Revealing the Significance of Catalytic and Alkyl Exchange Reactions during GaAs and GaP Growth by Metal Organic Vapor Phase Epitaxy

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ABSTRACT: Tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) are getting more and more established as group V precursors for the growth of V/III semiconductors by metal organic vapor phase epitaxy (MOVPE). Due to this development, the thermal decomposition of these precursors was studied during the growth of GaAs and GaP utilizing the Ga precursors, trimethylgallium (TMGa), triethylgallium (TEGa), and triteriarybutylgallium (TTBGa), in a horizontal AIXTRON AIX 200 GFR MOVPE system. The decomposition and reaction products were measured in line with a real-time Fourier transform quadrupole ion trap mass spectrometer from Carl Zeiss SMT GmbH. The decomposition temperatures and the related activation energies were determined for all the mentioned precursors under comparable reactor conditions. The decomposition curves suggest, on the one hand, a catalytic effect of the GaAs surface on the decomposition of TBAs. On the other hand, the decomposition products indicate alkyl exchange as a relevant step during the bimolecular decomposition of TBAs and TBP with the Ga precursors TMGa, TEGa, and TTBGa. The catalytic reaction reduces the decomposition temperature of TBAs and TBP by up to 200 °C. In addition, for the growth of GaAs with TBAs and TEGa and for the growth of GaP with TBP and TEGa, a significant decrease of the decomposition temperature with an increasing V/III ratio is observed. This behavior, which is related to an alkyl exchange reaction, gives insights into the low-temperature growth of GaAs and GaP and is converted into an effective V/III ratio. Finally, the growth of GaAs with TTBGa and TBAs is realized at 300 °C below the unimolecular decomposition temperature of TBAs, underlining the catalytic effect of the GaAs surface. Altering the growth surface with trimethylbismuth led to the prevention of the catalytic effect.

1. INTRODUCTION

Metal organic vapor phase epitaxy (MOVPE) is a well-established commercial production technique for many kinds of electronic and photonic devices based on semiconductor materials, such as light emitting diodes, laser diodes, solar cells, high electron mobility transistors, integrated circuits, and many more.¹ Large amounts of these applications are based on III/V semiconductor materials. To realize these devices by MOVPE, the choice of the right metal organic precursor (MO) is essential to achieve the desired material compositions and purity. On the one hand, small changes in the gas-phase mixture can have a significant impact on the growth characteristics, which influence the incorporation behavior. Consequently, the material composition is altered, which changes the device properties. On the other hand, the purity of the layer in the device is crucial because even impurities in the parts per million level can result in high defect densities within the crystal structure, which results in poor device performance.² To address these issues, a thorough understanding of the gas-phase reactions and an in situ gas-phase analysis under real process conditions is desired to enhance the current understanding of the growth process during MOVPE and improve process control for the fabrication of semiconductor devices. Different experimental setups using mass spectrometry have been invented in the past to enable decomposition analysis for III/V semiconductor materials. The need of decomposition studies started in the late 80’s and early 90’s with the development of novel precursors like tertiarybutylarsine (TBAs) and triethylgallium (TEGa).³⁴ Unfortunately, the decomposition experiments in the early studies were done
in various setups, which showed that changes of the experimental conditions like, for example, the choice of the carrier gas, the reactor pressure, the partial pressures of the MO precursors, and the surface area have a severe impact on the decomposition.\textsuperscript{5–10} Furthermore, due to the use of linear quadrupole mass spectrometers or time-of-flight mass spectrometers, additional pressure reduction stages were used in these setups to allow the transition from the rough vacuum or ambient pressure in the reactor to high vacuum (<10\(^{-3}\) mbar) conditions needed for mass spectrometry.\textsuperscript{11} This pressure reduction can lead to changes in the gas phase, which makes in situ measurements very challenging. Nevertheless, the combination of all these studies has founded a basic knowledge for decomposition reactions of single precursors in the gas phase (unimolecular reactions) for many different MO precursors.\textsuperscript{5–9,12–18} In addition, the decomposition of single precursors influenced by different surfaces (heterolytic reactions) was studied.\textsuperscript{5} Also, some approaches to study the simultaneous decomposition of different combinations of group V and group III precursors (bimolecular reactions) during the growth of GaAs, GaP, and other III/V semiconductors is given.\textsuperscript{9,19,20} However, especially the studies of bimolecular reactions do not cover all available precursor combinations and the mentioned use of different experimental setups makes a satisfying comparison difficult.

Therefore, to enhance the current understanding of the bimolecular decomposition reactions and reaction products, the growth of GaAs and GaP with the group V precursors TBAs and tertiarybutoxyphosphine (TBP) and the group III precursors trimethylgallium (TMGa), TEGa, and tritertiarybutoxygallium (TTBGa) are studied in this work. Especially, the combination of TTBGa with TBAs and TBP has not been studied so far, and our results for the other precursor combinations show some deviation compared to the data from the literature. The decomposition and reaction products are investigated by mass spectrometry in a novel setup for in situ gas-phase analysis, which is attached in line in a commercial AIXTRON AIX 200 MOVPE system. In contrast to the setups used in the past, the used mass spectrometer is based on a quadrupole ion trap that uses fast Fourier transformation (FFT) for the generation of the mass spectrum.\textsuperscript{21} Due to the resistance of the setup and the utilization of an atomic layer deposition valve, the process gas can be transferred into a mass spectrometer without the need of pressure reduction stages. This should reduce pressure-induced changes of the gas phase. Another huge advantage is the high sensitivity of the ion trap allowing the detection in the parts per trillion level, which gives new insights into the decomposition reactions. Furthermore, the FFT-based concept allows the detection of a full mass spectrum in less than 2 s, which allows real-time measurements during the MOVPE process.

In this study, this setup is used for in situ analysis during growth of GaAs and GaP. First, the unimolecular decomposition of the precursors TMGa, TEGa, TTBGa, TBAs, and TBP is discussed to support the literature data because these have not been measured in the same reactor system until now. Second, the influence of the Ga precursors on the decomposition of TBAs and TBP is shown, which results in a large reduction of the decomposition temperature under the chosen conditions. The detected decomposition products reveal that an alkyl exchange reaction is an important step in the bimolecular decomposition reaction, and the reaction products are compared to the findings in the literature. In the last part, the growth of GaAs with TEGa and TBAs shows a dependence of the decomposition temperature on the V/III ratio, which has so far not been systematically identified. From these results, an effective V/III ratio is determined, which could especially help to understand the growth at comparably low temperatures (<400 °C), which is required for novel materials or device concepts and allows the transfer of the collected data to other reactor setups.

