Article

Relation between Ga Vacancies, Photoluminescence, and Growth Conditions of MOVPE-Prepared GaN Layers

Alice Hospodková 1,*, Jakub Čížek 2, František Hájek 1,3, Tomáš Hubáček 1, Jiří Pangrác 1, Filip Dominec 1, Karla Kuldová 1, Jan Batysta 1,3, Maciej O. Liedke 4, Eric Hirschmann 4, Maik O. Liedke 4 and Andreas Wagner 4,*

1 Institute of Physics CAS, Cukrovarnická 10, 162 00 Prague, Czech Republic
2 Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague, Czech Republic
3 Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Břehová 7, 115 19 Prague, Czech Republic
4 Institute of Radiation Physics, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany
* Correspondence: hospodko@fzu.cz

Abstract: A set of GaN layers prepared by metalorganic vapor phase epitaxy under different technological conditions (growth temperature, carrier gas type and Ga precursor) were investigated using variable energy positron annihilation spectroscopy (VEPAS) to find a link between technological conditions, GaN layer properties, and the concentration of gallium vacancies (V$_{Ga}$). Different correlations between technological parameters and V$_{Ga}$ concentration were observed for layers grown from triethyl gallium (TEGa) and trimethyl gallium (TMGa) precursors. In case of TEGa, the formation of V$_{Ga}$ was significantly influenced by the type of reactor atmosphere (N$_2$ or H$_2$), while no similar behaviour was observed for growth from TEGa. V$_{Ga}$ formation was suppressed with increasing temperature for growth from TEGa. On the contrary, enhancement of V$_{Ga}$ concentration was observed for growth from TMGa, with cluster formation for the highest temperature of 1100 °C. From the correlation of photoluminescence results with V$_{Ga}$ concentration determined by VEPAS, it can be concluded that yellow band luminescence in GaN is likely not connected with V$_{Ga}$; additionally, increased V$_{Ga}$ concentration enhances excitonic luminescence. The probable explanation is that V$_{Ga}$ prevent the formation of some other highly efficient nonradiative defects. Possible types of such defects are suggested.

Keywords: GaN; defects; positron annihilation spectroscopy; photoluminescence; MOVPE

1. Introduction

Optimization of methods for high-quality GaN growth in the 1990s paved the way for GaN-based power-efficient optoelectronic devices [1]. Highly efficient InGaN blue and white LEDs are now commercially available [1]. Thanks to the high polarization coefficient and ability to form heterostructures, AlGaN/GaN high electron mobility transistors can be manufactured, and these can be found in many applications these days [2]. Other applications of GaN-based devices include UV detectors [3], photovoltaic cells [4], and scintillators [5]. Despite extensive research on both the application and basic properties of GaN and related materials in the past three decades, several fundamental questions remain unanswered. One of them is the role or even the presence of Ga vacancies in GaN.

Defects related to Ga vacancies (V$_{Ga}$) in GaN are extremely important for optoelectronic applications since they are believed to be the main cause for the nonradiative recombination of carriers [6]. Other scholars have proposed that V$_{Ga}$ are responsible for yellow band luminescence and form nonradiative centres if they are in a complex with donors [7–9]. V$_{Ga}$-related defects deteriorate the frequency properties of high electron mobility transistors (HEMTs), since trapping and releasing a charge in deep levels is a rather slow process,
decreasing the cut-off frequency. $V_{Ga}$ can also decrease electron channel mobility. Another problem of these defects is shortening of the device lifetime, since vacancies enhance the diffusion of atoms in the structure, which can lead to the decomposition of quantum wells (QWs) [10] or the back-diffusion of Mg atoms from the GaN capping layer through the AlGaN barrier [11,12] to the channel region in HEMT structures. Although $V_{Ga}$ and their complexes are very important defects in nitrides, there is a lack of knowledge about the link between formation of these defects and the technological parameters of the preparation of high-quality epitaxial layers by metalorganic vapor phase epitaxy (MOVPE), as well as the influence of vacancies on semiconductor properties.

2. Materials and Methods

The studied samples were prepared by Aixtron CCS 3 × 2 MOVPE apparatus with dynamic adjustment of showerhead height. The following precursors were used for epitaxy: trimethylgallium (TMGa), triethylgallium (TEGa), and ammonia (NH$_3$). The set of prepared samples is specified in Table 1.

