Characterization of native point defects in GaN by positron annihilation spectroscopy

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1. INTRODUCTION

Gallium nitride exhibits electronic, optical, and thermal properties, which make it a promising material for optoelectronic and high-power devices. Especially, its large direct band gap (3.4 eV) and strong interatomic bonds enable the construction of very efficient blue light-emitting diodes and promise the development of long-lifetime blue lasers. Unfortunately, GaN and related materials are difficult to fabricate. Since lattice-matched substrates for GaN epitaxy are generally not available, dislocation densities as high as $10^{10}$ cm$^{-2}$ are common in overlayers grown by metal-organic chemical vapor deposition (MOCVD) on sapphire. These and other extended defects have been studied extensively (for example, see Refs. [1-7] and citations therein). Much less is know about simple point defects such as vacancies and interstitial atoms, although it is likely that they are formed at high concentrations in the crystal growth of GaN.

Point defects induce localized electron levels into the band gap of the semiconductor. These states can trap charge carriers, thus inducing compensation, scattering of free carriers, and subsequent change of electrical properties. Moreover, the states interact with light, inducing increase in the absorption or emission photons in radiative recombination processes. For example, the parasitic optical transition leading to yellow luminescence is observed in both GaN bulk crystals and epitaxial layers. The atomic structure of the defect responsible for the yellow emission has been much debated, although even the positions of the electronic levels participating in this optical process have been under discussion [8-11].

The understanding and control of these effects requires both the identification of the defects as well as the characterization of their physical properties. Traditionally the experimental information on point defects has been obtained by electrical and optical characterization techniques, such as Hall measurements and infrared absorption. Although the defects can be detected in these experiments, their atomic structures remain very often unresolved. The methods based on electron paramagnetic resonance (EPR) are more sensitive to the structure of defects, but so far these techniques have given only limited information in GaN materials. An experimental technique is thus needed for the unambiguous defect identification. This goal is reached for vacancy-type defects by utilizing the positron annihilation spectroscopy.

Thermalized positrons in solids get trapped by the vacant lattice sites. The reduced electron density at the vacancies increases positron lifetime and narrows the positron-electron momentum distribution. The detection of these quantities yields direct information on the vacancy defects in solids. Positron lifetime measurements can be used to probe homogeneous defect distributions in semiconductor substrates. This technique is relatively simple to implement, but yet very powerful in identifying the atomic structure of the defect, its charge state and concentration. Defects in the near-surface region 0 – 3 µm can be studied by a monoenergetic positron beam. This technique is well suited for the defect studies of epitaxial semiconductor materials. The information provided by positron experiments is especially useful
when combined with those of other spectroscopies. The correlation of positron measurements with electrical and optical methods enables quantitative studies of technologically important phenomena such as electrical compensation, light absorption and photoluminescence.

In this chapter we present a brief overview of positron annihilation spectroscopy in Sec. 2. The goal is to introduce the reader with this technique at the level which is needed for understanding the results in GaN materials. More extensive reviews of the experimental methods can be found in the literature (see Refs. [12-16]). The positron results concerning the native defects in GaN bulk crystals are presented in Sec. 3. The vacancies in GaN layers on sapphire are discussed in Sec. 4 by summarizing the existing data in samples doped n-type with O or Si or p-type with Mg. The formation of point defects at various growth conditions of GaN layers are reviewed in Sec. 5. These include studies of stoichiometry, dislocation density and substrate material. Sec. 6 is a brief summary.
2. POSITRON ANNIHILATION SPECTROSCOPY

In this section we review the principles of positron annihilation spectroscopy and describe the experimental techniques. The thermalized positrons in lattices behave like free electrons and holes. Analogously, positrons have shallow hydrogenic states at negative ions such as acceptor impurities. Furthermore, vacancies and other centers with open-volume act as deep traps for positrons. These defects can be experimentally detected by measuring either the positron lifetime or the momentum density of the annihilating positron-electron pairs.

2.1. Positron implantation and diffusion in solids

The basic positron experiment is schematically shown in Fig. 1. Positrons are obtained from $\beta^+$ active isotopes like $^{22}$Na, $^{58}$Co, $^{64}$Cu and $^{68}$Ge. The most commonly used isotope is $^{22}$Na, where the positron emission is accompanied by a 1.28 MeV photon. This photon is used as the time signal of the positron birth in positron lifetime experiments. The stopping profile of positrons from $\beta^+$ emission is exponential. For the $^{22}$Na source ($E_{\text{max}} = 0.54$ MeV), the positron mean stopping depth is 110 $\mu$m in Si and 40 $\mu$m in GaN. The positrons emitted directly from a radioactive source thus probe the bulk of a solid [12-16].

Low-energy positrons are needed for studies of thin layers and near-surface regions. Positrons from $\beta^+$ emission are first slowed down and thermalized in a moderator. This is usually a thin film placed in front of the positron source and made of a material (e.g. Cu or W) which has a negative affinity for positrons. Thermalized positrons close to the moderator surface are emitted into vacuum with an energy of the order of 1 eV and a beam is formed using electric and magnetic fields. The positron beam is accelerated to a variable energy of 0 - 40 keV and in this way the positron stopping depth in the sample is controlled. The typical positron beam intensity is $10^4$ - $10^6$ e$^+$ s$^{-1}$ [12-17].

For monoenergetic positrons, the stopping profile can be described by a derivative of a Gaussian function with the mean stopping depth [16,18]

$$\bar{x} = AE^n[keV], \quad (1)$$

where $E$ is the positron energy, $A = (4/\rho)\mu g/cm^2$; $n = 1.6$, and $\rho$ is the density of the material. The mean stopping depth varies with energy from 1 nm up to a few $\mu$m. A 20 keV energy corresponds to 2 $\mu$m in Si and 0.8 $\mu$m in GaN. The width of the stopping profile is rather broad and the positron energy must be carefully chosen so that e.g. the signal from an overlayer is not contaminated by that from the substrate or surface.

In a solid, the fast positron rapidly looses its energy via ionization and core electron excitations. Finally, the positron momentum distribution relaxes to a Maxwell-Boltzmann one.
via electron-hole excitations and phonon emissions. The thermalization time at 300 K is 1 - 3 ps, i.e. much less than a typical positron lifetime of 200 ps [19,20]. Positron behaves thus as a fully thermalized particle in semiconductors.

The transport of thermalized positrons in solids is described by diffusion theory. The positron diffusion coefficient has been measured in several semiconductors by implanting low-energy positrons at various depths and observing the fraction which diffuses back to the entrance surface [21-23]. The diffusion coefficient at 300 K is in the range of 1.5 - 3 cm$^2$ s$^{-1}$. The total diffusion length during the finite positron lifetime $\tau$ is

$$L_x = (6D_x \tau)^{1/2} \approx 5000 \text{Å}. \quad (2)$$

If defects are present, the positron may get trapped before annihilation and this naturally reduces the effective diffusion length.

**FIG. 1.** Schematic figure of positron experiment, where positron is implanted into a sample from $^{22}$Na source. The positron lifetime is determined as a time difference between 511 keV annihilation photons and a 1.28 MeV photon emitted together with a positron from $^{22}$Na. The Doppler shift $\Delta E$ and the angular deviation $\theta$ result from the momentum of the annihilating electron-positron pairs.
2.2. Experimental techniques

2.2.1. Positron lifetime spectroscopy

Lifetime spectroscopy is a powerful technique in defect studies, because the various positron states appear as different exponential decay components. The number of positron states, their annihilation rates and relative intensities can be determined. In a positron lifetime measurement, one needs to detect the start and stop signals corresponding to the positron entrance and annihilation times in the sample, respectively (Fig. 1). A suitable start signal is the 1.28 MeV photon accompanying the positron emission from the $^{22}\text{Na}$ isotope. The 511 keV annihilation photon serves as the stop signal. The positron source is prepared by sealing about 10 $\mu$Ci of radioactive isotope between two thin foils. The source is then sandwiched between two identical pieces (e.g. 5×5×0.5 mm$^3$) of the sample material. This technique is standard for bulk crystal studies. Pulsed positron beams have been constructed for lifetime spectroscopy of thin layers [24,25], but so far they have not been used much in defect studies.

The standard lifetime spectrometer consists of start and stop detectors, each of them made by coupling a fast scintillator to a photomultiplier. The timing pulses are obtained by differential constant-fraction discrimination. The time delays between the start and stop signals are converted into amplitude pulses, the heights of which are stored in a multichannel analyzer. About $10^6$ lifetime events are recorded in one hour. The experimental spectrum represents the probability of positron annihilation at time $t$ and it consists of exponential decay components

$$-rac{dn(t)}{dt} = \sum_i I_i \exp[-\lambda_i t],$$

where $n(t)$ is the probability of positron to be alive at time $t$. The decay constants $\lambda_i = 1/\tau_i$ are called annihilation rates and they are the inverses on the positron lifetimes $\tau_i$. Each positron lifetime has the intensity of $I_i$. In practise the ideal spectrum of Eq. (3) is convoluted by a Gaussian resolution function which has a width of 200 - 250 ps (full width at half maximum, FWHM). About 5 - 10 % of positrons annihilate in the source material and proper "source corrections" must be made. Due to the finite time resolution, annihilations in the source materials, and random background, typically only 1 - 3 lifetime components can be resolved in the analysis of the experimental spectra. The separation of two lifetimes is successful only, if the ratio $\lambda_1/\lambda_2$ is $> 1.5$.

Fig. 2 shows positron lifetime spectra recorded in undoped and Mg-doped GaN bulk crystals [26]. Positrons enter the sample and thermalize at the time $t = 0$. The vertical axis of Fig. 2 gives the number of annihilations at a time interval of 25 ps. In the heavily Mg-doped sample the positron lifetime spectrum has a single component of 165±1 ps at 300 K.
corresponding to positron annihilations in the defect-free lattice. The undoped sample has two lifetime components, the longer of which ($\tau_2 = 235$ ps) is due to positrons annihilating as trapped at native Ga vacancies. For more discussion see Sec. 3.

The experimental results are often presented in terms of the average positron lifetime $\tau_{av}$ defined as

$$
\tau_{av} = \int_0^\infty dt t \left( -\frac{dn}{dt} \right) = \int_0^\infty dt n(t) = \sum_i I_i \tau_i .
$$

The average lifetime is a statistically accurate parameter, because it is equal to the center-of-mass of the experimental lifetime spectrum. Hence it can be correctly calculated from the intensity and lifetime values even if the decomposition represented only a good fit to the experimental data without any physical meaning. For example, the positron average lifetimes in the two...
spectra of Fig. 2 are 191 ps (undoped GaN) and 165 ps (Mg-doped GaN). The difference is very significant because changes below 1 ps can be reliably observed in the experiments.