## 2. RESULTS AND DISCUSSION

In the first part, the unimolecular decomposition of TMGa, TEGa, TTBGa, TBP, and TBAs is discussed. For these experiments, the susceptor was kept uncoated. However, a small coating with Ga during the decomposition of the Ga precursors occurs, which can change the surface properties. During the decomposition of TBAs and TBP, the reactor parts are being coated over time with arsenic or phosphorus, respectively.\textsuperscript{22}

### 2.1. Unimolecular Decomposition of TMGa, TEGa, TTBGa, TBP, and TBAs

The decomposition curves of TMGa (114 u), TEGa (156 u), TTBGa (240 u), TBP (90 u), and TBAs (134 u) are shown in Figure 1. The partial pressures (P\(_p\)) were chosen all in the same magnitude with P\(_p\) (TMGa) = 9.5 × 10\(^{-3}\) mbar, P\(_p\) (TEGa) = 7.5 × 10\(^{-3}\) mbar, and P\(_p\) (TTBGa) = 3 × 10\(^{-3}\) mbar with values comparable to actual growth conditions. The temperature at which the intensity drops to half of its intensity (T\(_{50}\)) is marked by the gray dashed line and is defined as the decomposition temperature of the precursor.

![Figure 1. Temperature-dependent decomposition curves of TBAs, TBP, TMGa, TEGa, and TTBGa on the bare graphite susceptor. Due to the electron impact ionization the Ga precursors are tracked by the largest detected fragment DMGa (100 u), DEGa (128 u), and DTTGa (183 u). The partial pressures are chosen with P\(_p\) (TBAs) = 7.5 × 10\(^{-3}\) mbar, P\(_p\) (TBP) = 8.2 × 10\(^{-3}\) mbar, P\(_p\) (TMGa) = 9.5 × 10\(^{-3}\) mbar, P\(_p\) (TEGa) = 7.5 × 10\(^{-3}\) mbar, and P\(_p\) (TTBGa) = 3 × 10\(^{-3}\) mbar with values comparable to actual growth conditions. The temperature at which the intensity drops to half of its intensity (T\(_{50}\)) is marked by the gray dashed line and is defined as the decomposition temperature of the precursor.](https://doi.org/10.1021/acsomega.1c04316)
Table 1. Determined Decomposition Temperature (T_{decomp}), Activation Energies (E_a), and Attempt Frequency Factors (A_0) from Arrhenius Plots of the Decomposition Data of Figures 1, S6, and S12.

| experiment | E_a in [eV] | E_a in [kcal/mol] | log(A_0) in [1/s] | T_{decomp} in [°C] | experiment | E_a in [eV] | E_a in [kcal/mol] | log(A_0) in [1/s] | T_{decomp} in [°C] |
|------------|-------------|-------------------|-------------------|-------------------|------------|-------------|-------------------|-------------------|-------------------|
| TBAs       | 1.4 ± 0.2   | 31 ± 5            | 28 ± 4            | 360 ± 10          | V/III = 10 | 1.7 ± 0.1   | 39 ± 2            | 37 ± 2            | 310 ± 10          |
| TBP        | 1.6 ± 0.2   | 37 ± 5            | 31 ± 3            | 400 ± 10          | V/III = 1  | 1.5 ± 0.1   | 34 ± 2            | 33 ± 2            | 310 ± 10          |
| TMGa       | 1.2 ± 0.1   | 26 ± 2            | 25 ± 2            | 340 ± 10          | V/III = 2  | 1.3 ± 0.1   | 29± 3            | 29 ± 3            | 290 ± 10          |
| TEGa       | 1 ± 0.1     | 23 ± 2            | 25 ± 2            | 250 ± 10          | V/III = 1  | 1.1 ± 0.1   | 26 ± 2            | 28 ± 2            | 250 ± 10          |
| TTBGa      | 0.7 ± 0.1   | 17 ± 1            | 24 ± 1            | 140 ± 10          | V/III = 0.75 | 0.9 ± 0.1 | 20 ± 1 | 22 ± 1 | 235 ± 10 |
| TBAs + TMGa| 1.3 ± 0.2   | 30 ± 6            | 29 ± 5            | 310 ± 10          | V/III = 0.5 | 0.8 ± 0.1 | 17 ± 1 | 21 ± 2 | 220 ± 10 |
| TBAs + TEGa| 0.9 ± 0.2   | 21 ± 4            | 24 ± 4            | 260 ± 10          | TBAs-coated | 0.6 ± 0.1 | 15 ± 1 | 17 ± 1 | 250 ± 10 |
| TBP + TTBGa| 0.8 ± 0.1   | 18 ± 2            | 21 ± 2            | 170 ± 10          |           |             |           |           |           |
| TBP + TEGa | 1.4 ± 0.2   | 32 ± 6            | 21 ± 5            | 350 ± 10          |           |             |           |           |           |
| TBP + TTBGa| 1.3 ± 0.2   | 30 ± 4            | 28 ± 3            | 315 ± 10          |           |             |           |           |           |
| TBP + TTBGa| 0.8 ± 0.1   | 18 ± 2            | 21 ± 2            | 250 ± 10          |           |             |           |           |           |

*Determined with Arrhenius plots assuming first-order kinetics for data from: Figure 1: unimolecular decomposition. Figure 2: bimolecular decomposition. Figure 4: V/III variation. Only a few data points could be used due to the steep decomposition curve.*

respective figures marks this point. The decomposition temperatures (T_{decomp}) are determined with T_{TBP_{decomp}} = 340 ± 10 °C, T_{TEGa_{decomp}} = 250 ± 10 °C, T_{TTBGa_{decomp}} = 140 ± 10 °C, T_{TTBGa_{decomp}} = 400 ± 10 °C, and T_{TBAs_{decomp}} = 360 ± 10 °C. These and the values of the experiments shown in the next parts are listed in Table 1 to give a general overview and comparison between the experiments done in this study. The decomposition temperatures determined from the data of TBMGa, TEGa, and TTBGa reduces strongly with the increasing size of the alkyl groups in the molecule. This follows the behavior seen in detail for various As precursors and fits to the trend in decomposition temperatures from data published in the literature with T_{TBMGa_{decomp}} = 430 °C, T_{TEGa_{decomp}} = 290 °C, and T_{TTBGa_{decomp}} = 290 °C.

