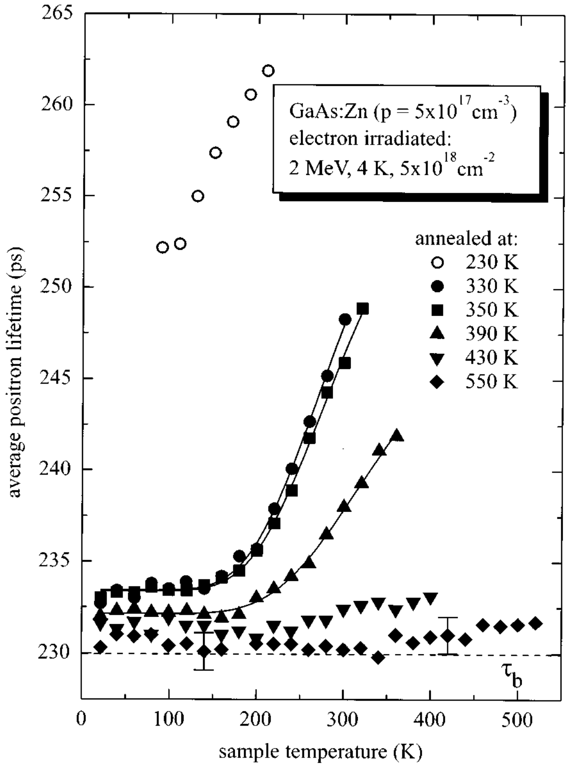

FIG. 7. Average positron lifetime is presented as a function of sample temperature in electron-irradiated GaAs:Zn after different annealing steps. The full lines are the fits corresponding to the two-defect trapping model with detrapping from one defect. The positron binding energy to shallow traps was determined to be $E_b=(90\pm12)$ meV.

neals in one stage between 200 and 500 K in analogy to the defect in electron-irradiated compensated GaAs:Te. We conclude that the annealing stage observed in electron-irradiated *p*- and *n*-doped GaAs is due to a complex containing a monovacancy associated with an intrinsic defect or with the dopant rather than an isolated monovacancy. We investigated also irradiated undoped material to decide between these possibilities of the constituent X of the complex (see Sec. IV D).

2. Temperature-dependent measurements

Figure 7 shows the temperature-dependent positron-lifetime measurements on GaAs:Zn electron irradiated with a fluence of 5×10^{18} cm^{-2} after different annealing steps. After annealing between 230 and 390 K, $\overline{\tau}$ increases with increasing temperature. This strong temperature dependence is due to the competitive positron trapping in negative ions and in the irradiation-induced vacancylike defects (see discussion above). The determination of the trapping rate for the shallow positron traps is difficult because no saturated trapping in the vacancy defects is reached at high temperatures. The binding energy of positrons to shallow traps E_b and the concentration of shallow traps C_{ST} are dependent on each other in the fitting procedure as far as the positron-lifetime curve as a function of temperature shows a point of inflection.

In order to estimate the positron binding energy to the shallow traps, a fit was applied to the temperature-dependent average positron lifetime (after annealing at 330, 350, and 390 K) according to the positron trapping model. In the fitting procedure, the temperature independence of the trapping rate of the vacancy defect was assumed. The decrease in the average lifetime with decreasing temperature is described in the trapping model considering detrapping of positrons from shallow traps. In this case four parameters were used for the fit: the trapping rate for the shallow traps κ_{ST}, the binding energy E_b of the positrons to the shallow traps, the concentration of shallow traps C_{ST} [see Eq. (2)], and the trapping rate of the vacancy defect κ_V. The fit gives $E_b=(90\pm12)$ meV. A binding energy of about 40 meV has been obtained earlier for shallow positron traps in electron-irradiated semi-insulating GaAs.[10] The numerical accuracy of the other parameters was low due to their mutual dependency. In Fig. 7 the fit curves are drawn.

After annealing at 430 K, the positron lifetime is nearly independent of temperature, the irradiation-induced vacancy defect is annealed, and the positron lifetime of bulk material was measured over the whole temperature range. The shallow positron traps are no longer detectable.

