Growth kinetics of $\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowires using triethylgallium as Ga precursor

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Abstract

$\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowire arrays are promising for various optoelectronic applications with a tunable band-gap over a wide range. In particular, they are well suited as the top cell in tandem junction solar cell devices. So far, most $\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowires have been synthesized by the use of trimethylgallium (TMGa). However, particle assisted nanowire growth in metal organic vapor phase epitaxy is typically carried out at relatively low temperatures, where TMGa is not fully pyrolysed. In this work, we developed the growth of $\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowires using triethylgallium (TEGa) as the Ga precursor, which reduced Ga precursor consumption by about five times compared to TMGa due to the lower homogeneous pyrolysis temperature of TEGa. The versatility of TEGa is shown by synthesis of high yield $\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowire arrays, with a material composition tunable by the group III input flows, as verified by x-ray diffraction measurements and photoluminescence characterization. The growth dynamics of $\text{Ga}_x\text{In}_{(1-x)}\text{P}$ nanowires was assessed by varying the input growth precursor molar fractions and growth temperature, using hydrogen-chloride as in situ etchant. We observed a complex interplay between the precursors. First, trimethylindium (TMIn) inhibits Ga incorporation into the nanowires, resulting in higher In composition in the grown nanowires than in the vapor. Second, the growth rate increases with temperature, indicating a kinetically limited growth, which from nanowire effective binary volume growth rates of InP and GaP can be attributed to the synthesis of GaP in $\text{Ga}_x\text{In}_{(1-x)}\text{P}$. We observed that phosphine has a strong effect on the nanowire growth rate with behavior expected for a unimolecular Langmuir–Hinshelwood mechanism of pyrolysis on a catalytic surface. However, growth rates increase strongly with both TEGa and TMIn precursors as well, indicating the complexity of vapor–liquid–solid growth for ternary materials. One precursor can affect the decomposition of another, and each precursor can affect the wetting properties and catalytic activity of the metal particle.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Epitaxially grown semiconductor nanowires show important benefits for photovoltaics (PV) such as efficient absorption of light [1–5] and strain relaxation via the free surface [6–8]. The progress of III–V semiconductor nanowires for PV has been demonstrated by numerous research groups [9–19]. In particular, high efficiency InP [10, 19] and GaAs [11] nanowire solar cells have recently been reported with nanowires covering only a fraction of the substrate surface while still showing bulk-like photocurrent generation level. Moving forward, tandem solar cell development is an important goal
and a starting point is development of a higher band-gap top cell.

For InP, GaAs, and Si bottom cells, Ga\(_{x}\)In\(_{1-x}\)P can be tuned in materials composition to have a suitable band-gap for the top cell in a tandem configuration. So far, most of the reported Ga\(_{x}\)In\(_{1-x}\)P nanowire synthesis have been performed by using trimethylgallium (TMGa) as the Ga precursor [20–24]. However, particle assisted nanowire growth in metal organic vapor phase epitaxy (MOVPE) is typically carried out at relatively low temperatures (i.e. 440 °C [25]), where TMGa is not fully pyrolysed. Triethylgallium (TEGa), on the other hand, is known to have a lower homogeneous pyrolysis temperature (≈350 °C) than TMGa (≈480 °C), similar to trimethylindium (TMIn) (≈350 °C) [26]. This should result in a simplified growth mechanism during precursor and temperature variations since both group III precursors would be expected to be fully pyrolysed. In fact, TEGA is commonly used for low temperature Ga\(_{x}\)In\(_{1-x}\)P layer by layer growth [27, 28] since at lower growth temperature the use of TMGa instead of TMGa leads to higher material quality due to reduced carbon incorporation in layers [26]. Additionally, a more complete pyrolysis of TEGA compared to TMGa at nanowire growth temperatures can lead to a more efficient use of growth precursors.

