Comparison of Triethylgallium and Trimethylgallium Precursors for GaInP Nanowire Growth

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Nanowire (NW) arrays containing a top segment of Ga$_x$In$_{1-x}$P are investigated, comparing NWs grown using two different Ga precursors, trimethylgallium (TMGa) and triethylgallium (TEGa). TMGa is the precursor commonly used for the particle-assisted vapor–liquid–solid (VLS) growth of Ga$_x$In$_{1-x}$P NWs. However, it shows inefficient pyrolysis at typical NW growth conditions. The use of the alternative precursor TEGa is investigated by making a direct comparison between NWs grown using TEGa and TMGa at otherwise identical growth conditions. Growth rates, resulting NW materials composition, and time-resolved photoluminescence (TRPL) lifetimes are investigated. With increasing Ga content of the NWs, the TRPL lifetimes decrease, indicating trap states that are associated with GaP. Somewhat longer TRPL lifetimes for the samples grown using TEGa indicate a lower concentration of deep trap states. For doped NWs, it is found that the strong effect of the p-type dopant diethylzinc (DEZn) on the NW composition, observed for Ga$_x$In$_{1-x}$P NWs grown using TMGa, is absent when using TEGa.

1. Introduction

Semiconductor nanowires (NWs) offer the unique possibility to form heterojunctions using materials with a relatively large lattice mismatch, enabled by strain relaxation along the radial direction of the NW.[1-3] This allows for flexible design of bottom–up synthesised III–V semiconductor NWs that are promising candidates for next generation photonic and optoelectronic devices.[4] Vertical arrays of NWs with optimized diameter and pitch support efficient light coupling due to nanophotonic resonance.[4-6] For photovoltaic applications, Ga$_x$In$_{1-x}$P, in particular, is suitable as a top cell material with a higher bandgap than the bottom cell in a tandem junction NW solar cell configuration, ideally in combination with an InP, GaAs, or Si bottom cell.[7-9] In this article, we will focus on arrays of NWs containing a Ga$_x$In$_{1-x}$P top segment and an InP bottom segment.

III–V NWs can be synthesized bottom–up using metal-organic vapor phase epitaxy (MOVPE) by means of the vapor–liquid–solid (VLS) growth mechanism with Au seed particles.[10] For the growth of Ga$_x$In$_{1-x}$P NWs, the Ga precursor trimethylgallium (TMGa) is commonly used.[11-16] However, TMGa has the disadvantage of inefficient pyrolysis at typical NW growth temperatures (400–480 °C), which can complicate growth dynamics.[17] Triethylgallium (TEGa) can be used as an alternative Ga precursor for NW growth.[18,19] Recently, Dagyt et al. have investigated the growth dynamics of nominally intrinsic Ga$_x$In$_{1-x}$P NW arrays grown using TEGa.[20] However, more extensive knowledge about the properties of the Ga$_x$In$_{1-x}$P material grown by the use of TEGa is needed for its successful use in NW optoelectronic devices.

The aim of this article is to compare the growth and material properties of Ga$_x$In$_{1-x}$P NW segments grown using TEGa and TMGa as Ga precursors at otherwise identical conditions. We consider both nominally intrinsic NWs, as well as Ga$_x$In$_{1-x}$P segments uniformly doped by using the dopant precursors hydrogen sulfide (H$_2$S), tetraethyltin (TESn), and diethylzinc (DEZn). The direct comparison between Ga$_x$In$_{1-x}$P grown by the use of TEGa and TMGa will support an informed choice of the most suitable precursor for the growth of NW devices. By studying the growth dynamics of doped Ga$_x$In$_{1-x}$P grown using TEGa, we also pave the way toward the synthesis of pn junction NW devices containing Ga$_x$In$_{1-x}$P segments grown with this precursor.