3. Summary

In electron-irradiated GaAs:Zn ($p=5\times10^{17}$ cm^{-3}), defects were detected by positrons only when $\Phi\geqslant10^{18}$ cm^{-2}. For $\Phi\geqslant5\times10^{18}$ cm^{-2}, the positron lifetime clearly increased and the lifetime in the defect was determined to be 265 ps, being typical for a monovacancy. Between 200 and 500 K, the annealing of this defect was observed. The Hall-effect measurements showed that the Fermi level was shifted into the midgap direction due to irradiation-induced carrier compensation. Because of this shift, a positron trapping center was ionized and the trapping rate increased. This was indicated by the higher average positron lifetime.

This behavior may be explained by an irradiation-induced complex containing a vacancy (in the Ga or As sublattice) with an ionization level (+/0) of $E_d-E_v=(0.355\pm0.020)$ eV. The annealing behavior of this complex is similar to that in GaAs:Te and one can propose the annealing of the same defect. The vacancy could be connected with an intrinsic defect (As_{Ga}, Ga_{As}, As_i, Ga_i) or with the dopant (Te or Zn). The annealing of a V_{Ga}-X complex at about 300 K was also found by MCDA.[33]

Temperature-dependent measurements after different annealing steps show the presence of shallow positron traps. It is difficult to obtain quantitative information from these measurements due to the unknown trapping rate in the vacancy defect. The positron binding energy to shallow traps is estimated to be $E_b=(90\pm12)$ meV.

D. Undoped GaAs

The undoped samples were of *n*-type conductivity with a carrier concentration of $n=1\times10^{15}$ cm^{-3} prior to irradiation. The Fermi level was located near the conduction-band edge $E_f=E_c-0.162$ eV and As and Ga vacancies were then detectable (see Fig. 2). The average positron lifetime was determined to be 235 ps. Due to stoichiometric As vacancies, this value is higher than the positron lifetime in the bulk (230 ps).[8] Generally it is assumed that the concentration of Ga vacancies is below the sensitivity limit of positrons in as-grown material.[1,8]

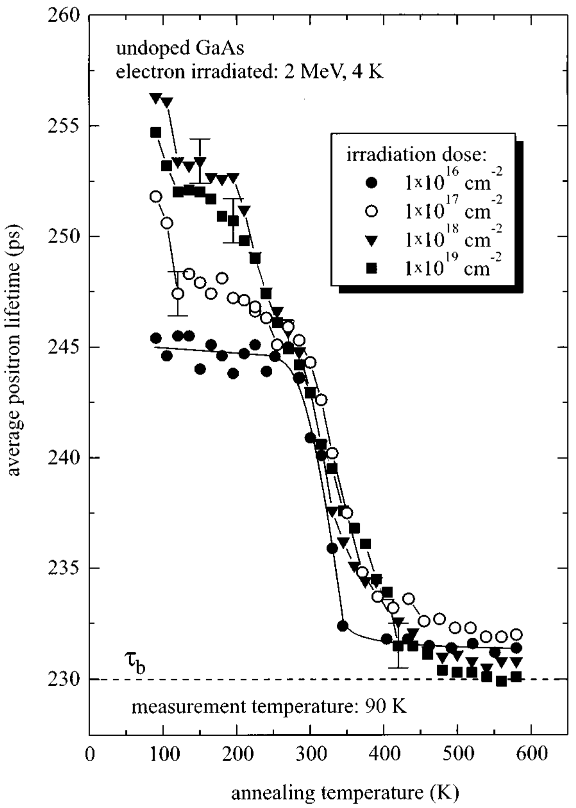

FIG. 8. Average positron lifetime is shown as a function of annealing temperature in undoped GaAs after electron irradiation with different fluences.

1. Compensating irradiation

After electron irradiation the average positron lifetime increased with increasing fluence (see Fig. 8) due to the occurrence of irradiation-induced defects. The decomposition of the spectra yields a defect component of (270±5) ps. The location of the Fermi level after irradiation and after annealing at 300 K was determined by Hall-effect measurements to be $E_f = E_c - 0.57$ eV for all samples. Therefore the samples were compensated (ρ=95 MΩ cm) already after irradiation with $\Phi = 10^{16}$ cm^{-2}.