2.2.2. Doppler broadening spectroscopy

The Doppler broadening spectroscopy is often applied especially in the low-energy positron beam experiments, where the lifetime spectroscopy is usually very difficult due to the missing start signal. The motion of the annihilating electron-positron pair causes a Doppler shift in the annihilation radiation (Fig. 1)

$$\Delta E = \frac{1}{2} cp_L,$$

where \( p_L \) is the longitudinal momentum component of the pair in the direction of the annihilation photon emission. This causes the broadening of the 511 keV annihilation line (Fig. 3). The shape of the 511 keV peak gives thus the one-dimensional momentum distribution \( \rho(p_L) \) of the annihilating electron-positron pairs. A Doppler shift of 1 keV corresponds to a momentum value of \( p_L = 3.91 \times 10^{-3} m_0 c \).

**FIG. 3.** Example of a Doppler broadening spectrum recorded in GaN bulk material. The energy resolution function (full-width-at-half-maximum FWHM = 1.3 keV) has been measured using the 514 keV photons of \(^{85}\)Sr source. The resolution function has been shifted to 511 keV and both curves have been normalized to the same peak-to-background ratio.
The Doppler broadening can be experimentally measured using a Ge gamma detector with a good energy resolution (Fig. 3). For measurements of bulk samples, the same source-sample sandwich is used as in the lifetime experiments. For layer studies, the positron beam hits the sample and the Doppler broadening is often monitored as a function of the beam energy. The typical resolution of a detector is around 1 keV at 500 keV (Fig. 3). This is considerable compared to the total width of 2 - 3 keV of the annihilation peak meaning that the experimental lineshape is strongly influenced by the detector resolution. Therefore, various shape parameters are used to characterize the 511 keV line. Their definitions are shown in Fig. 4, where the raw data such as in Fig. 3 has been (i) shown after background reduction, (ii) folded about the energy of 511 keV corresponding to $\Delta E = p_L = 0$, (iii) plotted as a function of the electron momentum $p_L$ using Eq. (5), and (iv) normalized to a unit area.

The low electron-momentum parameter $S$ is defined as the ratio of the counts in the central region of the annihilation line to the total number of the counts in the line (Fig. 4). In the same way, the high electron-momentum parameter $W$ is the fraction of the counts in the wing regions of the line (Fig. 4). Due to their low momenta, mainly valence electrons contribute to the region of the $S$ parameter. On the other hand, only core electrons have momentum values high enough to contribute to the $W$ parameter.

![Diagram](image)

**FIG. 4.** Positron-electron momentum distributions in the GaN lattice and at the Ga vacancy. The lineshape parameters $S$ and $W$ are defined as integrals of the shaded areas in the figure.
enough to contribute to the $W$ parameter. Therefore, $S$ and $W$ are called the valence and core annihilation parameters, respectively.

The high-momentum part of the Doppler broadening spectrum arises from annihilations with core electrons which contain information on the chemical identity of the atoms. Thus the detailed investigation of core electron annihilation can reveal the nature of the atoms in the regions where positrons annihilate. In order to study the high-momentum part, the experimental background needs to be reduced. A second gamma detector is placed opposite to the Ge detector and the only events that are accepted are those for which both 511 keV photons are detected [27,28]. This coincidence technique is utilized in the experimental data of Fig. 4. The coincidence detection of the Doppler broadening spectrum enables the measurement of electron momenta even up to $p \approx 60 \times 10^{-3} m_0 c \approx 8$ a.u.

2.3. **Positron states and annihilation characteristics**

2.3.1. Positron wave function, lifetime and momentum distribution

After implantation and thermalization the positrons in semiconductors behave like free carriers. The various positron states yield specific annihilation characteristics, which can be experimentally observed in the positron lifetime and Doppler broadening experiments. The positron wave function can be calculated from the one-particle Schrödinger equation [15]

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi^+ (\mathbf{r}) + V(\mathbf{r}) \Psi^+ (\mathbf{r}) = E \Psi^+ (\mathbf{r}),$$

(6)

where the positron potential consists of two parts:

$$V(\mathbf{r}) = V_{\text{Coul}} (\mathbf{r}) + V_{\text{cor}} (\mathbf{r}).$$

(7)

The first term is the electrostatic Coulomb potential and the second term takes into account the electron-positron correlation effects in the local density approximation. Many practical schemes exist for solving the positron state $\Psi^+$ from the Schrödinger equation [15].

A positron state can be experimentally characterized by measuring the positron lifetime and the momentum distribution of the annihilation radiation. These quantities can be easily calculated once the corresponding electronic structure is known. The positron annihilation rate $\lambda$, the inverse of the positron lifetime $\tau$, is proportional to the overlap of the electron and positron densities:

$$1/\tau = \lambda = \pi a_0^3 c \int d\mathbf{r} |\Psi^+ (\mathbf{r})|^2 n(\mathbf{r}) \gamma[n(\mathbf{r})].$$

(8)
where \( r_0 \) is the classical radius of the electron, \( c \) the velocity of light, \( n(r) \) the electron density, and \( \gamma[n] \) the enhancement factor of the electron density at the positron \([15]\). The momentum distribution \( \rho(p) \) of the annihilation radiation is a non-local quantity and requires knowledge of all the electron wave functions \( \Psi_i \) overlapping with the positron. It can be written in the form

\[
\rho(p) = \frac{\pi r_0^2 c}{V} \sum_i \left| \int d\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}} \Psi_+^*(\mathbf{r}) \Psi_i(\mathbf{r}) \sqrt{\gamma(\mathbf{r})} \right|^2, \tag{9}
\]

where \( V \) is the normalization volume. The Doppler broadening experiment measures the longitudinal momentum distribution along the direction of the emitted 511 keV photons, defined here as the \( z \)-axis:

\[
\rho(p_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp_x dp_y \rho(p). \tag{10}
\]

The momentum distribution \( \rho(p) \) of the annihilation radiation is that of the annihilated electrons, because the momentum of the thermalized positron is negligible.

The calculated positron density in a perfect GaN wurtzite lattice is shown in Fig. 5 \([29]\). The positron is delocalized in a Bloch state with \( k_+ = 0 \). Due to the Coulomb repulsion from positive ion cores, the positron wave function has its maximum at the interstitial space between the atoms. The positron energy band \( E_+(k) \) is parabolic and free particle-like with an effective mass of \( m^* \approx 1.5 m_0 \) \([15,30]\). The calculated positron lifetime is 156 ps \([29]\).

**FIG. 5.** The delocalized positron density in perfect GaN lattice according to theoretical calculations. The \( c \)-axis of the wurtzite structure is vertical in the figure. The positions of the Ga and N atoms are marked with open circles and diamonds, respectively. The contour spacing is 1/6 of the maximum value \([29]\).
2.3.2. Deep positron states at vacancy defects

In analogy to free carriers, the positron also has localized states at lattice imperfections. At vacancy-type defects where ions are missing, the repulsion sensed by the positron is lowered and the positron sees these kinds of defects as potential wells. As a result, localized positron states at open-volume defects are formed. The positron ground state at a vacancy-type defect is generally deep, the binding energy is about 1 eV or more [15]. Fig. 6 shows the calculated density of the localized positron at unrelaxed Ga and N vacancies in GaN [29]. The positron wave function is confined in the open volume formed at the vacancy. The localization is clearly stronger in the case of Ga vacancy because the open volume of VGa is much larger than that of VN.

In a vacancy defect the electron density is locally reduced. This is reflected in the positron lifetimes, which are longer than in the defect-free lattice. For example, the calculated lifetimes in the unrelaxed Ga and N vacancies are 209 ps and 160 ps, whereas the lifetime in the GaN lattice is 156 ps [29]. The longer positron lifetime at VGa is due to the larger open volume compared with that of VN. The positron lifetime measurement is thus a probe of vacancy defects in materials. Direct experimental information on vacancies is obtained when (i) the lifetime spectrum has long components associated with annihilations at vacancies, as seen in Fig. 2, and (ii) the average lifetime \( \tau_{av} \) (Eq. (4)) increases above that in defect-free lattice, i.e. \( \tau_{av} > \tau_B \), which is also evident in Fig. 2.

Positron annihilation at a vacancy-type defect leads to changes in the momentum distribution \( \rho(p) \) probed by the Doppler broadening experiment. The momentum distribution

![Image](https://via.placeholder.com/150)

FIG. 6. The localized positron densities in ideal Ga and N vacancies in GaN according to theoretical calculations. The c-axis of the wurtzite structure is vertical in the figure. The positions of the Ga and N atoms are marked with open circles and diamonds, respectively. The contour spacing is 1/6 of the maximum value [29].
arising from valence electron annihilation becomes narrower due to a lower electron density. In addition, the localized positron at a vacancy has a reduced overlap with ion cores leading to a considerable decrease in annihilation with high momentum core electrons. Experimentally, the increase of S parameter and decrease of W parameter are thus clear signs of vacancy defects in the samples. As an example, the experimental momentum distribution in the Ga vacancy is indeed much narrower than that recorded in the defect-free GaN lattice (Fig. 4).

2.3.3. Shallow positron states at negative ions

A negatively charged impurity atom or an intrinsic point defect can bind positrons at shallow states even if these defects do not contain open volume [31,32]. Being a positive particle, the positron can be localized at the hydrogenic (Rydberg) state of the Coulomb field around a negatively charged center. The situation is analogous to the binding of an electron to a shallow donor atom. The positron binding energy at the negative ion can be estimated from the simple effective-mass theory:

$$E_{\text{ion},n} = \frac{13.6 \, eV}{\varepsilon^2} \left( \frac{m^*}{m_e} \right) \frac{Z^2}{n^2} \approx 10-100 \, \text{meV}, \quad (11)$$

where $\varepsilon$ is the dielectric constant, $m^*$ is the effective mass of the positron, $Z$ is the charge of the negative ion, and $n$ is the quantum number. With $Z = 1 - 3$ and $n = 1 - 4$, Eq. (11) yields typically $E_{\text{ion}} = 10 - 100 \, \text{meV}$, indicating that positrons are thermally emitted from the Rydberg states at 100 - 200 K.

The hydrogenic positron state around negative ions has a typical extension of 10 Å and thus positrons probe the same electron density as in the defect-free lattice. Consequently, the annihilation characteristics (positron lifetime, positron-electron momentum distribution) are not different from those in the lattice. In the experiments we thus get $\tau_{\text{ion}} = \tau_B$, $S_{\text{ion}} = S_B$ and $W_{\text{ion}} = W_B$ for the lifetime, S and W parameters at the negative ions. Although the negative ions cannot be identified with these parameters, information on their concentration can be obtained in the positron lifetime and Doppler broadening experiments [31,32].

2.4. Positron trapping at point defects

2.4.1. Positron trapping rate and trapping coefficient

The positron transition from a free Bloch state to a localized state at a defect is called positron trapping. The trapping is analogous to carrier capture. However, it must be fast enough
to compete with annihilation. The positron trapping rate $\kappa$ onto defect D is proportional to its concentration $c_D$

$$\kappa_D = \mu_D c_D.$$  \hfill (12)

The trapping coefficient $\mu_D$ depends on the defect and the host lattice. Since the positron binding energy at vacancies is $> 1$ eV, the thermal emission (detrapping) of positrons from the vacancies can be usually neglected. Due to the Coulombic repulsion, the trapping coefficient at positively charged vacancies is so small that the trapping does not occur during the short positron lifetime [33]. Therefore, the positron technique does not detect vacancies in their positive charge states. The trapping coefficient at neutral vacancies is typically $\mu_D \approx 10^{14} - 10^{15}$ at. s$^{-1}$ independently of temperature [33-35]. This value means that neutral vacancies are observed at the concentrations $\geq 10^{16}$ cm$^{-3}$.

