Optically detected magnetic resonance studies of point defects in quaternary GaNAsP epilayers grown by vapor phase epitaxy

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Epitaxial III-V semiconductor light sources on silicon would tremendously increase the functionality of Si microelectronics and are promising for the realization of optoelectronic integrated circuits. For solar cell applications, Si-based multi-junction stacking would improve efficiency and reduce cost relative to conventional Si and III-V multi-junction cells. Direct epitaxial growth of conventional direct-band-gap III-V compounds (such as GaAs or InP) on Si is probably the most straightforward approach. However, due to a large lattice mismatch, high densities of threading or misfit dislocations and also point defects are formed in the III-V epitaxial films directly grown on Si substrates, preventing achievement of satisfactory performance. An exciting approach to circumvent this problem is epitaxial growth of compound semiconductors that are lattice matched to Si, such as the GaNxAsyP1-x-y quaternary alloy.

GaNAsP belongs to an interesting class of dilute nitrides that have recently attracted great attention owing to their fascinating physical properties. In dilute nitrides, the replacement of a small fraction (x ~ 1%) of phosphorus or arsenic atoms by nitrogen atoms causes highly nonlinear effects in the electronic properties of the host lattice. The pronounced effect of N on the band structure of GaP leads to a giant reduction in the bandgap energy and the N-induced crossover from an indirect bandgap in GaP to a quasi-direct bandgap in GaNP. This renders this material as having a high potential for visible light photonics. Therefore, detailed knowledge about nature and formation mechanisms of defects and their influence on physical properties of alloys is necessary in order to control them. Recently, we have demonstrated that Ga interstitial (GaI)–related defects are the dominant grown-in defects formed during molecular beam epitaxy (MBE) growth of both GaP and GaAs—based dilute nitrides. However, chemical identification of point defects in quaternary GaNAsP alloys is currently still lacking. The aims of the present work are: (a) to study and identify important grown-in defects in GaNAsP1-x-y, (b) to obtain information about the role of defects in carrier recombination processes, and finally, (c) to evaluate the obtained results in light of previous defects studies in dilute nitrides. Photoluminescence (PL) and optically detected magnetic resonance (ODMR) techniques will be employed for these purposes.

Defect properties of quaternary GaNAsP/GaP epilayers grown by vapor phase epitaxy (VPE) are studied by photoluminescence and optically detected magnetic resonance techniques. Incorporation of more than 0.6% of nitrogen is found to facilitate formation of several paramagnetic defects which act as competing carrier recombination centers. One of the defects (labeled as GaI-D) is identified as a complex defect that has a Ga interstitial (GaI) atom residing inside a Ga tetrahedron as its core. A comparison of GaI-D with other GaI-related defects known in ternary GaNP and GaNAs alloys suggests that this defect configuration is specific to VPE-grown dilute nitrides. © 2013 American Institute of Physics.

Optically detected magnetic resonance studies of point defects in quaternary GaNAsP epilayers grown by vapor phase epitaxy

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TABLE I. Parameters of the GaNAsP epilayers studied in this work.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>[N] (%)</th>
<th>[As] (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#15</td>
<td>0.6</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>#5</td>
<td>0.6</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>#14</td>
<td>0.6</td>
<td>11.5</td>
<td>400</td>
</tr>
<tr>
<td>#11</td>
<td>0.6</td>
<td>18</td>
<td>400</td>
</tr>
<tr>
<td>#13</td>
<td>0.9</td>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>#10</td>
<td>0.9</td>
<td>11.5</td>
<td>400</td>
</tr>
<tr>
<td>#12</td>
<td>1.2</td>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>#9</td>
<td>1.2</td>
<td>18</td>
<td>400</td>
</tr>
</tbody>
</table>
used for PL detection in the visible spectral range. ODMR signals were measured at X-band (9212 MHz) and Q-band (33 948 MHz) as spin-resonance induced changes of the PL intensity (detected by a Si photodiode) utilizing the lock-in technique in phase with an amplitude modulated microwave field at a frequency of 3 kHz.

Figure 1(a) shows effects of N and As incorporation on 5 K PL spectra of the GaNAsP alloys within the visible spectral range, which are dominated by excitonic emissions at N-related localized states. Incorporation of N and As induces a monotonous redshift in the peak position of these emissions reflecting a reduction in the alloy bandgap energy. In addition to the redshift, incorporation of both N and As also causes a strong decrease in the near-bandgap emission intensity. Such decrease is often caused by formation of defects during the growth that act as centers of competing carrier recombination. In order to study and identify these defects, detailed ODMR studies were carried out.