Table 1. Technological growth conditions of samples prepared for VEPAS measurement.

| Samples | $N_2$ atmosphere | $H_2$ atmosphere | Temperature | Precursor |
|---------|------------------|------------------|-------------|-----------|
| TEN1    | TEH1             |                  | 850 °C      | TEGa      |
| TEN2    | TEH2             |                  | 900 °C      | TEGa      |
| TEN3    | TEH3             |                  | 990 °C      | TEGa      |
| TMN1    | TMH1             |                  | 950 °C      | TMGa      |
| TMN2    | TMH2             |                  | 1025 °C     | TMGa      |
| TMN3    | TMH3             |                  | 1100 °C     | TMGa      |

Samples were prepared with the aim of finding a link between vacancy formation and some MOVPE technological parameters, namely temperature, type of carrier gas, and type of precursor. Growth of samples was always repeated in both atmospheres, $H_2$ or $N_2$. The growth temperature was changed from 850 °C to 1100 °C. TEGa was used for the growth in the temperature range of 850–950 °C; growth at higher temperatures with this precursor was not possible due to strong adduct formation. TMGa was used at the higher temperature range of 950–1100 °C. Growth at lower temperatures from TMGa was avoided due to strong carbon incorporation. Four samples, TEN3, TEH3, TMN1, and TMH1 were prepared at the same temperature (950 °C) to compare only the influence of precursor type. All samples had a 1 µm thick GaN layer prepared with relevant technological parameters. Their simple structure is shown in Figure 1a.

![Figure 1. (a) Structure of samples prepared for VEPAS and PL measurement, (b) Structure of samples prepared for SIMS.](image-url)
Positron annihilation spectroscopy (PAS) [13,14] is a well-established technique with high sensitivity to vacancies in solids. Positrons emitted by β+ radioisotopes have a continuous energy spectrum with a mean value in the order of hundreds keV. These energetic positrons are therefore called ‘fast positrons’. The mean penetration depth of fast positrons into solids is in the order of $10^2$–$10^3$ µm depending on the material density. Consequently, fast positrons can be used for investigations of bulk samples only. For defect studies of thin films, it is necessary to decrease positron energy. This can be achieved by the moderation of fast positrons. A material with negative positron work function [15] can be used as a moderator. A fraction of fast positrons stopped in the moderator diffuses to its surface and escapes into the vacuum due to the negative positron work function. These so-called ‘slow positrons’ are monoenergetic, with an energy of a few eV [16]. Slow positrons are collected in a slow positron beam and guided onto the sample. The energy of slow positrons in the beam can be increased using an electrostatic accelerator. Higher positron energy leads to higher positron penetration depth [16]. Hence, using a variable-energy slow positron beam one can probe the sample from the surface down to various depths. As an example, Figure 2 shows the implantation profiles of positrons with various energies implanted into GaN. The positron implantation profile is well-described by the Makhovian profile [17].

One can see in Figure 2 that varying the energy of slow positrons from 0.5 up to 12 keV enables variation in the mean positron penetration depth into GaN from to 2 to 347 nm. VEPAS is thus well-suited for defect studies of thin films or layered structure. The thickness of GaN films prepared for VEPAS studies is 1 µm (see Figure 1a). Hence, slow positrons are completely stopped inside the GaN layer even for the highest implantation energy of 12 keV used in measurement.

Measurement of a positron’s lifetime requires a start signal providing a time stamp when a positron was born and a stop signal when the positron was annihilated. The stop signal is given by a 511 keV gamma ray emitted during positron annihilation. In order to obtain the start signal, the positron beam has to be pulsed, i.e., positrons are allowed to appear only in narrow time intervals, providing the start signal. The efficiency of positron moderation is very low ($\leq 5 \times 10^{-3}$) [16] and pulsing of the slow positron beam leads to
further reduction in intensity. As a consequence, a pulsed variable-energy slow positron beam requires a strong positron source.

VEPAS studies in the present paper were carried out on a LINAC-based pulsed variable energy slow positron beam MePS [18] operating at the ELBE facility [19] at Helmholtz-Zentrum Dresden-Rossendorf. Primary fast positrons were created by pair production induced by electron bremsstrahlung radiation. A tungsten moderator was used to obtain slow positrons. A high-intensity LINAC electron beam (average electron beam current 1.6 mA, electron energy 35 MeV) enabled achieving a high intensity of fast positrons necessary for a pulsed slow positron beam. Moreover, narrow electron pulses of ELBE LINAC (width smaller than 10 ps) were used as start signals for precise measurement of positron lifetimes. The annihilation gamma rays providing stop signals were measured using a CeBr3 scintillation detector with digital signal processing. The time resolution of the spectrometer (FWHM of the resolution function) was 230 ps. The energy of slow positrons could be varied in the range from 0.5 to 12 keV.

Photoluminescence (PL) spectra of samples were collected using 325 nm excitation wavelength and a confocal microscope (LabRAM HR Evolution HORIBA, He–Cd laser, objective 74 CG, detector Synapse UV).

Two samples were also prepared for secondary ion mass spectroscopy (SIMS) measurement to study the connection between the contamination of layers and the technology of their preparation (see Figure 1b). These samples contained GaN layers with relevant technological parameters, with a thickness of 50 nm separated by 10 nm thick AlGaN layers that served as markers. All examined layers of the first and second sample were grown in H2 and N2 atmospheres, respectively. The concentrations of common contaminants (C, O, H, Si) were measured in EAG laboratories [20].