2. Experimental Section

We defined hexagonal arrays of Au catalyst particles using nanoimprint lithography on InP (111)B substrates, as described in the study by Otnes et al.[21] Electron beam evaporation was used to deposit 65 nm of Au, followed by a liftoff step to remove excess gold. The resulting Au particles had a diameter of 200 nm, forming a hexagonal array with a pitch of 500 nm.
From these, we grew NW arrays in an Aixtron 200/4 MOVPE reactor operating at a temperature of 440 °C and a total pressure of 100 mbar. Hydrogen was used as a carrier gas maintaining a total flow of 13 L min\(^{-1}\). To preserve the hexagonal pattern, the growth was started with a 60 s preanneal nucleation step at 280 °C, followed by annealing at 550 °C for 10 min under a flow of phosphine (PH\(_3\)) at a molar fraction of \(x_{\text{PH}_3} = 3.46 \times 10^{-3}\).\(^{[21]}\)

The NW growth was then initiated by introducing TMIn at a molar fraction of \(x_{\text{TMIn}} = 0.59 \times 10^{-4}\), as well as the in situ etchant HCl (\(x_{\text{HCl}} = 1.23 \times 10^{-4}\)) to prevent tapering. HCl leads to the chlorination of In- and Ga-based species which impedes parasitic shell growth.\(^{[22,23]}\) The temperature was held at 440 °C and the PH\(_3\) molar fraction at \(x_{\text{PH}_3} = 0.69 \times 10^{-2}\) during the growth of all samples. The growth temperature of 440 °C was chosen as a compromise between the optimal temperatures for InP and GaP binary growth.

We evaluated the NW length in situ using a LayTec EpiR DA UV optical reflectometry system.\(^{[24]}\) To mimic the structure and growth dynamics of the pursued tandem InP/Ga\(_{1-x}\)P NW solar cells, we grew 0.9 ± 0.1 μm long Ga\(_{1-x}\)In\(_x\)P segments on the top of 0.8 ± 0.1 μm long InP stubs. The growth time of each segment was adjusted in situ to match the desired length. While the flows of In and Ga precursors for the Ga\(_{1-x}\)In\(_x\)P segment were varied, the conditions for the InP growth were held constant for all samples, using \(x_{\text{TMIn}} = 0.59 \times 10^{-4}\) and without introducing intentional doping (i.e., nominally intrinsic). The key parameters for all samples grown in this article are shown in Table S1 in the Supporting Information.

In the first set of growth runs, we grew nominally intrinsic Ga\(_{1-x}\)In\(_x\)P segments on InP stubs. The molar fractions of the Ga and In precursors (TEGa/TMGa and TMIn, respectively) were varied, aiming for a Ga content in the Ga\(_{1-x}\)In\(_x\)P NWs in the vicinity of \(x = 0.3\) at an average growth rate around 1 nm s\(^{-1}\). We found the following growth parameters to match these requirements: \(x_{\text{TMIn}} = 0.25 \times 10^{-4}\) and \(x_{\text{TMGa}} = 2.9 \times 10^{-4}\) when using TEGa. \(x_{\text{TMIn}} = 0.59 \times 10^{-4}\) and \(x_{\text{TEGa}} = 0.75 \times 10^{-4}\) when using TEGa.

To identify the effects of adding dopant precursors to the reactor flow, we grew intended Ga\(_{0.7}\)In\(_{0.3}\)P on InP structures while introducing the dopant precursors during growth of the Ga\(_{1-x}\)In\(_x\)P segment. In each sample, one of the precursors H\(_3\)S at \(x_{\text{H}_3\text{S}} = 0.035 \times 10^{-4}\), TESn at \(x_{\text{TESn}} = 0.44 \times 10^{-4}\), and DEZn at \(x_{\text{DEZn}} = 0.15 \times 10^{-4}\) was introduced, while the other growth parameters were generally kept the same. The dopant precursors H\(_3\)S and TESn were known to lead to n-type doping in Ga\(_{1-x}\)In\(_x\)P NWs, whereas DEZn resulted in p-type doping.\(^{[12,13]}\) The dopant molar fractions were chosen similar to the established values used for the growth of pn junctions in InP NW solar cells.\(^{[25,26]}\)

All samples were inspected in a Zeiss LEO 1560 field emission scanning electron microscope both in a top-view configuration and at a 30° tilt angle towards the normal of the plane. We observed a high NW yield (>98%) for all samples. The elemental composition (i.e., \(x\) in Ga\(_{1-x}\)In\(_x\)P) was determined from X-ray diffraction (XRD) measurements by the use of Vegard’s law, based on the 2θ angle with the maximum XRD signal. The compositional variation of the NWs was assessed using the full width at half maximum (FWHM) of the XRD peak. Although there is also some variation between individual NWs, the XRD peak FWHM is predominantly determined by the compositional variation along the NW axis.\(^{[20]}\) The XRD measurements were performed normal to the (111)B plane (i.e., the sample surface) using Cu Kα radiation (\(λ = 1.541\) Å).