In this paper, we analyze MOVPE growth of a gold-seeded dense periodic array of Ga\(_{x}\)In\(_{1-x}\)P nanowires on an InP (111)B substrate, using TEGA, TMIn and phosphine (PH\(_3\)) as precursors, and hydrogen-chloride (HCl) as an in situ etchant [29–31]. We observe that the Ga precursor material consumption is reduced by about 5 times when using TEGA for nanowire synthesis at 440 °C with the same PH\(_3\) flow, Ga\(_{x}\)In\(_{1-x}\)P composition of around 30% Ga, and growth rate of around 1.4 nm s\(^{-1}\), as compared to using TMGa in our system [25]. Using TEGA, we observe highly uniform nanowire arrays for a wide growth parameter space, resulting in nanowires with a widely tunable composition range. In order to learn more about the precursor chemistry and kinetics under our experimental conditions using array geometry with efficient light absorption in InP nanowires [32], we vary growth temperature and precursor ratios.

TEGa has previously been used for nanowire growth of for instance GaAs [33–38], InGaAs [39], GaP [40], and Ga\(_{x}\)In\(_{1-x}\)P [41, 42]. Most of these articles are focused on crystal structure, stacking faults and defects, with only some investigating growth kinetics, where a direct comparison to our study is complicated by differences in the experimental methods, such as reactor design, choice of substrate material, catalyst particles and choice of precursors. For example, Persson et al [33] observe GaAs nanowire growth rate increase with both tertiarybutylarsine (TBAs) and TEGA pressures in their chemical beam epitaxy (CBE) reactor and suggest a vapor–solid–solid growth mechanism where at high TBAs pressures the diffusion of gallium in the gold phase is the rate-limiting step. On the other hand, Husanu et al [40] report a P-limited GaP nanowire growth rate grown with pre-cracked tertiarybutyl phosphine and TEGA in CBE system. More similar to our material system, the Ga\(_{x}\)In\(_{1-x}\)P nanowires grown in MOVPE with TEGA by Cerqueira et al [41] were grown on a Si substrate using InP powder as the source for In and P, whereas the Ga\(_{x}\)In\(_{1-x}\)P nanowires by Oliveira et al [42] were grown on a GaAs (100) substrate using TEGA in a CBE reactor. However, neither of these two articles on Ga\(_{x}\)In\(_{1-x}\)P nanowire growth by use of TEGA contain systematic investigation of growth dynamics. It is worth mentioning that Salehzadeh et al [35, 36] and Khorenko et al [34] compared TEGA and TMGa precursors for GaAs nanowire growth using MOVPE. Salehzadeh et al [36] report activation energies for GaAs planar film grown on (001) GaAs substrates using TMGa (135 ± 6 kJ mol\(^{-1}\)) and TEGA (102 kJ mol\(^{-1}\)) and compare them to lateral and axial activation energies for GaAs nanowire growth with TMGa (lateral: 127 ± 18 kJ mol\(^{-1}\), axial: 59 ± 7 kJ mol\(^{-1}\)), and TEGA (lateral: 96 ± 6 kJ mol\(^{-1}\), axial: not activated in the temperature range of 380 °C–500 °C). However, in addition to using a different substrate and material system, we use in situ etching by the use of HCl in order to take full control over axial versus radial nanowire growth, which is known to strongly affect the growth dynamics [29, 30, 43].

2. Methods

Ga\(_{x}\)In\(_{1-x}\)P nanowire arrays were grown by vapor–liquid–solid method on p-type, nominally Zn doped, InP (111)B substrates in a low pressure (100 mbar) MOVPE system with a total flow of 13 l min\(^{-1}\) using hydrogen as carrier gas. An array of circular Au disks (with typical thickness of around 60 ± 5 nm, bottom diameter 200 ± 10 nm, and top diameter 165 ± 10 nm), forming a hexagonal pattern of Au catalyst particles with a pitch of 500 nm, was defined on the surface by nano imprint lithography, metal evaporation (Au) and lift-off [44]. The deposited Au particle volume resulted in nanowire diameter of around 200 nm, where the exact final diameter depends on the growth conditions.