The unimolecular decomposition of TBP shows, like the TBAs decomposition, the formation of isobutene (56 u) and tert-butyl radicals (57 u), underlining the importance of homolytic fission or intramolecular coupling reactions, as well as the formation of isobutene (56 u), indicating β-H elimination reactions upon decomposition. The possibility of a β-H elimination reaction for the abstraction of the tert-butyl group was shown to become accessible under MOVPE conditions by calculations based on the density functional theory. Our data give evidence that the formation of isobutene (56 u) becomes more dominant at higher temperatures. The corresponding decomposition data and reaction schemes are shown in S2. Findings in the literature show a strong importance of bimolecular reactions, enhancing the TBP decomposition at higher input partial pressures under atmospheric pressure conditions. Dependence on the TBP partial pressure has not been systematically studied in our setup, but the gathered results show so far no influence of the partial pressure on the decomposition behavior. This can be explained because the probability of bimolecular reactions in the gas phase should be reduced in our setup due to the used rough vacuum of 50 mbar and low partial pressures in the 10⁻² to 10⁻³ mbar range compared to the partial pressures in the mbar range used in ref 6. They report in their study that, for partial pressures below 8 mbar in an atmospheric pressure reactor, the formation of isobutene (56 u) becomes dominant. The isobutene (56 u) formation correlates with an increase in the formation of H₂ in their experiments, which gives rise to a unimolecular chain reaction. In this chain reaction, the first decomposition of TBP into tert-butyl radicals (57 u) and PH₂ occurs, followed by H⁺ abstraction from the tert-butyl radicals (57 u) to form isobutene (56 u). This chain reaction cannot be excluded by our findings. However, the H abstraction reaction seems to be very unlikely from a chemical point of view due to the stability of the tert-butyl radicals because of hyper-conjugation. Therefore, the increase of isobutene (56 u) is attributed to the β-H elimination reaction in our study, which
is in agreement with the gas-phase calculations mentioned above. The determined decomposition temperature of TBP in our setup is given with about 70–90 °C lower compared to the values in the literature.6

In the case of the group III precursors, the decomposition is tracked by the largest available fragment of the precursors because the parent molecule in this case is fractured by the ionization. The decomposition products for the Ga precursors compare well to the findings in the literature and are shown in S5–S5. No influence of the partial pressures of the Ga precursors on the unimolecular decomposition is seen in our experiments. For the unimolecular decomposition of TMGa, mainly methane (16 u) and methyl radicals (15 u) are detected, indicating the homolytic fission of the methyl groups from TMGa. This leads to methyl radicals, which can attack the carrier gas (H2) to form methane and H+. Studies in the literature show that the methyl radicals can further react with TMGa to enhance the decomposition.13 In the literature, further formation of ethane (C2H6 – 30 u) is seen, which can be created in a chain termination step by the reaction of two methyl radicals. Some ethane is detected within our measurement as well. However, this can be fully attributed to the alkyl background in our setup. The lack of ethane in our experiment is explained by the lower reactor pressure of 50 mbar and partial pressures in the 10−3 mbar range. This makes the aforementioned chain reaction quite unlikely in our experiment. The collision of two reactive methyl radicals is very unlikely because the methyl radicals more likely collide with H2 first and react to methane.

The TEGa decomposition shows the formation of ethane (30 u), ethyl radicals (29 u), and ethene (28 u), which agree to the findings in the literature.7,16 The corresponding decomposition data and reaction schemes are included in S4. Ethane and ethyl radicals indicate the homolytic fission of the alkyl group from the TEGa. Ethane is most likely formed by the reaction of the ethyl radicals with the H2 carrier gas and shows a lower intensity compared to the detected ethyl and ethene signals. The ethene signal also drops at higher temperatures showing that the formation of ethane is more relevant at lower temperatures. The detected ethene is produced by the β-H elimination of the alkyl groups. The signal of ethene shows the highest intensity over the whole temperature range. This supports the findings in the literature that β-H elimination is the dominant decomposition process for TEGa.2,13 Surprisingly, the intensity of the ethyl radicals detected is high. This shows that the homolytic fission reaction is relevant for the TEGa decomposition at higher temperatures under the conditions used in our experiment.

TTBGa has received the least attention within the literature. The decomposition products measured for the decomposition of TTBGa and reaction pathways are shown in S5. Remarkably, the decomposition temperature of TTBGa is determined by TTTBGa = 140 ± 10 °C. Our determined value shows an about 100 °C lower decomposition temperature compared to TTTBGa and about 200 °C lower compared to TTMGa. TTTBGa which agrees well to the finding of TTTBGa < TTTBGa and TTMGa in refs 13, 18, and 23. The measured decomposition curve of TTBGa shows a steeper decay compared to TEGa and TMGa, which results in a lower activation energy of 0.7 eV compared to 1 and 1.2 eV for TEGa and TMGa, respectively. Upon the decomposition of TTBGa isobutane (58 u), tert-butyl radicals (57 u) and isobutene (56 u) are produced as major fragments. Isobutene (56 u) shows the highest intensity over the whole temperature range, showing that the β-H elimination of the tert-butyl groups is the dominant decomposition reaction. Nevertheless, isobutane (58 u) and tert-butyl radicals (57 u) are detected with high intensities as well, indicating that the homolytic fission of the tert-butyl group is an important step in the decomposition. Presumably, one of the tert-butyl groups is abstracted by homolytic fission upon the decomposition of TTBGa. The underlying reason could be a steric hindrance for the β-H elimination as a first reaction step because the molecule has to rearrange in the transition state. Additionally, Ga (69/71 u) is detected upon decomposition. On the one hand, this could be attributed to the desorption of Ga deposited on the reactor components. However, no Ga signal is detected in the decomposition of TMGa and TEGa. On the other hand, Ga could also be detected due to the formation of a larger Ga containing molecule. This could, for example, be the formation of tertiarybutylgallium (TBGa). This larger fragment can likely crack in the ionization process into tert-butyl radicals and Ga.