The positron trapping coefficient at negative vacancies is typically $\mu_D \approx 10^{15} - 10^{16}$ at. s$^{-1}$ at 300 K temperature [33-35]. The sensitivity to detect negative vacancies is thus $\geq 10^{15}$ cm$^{-3}$. The experimental fingerprint of a negative vacancy is the increase of $\mu_D$ with decreasing temperature [34,35]. The $T^{-1/2}$ dependence of $\mu_D$ is simply due to the increase of the amplitude of the free positron Coulombic wave as the thermal velocity of the positron decreases [33]. The temperature dependence of $\mu_D$ allows to distinguish experimentally negative vacancy defects from neutral ones.

The positron trapping coefficient $\mu_{\text{ion}}$ at the hydrogenic states around negative ions is of the same order of magnitude as that at negative vacancies [32,36]. Furthermore, the trapping coefficient exhibits a similar $T^{-1/2}$ temperature dependence. Unlike in the case of vacancy defects, the thermal emission of positrons from the negative ions plays a crucial role at usual experimental temperatures. The principle of detailed balance yields the following equation for the detrapping rate $\delta_{\text{ion}}$ from the hydrogenic state [15]

$$\delta_{\text{ion}} = \mu_{\text{ion}} \left( \frac{2\pi n^* k_B T}{\hbar^2} \right)^{3/2} \exp \left( -\frac{E_{\text{ion}}}{k_B T} \right).$$  \hfill (13)

Typically ion concentrations above $10^{16}$ cm$^{-3}$ influence positron annihilation at low temperatures ($T < 100$ K), but the ions are not observed at high temperatures ($T > 300$ K), where the detrapping rate (Eq. (13)) is large.

2.4.2. Kinetic trapping model

In practise the positron annihilation data is analyzed in terms of kinetic rate equations describing the positron transitions between the free Bloch states and localized states at defects.
Very often the experimental data show the presence of two defects, one of which is a vacancy and the other is a negative ion. The probability of positron to be in the free state is \( n_B(t) \), trapped at vacancies \( n_V(t) \) and ions \( n_{\text{ion}}(t) \). We can write the rate equations as

\[
\frac{dn_B}{dt} = -(\lambda_B + \kappa_V + \kappa_{\text{ion}})n_B + \delta_{\text{ion}}n_{\text{ion}},
\]

\[
\frac{dn_V}{dt} = \kappa_B n_B - \lambda_V n_V,
\]

\[
\frac{dn_{\text{ion}}}{dt} = \kappa_{\text{ion}} n_B - (\lambda_{\text{ion}} + \delta_{\text{ion}})n_{\text{ion}},
\]

where \( \lambda, \kappa \) and \( \delta \) refer to the corresponding annihilation, trapping and detrapping rates.

Assuming that the positron at \( t=0 \) is in the free Bloch state, Eqs. (14 - 16) can be solved and the probability of positron to be alive at time \( t \) is obtained as

\[
n(t) = n_B(t) + n_V(t) + n_{\text{ion}}(t) = \sum_{i=1}^{3} I_i \exp[-\lambda_i t],
\]

indicating that the lifetime spectrum \(-dn(t)/dt\) has three components. The fractions of positron annihilations at various states are

\[
\eta_B = \int_0^\infty dt \lambda_B n_B(t) = 1 - \eta_{\text{ion}} - \eta_V,
\]

\[
\eta_V = \int_0^\infty dt \lambda_V n_V(t) = \frac{\kappa_V}{\lambda_B + \kappa_V + \frac{\kappa_{\text{ion}}}{1 + \delta_{\text{ion}}/\lambda_{\text{ion}}}},
\]

\[
\eta_{\text{ion}} = \int_0^\infty dt \lambda_{\text{ion}} n_{\text{ion}}(t) = \frac{\kappa_{\text{ion}}}{(1 + \delta_{\text{ion}}/\lambda_{\text{ion}})\left(\lambda_B + \kappa_V + \frac{\kappa_{\text{ion}}}{1 + \delta_{\text{ion}}/\lambda_{\text{ion}}}\right)}.
\]

These equations are useful because they can be related with the experimental average lifetime \( \tau_{av} \), positron-electron momentum distribution \( \rho(p_L) \) and Doppler lineshape parameters \( S \) and \( W \) as

\[
\tau_{av} = \eta_B \tau_B + \eta_{\text{ion}} \tau_{\text{ion}} + \eta_V \tau_V,
\]
\[ \rho(p_L) = \eta_B \rho(p_L) + \eta_{ion} \rho_{ion}(p_L) + \eta_V \rho_V(p_L), \]  

(22)

\[ S = \eta_B S_B + \eta_{ion} S_{ion} + \eta_V S_V, \]  

(23)

\[ W = \eta_B W_B + \eta_{ion} W_{ion} + \eta_V W_V. \]  

(24)

Eqs. (18 - 24) allow the experimental determination of the trapping rates \( \kappa_V \) and \( \kappa_{ion} \) and consequently the defect concentrations can be obtained from Eq. (12). Furthermore, these equations enable the combination of positron lifetime and Doppler broadening results and various correlations between \( \tau_{av}, \rho(p_L), S \) and \( W \) can be studied.

At high temperatures all positrons escape from the hydrogenic state of the negative ions and no annihilations take place at them. In this case the lifetime spectrum has two components

\[ \tau_1^{-1} = \tau_B^{-1} + \kappa_V, \]  

(25)

\[ \tau_2 = \tau_V, \]  

(26)

\[ I_2 = 1 - I_1 = \frac{\kappa_V}{\kappa_V + \lambda_B - \lambda_D}. \]  

(27)

The first lifetime \( \tau_1 \) represents the effective lifetime in the lattice in the presence of positron trapping at vacancies. Since \( \kappa_V > 0 \) and \( I_2 > 0 \), \( \tau_1 \) is less than \( \tau_B \). The second lifetime component \( \tau_2 \) characterizes positrons trapped at vacancies, and it can be directly used to identify the open volume of the vacancy defect. When \( \eta_{ion} = 0 \) and \( \delta_{ion}/\lambda_{ion} \gg 1 \) the determination of the positron trapping rate and vacancy concentration is straightforward using Eqs. (18 - 24)

\[ \kappa_V = \mu_v c_v = \lambda_B \frac{\tau_v - \tau_B}{\tau_v - \tau_{av}} = \lambda_B \frac{S - S_B}{S_V - S} = \lambda_B \frac{W - W_B}{W_V - W}. \]  

(28)

Notice that in this case \( \tau_{av}, S \) and \( W \) depend linearly on each others. The linearity of experimental points in the \((\tau_{av}, S), (\tau_{av}, W)\) and \((S, W)\) plots provides thus evidence that only a single type of vacancy defect is trapping positrons in the samples.
3. NATIVE VACANCIES AND NEGATIVE IONS IN GaN BULK CRYSTALS

Bulk GaN crystals are ideal substrates for the epitaxy of GaN overlayers for optoelectronic components at the blue wavelength. Such material can be synthesized of liquid Ga in high N overpressure at elevated temperatures [37,38]. Nominally undoped GaN crystals show usually high n-type conductivity with the concentration of electrons exceeding $10^{19}$ cm$^{-3}$. This is most likely due to the residual oxygen atoms acting as shallow donors [39,40]. When GaN is doped with Mg the electron concentration decreases and for sufficiently high amount of Mg dopants the samples become semi-insulating. It is interesting to study how the movement of the Fermi level toward the midgap changes the formation of charged native defects such as the Ga vacancy. Another basic question concerns the mechanism of the electrical deactivation. One can consider either (i) the gettering role of Mg leading to the formation of MgO molecules [41] or (ii) electrical compensation of O$_{N^+}$ donors by Mg$_{Ga^-}$ acceptors.

In this section we review our recent works [26,29,42,43] and show that Ga vacancy acts as a native defect in GaN crystals. We pay special attention to the identification of $V_{Ga}$ by correlating the results of positron experiments with those of theoretical calculations. Our data indicate that the formation of Ga vacancies is suppressed by Mg doping. We show further that most of Mg is in a negative charge state, suggesting that the loss of n-type conductivity is due to compensation of O$_{N^+}$ donors by Mg$_{Ga^-}$ acceptors.

3.1. Samples and their impurity concentrations

The bulk GaN crystals were grown at the nitrogen pressure of 1.5 GPa and temperature of 1500 °C [38]. We studied three samples, where the Mg doping level was intentionally varied during the crystal growth (Table I). The Mg and O concentrations of the samples were determined experimentally by secondary ion-mass spectrometry (SIMS). The absolute concentrations were calibrated by implanting known amounts of O and Mg to undoped epitaxial GaN layers, where the residual Mg and O concentrations were well below $10^{18}$ cm$^{-3}$.

The secondary ion-mass spectrometry indicates that the oxygen concentration is about $4\times10^{19}$ cm$^{-3}$ in undoped GaN (Table I). The concentration of conduction electrons ($n = 5\times10^{19}$ cm$^{-3}$ at 300 K) in this sample is thus almost the same as oxygen concentration. This is in good agreement with the previous evidence [39,40] that the n-type conductivity of GaN is due to unintentional oxygen doping. In the lightly Mg doped GaN the concentration of oxygen is $12\times10^{19}$ cm$^{-3}$, which is slightly larger than the Mg concentration of $6\times10^{19}$ cm$^{-3}$. The electrical experiments indicate that the sample has n-type conductivity, but the carrier concentration is less than in the undoped sample. The heavily Mg-doped sample has the O concentration of $9\times10^{19}$ cm$^{-3}$ and the Mg concentration of $1\times10^{20}$ cm$^{-3}$. According to the electrical experiments the
sample is semi-insulating. This is reasonable since the impurity concentrations determined by SIMS show that $[\text{Mg}] \approx [\text{O}]$.

### 3.2. Positron lifetime results

The positron lifetime spectra in undoped and heavily Mg-doped GaN have been presented in Fig. 2 at Sec. 2. The temperature dependence of the average positron lifetime in various GaN crystals is shown in Fig. 7. Positrons annihilating in the heavily Mg-doped sample have only a single component of $165\pm1$ ps at 300 K (Fig. 2). The lifetime is almost constant as a function of temperature (Fig. 7).

These observations indicate that the heavily Mg-doped GaN is free of vacancy defects trapping positrons. In perfect GaN lattice the positron state is very delocalized and the positron density has its maximum in the interstitial region (see Fig. 5 in Sec. 2). The calculated lifetime in defect-free GaN lattice is 154 ps, which is in reasonable agreement with the experimental result $\tau_B = 165$ ps. The lifetime $\tau_B = 165$ ps can be estimated also on the basis of the lifetime decomposition at low temperature [42]. In heavily Mg-doped GaN all positrons thus annihilate in the delocalized state in the GaN lattice with the bulk lifetime $\tau_B = 165$ ps. The slight increase of the bulk lifetime as a function of temperature (Fig. 7) can be attributed to the lattice expansion.