The growth is initiated with an InP nucleation stub, which was grown according to the two-step pre-nucleation scheme as introduced by Otnes et al [44], which ensures pattern preservation. The scheme was slightly modified by introducing HCl from the beginning of the growth temperature (440 °C) nucleation step, thus growing InP nucleation stub for 60 s with molar fractions of TMIn, χ\(_{\text{TMIn}}\) = 0.89 × 10\(^{-4}\), PH\(_3\), χ\(_{\text{PH3}}\) = 0.69 × 10\(^{-2}\), and HCl, χ\(_{\text{HCl}}\) = 1.23 × 10\(^{-2}\). The growth of Ga\(_{x}\)In\(_{1-x}\)P nanowires was initiated by switching on TEGA supply to the reactor and setting TMIn, TEGA, PH\(_3\), and HCl molar fractions to the values given in the supplementary information tables S1–S6, available online at stacks.iop.org/NANO/29/394001/mmedia. These flows were then kept constant throughout the nanowire growth. The growth was stopped by switching off all precursors except PH\(_3\) and cooling the reactor down under a PH\(_3\)/H\(_2\) gas mixture.

TEGA, TMIn, PH\(_3\), and HCl growth series were performed at 440 °C by changing the molar flow of each individual precursor in the ranges χ\(_{\text{TEGA}}\) = (0.15–1.19) × 10\(^{-4}\), χ\(_{\text{TMIn}}\) = (0.15–1.34) × 10\(^{-4}\), χ\(_{\text{PH3}}\) = (0.15–3.46) × 10\(^{-2}\), χ\(_{\text{HCl}}\) = 0–1.54 × 10\(^{-4}\) respectively for each series. The other
precursor flows for each series were fixed at what we call standard values of the precursor molar fractions: $\chi_{\text{TmIn}} = 0.45 \times 10^{-4}$, $\chi_{\text{TEGa}} = 0.60 \times 10^{-4}$, $\chi_{\text{PH3}} = 2.08 \times 10^{-2}$, and $\chi_{\text{HCl}} = 1.23 \times 10^{-4}$. The total group III series was performed by keeping the $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TmIn}})$ ratio fixed to 0.57 and changing the total group III molar flow. The temperature dependent series was performed by synthesis at different growth temperatures in the range 380°C–490°C (see table S6). For most samples, an InP nucleation was carried out at the same growth temperature as the main GaIn$_{1-x}$P nanowire growth part, except for synthesis at 380°C and 400°C where nucleation turned out to be problematic for the chosen precursor flows, reducing the yield of the array. Thus, for the 380°C and 400°C growth temperatures, the nucleation step was carried out at 440°C after which a growth interruption was used by stopping the supply of TMIn and HCl to the reactor. The temperature was then reduced to the growth temperature and growth restarted by re-supplying TMIn, TEGa and HCl precursors to the reactor.

Ternary materials pose additional challenges in analyzing growth chemistry due to complex interactions between the precursors, where the total growth rate can originate from either of the binary components. In this paper, we choose to plot binary volume growth rates in order to separate TMIn and TEGa influence on the growth dynamics. In such a way, the growth rate figures simultaneously illustrate total nanowire growth rate, binary behavior, and the nanowire composition. To obtain the binary volume growth rates, we measure total volume growth rate and the average nanowire composition as detailed below.

Nanowire synthesis was monitored by LayTec EpiR DA UV optical reflectometry system for real time information on the nanowire growth rate and length [45], which was used to control the length of the nanowires to be around 1300 ± 100 nm by adjusting the growth time for each sample.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) imaging was carried out using a Zeiss LEO 1560 thermal field emission SEM operated at 15 kV and a JEOL 3000 F TEM operated at 300 kV. As an example, a representative SEM image of a GaIn$_{1-x}$P nanowire array grown at 440°C is shown in figure 1. To verify length and diameter measurements by LayTec, approximately 30 nanowires per sample were measured by SEM from two different positions to confirm sample homogeneity. The growth time was then used to evaluate the average nanowire volume growth rates ($R_v$) by assuming a constant growth rate of the nanowires. Such an assumption is confirmed for most of the samples by LayTec measurements (see figure S1 in supplementary information), except for an observed decreasing growth rate along the length of the nanowire for the lowest PH$_3$ flow. The InP nucleation segment length was measured by LayTec system and subtracted from the total nanowire length in order to calculate the GaIn$_{1-x}$P nanowire growth rates. For TEM imaging, nanowires were mechanically broken off and transferred onto lacey carbon film covered Cu-grids.