2.2. Influence of TMGa, TEGa, and TTBGa on the Decomposition of TBAs and TBP. In this section, the influence of TMGa, TEGa, and TTBGa on the decomposition of TBAs and TBP during the growth of GaAs and GaP will be discussed, respectively.

The decomposition temperatures evaluated from the decomposition curves of TBAs (S6) during the growth of GaAs with TMGa, TEGa, and TTBGa is shown in Figure 2.

![Figure 2. Decomposition temperatures of TBAs (134 u) during growth of GaAs by addition of the three different Ga sources TMGa, TEGa, and TTBGa. The partial pressures are chosen with Pp(TBAs) = 8.2 × 10−3 mbar and Pp(TXGa) = 8.2 × 10−3 mbar. For a direct comparison, the determined decomposition temperatures of TBP (90 u) during growth of GaP by the addition of the same Ga sources TMGa, TEGa, and TTBGa are included. The partial pressures are chosen with Pp(TBP) = 8.2 × 10−3 mbar and Pp(TXGa) = 8.2 × 10−3 mbar during growth and with Pp(TBP*) = 4.6 × 10−2 mbar for TBP alone.](https://doi.org/10.1021/acsomega.1c04316)
decomposition temperatures are reduced to $T_{\text{TBAs+TEGa}}^\text{decomp} = 310 \pm 10 \, ^\circ\text{C}$, $T_{\text{TBAs+TTBGa}}^\text{decomp} = 260 \pm 10 \, ^\circ\text{C}$, and $T_{\text{TBAs+TMGa}}^\text{decomp} = 170 \pm 10 \, ^\circ\text{C}$ compared to the unimolecular decomposition temperature of TBAs ($T_{\text{TBAs}}^\text{decomp} = 360 \pm 10 \, ^\circ\text{C}$). This shows a significant reduction in the decomposition temperature of TBAs in all three cases. The decomposition temperature of the Ga precursors has been measured within the same experiment. These are determined with $T_{\text{TMGa+TBAs}}^\text{decomp} = 310 \pm 10 \, ^\circ\text{C}$, $T_{\text{TEGa+TBAs}}^\text{decomp} = 230 \pm 10 \, ^\circ\text{C}$, and $T_{\text{TTBGa+TBAs}}^\text{decomp} = 150 \pm 10 \, ^\circ\text{C}$ and show no deviation from the unimolecular decomposition, within the error of the measurement. The corresponding data are added into S7 for completeness.

The decomposition temperature of TBP lowers significantly due to the addition of the Ga precursors in our study. The deviation in the decomposition temperatures correlates with some degree to the difference between the decomposition temperatures of the unimolecular decomposition of TBP and TBAs of 40–50 $^\circ\text{C}$, as shown in Figure 2. This suggests a higher stability of TBP compared to TBAs, which can be related to a higher bond strength of the C–P instead of the C–As bond. The absolute reduction in the case of TBP is comparable to the findings of TBAs; however, the decomposition temperature is not reduced completely to the decomposition temperature of the respective Ga source. These findings cannot only be explained by the higher stability of TBP together with a simple catalytic effect of the Ga deposited on the reactor surfaces. If only the elemental Ga is involved,
the TBP decomposition temperature should fit to that of the Ga precursor, at least at higher temperatures. This suggests that the Ga alkyl groups need to be involved in the decomposition reaction. Similarly, in the case of the bimolecular decomposition of TBP and TMGa, the formation of CH₄ and methlyphosphane (48 u) was detected in the literature, which is believed to occur by alkyl exchange on the surface. The idea of an exchange of the alkyl groups of the Ga sources with the tert-butyl groups of TBP and TBAs on the surface could explain the change in the decomposition temperature. These reactions have to be dependent on the bond strength within both molecules, and therefore can account for the higher decomposition temperatures for TBP compared to the values determined in the case of TBAs. Due to the higher bond strength, the alkyl exchange should occur at higher temperatures for TBP compared to TBAs, as supported by our data. The possibility for this alkyl exchange on the surface should be given because many studies report a site blocking effect by the alkyl groups sticking to the adsorbed Ga precursor at low temperatures.

Some more evidence for these reactions will be discussed in the next part of this paper.

2.3. Reaction Products of the Bimolecular Decomposition of TBAs. In the next part, the decomposition products detected during the bimolecular decomposition of TBAs and the Ga precursors TMGa, TEGa, and TTBGa will be discussed.

The temperature-dependent evolution of the main fragments for the combination of TMGa and TBAs is shown in Figure 3. For the bimolecular decomposition of TBAs and TMGa, the decomposition products isobutane, tert-butyl radicals, and isobutene as well as propyne arising from the fragmentation of isobutane are detected. These fragments originate from the decomposition of the tert-butyl groups of TBAs, as discussed in Section 2.1. Compared to the unimolecular decomposition of TBAs, the detected intensities of isobutane and of the tert-butyl radicals are increasing. This indicates that the homolytic fission of the tert-butyl group is enhanced. In contrast to the unimolecular decomposition of TBAs, no drop in the isobutane intensity for higher temperatures is seen, which shows that the homolytic fission dominates over the whole temperature range. In addition, a mass of 106 u is detected, whose intensity rises, as soon as the TBAs molecule starts to decompose. This fragment is identified with dimethylarsane (DMAs - 106 u). The occurrence of DMAs fits to the decomposition data in refs 20 and 26. In both studies, the formation of an As compound with 1 or 2 attached methyl groups is reported. The formation of DMAs likely indicates that an alkyl exchange reaction occurs as the reaction step in the catalyzed TBAs decompositions. The detected DMAs signal drops around a temperature of 360 °C. DMAs was found to be more stable compared to the TBAs and decomposes at 450 °C in an unimolecular decomposition. The drop of the DMAs at 360 °C is expected because the temperature fits to the unimolecular decomposition temperature of TBAs. Above this temperature, the majority of the TBAs molecules are decomposed by unimolecular reactions before adsorbing on the surface. This severely reduces the possibility of an alkyl exchange, which could be the reason for the drop of the DMAs signal.