Figure 8 shows the results of the isochronal (15 min) annealing experiments of undoped n-GaAs after electron irradiation with fluences of $\Phi = 10^{16}$–10^{19} cm^{-2}. The samples were annealed in the temperature range between 90 and 580 K. For all samples a wide main annealing stage between 200 and 500 K was observed. The positron lifetime in the defect of 270 ps is a typical value for a monovacancy defect. After the 580-K annealing step, the positron lifetime of the bulk (230 ps) was measured at 90 K and no temperature dependence was detected. The irradiation-induced defect is annealed.

The irradiated samples are compensated and the Fermi level ($E_f = E_c - 0.57$ eV) is located below the lowest ionization level (0/+) of the As vacancy (see Fig. 2). Therefore As vacancies are positively charged and undetectable, while Ga vacancies remain detectable by positrons. We concluded from the investigations on irradiated GaAs:Zn (Sec. IV C) that the isolated Ga monovacancies were not observed and the increased positron lifetime is caused by another vacancy defect. It has also been assumed earlier that the isolated Ga vacancy anneals below 100 K.[5]

Therefore the assumption is supported that the annealing stage between 200 and 550 K in electron-irradiated GaAs is due to the disappearance of a defect complex connected with an As or a Ga vacancy.

We conclude from the same annealing temperature (see also discussion in Sec. IV E) in electron-irradiated doped and undoped GaAs that the dominating irradiation-induced defect is a monovacancy connected to an intrinsic defect (interstitial, antisite) but not to a dopant atom. There are different possibilities to combine these defects. A vacancy and a nearest-neighbor interstitial form an unstable complex due to the high mobility of interstitials. Therefore the favorable combination is a monovacancy linked with an antisite defect. Assuming a Coulombic repulsion between two acceptors (V_{Ga}-Ga_{As}) or two donors (V_{As}-As_{Ga}), the most probable complexes are V_{Ga}-As_{Ga} or V_{As}-Ga_{As}. In good agreement with this conclusion is the fact that a dominating defect, which anneals at 300 K, was found after low-temperature electron irradiation in semi-insulating, n-, and p-type GaAs by ESR (electron spin resonance) and was assigned to V_{Ga}-X.[33,34] However, the connection of this complex with a Ga vacancy was concluded from positron annihilation measurements,[9] where the detected annealing stage at about 300 K was attributed to the isolated Ga vacancy. Therefore the decision between V_{Ga}-As_{Ga} and V_{As}-Ga_{As} is not possible.

A discrepancy between the annealing curves of undoped and doped GaAs was observed. The end of an annealing stage for irradiation fluences $\Phi \geqslant 10^{17}$ cm^{-2} in undoped GaAs was to be seen below a temperature of 120 K. The effect is small and a decomposition of the spectra was very difficult due to the influence of shallow positron traps at the measurement temperature. There are two possible explanations for the annealing below 120 K. At first, the annealing of isolated Ga vacancies is assumed to occur below 100 K (Ref. 5) and can cause the annealing stage. Secondly, the thermally stimulated reconversion of the $EL2$ defect from the metastable to the stable state may give rise to this annealing effect.[36] The $EL2$ defect converts under illumination at low temperatures to the metastable configuration and reconverts at about 120 K. The metastable state contains a vacancy detectable by positrons.[37] Because the samples were prepared in liquid nitrogen by daylight (30 min) the metastable state of $EL2$ may be created. This annealing stage at 100 K was not observed after irradiation with 10^{16} cm^{-2}. An explanation is the low introduction rate for metastable vacancies (0.3 cm^{-1}) (Ref. 38) by electron irradiation in GaAs. Therefore, the concentration of the irradiation-induced metastable vacancies is below the sensitivity range of positrons ($<5\times10^{15}$ cm^{-3}).