The average nanowire composition of each sample was evaluated by use of x-ray diffraction (XRD) (see supplementary information figure S2 for all XRD data of the samples included in the main text). The measured XRD scattering angle (2θ) has been converted to chemical composition values by use of diffraction equation and Vegard’s law:

$$x = \frac{\sqrt{3} \lambda/2 \sin \theta - a_{\text{InP}}}{a_{\text{GaP}} - a_{\text{InP}}}$$

where $x$ is the Ga content in GaIn$_{1-x}$P, $\lambda = 1.541 \text{ Å}$ is the x-ray wavelength, and $a_{\text{InP}}$, $a_{\text{GaP}}$ are the lattice constants of InP and GaP respectively, and the $\sqrt{3}$ appears because the measurement is done along [111]. The average composition was then used to estimate effective binary volume growth rates of the ternary nanowires by multiplying the nanowire volume growth rate by the determined composition. The full width half-maximum (FWHM) of the observed rocking curve peaks was taken as a measure of the compositional variation. Note that strictly, the width of the peak can actually depend on several factors, as has been detailed by Kriegner et al [46] for GaInP nanowires. In our case, this width most likely depends on the chemical composition variation both along each nanowire (as observed by TEM for some samples), although due to growth edge effects, variation across the sample is also expected. The accuracy of the estimated binary volume growth rates is obtained by error propagation, which includes compositional variation (FWHM) and volume measurement error, which includes standard deviation of nanowire total length and diameter measured by SEM, as well as the standard deviation of the InP nucleation stub length as measured by LayTec measurement system.

Steady state photoluminescence (PL) of as-grown nanowire arrays was measured at room temperature. The as-grown arrays were excited by a near-UV laser diode module with a wavelength of 375 nm. The PL emitted from the sample was collected by an objective with a numerical aperture of 0.45 (20x magnification), dispersed by a fiber spectrometer and detected by a CCD camera.
3. Results

3.1. Ga incorporation

As shown in figure 2(a), within our varied parameter set, we achieved a wide range of compositions for GaIn_{1-x}P nanowires by varying TMIn or TEGa flow separately (0%–80% Ga content in the solid for this choice of precursor flows; GaP growth is also possible, although slight adjustment of the growth parameters was needed in order to optimize the yield (see supplementary information)). The yield and morphology of all these samples are similar to that shown in figure 1, with some instability in the Au particle wetting angle at the highest TEGa flow and lowest PH3 flow accompanied by an observed roughened nanowire surface. As expected, the Ga content in the solid increases with increased $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TMIn}})$ ratio by increasing (decreasing) $\chi_{\text{TEGa}}$ ($\chi_{\text{TMIn}}$) (figure 2(a)). Interestingly, the relative increase in Ga content is not linear with the $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TMIn}})$ ratio, which indicates a complex interplay between the precursors during synthesis. First, there seems to be a minimum $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TMIn}})$ ratio required to incorporate Ga into the solid (within detection limit). At this point, we note that Ga solubility in Au can be affected by the presence of TMIn as has been previously reported [47]. Second, once some Ga is incorporated in the solid, an increase (decrease) in $\chi_{\text{TEGa}}$ ($\chi_{\text{TMIn}}$) molar fraction leads to a superlinear increase of the Ga content in the solid. At high (low) $\chi_{\text{TEGa}}$ ($\chi_{\text{TMIn}}$) in the vapor, a similar incorporation efficiency of Ga and In into the crystal is observed, indicating that TMIn and its related decomposition species inhibit Ga incorporation into the crystal for lower $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TMIn}})$ ratios. Even though the pyrolysis temperatures of TMIn and TEGa are expected to be similar.
[26], we observe that the incorporation efficiency of Ga and In is different, and $\chi_{\text{TEGa}}/(\chi_{\text{TEGa}} + \chi_{\text{TMIn}})$ ratio dependent (figure 2(a)). In order to understand this effect in more detail, we performed temperature dependent growth experiments, and found that the solid composition approaches that of the vapor with increased growth temperature (table S6 of supplementary information), which could indicate that one element is temperature limited in pyrolysis, or that the inhibition effect by TMIn is a temperature dependent process.