3. Results and Discussion
3.1. Variable Energy Positron Annihilation Spectroscopy

A positron lifetime spectrum is in general a sum of exponential components convoluted with the response function of the spectrometer. Each component corresponds to a certain positron state and is characterized by its lifetime \(\tau_i\) and relative intensity \(I_i\). A single-component fit of positron lifetime spectra yields the mean positron lifetime, representing the weighted average of lifetimes of various components, \(\bar{\tau} = \sum \tau_i I_i\). An example of a single-component fit of positron lifetime spectrum for the TEH1 sample for positron energy \(E = 10\) keV is shown in Figure 3a. The mean positron lifetime is a robust parameter not affected by mutual correlations among fitting parameters and provides useful information about trends in the series of GaN films studied. The mean positron lifetime for GaN layers studied is plotted in Figure 4 as a function of the positron energy. At low energies, almost all positrons are annihilated on the surface and the mean positron lifetime corresponds to the surface state. With increasing energy, positrons penetrate deeper into the GaN layer and the fraction of positrons diffusing back to the surface gradually decreases. Consequently, the mean positron lifetime gradually decreases with increasing positron energy from the surface value down to a value corresponding to when all positrons are annihilated in the GaN layer.

Positrons are attracted and captured by negatively charged Ga vacancies (\(V_{Ga}\)). In the empty volume of a \(V_{Ga}\), positrons have lower overlap with the electrons of crystal atoms, which decreases the probability of their annihilation and, hence, the lifetime of positrons trapped in the vacancy is increased. Figure 4 also shows the calculated lifetime values of free positrons in a perfect GaN crystal without defects (bulk) as well as that of positrons trapped in \(V_{Ga}\) and of positrons trapped in different clusters with nitrogen vacancies (\(V_N\)). Positron lifetime increased with increased empty volume in the defect. Positrons annihilated on the surface influenced the measured mean lifetime values up to the mean penetration depth of 200–300 nm due to the back-diffusion of positrons toward the surface. For higher penetration depths, i.e., incident positron energy above 8 keV, the fraction of positrons diffusing back to the surface becomes negligible and almost all
positrons are annihilated in the GaN layer. The mean positron lifetime values for energies above 8 keV were, therefore, supposed to be relevant for determination of defect type and concentration.

From inspection of Figure 4, one can conclude that the mean positron lifetime at high energies (E > 8 keV) approaches values located between the calculated bulk positron lifetime (i.e., lifetime of free positrons in a defect-free lattice) and the calculated lifetime of positrons trapped in V_{Ga}. This indicates that GaN films contain V_{Ga}, and some positrons are trapped and annihilated in V_{Ga} while the remaining positrons are annihilated in the free state, i.e., not trapped at defects. The only exception comprises TMN3 and TMH3 samples grown at the highest temperature of 1100 °C. In TMN3 and TMH3, the mean positron lifetime at high energies approached a value that was higher than the calculated lifetime for V_{Ga}. This indicates that TMN3 and TMH3 contain defects with a higher open volume than V_{Ga}.

![Figure 3](image_url)

**Figure 3.** An example of positron lifetime spectrum measured for the TEH1 sample and energy of incident positrons E = 10 keV. Solid line shows fit of the spectrum by model function. (a) Single-component fit yielding the mean positron lifetime; (b) Two-component fit considering contribution of free positrons (lifetime τ_1) and positrons trapped at defects (lifetime τ_2). Individual components are plotted by dashed lines.
Figure 3. An example of positron lifetime spectrum measured for the TEH1 sample and energy of incident positrons \( E = 10 \text{ keV} \). Solid line shows fit of the spectrum by model function. (a) Single-component fit yielding the mean positron lifetime; (b) Two-component fit considering contribution of free positrons (lifetime \( \tau_1 \)) and positrons trapped at defects (lifetime \( \tau_2 \)). Individual components are plotted by dashed lines.

Figure 4. Dependence of the mean positron lifetime on the energy of incident positrons entering the GaN layer prepared under different growth conditions in (a) nitrogen and (b) hydrogen atmosphere. Upper x-axis shows the mean positron penetration depth.

An example of the decomposition of the positron lifetime spectra for the TEH1 sample and the energy of incident positrons \( E = 10 \text{ keV} \) is shown in Figure 3b. From comparison of Figure 3a to Figure 3b it is clear that fitting by two components results in better agreement with experimental points than the single-component fit. The development of positron lifetimes \( \tau_1 \) and \( \tau_2 \) and corresponding intensities \( I_1 \) and \( I_2 \) for sample TEH1 with positron energy is shown in Figures 5a and 5b, respectively. It can be noticed that for penetration depth 300 nm, the positron lifetime \( \tau_2 \) reached the value calculated for positrons trapped in \( V_{Ga} \), testifying that the TEH1 sample contains \( V_{Ga} \). Results of the breakdown of positron lifetime spectra for other samples are collected in Supplementary Materials. Similar results
as for TEH1 were also obtained for other GaN films deposited at temperatures below 1100 °C. The results of the decomposition of positron lifetime spectra for the TMH3 sample deposited at 1100 °C are plotted in Figure 6. In contrast to the films deposited at lower temperatures, the lifetime τ2 for the TMH3 sample at high energies approaches a significantly higher value, corresponding to the calculated lifetime of positrons trapped in a complex consisting of two Ga and two N missing ions (2VGa+2VN complex). A similar result was obtained for TMN3 film deposited at 1100 °C using N2 carrying gas (see Supplementary Materials). The development of the lifetime τ2 measured at the highest positron energy of 12 keV on different GaN film deposition temperatures is plotted in Figure 7a. For deposition temperatures lower than 1100 °C, the lifetime τ2 remains close to the calculated value for VGa. However, for films deposited at 1100 °C the lifetime τ2 increases to the value corresponding to a 2VGa + 2VN complex. Thus, one can conclude that GaN films grown at temperatures below 1100 °C contain VGa. However, at higher temperatures the nature of the defects changes and films grown at 1100 °C contain 2VGa + 2VN complexes.