The positron lifetime spectrum recorded in undoped GaN is clearly different from that in highly Mg-doped sample (Fig. 2). The annihilation probability at $t > 0.5$ ns is much larger in the undoped GaN, indicating that the average positron lifetime $\tau_{av}$ is longer than $\tau_B = 165$ ps. In

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen concentration (cm$^{-3}$)</th>
<th>Magnesium concentration (cm$^{-3}$)</th>
<th>Ga vacancy concentration (cm$^{-3}$)</th>
<th>Negative ion concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>$4 \times 10^{19}$</td>
<td>$1 \times 10^{18}$</td>
<td>$2 \times 10^{17}$</td>
<td>$3 \times 10^{18}$</td>
</tr>
<tr>
<td>Lightly Mg doped</td>
<td>$12 \times 10^{19}$</td>
<td>$6 \times 10^{19}$</td>
<td>$7 \times 10^{16}$</td>
<td>$6 \times 10^{19}$</td>
</tr>
<tr>
<td>Heavily Mg-doped</td>
<td>$9 \times 10^{19}$</td>
<td>$10 \times 10^{19}$</td>
<td>&lt; $10^{16}$</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE I.** The concentrations of impurities and defects in the studied GaN bulk crystals. The magnesium and oxygen concentrations were determined by secondary ion mass spectrometry. The concentrations of Ga vacancies and negative ions are obtained from the positron annihilation data.
fact, $\tau_{av} = 167$ ps at $T = 10 - 150$ K, and it increases up to $\tau_{av} = 190$ ps at 500 K (Fig. 7). In lightly Mg-doped GaN the positron lifetime is equal to $\tau_B = 165$ ps at low temperatures of 10 - 200 K (Fig. 7). At 200 - 500 K, however, $\tau_{av}$ is clearly larger than $\tau_B$ and reaches a value of 180 ps at 500 K. Since $\tau_{av} > \tau_B$ in both undoped and lightly Mg-doped samples, we can conclude that these GaN crystals contain vacancy defects.

The lifetime spectra recorded at 300 - 500 K in the undoped and lightly Mg-doped GaN can be decomposed into two exponential components (Figs. 2 and 7). The positrons trapped at vacancies annihilate with the longer lifetime $\tau_V = \tau_2 = 235 \pm 5$ ps. Roughly the same lifetime has been observed also in thick epitaxial films on sapphire [44]. Within experimental accuracy the lifetime $\tau_V = 235 \pm 5$ ps is the same in the n-type undoped crystal and in the lightly Mg-doped sample (Fig. 7), indicating that the same vacancy is present.

![Graph showing positron lifetime vs. temperature for GaN crystals](image)

**FIG. 7.** The average positron lifetime and the second lifetime component $\tau_2$ vs. measurement temperature in GaN bulk crystals. The solid lines correspond to the analyses with the temperature dependent positron trapping model, where concentrations of Ga vacancies and negative ions (Table I) are determined as fitting parameters [29,42].
3.3. Identification of the native vacancy

Positron trapping and annihilation with the lifetime $\tau_V = 235$ ps is observed at native vacancies in n-type GaN crystals. This value is typical for a monovacancy in materials which have the same atomic density as GaN, such as Al. It is also highly improbable that the N vacancy could induce such a long lifetime of $\tau_V = 235$ ps because the open volume at $V_N$ is very small. It is thus rather straightforward to associate the observed lifetime $\tau_V = 235$ ps with Ga vacancy or a complex involving $V_{Ga}$.

The identification of the Ga vacancy can be put on a firm theoretical basis by calculating the positron lifetimes theoretically from Eqs. (6 - 8). The electron densities were constructed using the atomic superposition method. The positron states (Eq. (6)) were solved in a supercell of 256 atomic sites in a periodic superlattice using the generalized gradient approximation for electron-positron correlation [27,45].

The calculated positron densities at ideal Ga and N vacancies have been shown in Fig. 6 in Sec. 2. Both vacancies are able to localize the positron. However, the localization is clearly stronger in the case of Ga vacancy, because the open volume of $V_{Ga}$ is much larger than that of $V_N$. This fact is reflected in the calculated positron lifetimes, which are $\tau_V = 209$ ps and $\tau_V = 160$ ps for unrelaxed Ga and N vacancies, respectively. The experimental value of 235 ps can thus be associated with the Ga vacancy but not with the N vacancy.

![Ga-vacancy (relax 5%)](image)

**FIG. 8.** The localized positron densities in a Ga vacancy in GaN according to theoretical calculations. The structure of the Ga vacancy has been relaxed 5% outwards. The c-axis of the wurtzite structure is vertical in the figure. The positions of the Ga and N atoms are marked with open circles and diamonds, respectively. The contour spacing is 1/6 of the maximum value [29].
The positron lifetime experiments show thus unambiguously that the native vacancies in GaN crystals belong to the Ga sublattice and have an open volume of a monovacancy. According to theoretical calculations [9,10,46], the Ga vacancy is negatively charged in n-type and semi-insulating GaN and thus acts as an efficient positron trap. On the other hand, the N vacancy is expected to be positive and repulsive to positrons [9,10,46,47]. In fact, the experimental and calculated positron lifetimes at VGa are in very good agreement if the lattice relaxation around VGa is taken into account. Fig. 8 shows the calculated positron density at the Ga vacancy, where the neighboring N atoms are relaxed 5 % outwards. The relaxation lowers the electron density and increases positron lifetime. For the structure shown in Fig. 8 the calculated difference $\tau_{V} - \tau_{B}$ is equal to the experimental value $\tau_{V} - \tau_{B} = 70$ ps, thus yielding evidence that the N atoms surrounding VGa are indeed relaxed about 5 % outwards. In fact, such a relaxation is expected for the Ga vacancy on the basis of theoretical calculations [9,10]. Unfortunately, the present positron experiments do not tell whether VGa is an isolated defect or part of a larger complex.

### 3.4. Positron trapping at negative ions

At low temperatures the average positron lifetime decreases and the lifetime at the Ga vacancy $\tau_{V}$ remains constant (Fig. 7). This behavior indicates that the fraction $\eta_{V} = (\tau_{av} - \tau_{B}) / (\tau_{V} - \tau_{B})$ of positrons annihilating at vacancies decreases. Since the positron trapping at negative Ga vacancies should be enhanced at low temperatures (Sec. 2), the decrease of $\eta_{V}$ is due to other defects which compete with Ga vacancies as positron traps. Negative ions are able to bind positrons at shallow (< 0.1 eV) hydrogenic states in their attractive Coulomb field (Sec. 2). Since they possess no open volume, the lifetime of positrons trapped at them is the same as in the defect-free lattice, $\tau_{ion} = \tau_{B} = 164\pm1$ ps. The average lifetime increases above 150 K, when positrons start to escape from the ions and a larger fraction of them annihilates at vacancies.

The temperature dependence of the average lifetime can be modeled with kinetic trapping equations introduced in Sec. 2. Positron trapping coefficients at negative Ga vacancies $\mu_{V}$ and negative ions $\mu_{ion}$ vary as $T^{-1/2}$ as a function of temperature [12,15]. The positron detrapping rate from the ions can be expressed as $\delta(T) \propto \mu_{ion} T^{-3/2} \exp(-E_{ion}/k_{B}T)$, where $E_{ion}$ is the positron binding energy at the Rydberg state of the ions (Eq. 13). The fractions of annihilations at Ga vacancies $\eta_{V}$ and at negative ions $\eta_{ion}$ are given in Eqs. (19 – 20) and they depend on the concentrations $c_{V} = \kappa_{V} / \mu_{V}$ and $c_{ion} = \kappa_{ion} / \mu_{ion}$ of Ga vacancies and negative ions (Eq. 12), respectively, as well as on the detrapping rate $\delta_{ion}(T)$ (Eq. 13). We take the conventional value $\mu_{V} = 2\times10^{15}$ s$^{-1}$ for the positron trapping coefficient at 300 K [12,13]. Inserting the annihilation fractions $\eta_{B}$, $\eta_{ion}$, and $\eta_{V}$ from Eqs. (18 - 20) into the equation for the average lifetime $\tau_{av} = \eta_{B}\tau_{B} + \eta_{ion}\tau_{ion} + \eta_{V}\tau_{V}$ (Eq. (21)) the resulting formula can be fitted to the experimental data of Fig. 7 with $c_{V}$, $c_{ion}$, $\mu_{ion}$ and $E_{ion}$ as adjustable parameters. As indicated by the solid lines in
Fig. 7, the fits reproduce well the experimental data with the positron binding energy of $E_{\text{ion}} = 60\pm10$ meV and trapping coefficient $\mu_{\text{ion}} = (7\pm4)\times10^{16} \ (T/K)^{-0.5}$. These values are close to those obtained previously in GaAs [36,48].

3.5. **Defect concentrations and electrical compensation**

The analysis explained above yields estimates for the concentrations of $V_{\text{Ga}}$ and negative ions (Table I). The Ga vacancy concentration is $c_V = 2\times10^{17}$ cm$^{-3}$ in the undoped GaN and $c_V = 7\times10^{16}$ cm$^{-3}$ in the lightly Mg-doped crystal. In the heavily Mg-doped GaN no Ga vacancies are observed indicating that their concentration is below the detection limit of $10^{16}$ cm$^{-3}$. The concentration of $V_{\text{Ga}}$ thus decreases with increasing Mg doping and the Ga vacancies disappear completely when the material gets semi-insulating, i.e. $[O] \approx [\text{Mg}]$. The same observation has been done also in Mg-doped GaN layers on sapphire [49,50]. This behavior is in good agreement with the results of theoretical calculations, which predict a low formation energy for the Ga vacancy and $V_{\text{Ga}}\text{O}_N$ complex only in n-type material [9,10,46]. The creation of Ga vacancies in the growth of GaN crystals seems to follow thus the trends expected for acceptor defects in thermal equilibrium.

The concentration of negative ions is $3\times10^{18}$ cm$^{-3}$ in undoped GaN and about $6\times10^{19}$ cm$^{-3}$ in lightly Mg-doped crystal. The ion concentration cannot be determined in heavily Mg-doped sample because no competitive positron trapping at Ga vacancies is observed and the positron annihilations at the ions cannot be distinguished from those in the GaN lattice. Due to the uncertainties in the values of positron trapping coefficients $\mu_V$ and $\mu_{\text{ion}}$ the experimental errors of the absolute concentrations of negative ions are large, of the order of 50%. In the lightly Mg-doped sample $c_{\text{ion}}$ represents the lower limit concentration only, because at temperatures of $T < 200$ K the average lifetime saturates at the value $\tau_B$ corresponding to annihilations in the GaN lattice.