Similar observations of changes in effective incorporation of Ga into the solid with precursor flows and temperature have been reported by Carlin et al [49] for CBE growth of planar Ga$_{1-x}$In$_x$P with TEGa, TMIn, and pre-cracked PH$_3$ precursors. Note that growth dynamics in CBE is very different from MOVPE. CBE is a vacuum system, which leads to much stronger desorption effects than in MOVPE. We note, however, that the use of HCl during MOVPE growth to much stronger desorption effects than in MOVPE. We see, however, that the use of HCl during MOVPE growth note, however, that the use of HCl during MOVPE growth has been observed to induce desorption by chlorination of growth species [20, 29, 30]. Hence, we cannot rule out the similarity of the findings as a mere coincidence. In the article, Carlin et al [49] clearly see an inhibition effect of Ga by TMIn in ternary materials, which they speculate could be related to presence of In atoms at the surface and increase of TMIn in ternary materials, which they speculate could be compensated by group III precursor during growth to obtain homogeneous composition throughout the nanowire [24].

The normalized PL signal in figure 2(c) illustrates the wide range of band-gaps achieved by changing the total group III flow as shown in figure 2(b). Figure 2(d) shows, however, that the most intense signal is achieved at around 1.5 eV, after which the signal intensity starts decreasing with higher band-gap energies. Decreasing quantum yield with increased Ga content in Ga$_{1-x}$In$_x$P nanowires grown using TEGa as Ga precursor has been previously observed by Zhang et al [52] and was attributed to faster trapping of electrons and holes, as well as faster non radiative recombination with higher Ga content. Furthermore, at Ga content close to 67% ($E_g(L) = 2.16$ eV at 300 K) zincblende Ga$_{1-x}$In$_x$P becomes indirect, which is expected to lead to a significant drop in PL intensity. The performed TEM measurements on samples from PH$_3$ and TEGa series show nanowires with zincblende crystal structure. However, XRD measurements on some of the other samples, reveal peaks below the bulk InP peak (shown as negative values for solid Ga content, $x$ in figure 2(a) and tables S2, S6, and S7 in the supplementary information), which indicates InP nanowires with presence of wurzite crystal structure [53].

3.2. Group III influence

In an attempt to understand more about the Ga incorporation inhibition by TMIn, we investigated the extracted effective binary growth rates as a function of TEGa, TMIn, and total group III molar fractions (see figure 3). As expected, the effective GaP volume growth rate increases with increasing $\chi_{\text{TEGa}}$ and correspondingly, the effective InP growth rate increases with an increase of $\chi_{\text{TMIn}}$. However, the effective GaP volume growth rate decreases with increasing $\chi_{\text{TMIn}}$. This indicates a mechanism where TMIn inhibits Ga incorporation in the nanowire crystal that fits well with our observations in previous section. A similar behavior has been observed by Jacobsson et al for Ga$_{1-x}$In$_x$P nanowires grown with TEGa, TMIn and PH$_3$ precursors [20], where the total Ga content in the nanowires decreases with increasing TMIn, even though TEGa
was kept constant. Jacobson et al speculate that this may indicate that the methyl groups from TMIn affect the catalytic decomposition and incorporation of Ga species, by for example catalyzing HCl decomposition that then leads to InCl and GaCl formation [20]. The binding energy of the chlorides is 4.9 eV for Ga–CI [54] and 4.5 eV [55] for In–Cl, which is relatively strong and some of the reaction products may desorb leading to possibly different desorption pathways of Ga and In. From our HCl growth series (supplementary information, figure S3), we observe a significant reduction in In incorporation with increasing HCl, whereas the effective GaP volumetric growth rate seems to stay constant, which we associate with a more efficient chlorination of In species, similar to conclusion made by Jacobson et al [20]. However, this also indicates that Ga incorporation is not limited by the increase of HCl. Interaction between the TMIn and TEGa precursors is also observed in the total group III series (figure 3(c)), as discussed previously in terms of composition (figures 2(b)–(d)). Here, we see that the InP growth rate is increasing, but the GaP growth rate is nearly constant, despite both molar fractions of TMIn and TEGa being increased equally, keeping TEGa/TMIn = 1.33, supporting the previously mentioned hypothesis that Ga solubility in the Au particle is affected by the presence of TMIn [47].