Temperature-dependent measurements were also performed after different annealing steps. The results are comparable with those of the Zn-doped samples. The observed increase of $\overline{\tau}$ with the temperature is due to the competitive positron trapping in shallow traps and in the irradiation-induced vacancylike defects (see discussion above). The determination of the trapping rates for vacancies and shallow positron traps is difficult because no saturated trapping in the vacancy defects is reached at high temperatures (see discussion in Sec. IV B 2.). After annealing at 500 K, the positron

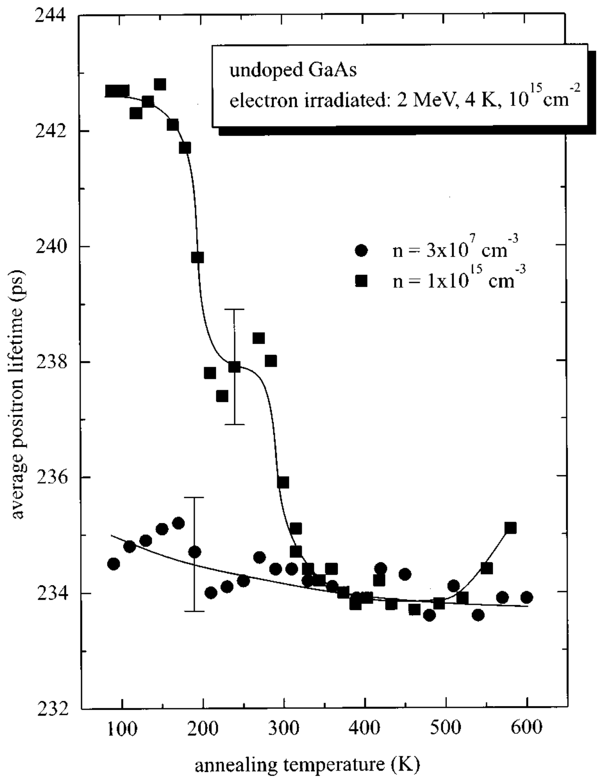

FIG. 9. Average positron lifetime is shown as a function of annealing temperature in n-type and semi-insulating undoped GaAs after electron irradiation.

lifetime is independent of the temperature. The irradiation-induced vacancy defect is annealed, and the positron lifetime equals the bulk value over the whole temperature range. The shallow positron traps are no longer detectable but may be present.

2. Annealing experiments on undoped GaAs after low-dose irradiation

The annealing behavior of positron lifetime after low-dose irradiation ($\Phi=10^{15}$ cm^{-2}) is different from the curves obtained after compensating doses ($\Phi=10^{16}$–10^{19} cm^{-2}). Figure 9 shows the average positron lifetime as a function of annealing temperature for two undoped GaAs samples. The first sample is of n-type conductivity (see Sec. IV D 1, $n=1\times10^{15}$ cm^{-3}, $E_f=E_c-0.162$ eV) and after irradiation still of n type proved by Hall-effect measurements ($n=6.9\times10^{14}$ cm^{-3}, $E_f=E_c-0.17$ eV). The second sample is semi-insulating before and after irradiation ($n=3\times10^7$ cm^{-3}).

For the sample of n-type conductivity (filled squares) an increase of average positron lifetime from 235 to 242 ps after irradiation was observed. This increase is unexpectedly strong and the average positron lifetime in the defect is (270$\pm$5) ps due to irradiation-induced vacancy defects. The trapping rate is $\kappa=2\times10^9$ s^{-1}. Assuming that 10^{15} cm^{-3} defects were induced by irradiation ($\Phi=10^{15}$ cm^{-2}), the estimation of the positron trapping coefficient results in $\mu=8.8\times10^{16}$ s^{-1}. This value is very high but it is possible for a negatively charged trapping center at low temperatures. This unexpectedly strong increase of the positron lifetime was also observed after low-dose irradiation in GaAs:Te.

Instead of a wide annealing stage between 200 and 500 K detected in compensated GaAs, two steps at 200 and at 300 K appear. We assume the annealing of the same complex observed in compensated samples at 300 K. Additionally, the annealing of another vacancylike defect at 200 K was observed only in n-type material. Therefore the 200-K annealing stage may be due to a donorlike defect detectable by positrons. A possible candidate is the irradiation-induced As vacancy. This is in agreement with an earlier assumption that V_{As} recombine with mobile Ga_i in the annealing stages I and II, which occurs at about 250 K.[5]

The positron lifetime reaches the value measured prior to irradiation after annealing at 350 K and the assumed growth-induced vacancies are still detectable. Moreover, this means that the concentration of shallow positron traps introduced by irradiation is too low to decrease the average lifetime at the measurement temperature of 90 K distinctly. After annealing at 550 K, a weak increase of positron lifetime was measured. This behavior is possibly caused by the same defect reaction observed in uncompensated n-type GaAs:Te (see Sec. IV B).