Figure 5. Breakdown results of positron lifetime spectra for sample TEH1 (a) lifetimes τ1 and τ2 of components resolved in spectra and (b) intensities I1 and I2 of the components. Dashed lines indicate calculated bulk positron lifetime and lifetimes of positrons trapped in various defects. The mean positron penetration depth is shown in the upper x-axis. The solid lines serve to guide the eye.

Figure 6. Results of breaking down positron lifetime spectra for the TMH3 sample (a) lifetimes τ1 and τ2 of the components resolved in spectra and (b) intensities I1 and I2 of the components. Dashed lines indicate calculated bulk positron lifetime and the lifetimes of positrons trapped in various defects. The mean positron penetration depth is shown in the upper x-axis. The solid lines serve to guide the eye.
The \( V_{Ga} \) concentration was calculated from the lifetimes and intensities of both components using the two-state trapping model [21]. Data measured for the highest positron energy of 12 keV corresponding to the highest positron penetration depth were used for determination of the vacancy concentration for all samples. Results for all samples are summarized in Figure 7b. \( V_{Ga} \) formation is not only influenced by the temperature, but it is also strongly dependent on the choices of precursor and carrier gas. The temperature dependence of \( V_{Ga} \) concentration for samples grown from TEGa and TMGa precursors have opposite characters. Unfortunately, there was not sufficient overlap of temperature intervals in which both precursors could be used for epitaxy; only around 950 °C could both types of precursors be used. TEGa is preferred for temperatures below 950 °C, since at this temperature range TMGa is less decomposed and too much carbon would be incorporated into the layers. At temperatures above 950 °C, TEGa cannot be used due to adduct formation, which impacts the growth rate.

Very characteristic of layers grown from TEGa is that the measured \( V_{Ga} \) concentration is significantly higher in a nitrogen atmosphere compared to samples grown in hydrogen. In the case of TEGa grown in nitrogen, \( V_{Ga} \) concentration decreases with temperature. This is unexpected from a thermodynamic point of view, since the vacancy concentration should be increasing with temperature as \( \exp\left(-\frac{E_f}{kT}\right) \), where \( E_f \) is the vacancy formation energy [22]. Several possible hypotheses explaining this behaviour can be suggested. Since the TEGa precursor should be fully decomposed in the studied temperature range [23], limited Ga precursor decomposition can be ruled out. One of the possible explanations is the influence of surface morphology on vacancy formation, because in a N\(_2\) atmosphere the epitaxial surface is rather rough (V-shape defects are formed). A lower \( V_{Ga} \) concentration in a H\(_2\) atmosphere can be due to passivation or filling of \( V_{Ga} \) by hydrogen incorporated in the GaN lattice. In complexes of \( V_{Ga} \) associated with H atoms positrons cannot be trapped or their lifetime is much shorter. For comparison, the lifetime of a positron trapped in a \( V_{Ga} \) is 200–211 ps, while positron lifetime for \( V_{Ga} \cdot H \) complexes is shortened to 180 ps and for \( V_{Ga} \cdot 2H \) it is further shortened to 150 ps, so it is even shorter than 155 ps, which is the bulk positron lifetime for GaN, i.e., lifetime of free positrons in a perfect (defect-free) GaN crystal [24].

When TMGa is used as the precursor, \( V_{Ga} \) concentration is not influenced by the choice of atmosphere in the MOVPE reactor, but it is strongly enhanced with increasing temperature. The lifetime corresponding to a cluster \( 2V_{Ga} \cdot 2V_{N} \) was measured for the highest growth temperature of 1100 °C, which means that the actual \( V_{Ga} \) concentration was twice the concentration of \( 2V_{Ga} \cdot 2V_{N} \) complexes shown in Figure 7b, since each complex contains two \( V_{Ga} \). Significantly different \( V_{Ga} \) concentration when TMGa or TEGa was used for the GaN growth suggests that the reaction pathway has important influence on the
vacancy formation. This could be a reason why theoretical predictions of $V_{Ga}$ concentration based on formation energy [25] are underestimated. In the future, layers grown from novel precursors and the vacancy formation in them might help to understand the growth kinetics, as suggested in [26,27].