Typical ODMR spectra obtained by monitoring the excitonic emissions are presented in Fig. 1(b), as function of N and As compositions. Incorporation of N caused an appearance of several ODMR signals that were, however, somewhat quenched in the As-containing alloys. All observed ODMR signals are negative, i.e., correspond to a decrease in the near-band-edge PL intensity (they are shown as positive in Fig. 1(b) merely for easy viewing). Before discussing effects of N and As incorporation on the defect formation, let us first provide a brief overview of the detected ODMR signals, which can be attributed to several different paramagnetic centers. The first signal consists of a single, and rather narrow line which is related to a paramagnetic center with an effective electron spin $S = 1/2$ and $g$-value close to 2. It is detected only in the ternary GaNP with the lowest N content of 0.6% (sample #15 in Fig. 1(b)). Positive identification of the corresponding defect is not possible, unfortunately, due to a lack of resolved hyperfine structure. For higher N compositions (samples #13, #10, #12, and #9), the ODMR spectra contain a rich pattern of lines spreading over a wide field range. The corresponding multiline ODMR spectra were analyzed using the spin Hamiltonian applicable for defects with an effective electronic spin $S = 1/2$. $H = \mu_B B \cdot S + AS \cdot I$. Here, $\mu_B$ is the Bohr magneton, $B$ is the external magnetic field, and $A$ is the central hyperfine parameter that describes coupling of the electron spin with a nuclear spin $I$. The electronic $g$-factor and the $A$ parameter are scalars here, since all observed ODMR signals are isotropic. As shown in Fig. 2, the structure of the multiline ODMR spectra can be accurately reproduced by assuming a paramagnetic defect center with $S = 1/2$ and a strong hyperfine interaction between the localized electron spin and the nuclear spin of a Ga atom (60% 69Ga, 40% 71Ga, both with $I = 3/2$). The best fit to the experimental data is obtained by using the following spin-Hamiltonian parameters: $g = 2.01 \pm 0.01$, $A(69\text{Ga}) = 0.059 \pm 0.002 \text{cm}^{-1}$, and $A(71\text{Ga}) = 0.0749 \pm 0.002 \text{cm}^{-1}$. The ODMR curves simulated by using these parameters and assuming involvement of both Ga isotopes are shown in Fig. 2. To further confirm the validity of this assignment, measurements at two different MW frequencies were performed and are displayed in Figs. 2(a) and 2(b). The agreement between the simulations and the experimental results is excellent, thus justifying the assignments of the defects and reliability of the obtained fitting parameters.

We note that the defect center with the same parameters was previously detected in the MBE-grown GaNAs and was identified as a Ga-interstitial complex denoted by Ga$_i$-D. Based on this similarity, the same Ga$_i$-D label will also be used for the defect discussed in the present study. The modeling has also revealed that, in addition to Ga$_i$-D, two signals labeled as L1 and L2 in Fig. 2 contribute to the measured ODMR spectra. They originate from two different paramagnetic centers of an effective electron spin $S = 1/2$ with $g = 2.010$ and $g = 1.956$ for L1 and L2, respectively. A lack of a resolved hyperfine structure hinders chemical identification of the corresponding defects which, therefore, will be omitted from further discussion in the paper.

In principle, ODMR studies alone are incapable of determining absolute defect concentrations. However, they yield information on relative defect content in the samples and therefore, allow us to analyze the defect formation in the GaNAsP alloys as a function of the nitrogen and arsenic content. According to the results displayed in Fig. 1(b), the formation of Ga$_i$-D is facilitated by an increase in the N content above 0.6%. This is in analogy to the behavior of other Ga$_i$-related defects in ternary GaNP alloys grown by MBE, where the defect formation was found to be largely promoted by the presence of nitrogen. This indicates that either an N atom(s) is directly involved as a part of the Ga$_i$-related complexes, or N incorporation provides favorable conditions for...
defect formation energetically favorable. Consistent with vicinity of N could then reduce the strain energy making the concluded that the formation energy for Ga\textsubscript{i} defects is very which further supports our previous conclusions on technological importance of this class of defects. effects induced by surrounding N atoms. This means that low and could become even negative due to local bonding

This may mean that the presence of As decreases the local tensile strain which results in an increase in the formation energy and, therefore, a lower concentration of Ga\textsubscript{i}. Alternatively, the As-rich conditions may facilitate formation of other defects that are competing with Ga\textsubscript{i}-D in carrier recombination but cannot be detected by the ODMR technique. The last alternative seems to be more plausible. Indeed, all revealed ODMR signals are negative which means that enhancement of carrier recombination via the involved paramagnetic centers under the magnetic resonance conditions leads to a decrease of the monitored near-band-edge emission. This fact unambiguously proves that the corresponding defects act as efficient recombination centers that compete with the monitored radiative recombination. Consistently, the overall intensity of the near-band-edge PL decreases with increasing N content, i.e., under the conditions when the Ga\textsubscript{i}-D defects are effectively formed in the alloy. However, a decrease in the ODMR intensity in the As-containing alloys does not lead to an increase in the PL intensity which in fact is further reduced upon As incorporation. This suggests the formation of other defects that compete with radiative recombination but could not be detected by the ODMR technique (e.g., are not paramagnetic).