As we are not able to identify a single explanation for the observed complex effects, we suggest some considerations for explaining the hindering mechanism of Ga incorporation: (i) heterogeneous reactions at the surface leading to parasitic layer growth, (ii) In atoms at the particle surface hindering catalysis of TEGa, (iii) In in the Au particle suppressing the solubility of Ga, (iv) TEGa and TMIn forming a complex in the vapor phase that would allow the exchange of ligands, resulting in formation of mixed species such as ethyldimethylindium and methyldiethylgallium.

**3.3. Temperature dependence**

To investigate growth dynamics in more depth, we look into temperature dependence series, where we observe an increase in ternary growth rate from 400 °C to 460 °C by a factor of 2. At higher temperatures, the nanowire growth rate is reduced due to parasitic reactions on the surface. If we split the ternary parameters into effective binaries (figure 4), we see that the effective InP volume growth rate follows a weak trend of slightly reducing growth rate with increased temperature due to kinetically activated parasitic surface growth of InP. The effective GaP volume growth rate, however, increases with increasing growth temperature in the range of 400 °C–470 °C. By fitting the temperature dependent effective volume growth rate of the GaP extracted from the ternary GaIn0.1–xP, we estimate the activation energy to be 165 ± 13 kJ mol⁻¹ (figure 4(b)), which is in the range of the reported value of 151 kJ mol⁻¹ for PH₃ decomposition on an InP surface [56].

Although the discussion above indicates a thermally activated catalytic PH₃ decomposition, the growth rate increase with increased group III precursor molar fractions observed in figure 3 introduces additional complexity to the system. In order to confirm our analysis, we grew GaP nanowires as a reference by ramping down the TMIn precursor flow after the InP nucleation segment and finally switching it off. Surprisingly, from a temperature series of GaP binary nanowires, we find an activation energy of 93 ± 6 kJ mol⁻¹ (see supplementary information, figure S4), nearly a factor of two lower than what we obtained in the GaIn0.1–xP case. The 93 kJ mol⁻¹ obtained for the binary GaP growth is at the low end of the wide range of TEGa decomposition activation energies reported for planar structures (63–330 kJ mol⁻¹) [36, 57–63]. This could be a reasonable value for TEGa decomposition activation energy in our structures, since activation energies in nanowires are often observed to be lower than in bulk due to Au acting as a catalyst [64, 65], where the activation energy can depend on the density of the nanowire array [64]. However, since TEGa decomposition temperature is expected to be around ≈350 °C [26], and Salehzadeh et al reported TEGa to be not thermally activated for axial growth of GaAs nanowires [36], we are inclined to assign the activation energy to the catalytic PH₃ decomposition. At this point, we cannot identify the reason for such a large difference in observed activation energies for GaP and GaIn0.1–xP nanowires, but it is worth keeping in mind that GaP series were performed at lower
PH$_3$ ($\chi_{PH3} = 0.69 \times 10^{-2}$) and higher HCl ($\chi_{HCl} = 3.08 \times 10^{-4}$) flows than for Ga$_x$In$_{1-x}$P series. One speculation to explain the large difference in activation energies could be a change in alloy composition when TMIn is introduced in the reactor, which could lead to a change in the catalytic behavior of the Au-alloy particle [64, 65]. Alternatively, additional effects could also be expected if the inhibition effect by TMIn is temperature dependent. Furthermore, we also cannot rule out that the activation energy observed is related to InCl desorption as a rate-limiting step (InCl desorption in InP films was found to be 86 kJ mol$^{-1}$ [66]). Such findings indicate complex processes taking place when TMIn is added to obtain a ternary.