3.2. Photoluminescence

Knowing the $V_{Ga}$ concentration in particular GaN layers, we investigated its correlation with PL properties. It could bring valuable insight into the quest for yellow band (YB) luminescence origin. In previous works, YB luminescence was attributed to a $C_N$ defect [28], $C_{N-O_N}$ complex [29], which is energetically favourable, or $C_{N-Si_{Ga}}$ [30] in n-type GaN layers. Other sources of YB luminescence that were proposed in the literature were $V_{Ga}$-3H and $V_{Ga}$-$O_{N}$-2H complexes [31] or $V_{Ga}$-$O_{N}$ [32]. $V_{Ga}$ were also supposed to be responsible for nonradiative recombination [6].

Typical room-temperature PL spectra for MOVPE-prepared GaN layers (samples TEN1 and TEH1) are shown in Figure 8 to illustrate the position of PL bands. Contrary to expectations, for sample TEN1, with a higher $V_{Ga}$ concentration, neither an increase in YB intensity nor a decrease of PL efficiency was observed.

![Figure 8. Room-temperature photoluminescence spectra of samples TEN1 and TEH1.](image)

In Figure 9a,b, correlation between excitonic and YB intensity with respect to the $V_{Ga}$ concentration is shown, summarizing the data obtained from all studied layers. No correlation between $V_{Ga}$ concentration and YB luminescence intensity was observed, which suggests that $V_{Ga}$ are not the dominant reason for YB luminescence.
was approximately three times higher than for samples grown in a N\textsubscript{2}\ atmosphere, we can also suppose the formation of V\textsubscript{Ga} complexes is much more probable than formation of isolated V\textsubscript{Ga}. The smallest formation energy of V\textsubscript{Ga} is found when the Fermi level is near the conduction band minimum but still reaches a value around 4.5 eV. On the other hand, at the same Fermi level position, the formation energy of \textit{V\textsubscript{Ga}-3H}, \textit{V\textsubscript{Ga}-2H}, and \textit{V\textsubscript{Ga}-O\textsubscript{N}-2H} is around 3 eV, 2.6 eV, and 0.5 eV, respectively [33]. Since none of these defects can be detected by VEPAS due to the small

3.3. Secondary Ion Mass Spectroscopy

To find possible candidates for nonradiative defects that are anticorrelated with V\textsubscript{Ga} and to elucidate whether V\textsubscript{Ga} form complexes with atoms from impurities, we prepared multilayer samples designed for SIMS characterization according to the scheme in Figure 1b. Hydrogen, oxygen, carbon, and silicon concentration profiles were measured by SIMS. There was one significant feature observed in all GaN layers—contamination from all four elements was higher when H\textsubscript{2} was used for the reactor atmosphere. Interesting correlations between V\textsubscript{Ga} and carbon for samples grown from TMGa, and between V\textsubscript{Ga} and hydrogen for samples grown from TEGa were observed. The obtained hydrogen and carbon concentrations for GaN layers prepared according to the above-defined technological parameters are summarized in Figure 10a,b.

In layers grown in a H\textsubscript{2} atmosphere at lower temperatures, hydrogen contamination was approximately three times higher than for samples grown in a N\textsubscript{2} atmosphere. We suppose that NH\textsubscript{3} is less efficiently decomposed in a H\textsubscript{2} atmosphere and hydrogen could be incorporated into the epitaxial layer. Hydrogen can form complexes with V\textsubscript{Ga} that are invisible to PAS methods, as was explained above. Since in samples grown from TEGa in a H\textsubscript{2} atmosphere the oxygen concentration measured by SIMS was in the order of 10\textsuperscript{17} cm\textsuperscript{-3} (not shown here), we can also suppose the formation of \textit{V\textsubscript{Ga}-O\textsubscript{N}-2H}, which is energetically favourable. In fact, if H and O are abundant, formation of \textit{V\textsubscript{Ga}-3H}, \textit{V\textsubscript{Ga}-2H}, or \textit{V\textsubscript{Ga}-O\textsubscript{N}-2H} complexes is much more probable than formation of isolated V\textsubscript{Ga}. The smallest formation energy of V\textsubscript{Ga} is found when the Fermi level is near the conduction band minimum but still reaches a value around 4.5 eV. On the other hand, at the same Fermi level position, the formation energy of V\textsubscript{Ga}-3H, V\textsubscript{Ga}-2H, and V\textsubscript{Ga}-O\textsubscript{N}-2H is around 3 eV, 2.6 eV, and 0.5 eV, respectively [33]. Since none of these defects can be detected by VEPAS due to the small

Figure 9. Maximum intensity of (a) excitonic and (b) yellow band luminescence as a function of V\textsubscript{Ga} concentration.

However, there is unexpected and clear positive correlation between V\textsubscript{Ga} concentration and excitonic luminescence. It means that V\textsubscript{Ga} cannot be efficient nonradiative centre. Since there is no known mechanism in which V\textsubscript{Ga} presence would enhance free-exciton emission in GaN, we suggest the following explanation for the correlation observed in Figure 9a: higher exciton intensity is caused by the suppression of other recombination channels, especially the nonradiative ones (because enhancement of yellow luminescence was not observed with increasing V\textsubscript{Ga} concentration, Figure 9b). Correlation between V\textsubscript{Ga} concentration and GaN exciton intensity means that there exists an anticorrelation between nonradiative centre concentration and V\textsubscript{Ga} concentration. In other words, the formation of an unknown nonradiative centrum is suppressed when the Ga vacancies are present.
open volume of the defects, their presence may explain the significantly lower detected $V_{Ga}$ concentration in layers grown from TEGa in a H$_2$ atmosphere. Some of these defects probably also act as nonradiative centres [33].