For the initially semi-insulating GaAs sample a positron lifetime equal to the value of 230 ps was measured before irradiation at room temperature. In the irradiated sample, the average positron lifetime increased up to 235 ps (filled circles) and no significant effect was observed up to an annealing temperature of 600 K. After this annealing step, the room-temperature measurement results in an average positron lifetime of 230 ps. This means that no defects are detectable by positrons at 300 K and that a defect with a significant trapping rate at 90 K is present in this sample with a low concentration.

3. Summary

In Sec. IV D it was shown that a vacancylike irradiation-induced defect anneals in the temperature range between 200 and 500 K analogously to doped GaAs. The detection of annealing of isolated As monovacancies can be excluded for the compensated samples ($\Phi\geqslant10^{16}$ cm^{-2}) because of the location of the Fermi level in midgap position. We deduce from the same annealing temperature in electron-irradiated doped and undoped GaAs that the dominating irradiation-induced defect is a monovacancy connected to an intrinsic defect (antisite).

Instead of a wide annealing stage between 200 and 500 K detected in compensated undoped GaAs two steps at 200 and at 300 K appear after low-dose irradiation of n-type GaAs. We assume the annealing of the same complex observed in compensated samples at 300 K and additionally the annealing of another vacancylike defect at 200 K only visible in n-type material. A possible candidate is the irradiation-induced As vacancy.

The positron lifetime weakly increased for the initially semi-insulating GaAs sample due to irradiation and no significant effect was observed up to an annealing temperature of 600 K.

E. Annealing kinetics of compensated GaAs samples

We tried to determine the activation energy E_a of the annealing processes in doped and undoped GaAs after compensating electron irradiation. In the common model of defect annealing, the number of defects N which disappear per unit time is proportional to $f(N)$, where $f(N)$ can be any kind of monotonically increasing function independent of temperature:

$$-\frac{dN}{dt}=Kf(N). \tag{3}$$

If $f(N)=N^{\alpha}$, the parameter α is called the order of reaction. The rate constant K has the form

$$K=K_0\exp\left(-\frac{E_a}{k_BT}\right), \tag{4}$$

where K_0 is a constant containing the vibrational frequency associated with the annealing process and E_a the corresponding activation energy.

The measurement procedure was realized in the following way: The defect concentration N was determined at the reference temperature T_m (in our investigations: 90 K). Afterwards, the sample was heated at the temperature $T_a=T_m+\Delta T$ for a given time t_a ($\Delta T=30$ K, $t_a=900$ s), then cooled down to T_m for the determination of N. It is then heated at $T_a=T_m+2\Delta T$ for the same time and again cooled to the reference temperature for the measurement and so on. The mathematical specification is

$$-\frac{\Delta N}{N^{\alpha}}=K_0\exp\left(-\frac{E_a}{k_BT_a}\right)\Delta t. \tag{5}$$

The only difficulty of the isochronal annealing is the requirement that the time of the temperature increase is short enough in order to minimize the amount of annealing which occurs during cooling and heating, as compared to the effect at annealing temperature during t_a.

The fits were applied to the positron trapping rate ($\kappa\sim N=C_d$) in the vacancy defect as a function of annealing temperature. The trapping rates were determined according to the two-defect trapping model. Since shallow positron traps were also induced by electron irradiation and act at the measurement temperature of 90 K, they must be considered. Their concentration and therefore their trapping rate are difficult to determine (see discussion in Sec. IV C). We assumed different trapping rates in shallow traps (10^{10}–10^{12} s^{-1}) and calculated the trapping rate in the vacancy defect according to the two-defect trapping model. The fits showed no distinct influence of the trapping rate in shallow traps on the determination of the activation energy and therefore we used for all annealing fits the average value of $\kappa_{ST}=10^{11}\ s^{-1}$.