In spite of the experimental inaccuracies the data indicates clearly that the concentration of negative ions increases by at least an order of magnitude with the Mg doping. Furthermore, the estimated concentrations of negative ions are close to those of Mg impurities as determined by the SIMS measurements (Table I). Hence, it is natural to attribute the negative ions to $\text{MgGa}^-$. The positron results thus show that a substantial part of the Mg impurities is in the negative charge state in Mg-doped GaN bulk crystals. This suggests that the conversion of n-type GaN to semi-insulating with Mg doping is mainly due to an electrical compensation of oxygen donors with negatively charged Mg acceptors. The electrons originating from O donors are transferred to Mg acceptors charging them negatively. Since positron trapping at $\text{MgGa}^-$ requires long-range Coulomb attraction, we can infer that $\text{MgGa}^-$ ions are not spatially correlated with positive $\text{O}_N^+$ donors. However, we cannot exclude the formation of MgO molecules [41], which may also contribute to some extent in the electrical deactivation of Mg-doped GaN crystals.
3.6. Conclusions

The positron experiments show the presence of Ga vacancies and negative ions in GaN crystals. The concentration of Ga vacancies decreases with increasing Mg doping, in good agreement with the trends expected for the $V_{Ga}$ formation energy as a function of the Fermi level. The concentration of negative ions increases with Mg doping and correlates with the Mg concentration determined by SIMS. We thus associate the negative ions with $Mg_{Ga}^{-}$. The negative charge of Mg suggests that the loss of n-type conductivity in the Mg doping of GaN crystals is mainly due to compensation of $O_{N}^{+}$ donors by $Mg_{Ga}^{-}$ acceptors.
4. DEFECTS AND DOPING IN GaN LAYERS GROWN ON SAPPHIRE

The growth of thin epitaxial overlayers form the basis of electronic and optoelectronic device structures made of GaN and related alloys. The defects in such materials are thus technologically very important. From scientific point of view it is interesting to compare the structure and properties of defects in GaN layers with those in the GaN crystals. The influence of doping on the formation of vacancy-type defects in GaN layers is the topic of this section. We review systematic positron experiments [42,49,50] in variously doped 1 – 3 µm thick GaN layers grown by metal-organic chemical vapor deposition (MOCVD) on sapphire substrates.

4.1. Mg doped GaN layers

Positron studies of thin 1 - 3 µm epitaxial layers are performed by implanting typically E = 0 - 50 keV positrons into the sample utilizing a monoenergetic positron beam. The positron lifetime spectroscopy requires a pulsed positron beam, which are not yet in routine use. Hence, most of positron studies in thin overlayers are done with the Doppler broadening technique [42,49,50]. This is the case also in GaN layers, where no positron lifetime results are published yet.

In Doppler broadening spectroscopy the 511 keV annihilation line is described using the conventional low-momentum parameter S (see Sec. 2). Fig. 9 shows the S parameter as a function of the incident positron energy in three Mg-doped GaN samples. One of them is a heavily Mg-doped GaN bulk crystal, which is free of vacancies as explained in Sec. 3. The two other samples are Mg-doped GaN layers on sapphire. The as-grown layer is semi-insulating, but the sample annealed at 750 °C exhibits p-type conductivity.

The incident positron energy can be converted into the mean positron implantation depth (top axis of Fig. 9) using Eq. (1). For a given positron implantation energy E, the S(E) parameter is a linear superposition of the values characterizing different positron annihilation states, weighted with the annihilation fraction η(E) for the corresponding state (see Eqs. (21 – 24))

\[ S(E) = \eta_S(E)S_S + \eta_L(E)S_L + \eta_{Subs}(E)S_{Subs} . \]  

(29)

In Eq. (29) S_S, S_L, and S_{Subs} represent the values of S parameter at the surface, in the GaN layer, and in the substrate, respectively. When the layer contains defects we can write

\[ \eta_L(E)S_L = \eta_B(E)S_B + \sum_i \eta_{Di}(E)S_{Di} , \]  

(30)

where S_B and S_{Di} are the S parameters in the GaN lattice and in the defect i, respectively. In the GaN(Mg) bulk crystals no positrons annihilate at defects (η_{Di} = 0) and thus the surface
annihilation fraction $\eta_S(E)$ depends only on the positron diffusion length and implantation depth. As seen in Fig. 9 at $E = 0$ positrons annihilate with the S parameter $S_S = 0.475$ on the surface of the sample. When positron incident energy increases S parameter decreases and finally saturates at $S_L = S_B = 0.435$. Since the heavily Mg-doped GaN crystals are free of vacancies (Sec. 3), the S parameter $S_B = 0.435$ characterizes positron annihilations at the defect-free GaN lattice.

In the Mg-doped GaN layers the S parameter (Fig. 9) decreases rapidly with increasing energy from the surface value $S_S$, whereafter it reaches a plateau. This plateau is the same as the the value $S_B = 0.435$ in the defect-free GaN(Mg) crystal, indicating that no positron annihilations take place in the open volume defects. At $E > 25$ keV the S parameter decreases rapidly in Fig. 9. At these incident energies, positrons penetrate and annihilate in the sapphire substrate with a very low S parameter $S_{Subs} = 0.41$.

No vacancy-type defects are thus observed in GaN(Mg) layers in the experiment of Fig. 9. The absence of positron trapping at vacancies has been further confirmed by temperature-
dependent experiments [50]. The S parameter in GaN(Mg) layers is almost constant as a function of temperature in the range T = 10 - 600 K, which is typical for positron annihilations in the defect-free lattice. Although no vacancies are detected in p-type and semi-insulating GaN(Mg) layers, these samples may contain open-volume defects in positive charge states. For example, the nitrogen vacancy is expected to be positive both in semi-insulating and p-type GaN according to theoretical calculations [9,10,46] and experiments [47]. Furthermore, its formation energy should be low in p-type doping conditions [9,10,46]. Unfortunately, positron experiments give no information of VN, because its repulsive positive charge prevents positron trapping.

4.2. Nominally undoped n-type GaN layers

Nominally undoped GaN layers grown by MOCVD on sapphire show n-type conductivity typically in the n = 10^{17} - 10^{18} cm^{-3} range. This conductivity has been attributed to nitrogen vacancies [8,51], but more recent evidence shows that it is rather induced by the residual oxygen.

![Diagram](image-url)

**FIG. 10.** The low electron-momentum parameter S as a function of the positron implantation energy in three nominally undoped GaN layers, which show n-type conductivity. The Mg-doped GaN reference sample indicates the level corresponding to positron annihilations in defect-free GaN. The top axis shows the mean stopping depth corresponding to the positron implantation energy [50].
acting as shallow donors in GaN [9,10,52]. Secondary ion-mass spectrometry indicates that the oxygen concentrations are > 10^{18} \text{ cm}^{-3} in the undoped samples studied by positron spectroscopy. In fact, the "undoped" GaN layers are thus heavily doped with oxygen.

4.2.1. Observation of native vacancies

Fig. 10 shows the S parameter as a function of the incident positron energy E in the defect-free Mg-doped GaN reference sample and in two undoped GaN layers. The surface induces a large S parameter of S_S = 0.47 at E = 0. When E increases S parameter decreases until it levels off at E = 5 - 15 keV to a plateau value S_L, which characterizes the GaN layer. At larger incident energies S parameter decreases as annihilations start to take place at the sapphire substrate.

The difference between the undoped and Mg-doped layers is clear. In the undoped n-type samples S parameter at the GaN layer S_L is clearly larger than in the Mg-doped reference sample, i.e. S_L > S_B. As explained in Sec. 2, the reduced electron density at open-volume

FIG. 11. The low electron-momentum parameter S vs. measurement temperature in various undoped GaN samples. The carrier concentrations of the GaN layers are indicated in the figure [42]. The solid lines are fits to the temperature dependent positron trapping model (Refs. [32,36])
defects narrows the positron-electron momentum distribution and increases the S parameter. Hence, the experiment of Fig. 10 shows that nominally undoped n-type GaN layers contain vacancy defects.

The vacancies in the undoped layers were further studied by recording the low-momentum parameter S as a function of temperature (Fig. 11). This experiment was performed at a fixed positron energy of 10 keV, because at this energy the contributions of the annihilation events at the surface and in the substrate are negligible and all annihilations take place at the GaN layer ($\eta_L = 1$). The low-momentum annihilation parameter S in the GaN(n = 2.0×10^{18} cm^{-3}) layer increases only slightly as a function of temperature (Fig. 11). This increase is similar as observed in defect-free GaN(Mg) sample, and it can be attributed to the thermal expansion of the lattice. The S parameter in all other GaN layers is clearly larger (Fig. 11), indicating again that vacancies are present. The temperature dependence of the S parameter in GaN(n = 3.7×10^{17} cm^{-3}) and GaN(n = 1.2×10^{18} cm^{-3}) samples is similar to that of the average positron lifetime or S parameter in the GaN bulk crystal. The low-momentum parameter S decreases at low temperatures because less positrons annihilate at vacancies. As explained in Sec. 3 this behavior can be attributed to shallow positron traps such as negative ions.

4.2.2. Identification of vacancies

The positron lifetime spectrum in bulk samples can be analyzed with two components thus enabling the distinction between free and trapped positron annihilation events. However, the Doppler broadened annihilation line cannot be decomposed directly into momentum density spectra originating from the lattice and the vacancies. The identification of the vacancies is thus less direct. On the other hand, the combined lifetime and Doppler experiments in GaN bulk crystals allow the detailed analysis of the data recorded also in the GaN layers.

The number of different vacancy-type positron traps in the material can be studied by investigating the linearity between the annihilation parameters $\tau_{av}$, S and W. If only a single type of a vacancy is present, these parameters depend linearly on each other (Sec. 2), when the fraction $\eta_V$ of positron annihilations at vacancies varies: $A = (1 - \eta_V)A_B + \eta_VA_V$, where A is $\tau_{av}$, S or W. The data in all GaN samples at various temperatures form a straight line in the (S, W) plane (Fig. 12). The same type of vacancy is thus present in the bulk crystal as well as in all GaN layers.

In the GaN bulk crystal the positron lifetime experiments show that the native vacancies are in the Ga sublattice (Sec. 3). On the other hand, the results of Fig. 12 indicate that the vacancy in the layers is the same as that in the bulk crystals. We can thus assign the native vacancies in the nominally undoped GaN layers with the Ga vacancy. The (S, $\tau_{av}$) and (W, $\tau_{av}$) plots can be used to determine the S and W parameters corresponding to the lifetimes $\tau_B = 165$
ps in the lattice and $\tau_V = 235$ ps at the vacancy. The relative changes of S and W due to positron trapping at the vacancy with $\tau_V = 235$ ps are $S_V / S_B = 1.038(2)$ and $W_V / W_B = 0.86(2)$.

To confirm the identification of the Ga vacancy the high-momentum part of the Doppler broadening spectrum can be recorded using the coincidence of two $\gamma$ ray detectors for background reduction [29,42,49]. This experiment yields the superimposed electron momentum distribution $\rho(p) = (1 - \eta_V) \rho_B(p) + \eta_V \rho_V(p)$, where $\rho_B(p)$ and $\rho_V(p)$ are the momentum distributions in the lattice and at the vacancy, respectively. For a sample with the measured $(S, W)$ values $\eta_V$,

$$
\eta_V = \frac{S / S_B - 1}{S_V / S_B - 1} = \frac{W / W_B - 1}{W_V / W_B - 1},
$$

(31)
can be determined using the positron trapping model and the parameters $S_V / S_B = 1.038(2)$ and $W_V / W_B = 0.86(2)$ deduced above (see Eqs. (18 – 24)). Since the momentum distribution in the lattice $\rho_B(p)$ can be measured in the defect-free reference sample such as heavily Mg-doped GaN crystal, the distributions $\rho_V(p)$ at vacancies can be decomposed from the measured spectrum $\rho(p)$.