We used time-resolved photoluminescence (TRPL) to study the dynamics of photogenerated charge carriers in several nominally intrinsic samples. The output of a Ti:Sapphire laser (Spectra-Physics, Tsunami, repetitive pulse frequency of 80 MHz, pulse duration of 100 fs, and \(λ = 800\) nm) was frequency doubled to 400 nm. The excitation beam was introduced at a 70° angle of incidence, which is close to the Brewster angle of the InP substrate. The samples were kept in an N\(_2\) atmosphere chamber during the measurement. The photoluminescence (PL) emission from the Ga\(_{1-x}\)In\(_x\)P NW arrays was collected by a spectrometer (Chromex), and the output of the spectrometer was transferred to a streak camera (Hamamatsu C6860). The detected TRPL images were calibrated by a standard lamp (Ocean Optics, LS-1-CAL).

### 3. Results and Discussion

During the first set of growth experiments, where we grew nominally intrinsic Ga\(_{1-x}\)In\(_x\)P on InP, we varied the flows of the In and Ga precursors, and thereby explored the growth parameter space with respect to the group III precursor molar fractions. Such a mapping of the parameter space is so far available in the literature for Ga\(_{1-x}\)In\(_x\)P grown with TEGa,\(^{[20]}\) but not for TMGa as a precursor. Information on how the composition and growth rate of a ternary material varies with precursor flows is important for finding suitable growth parameters and for comparing the results after growth using different precursors for synthesis, which is the aim of this article.

Using TMGa, we grew seven samples with the molar fractions varying in the ranges \(x_{\text{TMIn}} = 0.15–0.46 \times 10^{-4}\) and \(x_{\text{TMGa}} = 2.9–23.9 \times 10^{-4}\). The growth rates of the Ga\(_{1-x}\)In\(_x\)P segment were observed to be between 0.8 and 2.9 nm s\(^{-1}\) as determined by in situ optical reflectometry. They are plotted as a function of both \(x_{\text{TMIn}}\) and \(x_{\text{TMGa}}\) as shown in Figure 1a. The corresponding Ga content \(x\) of the Ga\(_{1-x}\)In\(_x\)P varied between 0.17–0.68 and is shown in Figure 2a. Please note that the x and y axes are arranged in different ways when comparing Figure 1 and 2.

For the Ga\(_{1-x}\)In\(_x\)P NW growth using TEGa, we can rely on the extensive study of growth kinetics by Dagyte et al. at similar conditions.\(^{[20]}\) To have robust data to compare TEGa and TMGa growth kinetics, we used the data from the study by Dagyte et al.\(^{[20]}\) for Figure 1b and Figure 2b. To verify the status of the reactor, we synthesized Ga\(_{1-x}\)In\(_x\)P with parameters developed in the study by Dagyte et al.\(^{[20]}\) with similar results.

The (purely phenomenological) planes fitted to the data points shown in Figure 1 and 2 are helpful for understanding the effect of precursor molar fractions on the growth dynamics within the studied ranges. For example, we can follow mesh lines in Figure 1a,b to observe the effect of TMIn molar fraction on the Ga\(_{1-x}\)In\(_x\)P growth rate \(R\) at a constant \(x_{\text{TMGa}}\) or \(x_{\text{TEGa}}\). We observe that an increasing TMIn molar fraction leads to a higher Ga\(_{1-x}\)In\(_x\)P growth rate, irrespective of the used Ga precursor. This would of course be expected based on increased In
incorporation. Similarly, an increase in the Ga precursor molar fractions, $\chi_{\text{TMGa}}$ and $\chi_{\text{TEGa}}$, also leads to an increased growth rate. However, note that the magnitude of the used Ga precursor flow is very different in the two cases. A molar fraction $\chi_{\text{TMGa}}$ that is one order of magnitude higher than typical values for both $\chi_{\text{TMIn}}$ and $\chi_{\text{TEGa}}$ had to be used to achieve a noted increase in the growth rate $R$. This is supported by the low value of $\Delta R/\Delta \chi_{\text{TMGa}} = 0.065 \times 10^4 \text{nm}$ in Table S2, Supporting Information, where we compiled the slopes characterizing the fitted planes shown in Figure 1 and 2. For comparison, $\Delta R/\Delta \chi_{\text{TEGa}}$ and $\Delta R/\Delta \chi_{\text{TMIn}}$ are all on the order of $1 \times 10^4 \text{nm}$. The low efficiency of Ga incorporation when using TMGa as a precursor for Ga$_x$In$_{1-x}$P NW growth has been noted previously. It can be attributed to an inefficient pyrolysis in combination with an inhibitory effect of TMIn on the Ga incorporation.[15,20]