### 3.4. Ternary growth rates

In a further attempt to identify the process behind the observed activation energy, we plot the ternary growth rates as a function of TMIn, TEGa and PH$_3$ precursor molar fractions (figure 5(a)), as well as the inverses of these values in a so called Lineweaver–Burk plot (figure 5(b)). From figure 5(a) we see that the growth dynamics of ternary Ga$_x$In$_{1-x}$P is complex and an increase of...
precursors are included in every series and are marked in the data, the samples grown with standard molar fractions of kept in mind when analyzing the data. For easier comparison of position.

Furthermore, HCl also affects the growth rate and the composition (see supplementary information, figure S3), which has to be kept in mind when analyzing the data. For easier comparison of the data, the samples grown with standard molar fractions of precursors are included in every series and are marked in figure 5 with dashed-ellipses.

From the PH3 molar fraction series, the nanowire volume growth rate increases rapidly at low $\chi_{PH3}$ and levels off at higher $\chi_{PH3}$, demonstrating that PH3 has a strong effect on the nanowire growth rate (figure 5(a)). Such behavior (1st order for low flows and 0th order for high flows) is expected for a unimolecular Langmuir–Hinshelwood mechanism of pyrolysis on a catalytic surface, as is further confirmed by the linear behavior in the Lineweaver–Burk plot in figure 5(b). The group III series shown in figure 5(a) has been performed at a constant $\chi_{PH3}$ of $2.08 \times 10^{-2}$ and shows a strong increase in the nanowire growth rate with increased group III molar fractions. The total group III series also indicates a behavior similar to the unimolecular Hinshelwood–Langmuir mechanism. However, TMIn and TEGa series on their own deviate from such behavior. Note that methyl radicals are known to strongly enhance PH3 pyrolysis, which could result in growth rate increase with TMIn because of more PH3 pyrolysed. However, increasing the group III leads to the highest fractional increase of the growth rate, for which an explanation based on increased efficiency of extra PH3 pyrolysis is not sufficient.

In order to identify if the limiting process changes with PH3 flow, group III series were also performed at a low $\chi_{PH3}$ of $0.35 \times 10^{-2}$ value, as shown in supplementary information figure S5. However, despite an overall reduction of volume growth rate due to reduced PH3 flow, the behavior with TMIn, as well as total group III were very similar to the series with higher PH3 flow value shown in figure 5.

**3.5. Group V influence**

To further increase our understanding of the growth mechanisms with different PH3 molar fractions, we split the ternary into effective binaries, as shown in figure 6(a). Here, we see that group V increases effective growth rates of both GaP and InP binaries. However, it is important to remember that effective binary growth rates are obtained by picking the middle of the XRD peak as the average composition of the nanowires and the FWHM as the error bars. This is especially important here, because, as seen in figure 6(b), with decreased group V flow, the composition of the nanowires gets heavily broadened due to appearance of composition gradient along the nanowire axis as confirmed by TEM (see figure 6(d)).

To understand the origin of such inhomogeneity of composition along the nanowire axis for low group V, we investigated nanowires from two samples with TEM as shown in figures 6(c), (d): nanowire grown with a high PH3 molar flow ($\chi_{PH3} = 2.08 \times 10^{-2}$) (figure 6(c)), and nanowire grown with the lowest PH3 molar flow ($\chi_{PH3} = 0.15 \times 10^{-2}$) (figure 6(d)). The crystal structure is zincblende with twins for both nanowires. However, the low PH3 nanowire contains fewer twins that lead to the rough looking surface as compared to the high PH3 case, which has more twins. As expected from the XRD results, the nanowire grown with low PH3 flow has a long composition gradient with Ga content increasing slowly along the nanowire over around 900 nm until saturating to a nearly constant composition. Note that a short gradient in Ga composition is visible also for high PH3 case. Since we nucleate the nanowire with an InP stub, this gradient most likely occurs due to saturation of the alloy particle, where it takes time to transition from InP to specific Ga$_{x}$In$_{1-x}$P composition growth. Furthermore, for the low PH3 case a significant axial InP segment is grown under the particle during cool down. Such a segment seems to be either missing or very short in the high PH3 case, which could be explained by a faster growth rate and thus faster emptying of
the particle at temperatures close to the growth temperature, leading to composition and crystal structure more similar to the nanowire grown before cool down process started. We note that the final composition of the Au-alloy particle is very similar in the two cases (41% In for high PH₃ and 43% In for low PH₃). To complete the picture, we also note that from the in situ LayTec monitoring system we observe the growth rate to decrease with nanowire length for the low PH₃ case, but to stay relatively constant for the high PH₃ (see figure S1 for data of nanowire length dependence on growth time).