FIG. 12. The electron-momentum parameters S and W in the GaN samples at various temperatures. The straight line indicates that the same defect (Ga vacancy) is found in all samples.
Fig. 13 shows the core electron momentum distributions $\rho_B(p)$ and $\rho_V(p)$ in the perfect GaN lattice and at the vacancy defect present in the undoped GaN layers, respectively. The intensity of the core electron momentum distribution is clearly smaller in the vacancy than in the GaN lattice. However, the momentum distributions at vacancies and in the bulk have clearly similar shapes over a wide momentum range.

The core electron momentum distributions (Eq. (9)) can be theoretically calculated in a straightforward way, since the wave functions of free atoms can be applied (Sec. 2). The curves in Fig. 13 were calculated using the atomic superposition method [27], the generalized gradient approximation and the state-dependent enhancement scheme [45,53]. The theoretical results show that the annihilations with Ga 3d electrons give the clearly dominant contribution to the measured core electron momentum distribution at GaN lattice as well as at Ga and N vacancies.

FIG. 13. The lower panel presents experimental core electron momentum densities at the perfect GaN lattice and at the Ga vacancy. The upper panel shows the result of the theoretical calculation at perfect GaN and at N and Ga vacancies. The momentum distributions are normalized to unity [29,42].
The shape of the momentum distributions is thus similar in all these three systems. The calculated momentum distribution at the Ga vacancy has a clearly lower intensity than that in the GaN lattice (Fig. 13), because the contribution of Ga 3d is reduced due to the surrounding N atoms. At the N vacancy the neighboring Ga atoms yield a core annihilation component, which is as strong as in the bulk lattice (Fig. 13). The experimental curve is compatible with the Ga vacancy, but not with the N vacancy. The Doppler broadening experiments thus support the identification of the Ga vacancy in nominally undoped n-type GaN bulk crystals. However, the present results cannot be used to specify further if the Ga vacancy is isolated or part of a larger complex.

4.3. Si-doped n-type GaN layers and correlation with oxygen

Ga vacancies are experimentally observed in n-type GaN layers and bulk crystals, when the n-type conductivity is due to residual oxygen. It is interesting to study whether the formation of Ga vacancies is promoted by other impurities acting as shallow donors, such as Si. For this purpose a set of 3 - 5 µm GaN(Si) layers grown by MOCVD on sapphire was studied. These

![Graph showing positron energy and S parameter relationship]  

FIG. 14. The low electron-momentum parameter S as a function of the positron implantation energy in three Si-doped GaN layers. The Mg-doped GaN reference sample and the dashed line indicate the level corresponding to positron annihilations in defect-free GaN. The top axis shows the mean stopping depth corresponding to the positron implantation energy [50].
samples contain an order of magnitude less oxygen than Si as determined by magneto-optical measurements [54].

The $S$ parameter in GaN(Si) samples is shown in Fig. 14 as a function of the positron implantation energy $E$. A high $S_S$ parameter is recorded at the surface of the sample at $E = 0$, but with increasing energy $S(E)$ curve decreases and saturates to a value $S_L$ characterizing the layer at $E > 15$ keV. It is remarkable that the layer-characteristic value $S_L$ is equal to the bulk value $S_B$ recorded in the Mg-doped reference sample. No vacancies are thus observed in GaN(Si) samples, indicating that their concentration is $\leq 10^{16}$ cm$^{-3}$. The $S$ parameter in the GaN(Si) varies with temperature in a similar way as in the GaN(Mg) reference sample, further confirming that positrons detect no Ga vacancies in the Si-doped GaN layers.

4.4. Summary and comparison with theoretical calculations

Positron experiments detect Ga vacancies in various GaN layers grown by MOCVD on sapphire. The following trends can be summarized for the formation of $V_{Ga}$ as a function of doping: (i) No Ga vacancies are found in p-type or semi-insulating Mg-doped layers. (ii) Ga vacancies are found at concentrations $> 10^{17}$ cm$^{-3}$ in nominally undoped GaN layers, which show n-type conductivity due to residual oxygen. (iii) Much lower Ga vacancy concentrations are observed in samples, where the n-type doping is done with Si impurities and the amount of residual oxygen is reduced.

According to the positron experiments the presence of Ga vacancies in GaN layers depends both on the Fermi level and impurity atoms in the samples. The same general trend is found in the epitaxial layers as in the bulk crystals: Ga vacancies are formed only in n-type doping concentrations when oxygen is present. However, if a similar doping is done with Si donors, no Ga vacancies are formed. A natural way to explain this behavior is to associate the observed Ga vacancies with complexes involving oxygen, such as $V_{Ga} - O_N$. Although the direct observation of oxygen surrounding $V_{Ga}$ has not been conclusive in the positron experiments so far, this is in principle possible using the Doppler broadening technique to probe the electron momentum density (Sec. 2).

Theoretically the formation energies of charged defects in thermal equilibrium depend on the position of the Fermi level in the energy gap, as shown in the calculated results of Fig. 15 [9,10,46]. The negatively charged defects such as the Ga vacancy have their lowest formation energy when the Fermi level is close to the conduction band, i. e. in n-type material (Fig. 15). On the other hand, the formation energy of $V_{Ga}$ is high in semi-insulating and p-type material. These trends correlate well with the experimental observations with the positron spectroscopy, where Ga vacancies are observed only in n-type material. In fact, the theoretical results of Fig. 15 predict that the formation energy of $V_{Ga} - O_N$ pair is even lower than that of isolated $V_{Ga}$. This is consistent with the experimental arguments to associate the observed Ga vacancies with
the \( V_{\text{Ga}} - O_N \) complex. In general, the creation of Ga vacancies (or \( V_{\text{Ga}} \) complexes) in the growth of both GaN crystals (Sec. 3) and epitaxial layers seems to follow the trends expected for acceptor defects in thermal equilibrium.

The \( V_{\text{Ga}} - O_N \) complexes may form at the growth temperature, when mobile Ga vacancies are trapped by oxygen impurities. Similarly, one could expect the formation of \( V_{\text{Ga}} - Si_{\text{Ga}} \) complexes in Si-doped GaN, as suggested by Kaufmann et al. [55]. In the positron experiments of Fig. 14, however, these complexes are not observed. According to theory [9], the binding energy of \( V_{\text{Ga}} - O_N \) pair (about 1.8 eV) is much larger than that of \( V_{\text{Ga}} - Si_{\text{Ga}} \) complexes (0.23 eV). The difference in stability is due to the electrostatic attraction: \( V_{\text{Ga}} \) and \( O_N \) are nearest neighbors whereas \( V_{\text{Ga}} \) and \( Si_{\text{Ga}} \) are only second nearest neighbors. The \( V_{\text{Ga}} - O_N \) pairs are thus more likely to survive the cooldown from the growth temperature than \( V_{\text{Ga}} - Si_{\text{Ga}} \). Hence, Ga vacancy complexes are detected by positrons only in materials containing substantial concentrations of oxygen, but their concentration in Si-doped material is much lower. However, the \( V_{\text{Ga}} - Si_{\text{Ga}} \) may be present in other type of GaN samples [55], particularly since the formation of Ga vacancies depends also on the stoichiometry of growth conditions as shown in Sec. 5.1.

**FIG. 15.** The formation energies of various defects in GaN as a function of the Fermi level \( \mu_e \) according to theoretical calculations [10].
4.5. **Yellow luminescence**

The parasitic yellow luminescence band at about 2.2 - 2.3 eV is commonly observed in n-type GaN. There is an increasing amount of evidence that this transition takes place between a shallow donor and a deep acceptor [8-10,56], and the Ga vacancy has been suggested as the defect responsible for the acceptor level [9,10,57]. Since Ga vacancies can be both identified and quantified by positron annihilation spectroscopy, it is interesting to compare their concentration with the intensity of the yellow luminescence.

The Ga vacancies were studied by positron measurements in a set of undoped n-type GaN epilayers grown on sapphire by MOCVD. The results of the Doppler broadening experiments have been given in Figs. 10 – 11 in Sec. 4.2. The concentration of the Ga vacancies can be estimated using the simple formula (Eq. 28)

\[
[V_{Ga}] = \frac{N_{at} S - S_B}{\mu_v \tau_B (S_V - S)}
\]  

(32)

at the high temperature plateau of Fig. 11, where the influence of negative ions and other type of shallow positron traps can be neglected (N_{at} is the atomic density). Taking the positron trapping coefficient \(\mu_v \approx 10^{15} \text{ s}^{-1}\) and \(S_V / S_B = 1.038\) we obtain the concentrations in the \(10^{17} - 10^{18} \text{ cm}^{-3}\) range. They are shown by the horizontal axis of Fig. 16.

The luminescence experiments were performed by exciting with the 325 nm line of a He-Cd laser. In order to probe approximately the same region below the surface of the epilayer as in the positron experiments, the luminescence was excited from the substrate side of the sample. The emitted radiation was analyzed by a 0.5-m monochromator equipped with a photomultiplier. In order to compare the yellow luminescence of different samples its intensity was averaged over the surface of a particular sample and the same optical alignment was used to collect the light emitted by each sample. No special normalization to the band-edge luminescence was done, but it was rather assumed that the dominant recombination channels are non-radiative in each sample. In such a case the intensity of the yellow luminescence can be expected to be proportional to the concentration of defects participating in this optical transition.

Fig. 16 shows the intensity of the yellow luminescence in MOCVD layers as a function of the \(V_{Ga}\) concentration obtained from positron experiments. In this set of samples the yellow luminescence correlates perfectly with the concentration of the Ga vacancies. This correlation provides evidence that native Ga vacancies participate the luminescence transition by acting as the deep acceptors.

The experimental results in GaN bulk crystals support further that Ga vacancies are responsible for the yellow luminescence. The Ga vacancies are present at concentrations \(10^{17} - 10^{18} \text{ cm}^{-3}\) in undoped heavily n-type material (Sec. 3), which always shows strong emission of
yellow light [40]. Furthermore, no signs of $V_{Ga}$ nor yellow luminescence is observed in semi-insulating Mg-doped crystals (Sec. 3). Very interestingly, recent results provide evidence that yellow luminescence is due to defects acting as compensating acceptors in n-type GaN [58]. Together with the present positron data this suggests that the Ga vacancy is the dominating intrinsic acceptor (see also Sec. 5.1) as well as responsible for the yellow luminescence. However, correlations such as that in Fig. 16 are inherently complicated, mainly because the quantification of photoluminescence data is difficult. For example, the yellow luminescence has been observed to disappear after electron irradiation [59-61], most likely because other photoelectron recombination channels become possible due to the introduction of irradiation-induced defects.