This reduction of Ga incorporation efficiency by TMIn also affects the Ga$_x$In$_{1-x}$P composition, which is shown in Figure 2a,b. We observe that an increasing TMIn flow at a constant value of either $\chi_{\text{TMGa}}$ or $\chi_{\text{TEGa}}$ leads to a lower Ga fraction $x$ in Ga$_x$In$_{1-x}$P, corresponding to a higher In fraction $(1-x)$ in the solid. While a shift of the Ga$_x$In$_{1-x}$P composition based on increased incorporation of In into the solid is expected, the observed change in composition is stronger than one would expect from a linear relation. By plotting the effective binary growth rate $R_{\text{GaP}}$ (not shown), we find a reduction of $R_{\text{GaP}}$ with increasing $\chi_{\text{TMIn}}$. This means that the use of a higher $\chi_{\text{TMIn}}$ hinders the incorporation of Ga into the NW (irrespective of the Ga precursor), in accordance with previous reports using both TMGa and TEGa.[15,20] The mechanism responsible for this effect has not been identified conclusively yet.

In contrast, an increase in the Ga precursor molar fraction leads to different results for TMGa and TEGa. When using TEGa, increasing $\chi_{\text{TEGa}}$ results in a higher Ga fraction in the solid (Figure 2b). The GaP effective binary growth rate $R_{\text{GaP}}$ increases, almost linearly, whereas $R_{\text{InP}}$ remains constant (not shown). Using TMGa, the situation is observed to be more complex. Interestingly, a higher molar fraction $\chi_{\text{TMGa}}$ does not lead to an increased Ga content in the Ga$_x$In$_{1-x}$P, instead it remains...
essentially unchanged (Figure 2a). As we observe that the growth rate increases, this means that adding more TMGa precursor to the gas phase must lead to more incorporation of both Ga and In into the solid, by about equal amounts. The additional incorporation of In and the amount of it is surprising, and has not been analyzed in the literature yet.

We speculate that this effect may be explained by an increased surface diffusion of In containing species when supplying a high molar fraction of TMGa. TMGa decomposes in a three-step process, liberating one methyl group during each step. The third methyl–gallium bond is the most stable, with a bond energy of 65 kcal mol\(^{-1}\), which can result in an accumulation of monomethylgallium (MMGa), possibly even leading to the formation of a solid (GaCH\(_3\))\(_n\) polymer. The accumulation and diffusion of MMGa has previously been observed to play a significant role in the growth of GaP NWs. In the case of Ga\(_{1-x}\)In\(_x\)P, we speculate that MMGa species adsorb on the NW and substrate surface, saturating dangling bonds, and thereby increase the surface migration length of In containing species, effectively boosting the amount of In available at the catalytic Au particle. It is known that In incorporation is surface migration limited, which causes a lower In incorporation during the later stages of growth, and ultimately a compositional variation of the Ga\(_{1-x}\)In\(_x\)P along the NW. We observe that the compositional variation of the NWs, quantified in terms of the XRD peak FWHM (see Table S1, Supporting Information), is reduced for the samples where a high X\(_{\text{TMGa}}\) was used (especially when comparing with samples grown using TEGa), in agreement with the postulated longer In surface migration length.

Concluding the discussion of growth kinetics, Ga\(_{1-x}\)In\(_x\)P/InP NW growth has been achieved with high yield using both TMGa and TEGa precursors. We have observed that the inefficient pyrolysis of the TMGa precursor leads to a complex dependence of Ga\(_{1-x}\)In\(_x\)P NW growth rate and composition on the group III precursor molar fractions. These observations favor the use of the alternative Ga precursor TEGa for Ga\(_{1-x}\)In\(_x\)P NW growth when high control over reproducibility and materials’ compositional stability is necessary.