However, in samples grown from TMGa, hydrogen does not play a significant role. Instead, carbon contamination seems to be anticorrelated with $V_{Ga}$ concentration. It seems that for the lowest temperature of 950 °C, the carbon concentration is so high that it is filling not only $V_{N}$, but also $V_{Ga}$, thus forming n-type $C_{Ga}$ defects. On the other hand, at the highest temperature, when there is low carbon contamination, both types of vacancies remain unfilled and their concentration is so high that they can merge into clusters, as was observed at 1100 °C. According to the PL results, at the highest carbon concentration PL efficiency drops significantly, suggesting the formation of strong nonradiative defects, which could be $C_{Ga}$ according to [34], or it may be due to some complex related to $C_{Ga}$ such as $C_{Ga}-C_N$ or $C_{Ga}$-H$_2$.

4. Conclusions

Twelve samples with GaN layers prepared by MOVPE under different technological conditions were investigated by a unique VEPAS method to find a link between technological conditions and $V_{Ga}$ formation. Different correlations between $V_{Ga}$ concentration and technology parameters were observed for layers grown from TEGa and TMGa precursors. In the case of TEGa, $V_{Ga}$ formation was significantly influenced by the type of reactor atmosphere (N$_2$ or H$_2$), while no similar behaviour was observed for samples grown from TMGa. $V_{Ga}$ formation was suppressed with increasing temperature for growth from TEGa in a N$_2$ atmosphere. On the contrary, opposite temperature dependence for $V_{Ga}$ formation was observed for growth from TMGa, with cluster formation for the highest temperature of 1100 °C. Significantly different $V_{Ga}$ formation when TMGa or TEGa was used for the GaN growth suggests that the reaction mechanism has an important influence on formation of vacancies. This could be a reason why $V_{Ga}$ concentrations theoretically predicted from formation energies are underestimated. According to the correlation of PL results with $V_{Ga}$ concentrations determined by VEPAS, it can be concluded that Yb luminescence is not generally connected with $V_{Ga}$ in MOVPE-prepared GaN layers. Surprisingly, the presence of $V_{Ga}$ was correlated with intensity of excitonic luminescence. The probable explanation is that the $V_{Ga}$ concentration in GaN layers is anticorrelated with some efficient nonradiative defects. According to SIMS results and correlation with detected $V_{Ga}$ concentrations, we
have suggested several candidates for such nonradiative defects, which could be C\textsubscript{Ga}, C\textsubscript{Ga}-C\textsubscript{N}, or C\textsubscript{Ga}-H\textsubscript{i} in samples grown from TMGa and V\textsubscript{Ga}-3H, V\textsubscript{Ga}-2H, or V\textsubscript{Ga}-O\textsubscript{N}-2H complexes in samples grown from TEGa.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15196916/s1, Figure S1: Results of decompositions of positron lifetime spectra for the sample TEN1 plotted as a function of the energy of incident positrons. Figure S2: Results of decompositions of positron lifetime spectra for the sample TEN2 plotted as a function of the energy of incident positrons. Figure S3: Results of decompositions of positron lifetime spectra for the sample TEN3 plotted as a function of the energy of incident positrons. Figure S4: Results of decompositions of positron lifetime spectra for the sample TEH1 plotted as a function of the energy of incident positrons. Figure S5: Results of decompositions of positron lifetime spectra for the sample TEH2 plotted as a function of the energy of incident positrons. Figure S6: Results of decompositions of positron lifetime spectra for the sample TEH3 plotted as a function of the energy of incident positrons. Figure S7: Results of decompositions of positron lifetime spectra for the sample TMN1 plotted as a function of the energy of incident positrons. Figure S8: Results of decompositions of positron lifetime spectra for the sample TMN2 plotted as a function of the energy of incident positrons. Figure S9: Results of decompositions of positron lifetime spectra for the sample TMN3 plotted as a function of the energy of incident positrons. Figure S10: Results of decompositions of positron lifetime spectra for the sample TMH1 plotted as a function of the energy of incident positrons. Figure S11: Results of decompositions of positron lifetime spectra for the sample TMH2 plotted as a function of the energy of incident positrons. Figure S12: Results of decompositions of positron lifetime spectra for the sample TMH3 plotted as a function of the energy of incident positrons. References [35,36] are cited in the supplementary materials.