As additional products, mainly Ga (69/71 u) and a small increase of a mass around 84 u are seen. The produced Ga can either be attributed to Ga desorbed from the surface or it is a fragment of larger Ga containing fragments. These larger fragments are likely to be cracked in the ionization process. The detected fragment around 84 u is most likely methylgallium (MGa - 84 u). Additional decomposition products and fragments are detected by utilizing the stored waveform inverse Fourier transform (SWIFT) method of the ion trap. The corresponding mass spectrum with and without SWIFT is shown in S9. These additional fragments are related to methylarsane (MAs - 92 u), ethylgallium (EGa - 98/100 u), isopropylgallium (112/114 u), and TBGa (126/128 u). All these fragments are probably related to the fragmentation induced by the electron ionization (EI) of a larger Ga compound like TBGa, which is formed in the alkyl exchange reaction. However, the formation of a larger adduct cannot totally be excluded. Furthermore, one can think of a formation of the TBGa by the reaction of formed tert-butyl radicals with Ga on the surface, followed by desorption.
Similarly, the main fragments for the bimolecular decomposition of TEGa and TBAs are shown in Figure 4. For the bimolecular decomposition of TBAs and TEGa, the decomposition products isobutane, tert-butyl radicals, and isobutene as well as propyne arising from the fragmentation of isobutane are detected. The isobutane intensity is again detected with the highest intensity of the decomposition products and remains constant over the whole temperature range, like in the case of TMGa and TBAs. Furthermore, the isobutene signal, which is the result of the $\beta$-H elimination reaction, drops off and is detected with a lower intensity compared to the unimolecular decomposition of TBAs. This also indicates that the homolytic fission decomposition pathway is enhanced by surface catalytic reactions. Additional fragments such as gallium (69/71 u), MGa (84 u), a small amount of IPGa (112/114 u), and tert-butylgallium (TBGa 126/128 u), similar to the fragments seen for TMGa, are detected. These fragments show slightly higher intensities compared to the ones observed for TMGa. The produced Ga could be explained by the desorption of Ga from the surface but is more likely the fragment of a larger Ga containing compound. The MGa, IPGa, and TBGa are possibly additional fragments of the Ga-containing compound. A view on additional fragments is shown in the mass spectrum recorded with and without SWIFT in S10. The spectra show additional fragments, which are determined with galliumhydride (GaH $-$ 72 u), MAs (92 u), EGa (98/100 u), and ethylarsane (EAs $-$ 106 u). Besides ethene, GaH can be formed by H$_2$ abstraction from GaH$_3$, which is proposed to be formed by the $\beta$-H elimination of the ethyl groups from TEGa.$^7$,$^{35}$ EAs can be the result of an alkyl exchange reaction between the TEGa and the TBAs, as mentioned for the formation of MAs in the case of TMGa. The MAs is probably created by the fragmentation of EAs during the ionization process. The MGa, EGa, and IPGa signals are also attributed to the fragmentation of TBGa within the ion trap. The TBGa is formed within the alkyl exchange reaction between TEGa and TBAs, which additionally produces the EAs.

These findings are in contrast to ref 26. No influence between TBAs and TEGa is observed in the referred study. The aforementioned products are also seen in the bimolecular decomposition of TTBGa and TBAs, as shown in Figure 5. For the bimolecular decomposition of TBAs and TTBGa, mainly isobutane and propyne are detected as the decomposition products. The measured propyne arises from the fragmentation of isobutane. The higher isobutane signal compared to the intensity in the unimolecular decomposition of TBAs can be attributed to the addition of TTBGa. The tert-butyl groups of TTBGa can decompose either radically or by $\beta$-H elimination, leading to the detection of isobutane, tert-butyl radicals, and isobutene, as seen in Section 2.1. The lack of isobutene indicates an enhanced probability for the homolytic fission of the TBAs as well as for the TTBGa.

The additionally detected fragments are identified with Ga (69/71 u), MGa (84 u), EGa (98/100 u), IPGa (112/114 u), and TBGa (126/128 u). The Ga signal can again either be attributed to Ga desorbed from the surface or to the fragmentation of a larger Ga containing compound. The formations of MGa, EGa, IPGa, and TBGa are likely due to the cracking of a larger fragment like TBGa in the ionization process. The intensities of these fragments show higher values compared to the ones detected for TMGa and TEGa. Especially, the intensity of TBGa is significantly enhanced. This is related to the tert-butyl groups, which are more likely to undergo alkyl exchange and adduct formations, which has been seen in experiments done in ref 36. Another possibility is that the formed tert-butyl groups react with Ga on the surface to form the TBGa. GaH (72 u), MAs (92 u), and EAs (106 u) are seen as additional fragments in the sensitive SWIFT measurement in S11. GaH can be produced by H$_2$ abstraction from GaH$_3$ formed in the $\beta$-H elimination of the tert-butyl groups from TTBGa. The MAs and EAs are believed to be fragments of TBAs.

Conclusively, the bimolecular decomposition of TBAs and the Ga precursors indicates the possibility of an alkyl exchange reaction. This is mainly supported by the detection of a larger Ga fragment, which is likely to be TBGa. Additional As compounds, like MAs and EAs or DMAs, can be the result of the same alkyl exchange reaction. Another possibility would be
the occurrence of an adduct formation. However, no larger masses are detected, which could directly support an adduct formation. With the settings used in the mass spectrometer, any formed adduct should be detectable, if it is formed in the gas phase. Nevertheless, this does not completely exclude an adduct formation on the surface.

The alkyl exchange might also explain the strong change of the decomposition temperatures and consequently of the activation energies in dependence of the V/III ratio for the bimolecular decomposition of TBAs and TEGa, which will be discussed in the next section.

2.4. Dependence of the Bimolecular Decomposition of TBAs and TEGa on the V/III Ratio. As the next step, the influence of TEGa on the decomposition temperature of TBAs and TBP has been studied in dependence of the V/III ratio in the reactor. The determined decomposition temperatures are shown in Figure 6a. The corresponding decomposition curves of the bimolecular decomposition of TBAs and TBP with TEGa can be found in S12. With decreasing V/III ratio, a strong reduction of the decomposition temperature is seen in this case. The decomposition temperatures are determined with $T_{\text{TBAs-decomp}} = 360 \pm 10 \degree C$, $T_{\text{TBP-decomp}} = 250 \pm 10 \degree C$, $T_{\text{V/III = 10}}^{\text{decomp}} = 310 \pm 10 \degree C$, $T_{\text{V/III = 4}}^{\text{decomp}} = 310 \pm 10 \degree C$, $T_{\text{V/III = 2}}^{\text{decomp}} = 290 \pm 10 \degree C$, $T_{\text{V/III = 1}}^{\text{decomp}} = 250 \pm 10 \degree C$, $T_{\text{V/III = 0.75}}^{\text{decomp}} = 235 \pm 10 \degree C$, and $T_{\text{V/III = 0.5}}^{\text{decomp}} = 220 \pm 10 \degree C$. To determine the effect of the GaAs surface, which is created during the growth study on the reactor walls, the unimolecular decomposition of TBAs and TEGa has been measured on the coated liner. A similar study reports that the change from the uncoated SiO$_2$ surface of 1200 cm$^2$ to the GaAs-coated surface resulted in a decrease of the TBAs decomposition temperature by 70 °C.\textsuperscript{5} In our setup, with an effective surface area of 720 cm$^2$, an even larger effect is seen with a reduction of about 100 °C. This clearly underlines the catalytic effect of the GaAs surface on the TBAs decomposition, as described above.