For semiconductor solar cells, in situ doping is commonly used to create a pn junction for charge carrier separation and photovoltaic activity. It has been observed that the addition of dopant precursors, such as DEZn used for p-type doping, can strongly affect the NW growth dynamics, which limits the control over synthesis. For ternary materials, such as Ga\(_{1-x}\)In\(_x\)P, dopant-induced changes of the NW composition are especially concerning, as they can hamper the band structure design.

As detailed in the Experimental Section, we have grown NWs introducing the n-type dopant precursors H\(_2\)S and TESn as well as the p-type dopant precursor DEZn at concentrations relevant for the doping of NW solar cells. Although the doping of Ga\(_{1-x}\)In\(_x\)P NWs grown with TMGa has been studied before, that is not the case for Ga\(_{1-x}\)In\(_x\)P NWs grown using TEGa as a Ga precursor. Note that the effects of dopants can differ strongly between samples grown with or without the in situ etchant HCl, consequently, our results are primarily applicable to NW growth where HCl is used.

As expected from previous studies, H\(_2\)S and TESn doping did not affect the Ga\(_{1-x}\)In\(_x\)P NWs grown using TMGa strongly, only resulting in a slight decrease in the incorporated Ga fraction (by 0.06). Similarly, when using the precursor TEGa, we found that doping by the use of H\(_2\)S resulted in a slight decrease in the incorporated Ga fraction x by 0.05, whereas TESn did not affect the composition.

Doping with DEZn can reportedly affect the growth dynamics of Ga\(_{1-x}\)In\(_x\)P very strongly, as it enhances the pyrolysis of TMGa, leading to more Ga-rich NWs. We therefore reduced the TMGa flow to \(X_{\text{TMGa}} = 1.0 \times 10^{-4}\), whereas simultaneously increasing the TMIn flow to \(X_{\text{TMIn}} = 0.37 \times 10^{-4}\). Thereby, we reduced the group III precursor ratio from \(X_{\text{TMGa}}/X_{\text{TMIn}} = 11.4\) to \(X_{\text{TMGa}}/X_{\text{TMIn}} = 2.8\), that is to say by a factor of 4. This led to a Ga\(_{1-x}\)In\(_x\)P composition of \(x = 0.30\), which is comparable to the other doped NW samples in this article. Discussing the pyrolysis of TMGa in the presence of DEZn more specifically, ethyl radicals from the pyrolysis of DEZn are expected to attack the partially decomposed Ga compound MMGa via the generation of hydrogen radicals. Therefore, the presence of DEZn will enhance the supply of elemental Ga to the growth.

Conversely, the effect of the DEZn dopant on the composition and growth rate of the Ga\(_{1-x}\)In\(_x\)P segment grown with the alternative Ga precursor TEGa was minimal. We observed only a slight increase in the Ga content of the NWs by 0.06, in stark contrast to the dominant influence of DEZn on the growth kinetics when using TMGa. Clearly, this is due to the complete pyrolysis of TEGa at the growth temperature, which is therefore not affected by the addition of DEZn. This is favorable for the growth of Ga\(_{1-x}\)In\(_x\)P NW optoelectronic devices, such as pn junctions, where a constant materials’ composition is desirable.

As first shown by Algra et al. for InP and later confirmed for both InP and GaP, the addition of DEZn during NW growth can change the crystal structure of the NWs from a mixture of wurtzite (WZ) and zinc-blende (ZB) to predominantly ZB. Interestingly, for a high enough DEZn concentration, a twinning superlattice (TSL) is induced, characterized by regularly spaced twin planes in the ZB crystal structure. Although it is suggested that this TSL can be used for optoelectronic devices based on the indirect-bandgap material GaP, the longer ZB segments can act as electron traps and affect the electrical properties of NW negatively.

Scanning electron microscope images can be used for an estimation of the NW crystal structure. NWs with a mixed WZ/ZB or predominantly WZ crystal structure usually have smooth sidewalls. In contrast, the sidewalls of NWs with ZB segments separated by twin planes appear rough, as the alternating (111)A and (111)B side facets of each segment are tilted with respect to the NW axis. Finally, when the twin plane spacing is regular (i.e., forming a TSL), a periodic structuring of the sidewalls can be observed.