Let us now discuss possible local surrounding of the Ga\textsubscript{i}-D defect. In dilute nitrides, Ga\textsubscript{i}-related defects are formed in several configurations which differ by the hyperfine interaction strength and, therefore, local surrounding and/or a partner of the Ga\textsubscript{i} inside the complex. An interstitial atom in the zinc-blende III-V lattice may reside in three high symmetry positions. Two of these positions are of T\textsubscript{i} symmetry with group-III or group-V atoms in the nearest shell, whereas the third one with the D\textsubscript{3d} symmetry corresponds to an interstitial atom surrounded by both group-III and group V sublattices. Since As and P atoms have different nuclear spins and nuclear magnetic moments, exchanging one of these atoms in the nearest shell of a Ga\textsubscript{i} is expected to lead to an observable change in the HF interaction strength. Interestingly, we found that the HF interaction strength remains unaffected by an increase of the As content from 5\% to 18\% (sample #12 versus sample #9, see Fig. 1(b)). Moreover, Ga\textsubscript{i} with the same HF interaction strength was also observed in Ga\textsubscript{NAs} grown by metal organic chemical vapor deposition (MOCVD). The observed insensitivity of the HF interaction strength to the group-V element suggests that neither As nor P are a part of the nearest shell surrounding the Ga\textsubscript{i}-atom. This leads to the conclusion that Ga\textsubscript{i}-D resides at the center of a tetrahedron formed by four group-III atoms, e.g., Ga\textsubscript{r}. Such configuration was also found to be the most favorable from the total energy considerations. We need to note that the same local surrounding was also concluded for the Ga\textsubscript{i}-A defect in Ga(Al)NP\textsuperscript{7} and Ga(Al)NAs,\textsuperscript{8} which has the strength of hyperfine interaction of A\textsuperscript{(69Ga)} = 0.077 cm\textsuperscript{-1}, i.e., larger than that for Ga\textsubscript{i}-D. The reduced strength of the hyperfine interaction may imply that Ga\textsubscript{i}-D is likely a complex defect containing a Ga\textsubscript{i}, where weaker localization of the electron wavefunction on the Ga\textsubscript{i} atom is expected.

Although Ga\textsubscript{i}-related defects are commonly observed in both MBE and MOVPE grown dilute nitride alloys, different configurations of Ga\textsubscript{i} are formed in materials produced by these two growth techniques. The Ga\textsubscript{i}-D configuration seems to be unique to MOCVD-growth, the Ga\textsubscript{i}-D defect has so far only been found\textsuperscript{9} in the MOCVD-grown Ga\textsubscript{NAs}. On the

FIG. 2. Representative ODMR spectra measured at 5 K in (a) X-band and
(b) Q-band from the GaN\textsubscript{0.032}As\textsubscript{0.05}P\textsubscript{0.928} epilayer (sample #12). The uppermost curves in (a) and (b) are the experimental spectra measured by monitoring the total intensity of the PL emissions in the 630–710 nm spectral range. The simulated ODMR spectra from the three contributing defects are shown by the lowest three curves. The ODMR spectra simulated including the contributions of all three defects are labeled as “Σ” and are shown by the thick curves below the experimental spectra for an easy comparison. The applied magnetic field is directed parallel to the [001] crystallographic direction and the ODMR intensity is normalized to the PL intensity. The ODMR signals are isotropic and negative but they are shown as positive for easy viewing.
other hand, other Ga_{i}-species such as Ga_{i}-A, Ga_{i}-B, Ga_{i}-C, and Ga_{i}-E were detected in MBE-grown alloys. In principle, there could be several possible reasons for this effect, such as differences in growth temperature, residual contamination, or surface kinetics during the growth. We believe, however, that the growth temperature is not the main factor in the Ga_{i}-D formation, since we have not observed this defect in GaNP grown by MBE at 590 °C, i.e., at a similar growth temperature as was used during the MOCVD growth. Under the assumption that a residual contaminant is a part of the Ga_{i}-D defect, possible candidates known to be abundant in MOCVD-grown GaNP and Ga(In)NAs materials include carbon and hydrogen impurities. In both alloys, concentrations of H and C can easily surpass $10^{19}$ cm$^{-3}$ and are usually at least one order of magnitude higher than that typical for materials grown by solid source MBE.

The fact that only one Ga_{i} configuration is found in the MOVPE-grown dilute nitrides can be interpreted as an indication that this specific Ga_{i} configuration has the lowest formation energy in dilute nitrides grown by chemical reactions.

In conclusion, we have conducted a comprehensive study of the point defect formation in the GaNAsP epilayers grown by chemical vapor deposition. It is found that the incorporation of more than 0.6% of nitrogen facilitates formation of several paramagnetic defects which act as competing recombination centers and are, therefore, harmful to the performance of optoelectronic devices based on the GaNAsP alloy. One of the defects, namely Ga_{i}-D, is identified as a complex defect that has a Ga interstitial atom at its core. Based on the comparison of the deduced spin-Hamiltonian parameters for Ga_{i}-D with those known for other Ga_{i}-related defects in ternary GaNP and GaNAs alloys, the Ga_{i}-D configuration is concluded to be the dominant configuration of the Ga_{i}-related defects in MOVPE-grown dilute nitrides. It is also shown that Ga_{i}-D involves a Ga atom that is most likely surrounded by the group-III sublattice.

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12. Weaker intensities of the experimental ODMR lines at low fields as compared with that in the simulated spectra are because of modifications of recombination rates by mixing of states which become important at the low fields but were not included in the simulations.