For the bimolecular decomposition of TBAs, a dependence on the V/III ratio is seen. The V/III ratio was varied by keeping the TEGa partial pressure constant at 8.2 $\times$ 10$^{-3}$ mbar and changing the TBP partial pressure accordingly. This change in the decomposition temperature with increasing V/III ratio supports the idea of reactions occurring on the surface. Any simple stoichiometric reaction in the gas phase should not be affected by the additional TBAs that is supplied. In the stoichiometric case, the TBAs is expected to decompose only in part earlier if the V/III ratio is larger than one. The excess TBAs present in the reactor most likely influences the catalytic reaction that is occurring. One effect of the increasing V/III ratio in the reactor is a change of the GaAs (001) surface reconstruction, which has been studied in the past.\textsuperscript{17,38} With increasing V/III ratio, the surface reconstruction becomes more As rich. Therefore, it could reduce the possible reaction sites for TBAs on the surface and lead to a higher decomposition temperature of TBAs. Because the TBAs also decomposes at lower temperatures on the prepared GaAs surface, this cannot be the only reason. Another idea is an enhanced alkyl exchange on or near the surface. The excess TBAs in the presence of the TEGa should enhance the probability of these reactions. The TBAs and TEGa show that an alkyl exchange results in the formation of TBGa (126 u) and an As containing molecule like EAs (106 u) or diethylarsane (DEAs - 135 u). Furthermore, our data suggest that the formation of TBGa (126 u) is enhanced by increasing the V/III ratio in the reactor. The corresponding data are shown in S13. In the same exchange reaction, a higher amount of EAs or DEAs would be formed, which is probably stuck to the surface. Due to the higher stability, the EAs or DEAs might block the catalytic Ga sites on the surface.\textsuperscript{7} With increasing the V/III ratio, the probability that a TBAs molecule collides with a TEGa molecule at the surface is enhanced. This should enhance the probability of the alkyl exchange reactions and lead to a higher site blocking by the EAs or DEAs. This can
Figure 7. (a) High-resolution X-ray diffractogram of GaAs grown at 300 °C on an GaAs (001) substrate with an Ga(N,As) marker layer. From the dynamical modeling of the experimental diffractogram, a thickness of 42 nm and a growth rate of about 0.01 nm/s are obtained. The marker layer was grown at 550 °C and shows a N incorporation of 4.8 % and a thickness of 10 nm. (b) AFM image showing a few small droplets on a smooth surface of the low-temperature GaAs layer with an root mean square (rms) of 1.5 nm.

effectively reduce the number of catalytic sites on the surface and therefore prevent the catalytic reactions of TBAs. This would explain the increase in the decomposition temperature as well as the increase of the activation energy with increasing V/III ratio. Here, a higher activation energy compared to the unimolecular decomposition of TBAs is seen for high V/III ratios and a lower activation energy for V/III ratios smaller than 2. The site blocking also explains why the unimolecular decomposition of TBAs on the coated liner occurs at a lower temperature than during the growth of GaAs. In this case, the alkyl groups of the Ga precursor should be desorbed and are no longer present at the surface. This would prohibit the alkyl exchange reaction and consequently no blocking of the catalytic TBAs decomposition occurs. The lower activation energy of 0.6 eV for the heterolytic decomposition compared to the 1.4 eV in the unimolecular case support a catalytic energy of 0.6 eV for the heterolytic decomposition compared to the 1.4 eV in the unimolecular case. The site blocking also explains why the unimolecular decomposition of TBAs on the coated liner occurs at a lower temperature than during the growth of GaAs. In this case, the alkyl groups of the Ga precursor should be desorbed and are no longer present at the surface. This would prohibit the alkyl exchange reaction and consequently no blocking of the catalytic TBAs decomposition occurs. The lower activation energy of 0.6 eV for the heterolytic decomposition compared to the 1.4 eV in the unimolecular case support a catalytic energy of 0.6 eV for the heterolytic decomposition compared to the 1.4 eV in the unimolecular case.
formation, which hinders the growth. These most likely result in the strong reduction of the growth rate, as seen in ref 36. Because fragmentary products are detected at low temperatures, these can lead to the unwanted incorporation of, for example, C from the alkyl groups of the precursors. Because our results suggest the site blocking of the formed EAs or DEAs, this could furthermore lead to the formation of As antisites, as discussed in ref 39. Finally, one should emphasize that the determined effective V/III ratio could be used to transfer the gained knowledge to other reactor designs and might help for the interpretation of data from low-temperature growth.

2.5. Low-Temperature GaAs Growth and Prevention of the Catalytic Decomposition. To prove the catalytic decomposition, two additional experiments were carried out. In a first approach, the growth of GaAs with TTBGa and TBAs was conducted at a growth temperature of 300 °C. Here, a gas-phase ratio of V/III = 1 was chosen, by using partial pressures of \( P(\text{TBAs}) = 8.2 \times 10^{-3} \text{ mbar} \) and \( P(\text{TTBGa}) = 8.2 \times 10^{-3} \text{ mbar} \), respectively. According to the decomposition results in the previous sections, the TBAs precursor should not be decomposed at this temperature in the unimolecular case, but both precursors should be decomposed at 300 °C in the bimolecular reaction, which could enable the deposition of GaAs. To determine the growth rate and the layer thickness of the grown GaAs layer, an additional marker layer of Ga(N,As) at 550 °C with 4.8 % of nitrogen and a thickness of 10 nm was grown prior to the GaAs layer at 300 °C. With this, the structure could be analyzed by high-resolution X-ray diffraction (HR-XRD) and atomic force microscopy (AFM), which is shown in Figure 7.