Scanning electron microscope images of NWs doped with DEZn are shown in Figure 3a,b. The DEZn-induced TSL can
be observed as a distinctly periodic patterning along the NW axis, in agreement with the study by Algra et al.\[42\] This is correlated with a slightly reduced NW diameter (by about 5–10 nm). The changed surface energies in the presence of DEZn lead to a larger contact angle, and thereby reduced NW diameter.\[41\]

Interestingly, rough NW sidewalls are even seen in the TESn-doped NWs that were grown by the use of TEGa (Figure 3d), which suggests a prevalence of ZB crystal structure with irregularly spaced twin planes. Conversely, smooth sidewalls are observed when TMGa was used (Figure 3c), corresponding to a mixed or WZ-rich distribution of crystal structures.

Similarly, we have analyzed all the samples in this article with respect to the sidewall morphology. We found that all nominally intrinsic samples with low Ga content ($x < 0.4$) in the $\text{Ga}_x \text{In}_{1-x} \text{P}$ have smooth sidewalls, see, for example, Figure S1a,b, Supporting Information. The same is observed for the samples doped using $\text{H}_2\text{S}$. In contrast, we observe somewhat rougher NW sidewalls for the nominally intrinsic TEGa sample with a high Ga content of $x = 0.52$, see Figure S1d, Supporting Information. In the TMGa sample with a similarly high Ga content, we observe some NWs with a smooth sidewall, but the high density of misshapen NWs indicates unstable growth conditions, see Figure S1c, Supporting Information.

In summary, we observe that TEGa facilitates the formation of NWs with a higher proportion of ZB crystal structure. This becomes evident when growing $\text{Ga}_x \text{In}_{1-x} \text{P}$ with a high Ga content $x$ or doped with TESn. The reason is assumed to be a reduction of the liquid–solid interface energy of the ZB structure in the presence of TEGa, similarly to the (more pronounced) effect observed when doping by the use of DEZn.\[41\] Further experiments will have to be conducted to understand possible effects of the larger proportion of ZB segments in $\text{Ga}_x \text{In}_{1-x} \text{P}$ grown by the use of TEGa on the device performance.

To assess the materials' quality of the $\text{Ga}_x \text{In}_{1-x} \text{P}$ grown with different precursors, we have measured the TRPL of several nominally intrinsic NW array samples. The TRPL decays at an excitation photon flux of $2 \times 10^{11}$ photons cm$^{-2}$ pulse$^{-1}$ are shown in Figure 4a,b for samples grown by the use of TMGa and TEGa, respectively. For both precursors, we observe a faster TRPL decay with increasing Ga content. This is in line with

![Figure 3](image-url)

**Figure 3.** Scanning electron micrographs of InP/$\text{Ga}_x \text{In}_{1-x} \text{P}$ NW arrays, taken at a tilt angle of 30° toward the normal of the plane. Scale bar: 500 nm. The NWs contain a top segment of $\text{Ga}_x \text{In}_{1-x} \text{P}$ (800–900 nm long) and a bottom segment of InP (600–700 nm long). a,c) The NWs are grown using TMGa, b,d) the NWs are grown using TEGa. In the NWs shown in (a) and (b), the $\text{Ga}_x \text{In}_{1-x} \text{P}$ segment is doped by the use of DEZn, whereas in (c) and (d), it is doped using TESn. In the upper segments of the NWs in (a) and (b), the characteristic periodic structure of a TSL is observable. Also, the diameter of the $\text{Ga}_x \text{In}_{1-x} \text{P}$ segment is slightly reduced in these samples. Please note that the TSL can best be seen using a computer display, and might not be evident in the printed images. In (d), rough sidewalls are observed, suggesting a ZB crystal structure with irregular twin planes.