**Author Contributions:** Conceptualization, A.H., J.Č., F.H. and T.H.; methodology, J.Č., F.H., K.K., F.D., J.P. and T.H.; formal analysis, J.Č. and F.H.; investigation, J.Č., A.H., F.H., K.K., F.D., T.H., J.B., M.O.L., M.B., E.H. and A.W.; writing—original draft preparation, A.H., J.Č. and F.H.; writing—review and editing, J.Č., A.H., K.K., J.P., F.D. and T.H.; visualization, J.Č. and A.H.; project administration, J.Č. and A.H.; funding acquisition, A.H. and J.Č. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Czech Science Foundation, project GACR LA 22-28001K (VACCINES), CAS mobility project PAN-20-19 and MEYS CR Czech Nanolab infrastructure LM2018110. Parts of this research were carried out at ELBE at the Helmholtz-Zentrum Dresden-Rossendorf e. V., a member of the Helmholtz Association. We would like to thank the facility staff (X) for assistance. Partial support from the Operational Programme Research, Development and Education financed by European Structural and Investment Funds and the Czech MEYS (Project No. SOLID21 CZ.02.1.01/0.0/0.0/16_019/0000760 is also acknowledged).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Measured data can be provided upon request from hospodko@fzu.cz.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Nakamura, S. Nobel Lecture: Background story of the invention of efficient blue InGaN light emitting diodes. Rev. Mod. Phys. 2015, 87, 1139–1151. [CrossRef]
2. Mishra, U.K.; Parikh, P.; Wu, Y.F. AlGaN/GaN HEMTs—An overview of device operation and applications. Proc. IEEE 2002, 90, 1022–1031. [CrossRef]
3. Li, D.B.; Sun, X.J.; Song, H.; Li, Z.M.; Chen, Y.R.; Jiang, H.; Miao, G. Q Realization of a high-performance GaN UV detector by nanoplasmonic enhancement. Adv. Mater. 2012, 24, 845–849. [CrossRef] [PubMed]
4. Neufeld, C.J.; Toledo, N.G.; Cruz, S.C.; Iza, M.; DenBaars, S.P.; Mishra, U.K. High quantum efficiency InGaN/GaN solar cells with 2.95 eV band gap. Appl. Phys. Lett. 2008, 93, 143502. [CrossRef]
5. Hospodková, A.; Nikl, M.; Pacherová, O.; Oswald, J.; Brůža, P.; Pánek, D.; Foltynski, B.; Hulicius, E.; Beitlerová, A.; Heuken, M. InGaN/GaN multiple quantum well for fast scintillation application: Radioluminescence and photoluminescence study. Nanotechnology 2014, 25, 455501. [CrossRef]
6. Nykanen, H.; Suikkonen, S.; Kilanski, L.; Sopanen, M.; Tuomisto, F. Low energy electron beam induced vacancy activation in GaN. *Appl. Phys. Lett.* 2012, 69, 122105. [CrossRef]

7. Neugebauer, J.; Van de Walle, C.G. Gallium vacancies and the yellow luminescence in GaN. *Appl. Phys. Lett.* 1996, 69, 503–505. [CrossRef]

8. Saarinen, K.; Laine, T.; Kuisma, S.; Nissila, J.; Hautojarvi, P.; Dobrzynski, L.; Baranowski, J.M.; Pakula, K.; Stepniewski, R.; Wojdak, M.; et al. Observation of native Ga vacancies in GaN by positron annihilation. *Phys. Rev. Lett.* 1997, 79, 3030–3033. [CrossRef]

9. Lyons, J.L.; Van de Walle, C.G. Computationally predicted energies and properties of defects in GaN. *NPJ Comput. Mater.* 2017, 3, 12. [CrossRef]

10. Bojarska, A.; Muziol, G.; Skierbiszewski, C.; Grzanka, E.; Wisniewski, P.; Makarowa, I.; Czernecki, R.; Suski, T.; Perlin, P. Influence of the growth method on degradation of InGaN laser diodes. *Appl. Phys. Express* 2017, 10, 091001. [CrossRef]

11. Gutt, R.; Kohler, K.; Wiegert, J.; Kirste, L.; Passow, T.; Wagner, J. Controlling the Mg doping profile in MOVPE-grown GaN/AlGaN light-emitting diodes. *Phys. Status Solidi C* 2011, 8, 2072–2074. [CrossRef]

12. Chichibu, S.F.; Uedono, A.; Kojima, K.; Ikeda, H.; Fujito, K.; Takashima, S.; Edo, M.; Ueno, K.; Ishibashi, S. The origins and properties of intrinsic nonradiative recombination centers in wide bandgap GaN and AlGaN. *J. Appl. Phys.* 2018, 123, 161413. [CrossRef]

13. Krause-Rehberg, R.; Leipner, H. *Positron Annihilation in Semiconductors: Defect Studies*, 1st ed.; Springer: Berlin, Germany, 1999.