To explain such inhomogeneity of composition along the nanowire axis for low group V, we propose that different PH₃ flow leads to a change in nucleation conditions as well as surface tension of the alloy particle, which can result in different density of twin formations [67–71]. The rough surface at low PH₃ flow can then efficiently trap In at the sidewalls [70, 72] in order to minimize surface energies. In this case, In can incorporate into the nanowire efficiently, but as the nanowire grows longer, more of the In can get trapped at the sidewalls, thus resulting in reduced In incorporation along the nanowire length, as observed with EDX in figure 6(d), and supported by the reduced growth rate observed with LayTec (see supplementary information, figure S1). In addition, interplay between surface and gas diffusion lengths of TEGa and TMIn can also play a role determining the final compositions and growth rates of the nanowires. For example, as we discussed with respect to temperature dependence analysis, surface diffusion of TMIn can be suppressed by phosphorus species as it can trap In atoms [26]. However, 440 °C used for the PH₃ series here might not be sufficient to overcome kinetic hindrance for growth on the substrate.

4. Summary

In this work, we have developed the growth of GaₙIn₁₋ₓnP nanowires using TEGa as the Ga precursor, which reduced the Ga precursor material consumption by about five times when using TEGa for nanowire synthesis at 440 °C than compared to TMGAs in our system. Such growth resulted in high yield nanowire arrays with a band-gap and geometry suitable for solar cell applications. Additionally, the band-gap can be tuned over a wide range without affecting the high yield, indicating a wide parameter space for good quality growth. This nanowire array structure could be used for various optoelectronics applications. In particular, it is promising as the top cell in a tandem junction solar cell device with either a planar- or nanowire-based bottom cell.

By varying the available precursors and temperature, we have characterized the growth dynamics of GaₙIn₁₋ₓnP nanowires using TEGa, TMIn, and PH₃ as the growth precursors, as well as HCl as in situ etchant. We observed a complex interplay between the precursors. First, TMIn inhibits Ga incorporation into the nanowire, resulting in higher In composition in the grown nanowires than in the vapor. The increase (decrease) in χTEGa (χTMIn) molar fraction leads towards a similar incorporation efficiency of Ga and In into the crystal. Second, the growth rate increases with temperature, indicating a kinetically limited growth, which, from the effective InP and GaP volume growth rates, can be attributed to the synthesis of GaP in GaₙIn₁₋ₓnP. By investigating ternary average volume growth rate with TEGa, TMIn, and PH₃ precursor molar fractions, we identified that PH₃ has a strong effect on the nanowire growth rate with behavior expected for a unimolecular Langmuir–Hinshelwood mechanism of pyrolysis on a catalytic surface. Hence, the observed activation energy could be assigned to the catalytic pyrolysis of PH₃. However, as the growth rates also strongly increase with both TEGa and TMIn precursor molar fractions, the analysis becomes complicated. By performing additional growth of binary GaP nanowires, we extracted an activation energy that is nearly two times lower than the one extracted from the GaP binary part of the GaₙIn₁₋ₓnP nanowire growth. We speculate that such a difference could arise due to the modification of the catalytic effect of the Au-alloy particle by the presence of TMIn. However, further investigations would be needed to explain the strong influence of TMIn for nanowire growth in our conditions.

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