![Figure 4](image-url)

**Figure 4.** Composition-dependent normalized TRPL decays of $\text{Ga}_x \text{In}_{1-x} \text{P}$ NW arrays excited at 400 nm at a fluence of $2 \times 10^{11}$ photons cm$^{-2}$ pulse$^{-1}$. The $\text{Ga}_x \text{In}_{1-x} \text{P}$ NW composition is indicated in the legend. a) NWs grown using TMGa. b) NWs grown using TEGa.
previous experiments on Ga\textsubscript{x}In\textsubscript{1-x}P NWs grown using TMGa, where the effect was explained in terms of a higher concentration of deep trap states with increasing Ga content.\cite{46} These deep traps can be speculatively assigned to surface states occurring in GaP, possibly Ga vacancies at the NW surface.\cite{47,48}

When comparing the TRPL decay of samples with similar Ga content grown using TMGa and TEGa, we observe somewhat longer lifetimes for the NWs grown using TEGa. We interpret this as a lower density of deep trap states in these Ga\textsubscript{x}In\textsubscript{1-x}P NWs. This can lead to beneficial optoelectronic device characteristics when using TEGa as a Ga precursor. However, further studies will be needed to establish if the favorable characteristics of Ga\textsubscript{x}In\textsubscript{1-x}P NWs grown by the use of TEGa persist after surface passivation of the NWs, which can reportedly have a considerable effect on the TRPL lifetimes.\cite{49,50}

Excitation power-dependent TRPL decays of two representative samples with a similar Ga content are shown in Figure 5a,b (see Figure S2, Supporting Information, for the other measured samples). In the Ga\textsubscript{0.3}In\textsubscript{0.7}P NW array grown by the use of TEGa, seen in Figure 5b (and similarly in Figure S2b, Supporting Information, with a higher Ga content), we observe a slower PL decay at higher excitation powers. This type of power dependence was previously associated with the filling of trap states under high fluence, leading to a longer average lifetime of the excited carriers.\cite{46,51,52} In accordance with the model presented for Ga\textsubscript{x}In\textsubscript{1-x}P NWs in the study by Zhang et al.,\cite{46} we assign this observation to the filling of shallow trap states that coexist with the deep level traps mentioned earlier. Plotting the 1/e lifetimes as a function of excitation intensity supports the interpretation of coexisting deep and shallow trap states, particularly for the NW arrays grown by the use of TEGa (see Figure S4, Supporting Information). The fast initial TRPL decay at low excitation intensity is due to a loss of free carriers into shallow traps. Electrons and holes in shallow traps can be thermally excited and then recombine or be trapped again. Over time, trapping and thermally excited detrapping processes lead to a redistribution of charge carriers between the spatially and energetically distributed shallow traps.\cite{46} Therefore, the TRPL decay will slow down, which can be observed as a nonexponential TRPL decay. Please note that the shallow trap states observed primarily in the NWs grown by the use of TEGa will not necessarily impact NW solar cell device performance, where the steady-state illumination leads to a continuous generation of charge carriers, such that the shallow traps are expected to be filled constantly.\cite{53}

On the basis of the following argumentation, we interpret the observed shallow traps primarily found in the Ga\textsubscript{x}In\textsubscript{1-x}P samples grown by the use of TEGa as a spatial localization of electrons and holes in ZB- and WZ-rich areas of the NW, respectively. In general, the ZB and WZ crystal phases of Ga\textsubscript{x}In\textsubscript{1-x}P have different conduction band (CB) and valence band (VB) energies, with a staggered (type II) band alignment. Both the CB edge and VB edge lie lower in energy for ZB Ga\textsubscript{x}In\textsubscript{1-x}P compared to WZ, and the ZB crystal phase also has a lower bandgap.\cite{54} Electron states localized in ZB-rich regions of a Ga\textsubscript{x}In\textsubscript{1-x}P NW are therefore energetically favorable, as are hole states localized in WZ-rich regions.\cite{55} Recombination can occur between electrons and holes trapped in neighboring ZB/WZ segments of a NW, termed as type II recombination.\cite{56,57} The lower recombination rates of the spatially separated charge carriers lead to a fast decrease in PL intensity at early times due to the trapping of free carriers, but also to a slower (i.e., nonexponential) subsequent decay of the PL signal, as observed in the measured TRPL decays.

These results are in good agreement with our findings concerning the Ga\textsubscript{x}In\textsubscript{1-x}P crystal structure, where we observed a trend toward a higher proportion of ZB crystal structure in NWs grown by use of TEGa. The resulting longer segments of ZB Ga\textsubscript{x}In\textsubscript{1-x}P act as efficient (shallow) electron traps.\cite{44} This interpretation further agrees with the more pronounced effects of trap filling that we observe in the NWs grown using TEGa, and supports our assignment of charge carrier trapping in ZB/WZ segments of the NWs.