The experimental diffractogram and the dynamical simulation agree well, revealing a thickness of 42 nm for the GaAs layer. The growth time was set to 1 h, resulting in a growth rate of 0.012 nm/s. Furthermore, the measurement shows a good agreement with the interference fringes expected from this structure besides some deviation at higher relative angles, suggesting a decent quality of the GaAs layer and the interface between the Ga(N,As) and the GaAs layers. This is supported by the AFM image of the GaAs surface. Besides a few features, most likely small Ga droplets due to the low V/III ratio, the surface shows a smooth surface with a mean roughness of 1.5 nm. This proves the realization of GaAs growth at temperatures as low as 300 °C utilizing the surface catalytic effect.

In a second approach, the precursor trimethylbismuth (TMBi) was used. Because Bi is known to float on the growth surface and alters the surface reconstruction, supply of TMBi can be used to change the surface properties.40–44 The addition of TMBi leads to a prevention of the surface catalytic effect. On the one hand, the addition of TMBi to the GaAs layer at 300 °C resulted in no growth at all on the Ga(N,As) layer. On the other hand, mass spectrometry was applied to monitor the TBAs decomposition curve with the addition of TEGa and TMBi, which is shown in Figure 8.

Clearly, the addition of TMBi to the bimolecular decomposition of TBAs and TEGa results in a drastic impact on the TBAs decomposition (black data points). The respective decomposition curve of TBAs follows the decomposition curve of the TBAs with the TEGa experiment (blue data points), as long as no significant amount of TMBi is decomposed. Going toward higher temperatures, enough Bi is deposited on the growth surface to change the surface properties due to the increasing portion of decomposed TMBi (red data points). This is seen by an increase of the TBAs intensity due to the blocking of the catalytic surface sites. The TBAs intensity drops off again, as soon as the temperature is high enough for the unimolecular decomposition of TBAs to set in. From this point onward, the decomposition curve follows the unimolecular decomposition curve of TBAs (green data points). This implies that the catalytic decomposition process is blocked by the addition of TMBi on the surface. Furthermore, this suggests that the used TBAs precursor limits the possibility to grow Ga(As,Bi) at temperatures below 350 °C with this precursor combination.

3. EXPERIMENTAL PROCEDURE

All the decomposition studies are carried out in an AIXTRON AIX 200 horizontal GFR (gas foil rotation) reactor. In this system, the precursors are carried by high purified hydrogen (purity 9.0) into the reactor chamber. Notably, the precursors are carried through separate pipes for group V and group III precursors into the reactor and meet for the first time around 10 cm before the growth area. This effectively prevents possible pre-reactions of the precursors. The total flow in the reactor is kept constant with 6800 sccm. The thermal energy necessary to initiate the decomposition of the precursors, and therefore the crystal growth, is generated by a graphite susceptor uniformly heated by halogen lamps located beneath the reactor. The temperature is controlled and measured by a thermocouple in the center of the susceptor and the surface temperature is calibrated by observing the phase transition of an Al-coated Si substrate. Prior to the experiments, the susceptor was baked out at 800 °C to desorb residual fragments, which could potentially have remained from former experiments. For measurements of the unimolecular decomposition, the susceptor was kept uncoated and no substrate was added into the reactor. No substrate was used for the investigation of the bimolecular reactions, as well. Because...
deposition occurs on all surfaces above a specific temperature, the reactor walls and components are being coated throughout the experiment. To avoid coating-related effects, the exchangeable reactor components are cleaned in between the experiments. To stick to standard growth conditions, the growth area is rotated at 50–70 rpm, which is used to allow homogenous deposition in this reactor type. The reactor chamber exhibits a surface area of about 720 cm², including the surface area of the quartz liner and the graphite susceptor (100 cm²).\(^ {21}\)

For all experiments, TMGa, TEGa, and TTBGa are used as group III precursors and TBAs and TBP are used as group V precursors. Throughout the experiments, the partial pressures of the precursors have been adjusted within a range, which is used in the growth of semiconductor devices, and the exact values are given within each experiment. This should ensure a good insight into the growth process. The thermal decomposition and reaction products are analyzed by a quadrupole ion trap mass spectrometer (iTrap) from Carl Zeiss SMT GmbH. The ion trap is connected with a bypass system to the MOVPE system. A quartz crystal nozzle located right above the middle of the growth area of the susceptor collects the process gas. This bypass is operated under a stable gas flow and pressure conditions similar to the conditions in the reactor to minimize any disturbance of the system. Using an atomic layer deposition valve, the collected process gas is then pulsed into the ion trap with a gas inlet time in the milliseconds range. Therefore, in comparison to setups used in the past, no pressure reduction stages are needed.\(^ {7}\) The quadrupole of the ion trap is based on the principle of a Paul trap and consists of a top, a bottom, and a ring electrode. The anolyte is first ionized by EI at 70 eV. The created ions are then captured by an oscillating electric field, which is applied to the ring electrode of the ion trap. The applied field is oscillating in the radio frequency range with a used voltage between 80 and 400 V, which has to be adjusted in accordance with the desired mass range. The resulting motions of the ions within the ion trap induce a mirror image current in the top and bottom electrodes. After resonant excitation of the ions, a full mass spectrum can be generated by FFT of the detected damped mirror image current. Furthermore, the setup is capable of removing a selected range of mass over charge ratios \((m/z)\) from the trap by using SWIFT.\(^ {15,46}\) This concept was developed to enable very high sensitivity, which was demonstrated by the detection of a part per trillion volume of diborane \((\text{B}_2\text{H}_6)\) in \(\text{H}_2\). Additionally, due to the FFT-based concept, the measurement time of a single mass spectrum can be lower than 2 s, which makes this setup very suitable for real-time gas-phase analysis, and it should be capable for the detection of impurities within the reactor system. This setup is additionally described in more detail in ref \(^ {21}\) and has already been successfully used for gas-phase analysis of TBAs, a novel N–As precursor diteriarybutylaminoarsane and the corresponding P analogue diteriarybutylaminophosphane.\(^ {47,48}\)