There are three fit parameters in Eq. (5): the activation energy E_a, the constant K_0, and the order of reaction α. The first fit attempts yield an order of $\alpha\approx1$ and then this value was fixed.

Figure 10 shows the comparison between the annealing behavior of Te-, Zn-, and undoped GaAs after compensating

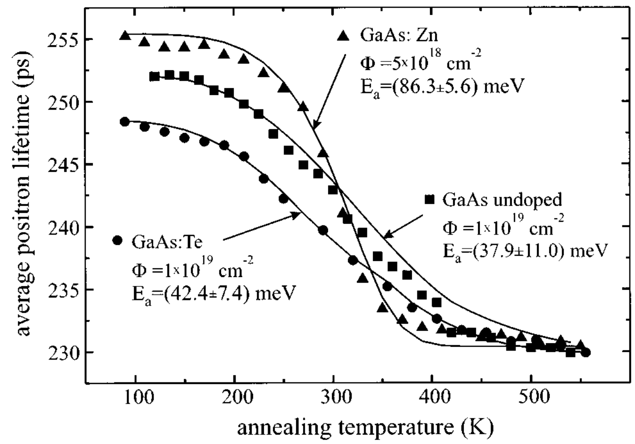

FIG. 10. The comparison between the annealing behavior of Te-, Zn-, and undoped GaAs after compensating irradiation is shown. The lines correspond to the fit applied to the trapping rate in the vacancy defect according to annealing kinetics.

irradiation. The lines correspond to the fit applied to the trapping rate in the vacancy defect according to Eq. (5).

The annealing temperature of about 300 K is the same for all electron-irradiated GaAs samples and therefore it seems likely to assume the annealing of the same defect which is not connected with a dopant but with an intrinsic defect. The fits result in the activation energy of about $E_a=(40\pm12)$ meV for n-type GaAs and $E_a=(86.3\pm5.6)$ meV for p-type GaAs. A possible explanation of this difference between the determined activation energies is a different charge state of the same vacancylike defect. For compensated n-GaAs the Fermi level is located about 0.85 eV above the valence-band edge and for compensated p-GaAs about 0.5 eV above E_v. Besides the estimated $+/0$ ionization level $E_d-E_v=(0.355\pm0.020)$ eV (see Sec. IV C) a second level $(0/-)$ could occur between 0.5 eV$\leqslant E_d-E_v\leqslant$0.85 eV.

V. CONCLUSIONS

A systematic study of electron-irradiation-induced defects in GaAs was carried out. The defect formation and annealing behavior were studied as a function of the fluence (10^{15}–10^{19} cm^{-2}) in undoped, n-, and p-doped GaAs.

It was shown that a vacancylike irradiation-induced defect anneals in the temperature range between 200 and 500 K in all conductivity types of GaAs. We doubt the annealing of the isolated Ga monovacancy and favor the annealing of an irradiation-induced complex containing a vacancy (in the Ga or As sublattice) and an intrinsic defect with an ionization level $(+/0)$ of $E_d+E_v=(0.355\pm0.020)$ eV. The activation energy of the isochronal annealing of about $E_a=(40\pm12)$ meV for n-type GaAs and $E_a=(86.3\pm5.6)$ meV for p-type GaAs was determined. This difference between the energies may be explained by a different charge state of the same vacancylike defect with an ionization level $(0/-)$ of about 0.5 eV $\leqslant E_d+E_v\leqslant$0.85 eV.

An additional defect was detected for n-GaAs samples retaining their n-type conductivity after irradiation and annealing at a temperature of 500 K. No Fermi-level shift in this annealing range was observed by Hall-effect measurements. Therefore we conclude that the increase of the positron lifetime is due to a structural change of defect complexes connected with a charge change of an involved vacancy in the As sublattice.

Temperature-dependent measurements after different annealing steps show the presence of shallow positron traps. It is difficult to derive quantitative information from these measurements due to the unknown trapping rate of the vacancy defect. The positron binding energy to shallow traps was estimated for several examples. A fit applied to the temperature-dependent average positron lifetime according to the positron trapping model shows the effectiveness of shallow traps up to 550 K if their concentration is sufficiently high.

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