PL spectra were extracted from the streak camera images at the time of peak intensity and at a delay time of 200 ps. Figure 6 shows the extracted PL spectra for representative Ga\textsubscript{0.3}In\textsubscript{0.7}P NW arrays grown by the use of TMGa and TEGa, respectively. The spectra of all further measured samples are shown in Figure S3, Supporting Information. We observe a redshift of the PL by 10–12 nm (corresponding to 25–40 meV) at a delay time of 200 ps after excitation in the samples grown by the use of TEGa, whereas such a shift is not observed for the TMGa samples. This observation further strengthens the proposed trapping of electrons in lower bandgap ZB segments of the NWs grown by the use of TEGa. Apparently, over time the charge

Figure 5. Excitation power-dependent normalized TRPL decays of Ga\textsubscript{0.3}In\textsubscript{0.7}P NW arrays excited at 400 nm under the indicated photon fluxes per pulse. a) Ga\textsubscript{0.3}In\textsubscript{0.66}P NWs grown using TMGa. b) Ga\textsubscript{0.3}In\textsubscript{0.7}P NWs grown using TEGa.
carriers are trapped in lower energy positions, which leads to a decrease in the emitted photon energies. The magnitude of the PL peak position shift of 25–40 meV appears reasonable considering the difference in bandgap between WZ and ZB being in the range of 45–84 meV for Ga\textsubscript{x}In\textsubscript{1–x}P, depending on the composition.[54]

4. Conclusion

In this article, we have compared the characteristics of Ga\textsubscript{x}In\textsubscript{1–x}P NW segments grown using TMGa and TEGa as Ga precursors. We have shown the complex dependence of NW growth on the TMGa and TMIn fluxes and confirmed the issue of low Ga incorporation efficiency when using TMGa as a precursor. Furthermore, we found that the strong influence of DEZn doping on the Ga\textsubscript{x}In\textsubscript{1–x}P NW composition grown using TMGa (leading to an increased Ga content) is absent when using TEGa, which is advantageous for the growth of doped NW optoelectronic devices with a uniform materials composition. From an analysis of the NW morphology, we have confirmed the strong effect of DEZn on the NW crystal structure, inducing a ZB crystal structure with regularly spaced twin planes. We discovered that TEGa also favors the formation of an increased proportion of ZB segments in Ga\textsubscript{x}In\textsubscript{1–x}P NWs. Further research is needed to establish if this influences the electrical properties of the resulting Ga\textsubscript{x}In\textsubscript{1–x}P NW devices.

Finally, we have measured the TRPL of NW arrays to characterize the Ga\textsubscript{x}In\textsubscript{1–x}P materials' quality. We observed a shorter lifetime with increasing Ga content in the NWs, which was associated with deep trap states. The somewhat longer lifetimes in NW arrays grown by the use of TEGa indicate a lower density of deep traps. By investigating the excitation power-dependent TRPL decays, we have detected the presence of shallow trap states, in particular, in the NWs grown using TEGa. We correlated these shallow traps with the crystal structure, and postulated that they correspond to electron and hole trapping in ZB- and WZ-rich parts of the NW, respectively.

In conclusion, we have compared the growth rates, composition, and optical properties of Au seeded Ga\textsubscript{x}In\textsubscript{1–x}P NWs grown by the use of TMGa and TEGa, and established the suitability of TEGa as a precursor for the growth of NW optoelectronic devices.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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GaInP, metal-organic vapor phase epitaxy, nanowires, triethylgallium, trimethylgallium

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[1] M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, C. M. Lieber, Nature 2002, 415, 617.
[2] G. E. Cirillo, V. G. Dubrovskii, I. P. Soshnikov, N. V. Sibirev, Yu. B. Samsonenko, A. D. Bouravlev, J. C. Harmand, F. Glas, Phys. Status Solidi RRL 2009, 3, 112.
[3] R. Yan, D. Gargas, P. Yang, Nat. Photon. 2009, 3, 569.
[4] N. Anttu, H. Q. Xu, Opt. Express 2013, 21, A558.
[5] N. Anttu, A. Abrand, D. Asoli, M. Heurlin, I. Åberg, L. Samuelson, M. Borgström, Nano Res. 2014, 7, 816.
[6] J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. Åberg, M. H. Magnusson, G. Siefer, P. Fuss-Kailuweit, F. Dimroth,