**FIG. 16.** The intensity of the yellow luminescence vs. the Ga vacancy concentration in GaN epitaxial layers. The inset shows the luminescence spectrum in the four studied layers, indexed according to the increasing Ga vacancy concentration [42].
5. POINT DEFECTS AND GROWTH CONDITIONS OF EPITAXIAL GaN

Epitaxial GaN layers can be grown using several methods, the most common of which are the metal-organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE). The lattice mismatch at the layer/substrate interface induces dislocations in the layers at concentrations up to $10^{10}$ cm$^{-2}$. The quality and the properties of the layers depend further on various parameters such as the stoichiometry of the growth conditions, growth temperature and the intermixing of the atoms between the layer and the substrate. In this section we review the positron results concerning the point defects formed in GaN layers under various kinds of growth conditions.

5.1. Stoichiometry of the MOCVD growth

The formation of Ga vacancies was studied in samples where the stoichiometry of growth conditions was varied in the MOCVD reactor [62]. The undoped GaN layers of thicknesses 1 – 5 µm were grown on sapphire substrates by MOCVD technique at 950 – 1100 °C, as described earlier [63]. The precursors employed were triethylgallium (TEGa) and ammonia (NH$_3$). The same TEGa flow was used for all samples and the NH$_3$ flow was adjusted to change the stoichiometry of the growth conditions. The V/III molar ratio varied from 1000 to 10000. As reported earlier [63], the growth rate as well as the electrical and optical properties of the samples change strongly with the V/III molar ratio. At lower ratios the photoluminescence shows broadened band edge structures and enhanced donor-acceptor pair recombination. The carrier concentrations at room temperature decrease from $10^{20}$ to $10^{16}$ cm$^{-3}$ when the V/III molar ratio increases from 1000 to 10000 [63].

All samples were investigated at room temperature as a function of the positron beam energy $E$ (Fig. 17). When positrons are implanted close to the sample surface with $E = 0 – 1$ keV, the same S parameter of $S = 0.49$ is recorded in all samples. This value characterizes the defects and chemical nature of the near-surface region of the sample at the depth 0 – 5 nm. At 5 – 15 keV the S parameter is constant indicating that all positrons annihilate in the GaN layer. The data recorded at these energies can thus be taken as characteristic of the layer. The lowest S parameter is obtained in the Mg-doped reference layer, where we get $S = 0.434$ at $E = 5 – 15$ keV. This value corresponds to positrons annihilating as delocalized particles in the defect-free GaN lattice.

The S parameter in all n-type layers is larger than in the Mg-doped reference sample (Fig. 17). The increased S parameter indicates that the positron-electron momentum distribution is narrower than in the defect-free reference sample. The narrowing is due to positrons annihilating as trapped at vacancy defects, where the electron density is lower and the probability of annihilation with high-momentum core electrons is reduced compared to that of delocalized
positrons in the lattice (Sec. 2). The increased S parameter is thus a clear sign of vacancy defects present in the n-type GaN layers.

The number of different vacancy defects trapping positrons can be investigated through the linearity between the low and high electron-momentum parameters S and W. If only a single type of vacancy is present, the W parameter depends linearly on the S parameter when the fraction of positron annihilations at vacancies $\eta_V$ varies. The plot of the W parameter vs. S parameter thus forms a line between the endpoints $(S_B, W_B)$ and $(S_V, W_V)$ corresponding to the defect-free lattice and the total positron trapping at vacancies, respectively. The S and W parameters of all samples are plotted in Fig. 18. All data points fall on the same line, which goes through the endpoint $(S_B, W_B) = (0.434, 0.069)$ obtained in the Mg-doped reference sample. The same type of vacancy is thus found in all samples. The positron trapping fraction $\eta_V$ and the S parameter vary from one sample to another due to the different vacancy concentrations.

**FIG. 17.** The low electron-momentum parameter $S$ as a function of the positron implantation energy in three GaN samples. The top axis shows the mean stopping depth corresponding to the positron implantation energy [62].
The slope of the line in Fig. 18 characterizes the vacancy defect present in all layers. The value $\Delta S/\Delta W = 2$ is the same as determined for the native Ga vacancy in Sec. 4. To confirm the identification, we recorded the positron-electron momentum distribution in the Mg-doped sample and the layer with V/III ratio of 8000 using the two-detector coincidence technique [27]. The high-momentum part of the momentum distribution was similar as observed for the Ga vacancy (Fig. 13 in Sec. 4). We can thus identify the native vacancy in the GaN layers as the Ga vacancy. As explained in Sec. 4, the presence of Ga vacancies can be expected in n-type undoped GaN due to their low formation energy. The different levels of the S parameter in Fig. 17 indicate that the concentration of the Ga vacancies seems to depend on the stoichiometry of growth.

In the samples with the V/III molar ratios 8000 and 5000 the Doppler broadening experiments were performed as a function of temperature at 20 - 500 K. The curves were qualitatively similar as shown in Fig. 11 in Sec. 4. At low temperatures $T < 150$ K the S parameter decreases indicating that positrons are trapped at shallow traps such as the Rydberg states of negative ions in addition to Ga vacancies. At high temperatures $T > 250$ K positrons are

![Graph](image)

**FIG. 18.** *The low and high electron-momentum parameters S and W in various samples. The V/III molar ratio of each sample is indicated in the figure. The straight line indicates that the same vacancy defect (Ga vacancy) is observed in all samples [62].*
able to escape from these traps. This effect increases the S parameter as a function of temperature, because more positrons are able to get trapped at vacancy defects. At 300 - 500 K the S parameter is constant indicating that the detrapping from the negative ions is complete. At these temperatures only Ga vacancies act as positron traps.

In order to quantify the concentration of V_{Ga} the S parameter data at 300 K was analyzed with the positron trapping model (Sec. 2.4.2). When Ga vacancies are the only defects trapping positrons, their concentration can be determined with the simple formula (Eq. (28))

\[ [V_{Ga}] = \frac{N_{at}}{\mu \tau_B} \frac{S - S_B}{S_V - S}, \]

where \( \tau_B = 165 \text{ ps} \) is the positron lifetime at the GaN lattice,[42] \( \mu = 10^{15} \text{ s}^{-1} \) is the positron trapping coefficient [12] and \( N_{at} = 8.775 \times 10^{22} \text{ cm}^{-3} \) is the atomic density of GaN. For the S parameter at the Ga vacancy we take \( S_V / S_B = 1.046 \). This value is slightly larger than presented

\[ \text{FIG. 19. The concentration of Ga vacancies vs. the V/III molar ratio in undoped GaN samples. The straight line is drawn to emphasize the correlation [62].} \]
earlier in Sec. 4, because the energy resolution of the gamma spectroscopy system used in this study (1.2 keV at 511 keV) is better than in our earlier study [42] (1.5 keV at 511 keV).

The results in Fig. 19 indicate that the concentration of Ga vacancies is proportional to the stoichiometry of the growth conditions. Rather low $[V_{Ga}] \approx 10^{16}$ cm$^{-3}$ is observed for the sample with the V/III molar ratio of 1000. When the V/III molar ratio becomes 10000, the $V_{Ga}$ concentration increases by almost three orders of magnitude to $[V_{Ga}] \approx 10^{19}$ cm$^{-3}$. This behavior shows that empty Ga lattice sites are likely formed in strongly N rich environment.

It has been shown in previous works that the V/III molar ratio has an influence on the growth rate as well as on the electrical and optical properties of the GaN layers [63]. The present results indicate that the formation of intrinsic point defects such as the Ga vacancy depend also heavily on the stoichiometry of the growth conditions. The Ga vacancy is negatively charged and thus acts as a compensating center in n-type material. Indeed, the Hall experiments show that the free electron concentration decreases from $10^{20}$ to $10^{16}$ cm$^{-3}$ when the V/III molar ratio increases from 1000 to 10000 [63]. Simultaneously, $[V_{Ga}]$ increases from $10^{16}$ to $10^{19}$ cm$^{-3}$ (Fig. 19). The charge state of $V_{Ga}$ in n-type material is 3- [9,10]. The compensation via the formation of Ga vacancies explains thus most of the decrease of the carrier concentration, when the V/III molar ratio increases from 1000 to 10000.

### TABLE II. The concentrations of free electrons, oxygen and Ga vacancies in the GaN layers grown with different V/III molar ratios. The oxygen concentrations were determined by secondary ion mass spectrometry and the concentrations of Ga vacancies were obtained from the positron annihilation data.

<table>
<thead>
<tr>
<th>V/III molar ratio</th>
<th>Carrier concentration (cm$^{-3}$)</th>
<th>Oxygen concentration (cm$^{-3}$)</th>
<th>Ga vacancy concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$10^{20}$</td>
<td>$&gt; 10^{20}$</td>
<td>$3 \times 10^{16}$</td>
</tr>
<tr>
<td>5000</td>
<td>$4 \times 10^{18}$</td>
<td>$4 \times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>8000</td>
<td>$10^{16}$</td>
<td>$1 \times 10^{19}$</td>
<td>$1 \times 10^{19}$</td>
</tr>
</tbody>
</table>
In order to obtain a more quantitative picture of the electrical compensation of GaN the oxygen concentrations were determined in some of the samples using secondary ion-mass spectrometry. As seen in Table II, the oxygen concentrations vary non-monotonously in the $10^{18} - 10^{20}$ cm$^{-3}$ range when the V/III ratio increases from 1000 to 8000. Interestingly, the carrier concentration seems to follow approximately the relation $n \approx [O] - [V_{Ga}]$ in the data of Table II. The SIMS, positron and electrical data are thus consistent with the simple picture that free electrons are supplied by shallow $O_{N}^+$ donors, which are partially compensated by negative Ga vacancies (or $V_{Ga}$ complexes) acting as dominant deep acceptors.

To summarize, we have applied positron annihilation spectroscopy to study the vacancy defects in undoped GaN layers, where the stoichiometry was changed by adjusting the V/III molar ratio. Gallium vacancies are observed in all samples. Their concentration increases from $10^{16}$ to $10^{19}$ cm$^{-3}$ when the V/III ratio changes from 1000 to 10000. Hence, the Ga vacancies are formed very abundantly when the growth conditions become more nitrogen rich. The decrease of free electron concentration with increasing V/III molar ratio correlates with the creation of Ga vacancies. This effect can be attributed to the compensation of impurities induced by the negatively charged Ga vacancies.

### 5.2. Dislocations and the formation of Ga vacancies in GaN layers

The results of Secs. 3 and 4 indicate that Ga vacancies (or complexes involving $V_{Ga}$) exist in GaN when the material is n-type and contains oxygen. The same trend is observed for both GaN bulk crystals and GaN grown by MOCVD on sapphire. However, the dislocation densities in these materials are very different. The lattice mismatch between GaN layer and sapphire substrate generates a highly dislocated region within a few hundred nanometers from the interface. The threading dislocations pass through the whole layer and have typically a high concentration of $10^{10}$ cm$^{-2}$ [1]. On the other hand, the dislocation density in GaN bulk crystals is only $10^5$ cm$^{-2}$. A relevant question is whether the formation of Ga vacancies in the GaN layers is related with the high concentration of dislocations.