As mentioned before, only the surface temperature of the susceptor is determined in our setup. Due to the distance of the gas collection point at the nozzle from the susceptor, the effective gas temperature is determined by the correlation of the TBAs decomposition results of ref \(^ {21}\) with data from ref \(^ {5}\). This leads to a larger error in the determined decomposition temperature. To estimate this error, first the error of mass spectrometry data is obtained by the standard deviation of at least three measurements at the same temperature for the decomposition curves given in Figures 1 and 3–5. For the evaluation of the decomposition temperatures, the curves are fitted with a Boltzmann function

\[
 f(x) = \frac{A_1 - A_2}{1 + e^{(x-x_0)/\Delta x}} + A_2
\]

with

\[
 y = \frac{y_0}{1 + e^{(x-x_0)/\Delta x}} + A_2
\]

to reproduce the sigmoid shape of the decomposition curve. The point where the decomposition curves drop to half of their value is given by \(x_0\) dx is the exponential “time” constant, while \(A_1\) is the initial and \(A_2\) is the final value, respectively. The fit results, depending on the measurement, in error for the decomposition temperature of around 2–3 °C. Even though the surface temperature is determined very reliably with the mentioned phase transition of the Al-coated Si substrate at 577 °C, the interpolated effective gas temperature suffers from the exact position of the nozzle above the susceptor. Therefore, the total error of the decomposition temperature is estimated with 10 °C, which is used in Figures 2 and 6 and in Table 1. This error is reasonable, as the reproduction of the same decomposition experiment from different sequential sessions lies within 10 °C.

The composition and layer thickness of the grown structures is analyzed by HR-XRD employing a PANalytical X’Pert Pro system that uses the Cu Kα, wavelength (1.5405 Å). The colected diffraction patterns around the GaAs (004) reflection are then simulated by X’Pert Epitaxy software. To analyze the surface morphology of the grown layers, a Nanoscope IIIa AFM in the tapping mode was used and the mean roughness \((\text{rms})\) was determined by Gwyddion software.

4. SUMMARY AND OUTLOOK

The influence of the Ga precursors TMGa, TEGa, and TTBGa on the decomposition of TBAs and TBP has been studied in an AIXTRON AIX 200 GFR MOVPE system. The unimolecular decomposition of all the mentioned precursors is studied on the bare graphite susceptor of the system. The products of the decomposition reactions are in good agreement with data published in the literature. However, some deviations occur due to the differences of the experimental setup compared to these studies. The decomposition temperatures of the unimolecular decomposition are determined with \(T_{\text{A}}\)\(^{\text{TMGa}}\)\(^{\text{decomp}}\) = 340 ± 10 °C, \(T_{\text{A}}\)\(^{\text{TEGa}}\)^{\text{decomp}} = 250 ± 10 °C, \(T_{\text{A}}\)\(^{\text{TTBGa}}\)^{\text{decomp}} = 140 ± 10 °C, \(T_{\text{A}}\)\(^{\text{TMGa}}\)^{\text{decomp}} = 400 ± 10 °C, and \(T_{\text{A}}\)\(^{\text{TBAs}}\)^{\text{decomp}} = 360 ± 10 °C. Our study allows a direct comparison between all the mentioned precursors because these are all investigated in the same reactor system. In the next step the bimolecular decomposition of TBAs and TBP with TMGa, TEGa and TTBGa is measured. For the used ratio of V/III = 1, the decomposition temperatures are severely reduced toward the unimolecular decomposition temperature of the Ga precursors. For TBAs, the decomposition temperatures are determined with \(T_{\text{A}}\)\(^{\text{decomp}}\) = 310 ± 10 °C, \(T_{\text{A}}\)\(^{\text{TBAs}}\)^{\text{decomp}} = 260 ± 10 °C, and \(T_{\text{A}}\)\(^{\text{TBAs+TEGa}}\)^{\text{decomp}} = 170 ± 10 °C. The reduction of the decomposition temperature is explained with a catalytic effect of the Ga on the deposited GaAs surface on the reactor components combined with an alkyl exchange reaction on the surface. Gas-phase reactions are believed to play a minor role due to a low reactor pressure of 50 mbar and the low partial pressures in the 10⁻² to 10⁻³ mbar range. The TBP decomposition temperature reduces to \(T_{\text{A}}\)\(^{\text{decomp}}\) = 350 ± 10 °C, \(T_{\text{A}}\)\(^{\text{TBAs+TEGa}}\)^{\text{decomp}} = 315 ± 10 °C, and \(T_{\text{A}}\)\(^{\text{TBAs+TTBGa}}\)^{\text{decomp}} = 250 ± 10 °C. Because the TBP decomposition is not reduced to a
temperature as low as the ones of the Ga precursors, the effect is believed to be not a simple catalytic effect. The additional decomposition products detected in the bimolecular reactions of TBAs and the Ga precursors suggest alkyl exchange reactions. The alkyl exchange depends on the bond strength of the group V precursor as well as on the bond strengths in the Ga precursors, which could explain the higher decomposition temperatures for the bimolecular decomposition of TBP with the Ga precursors compared to the findings for TBAs.

For the bimolecular decomposition of TBAs and TEGa, the dependence of the decomposition temperature on the V/III ratio is additionally investigated. The decomposition temperatures are determined with $T_{\text{decomp}} = 360 \pm 10 \, ^\circ\text{C}$ for TBAs and $T_{\text{decomp}} = 250 \pm 10 \, ^\circ\text{C}$ for TEGa. This effective V/III ratio is attributed to an enhanced probability of the alkyl exchange. The resulting As compounds could lead to the site blocking of the catalytic reaction sites on the surface and therefore prevent the catalytic decomposition. The lowered decomposition temperature of TBAs to $250 \pm 10 \, ^\circ\text{C}$ on the coated reactor supports the catalytic effect of the surface and shows that the additional supply of the Ga precursor changes the surface properties. The surface catalytic effect is proven by the realization of GaAs growth at $300 \, ^\circ\text{C}$, below the unimolecular TBAs decomposition temperature, and by preventing the catalysis by altering the surface with Bi. The bimolecular decomposition of TBP with TEGa shows the same tendencies by catalysis by altering the surface with Bi. The bimolecular decomposition temperature, and by preventing the catalytic decomposition of TBAs experiment. The decomposition data from the TBAs experiments are used to calculate an effective V/III ratio of growth temperatures below $350 \, ^\circ\text{C}$.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04316. Decomposition curves and detected mass spectra (PDF)

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**Notes**
The authors declare no competing financial interest.

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