14. Čiček, J. Characterization of lattice defects in metallic materials by positron annihilation spectroscopy: A review. *J. Mater. Sci. Technol.* 2018, 34, 577–598. [CrossRef]

15. Schultz, P.; Lynn, K.G. Interaction of positron beams with surfaces, thin films, and interfaces. *Rev. Mod. Phys.* 1988, 60, 701–801. [CrossRef]

16. Hugenschmidt, C. Positrons insurface physics. *Surf. Sci. Rep.* 2016, 71, 547–594. [CrossRef]

17. Puska, M.J.; Nieminen, R. Theory of positrons in solids and on solid surfaces. *Rev. Mod. Phys.* 1994, 66, 841–899. [CrossRef]

18. Wagner, A.; Butterling, M.; Liedke, M.O.; Potzger, K.; Krause-Rehberg, R. Positron Annihilation Lifetime Imaging and Doppler Broadening Spectroscopy at the ELBE Facility. *AIP Conf. Proc.* 1990, 1970, 40003. [CrossRef]

19. Gabriel, F.; Gippern, P.; Grosse, E.; Janssen, D.; Michel, P.; Prade, H.; Schamlott, A.; Seidel, W.; Wolf, A.; Wünsch, R. The Rosendorff radiation source ELBE and its FEL projects. *Nucl. Instrum. Methods Phys. Res. Sect. B* 2000, 161, 1143–1147. [CrossRef]

20. The Global Leader in Materials Testing Services. EAG Laboratories. Available online: https://www.eag.com/ (accessed on 21 October 2021).

21. West, R.N. Positron studies of condensed matter. *Adv. Phys.* 1973, 22, 263–383. [CrossRef]

22. Mendelev, M.I.; Bokstein, B.S. Molecular dynamics study of self-diffusion in Zr. *Philos. Mag.* 2002, 84, 110–124. [CrossRef]

23. Xing, G.; Ye, Z.Z. Selection of precursors and their influences on III-nitrides grown by MOCVD. *J. Appl. Phys.* 2015, 117, 207320. [CrossRef]

24. Hautakangas, S.; Makkonen, I.; Ranki, V.; Puska, J.; Saarinen, K.; Xu, X.; Look, D.C. Direct evidence of impurity decoration of Ga vacancies in GaN from positron annihilation spectroscopy. *Phys. Rev. B* 2006, 73, 163301. [CrossRef]

25. Xie, Z.J.; Siu, Y.; Buckeridge, J.; Catlow, C.R.A.; Keal, T.W.; Sherwood, P.; Walsh, A.; Farrow, M.R.; Scanlon, D.O.; Woodyl, S.M.; et al. Donor and acceptor characteristics of native point defects in GaN. *J. Phys. D Appl. Phys.* 2019, 52, 335104. [CrossRef]

26. dos Santos, R.B.; Rivelino, R.; Mota, F.D.; Kakanakova-Georgieva, A.; Gueorguiev, G.K. Feasibility of novel (H$_2$Cn$_3$)$_{3-n}$ compounds (X = B, Al, Ga, In): Structure, stability, reactivity, and Raman characterization from ab initio calculations. *J. Phys. Chem. C* 2015, 119, 262104. [CrossRef]

27. Freitas, R.R.Q.; Gueorguiev, G.K.; Mota, F.D.; de Castilho, C.M.C.; Satsfstrom, S.; Kakanakova-Georgieva, A. Reactivity of adducts relevant to the deposition of hexagonal BN from first-principles calculations. *Chem. Phys. Lett.* 2013, 583, 119–124. [CrossRef]

28. Lyons, J.L.; Janotti, A.; Van de Walle, C.G. Carbon impurities and the yellow luminescence in GaN. *Appl. Phys. Lett.* 2010, 97, 151208. [CrossRef]

29. Demchenko, D.O.; Diallo, L.C.; Reshchikov, M.A. Yellow Luminescence of Gallium Nitride Generated by Carbon Defect Complexes. *Phys. Rev. Lett.* 2013, 110, 87404. [CrossRef]

30. Christenson, S.G.; Xie, W.Y.; Sun, Y.Y.; Zhang, S.B. Carbon as a source for yellow luminescence in GaN: Isolated C-N defect or its complexes. *J. Appl. Phys.* 2015, 118, 135708. [CrossRef]

31. Lyons, J.L.; Alkauskas, A.; Janotti, A.; Van de Walle, C.G. First-principles theory of acceptors in nitride semiconductors. *Phys. Status Solidi B* 2015, 252, 900–908. [CrossRef]

32. Dreyer, C.E.; Alkauskas, A.; Lyons, J.L.; Speck, J.S.; Van de Walle, C.G. Gallium vacancy complexes as a cause of Shockley-Read-Hall recombination in III-nitride light emitters. *Appl. Phys. Lett.* 2016, 108, 141101. [CrossRef]

33. Zimmermann, F.; Beyer, J.; Roeder, C.; Beyer, F.C.; Richter, E.; Irmscher, K.; Heitmann, J. Current Status of Carbon-Related Defect Luminescence in GaN. *Phys. Status Solidi A* 2021, 218, 2100235. [CrossRef]

34. Čiček, J. PLRF Code for Decomposition of Positron Lifetime Spectra. *Acta Phys. Pol. A* 2020, 137, 177–187. [CrossRef]

35. Mogensen, O.E. *Positron Annihilation Chemistry*, 1st ed.; Springer: Berlin, Germany, 1995.