Fig. 20 shows the S parameter in two semi-insulating Mg-doped GaN layers on sapphire, grown by two different groups in different MOCVD reactors. The S vs. E curve decreases rapidly from the surface value $S_S$ and saturates at $E = 5 - 20$ keV to the value $S_L$ characterizing the Mg-doped layer. The layer-characteristic value $S_L$ is equal to that in defect-free GaN lattice, indicating that both layers are free of Ga vacancies trapping positrons (see Sec. 4.1). However, the S(E) curves in the two samples are very different at $E = 20 - 40$ keV, which corresponds to a depth of the GaN/sapphire interface. In sample #1 S parameter decreases at $E > 30$ keV since annihilations start to occur at the sapphire substrate. The S(E) data in sample #2 forms a maximum around $E = 30$ keV and decreases towards the sapphire value $S_{Subs}$ only at larger incident positron energies.
The increased S parameter seen at $E = 30$ keV is the fingerprint of open-volume defects, which are clearly present in the highly dislocated region at the GaN/sapphire interface in sample #2. According to the data of Fig. 20 these vacancies extend 100 - 300 nm from the interface into the GaN layer, but most of the Mg-doped layer is free of these defects. As concluded in Sec. 4.4 the absence of Ga vacancies in Mg-doped GaN can be explained by the high formation energy of these defects. The data of Fig. 20 suggests that the dislocations have influence on the vacancy formation only at depths close to the interface between GaN and sapphire.

The lattice mismatch and the high dislocation density can be avoided by growing GaN layers homoepitaxially on the GaN bulk crystals. Such a sample has been studied in Fig. 21, which shows the S(E) results in n-type homoepitaxial layer and in the Mg-doped reference GaN. The homoepitaxial layer is not intentionally doped and its n-type conductivity is most likely due to oxygen impurities. As seen in Fig. 21, the S parameter in the n-type homoepitaxial sample is

FIG 20. The low electron-momentum parameter S as a function of the positron implantation energy in two Mg-doped GaN layers grown on sapphire. The top axis shows the mean stopping depth corresponding to the positron implantation energy. The maximum of the $S(E)$ curve at $E = 30$ keV indicate the presence of open-volume defects at the highly dislocated GaN/Al$_2$O$_3$ interface [50].
clearly larger than in the Mg-doped reference layer. This indicates that vacancies are present in the homoepitaxial GaN. The defects can be identified as Ga vacancies using the W vs. S analysis similarly as in Secs. 4.2 and 5.1.

The presence of Ga vacancies in homoepitaxial n-type GaN and their absence in semi-insulating Mg-doped layers on sapphire are both indications that the formation of Ga vacancies depends much more on the doping than on the substrate material and dislocation density. Furthermore, the Ga vacancies are observed in n-type bulk crystals, where the dislocation density is $\leq 10^5 \text{ cm}^{-2}$. We conclude that the n-type doping (Sec. 4.2), presence of oxygen (Sec. 4.4) and the N rich growth conditions (Sec. 5.1) promote the formation of Ga vacancies, but the lattice mismatch, substrate material and dislocation density seem to have influence on the vacancy concentration only close to the layer/substrate interface.

![Figure 21](image.png)

**FIG. 21.** The low electron-momentum parameter $S$ as a function of the positron implantation energy in nominally undoped homoepitaxial GaN layer, which shows n-type conductivity. The Mg-doped GaN reference sample indicates the level corresponding to positron annihilations in defect-free GaN. The top axis shows the mean stopping depth corresponding to the positron implantation energy [50].
5.3. Interdiffusion of atoms at GaN layers grown by MBE on Si

Positron spectroscopy has been applied to study vacancy defects in GaN layers grown by molecular-beam epitaxy (MBE) on Si [64]. The SIMS experiments show that a strong intermixing of atoms takes place at the GaN/Si interface. The interdiffusion is accompanied by changes in the optical and electrical properties of the layers. New peaks appear in the photoluminescence and a highly p-type layer is formed at the GaN/Si interface [64].

The Doppler broadening of the 511 keV annihilation radiation was recorded as a function of the positron beam energy in nominally 0.78 µm thick undoped GaN layers grown at 660, 720, 760, and 780 °C directly on the Si(111) substrates without buffer layers. The S parameter vs. the positron beam energy E is shown in Fig. 22 for all measured samples. The S(E) curve is a superposition of the specific parameter values for different positrons states. The fraction of positrons in each states varies with the beam energy, i.e. the positron stopping depth. At E = 0 keV positrons annihilate at the GaN surface. Between 2 keV and 8 keV positrons stop and

![Graph showing the low electron-momentum parameter S vs. positron implantation energy in undoped GaN/Si(111) grown by MBE at various temperatures. The dashed lines indicate the specific S values for free positrons in the GaN lattice and trapped positrons in Ga vacancies [64].](image-url)
annihilate in the GaN overlayer. Above 10 keV an increasing fraction of positrons penetrate to the Si substrate and the S parameter shoots up towards the Si-specific value $S_{Si} = 0.520(1)$.

The level of the plateau from 2 keV to 8 keV characterizes the corresponding GaN layer. In the layer grown at 660 °C, the level is very close to that found for free positrons in the GaN lattice, $S_B = 0.434(1)$ (Sec. 4.1). In the other three layers the plateau levels are much higher, even above the specific values of the Ga vacancy determined earlier in Sec. 4. This is a clear indication of vacancy-type defects in the layers.

We use the (S,W) plot to illustrate the positron states and to estimate the specific $(S_D,W_D)$ values for the defect which trap positrons in the layers. The $(S(E),W(E))$ points have been marked on the plot in Fig. 23. The surface effects have been dropped out by skipping the points with $E < 5$ keV. The positions of the positron states in the defect-free GaN lattice and in the Si substrate have been indicated, too. For the sake of clarity, the plateau values averaged from 5 keV to 8 keV have been marked by bigger symbols. One can see that all the plateau points fall on one line which goes through the "GaN Lattice" point. This means that the annihilations in the plateau regions arise as superpositions of two states: the free positrons in the lattice and the
trapped positrons in defects. The defect is same in all layers and the specific defect state 
\((S_D, W_D)\) must lie on this line, too. If we extrapolate the \((S, W)\) points of high \(E\) through the Si
substrate state, we get a second line. The crossing point ("Vacancy cluster") is the positron state
in the common defect present in all layers. All the experimental points fall inside the triangle
"GaN Lattice - Vacancy cluster - Si" meaning that the experimental data in Fig. 23 can be
explained as superpositions of annihilations in these three positron states.

The defect which trap positrons in the GaN layers has the normalized specific values
\(S_D/S_B = 1.10(2)\) and \(W_D/W_B = 0.75(3)\). These values are clearly different from those of the Ga
vacancy \(S_{VGa}/S_B = 1.038\), \(W_{VGa}/W_B = 0.86\), which are also marked in Fig. 23. We conclude
that the defect is far from being a monovacancy. The decoration of a Ga vacancy by a Si impurity
cannot change much the specific \((S,W)\) values, as the Si atom occupies a substitutional site in the
second nearest shell. Therefore the defect cannot be a \(V_{Ga}\)-Si pair. The high \(S_D\) and low \(W_D\)
values of the defect suggest an open volume at least twice that of a monovacancy, i.e. the defect
is a vacancy cluster. Using the positron trapping coefficient of \(10^{15}\) \(s^{-1}\) we can estimate that the
vacancy-cluster concentrations are \(< 10^{17}\) \(cm^{-3}\), \(5\times10^{17}\) \(cm^{-3}\), \(8\times10^{17}\) \(cm^{-3}\), and \(1\times10^{18}\) \(cm^{-3}\) in
the layers grown at 660, 720, 760, and 780 °C, respectively.

The SIMS results clearly demonstrate the strong Si diffusion across the GaN/Si interface
when no buffer layer exists. The Si profile penetrates 100 - 300 nm to the GaN side. Looking
carefully the positron results, we see that the \(S(E)\) values at the interface regions \((E = 10 - 14
keV)\) increase rapidly above the plateau levels in Fig. 22, but the corresponding points in the S-W
plot of Fig. 23 still continue to follow the "GaN lattice - Vacancy cluster" line. This means that
at the interface regions the positrons encounter vacancy-cluster concentrations which are 5-10
times higher than in the plateau regions.

Vacancies are known to be vehicles for substitutional atoms. In GaN samples grown by
MBE on Si positrons do not detect Ga vacancies nor \(V_{Ga}\)-Si pairs. Instead, vacancy clusters are
observed which are evidently stable traces left by diffusion processes during the layer growth.
We can conclude that positron measurements detect vacancy clusters as a result of the strong
interdiffusion across the GaN/Si interface without a buffer layer.

The Ga vacancy has been identified in MOCVD layers grown on sapphire and their
concentration has been seen to correlate with the yellow luminescence intensity (Sec. 4.5). The
PL results in the GaN layers on Si show no traces of the yellow band. This is consistent with the
absence of the Ga vacancy signal in positron measurements.
6. SUMMARY

Positron annihilation spectroscopy can be used to identify vacancy defects in bulk semiconductor crystals and epitaxial layers. It yields quantitative information on vacancy concentrations in the range $10^{15} - 10^{20}$ cm$^{-3}$. Positron localization into the hydrogenic states around negative centers can be applied to study also ionic acceptors that have no open volume.

Positron experiments detect Ga vacancies as native defects in GaN bulk crystals. The concentration of $V_{\text{Ga}}$ decreases with increasing Mg doping, as expected from the behavior of their formation energy as a function of the Fermi level. The trapping of positrons at the hydrogenic state around negative ions gives evidence that most of the Mg atoms are negatively charged. This suggests that Mg doping converts n-type GaN to semi-insulating mainly due to the electrical compensation of $O_N^{+}$ donors by $Mg_{\text{Ga}}^{-}$ acceptors.

Ga vacancies are observed as native defects in various n-type GaN overlayers grown by MOCVD on sapphire. Their concentration is $> 10^{17}$ cm$^{-3}$ in nominally undoped material, which show n-type conductivity due to residual oxygen. When similar doping is done with Si impurities and less oxygen is present, the concentration of Ga vacancies is lower by at least an order of magnitude. No Ga vacancies are observed in p-type or semi-insulating layers doped with Mg. These trends agree well with the theoretical calculations, which predict that the formation energy of Ga vacancy is high in p-type and semi-insulating material, but greatly reduced in n-type GaN, and even further reduced due to the formation of $V_{\text{Ga}}^{-}O_N$ complexes.

In addition to doping, the presence of open-volume defects in GaN layers depends on the growth conditions. The concentrations of Ga vacancies increases strongly when more N rich stoichiometry is applied in the MOCVD growth. On the other hand, the lattice mismatch and associated dislocation density seem to have less influence on the formation of point defects than doping and stoichiometry - at least at distances $> 0.5$ µm from the layer/substrate interface. This suggests that the formation of point defect in both epitaxial layers and bulk crystals follows mainly the trends expected for defects in thermal equilibrium.
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