Decomposition Mechanisms of Ditertiarybutylaminoarsan (DTBAA)

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Abstract

III-V semiconductors containing small amounts of Nitrogen ("dilute nitrides") are very promising material systems for optoelectronic applications. Devices based on dilute nitrides currently suffer from problematic C incorporation. To overcome this problem a novel Nitrogen (N) and Arsenic (As) precursor for metalorganic vapor phase epitaxy (MOVPE) of dilute nitrides ditertiarybutylaminoarsan (DTBAA) has been introduced. DTBAA compared to the commonly used 1,1-dimethylhydrazine (UDMHy) showed a significantly improved N incorporation efficiency. The molecule exhibits no strong Carbon (C) - N bond and the C is only present in large alkyl groups which form less C radicals since β-H-elimination is the dominating decomposition process. This should significantly lower the problematic C incorporation in dilute nitrides and lead to high efficient devices. To understand the high N incorporation efficiency as well as the As incorporation the gas phase decomposition of this novel precursor has been studied with a real time Fourier transform (FT) quadrupole ion trap mass spectrometer from Carl Zeiss SMT GmbH in a horizontal Aixtron Aix 200 GFR MOVPE reactor. Formation of Isobutane and Isobutene proves a radical cleavage and β-H-elimination as decomposition processes of the tertiarybutyl groups attached to the molecule. Furthermore, the appearance of Ammonia (NH₃) has been detected. This indicates a direct cleavage of the As-N bond of the molecule resulting in the formation of an aminyl radical (NH₂•). The formation of NH₂• explains the high N incorporation efficiency of DTBAA as well as its limitations due to desorption of NH₃ at higher temperatures.

Keywords

1. Introduction

Metalorganic vapor phase epitaxy (MOVPE) is a well-established commercial production technique for many kinds of electronic and photonic devices, such as LEDs, laser diodes, solar cells, high electron mobility transistors, integrated circuits and many more [1]. MOVPE is suitable to grow basically all III/V and II/VI semiconductors, including metastable alloys like Nitrogen (N) containing III/Vs ("dilute nitrides"). High purified metalorganic precursors (MOs) and good process control is necessary to realize these devices since even impurity levels in the parts per million range can lead to high defect densities in these devices [2]. Especially for dilute nitrides a main remaining challenge is the unintentional carbon (C) incorporation which arises, especially in MOVPE, from the alkyl groups of used MOs. One source of C incorporation is the conventionally used N source 1,1-dimethylhydrazine (UDMHy). Due to strong C-N bonds in the precursor the C is likely to incorporate into the devices which leads, for example, to an increase of the threshold current density in (Ga,In)(N,As) lasers [3]. This is additionally shown by mass spectrometric decomposition studies of UDMHy showing the formation of CH₄ and larger stable fragments like (CH₃)₂NH and CH₃NCH₂ which presumably lead to C incorporation. Also the direct N-N bond within the molecule was found to be very stable and responsible for intermolecular coupling reactions which
result in the formation of N₂ [4]. Also quantum chemical gas phase calculations support the strength of the N-N bond [5]. This might explain the poor incorporation efficiency of the precursor.

In this work the thermal decomposition of a novel metal organic precursor ditertiarybutylaminoarsan (DTBAA) was investigated. The DTBAA molecule exhibits a direct As-N bond and can be used as Arsenic (As) as well as N source in MOVPE. Therefore, no additional As source is necessary to grow e.g. Ga(N,As) with DTBAA and triethylgallium (TEGa). Compared to UDMHy no direct C-N bond is present in DTBAA and the C is only present in large alkyl groups which are most probably sterically hindered from being incorporated into the growing layer [6]. In growth studies it has been shown that DTBAA is suitable for low temperature growth of dilute nitrides with up to 40 times higher incorporation efficiency compared to layers grown with UDMHy [5,7]. To understand the high N incorporation efficiency as well as the As incorporation, the decomposition pathways of DTBAA has been investigated with a novel real time FT quadrupole ion trap mass spectrometer from Carl Zeiss SMT GmbH in a horizontal Aixtron Aix 200 GFR MOVPE reactor [8,9].

In this paper first the thermal decomposition products and decomposition temperature of the introduced precursor molecule DTBAA are discussed. From the arising products the preferred reaction pathways during the decomposition of the DTBAA are examined. Afterwards the decomposition will be compared to the decomposition of UDMHy to show the advantages of the novel N precursor. Furthermore, from the results the activation energy of the decomposition reaction is determined and compared to literature results from DFT calculations as well as correlated to the N incorporation behavior of DTBAA.

2. Experimental procedure

The investigated precursors were carried by palladium purified Hydrogen (purity: 9.0) into an Aixtron Aix 200 horizontal GFR (gas foil rotation) reactor. The reactor is operated under a constant pressure of 50 mbar (37.5 Torr) and a total flux of 6800 sccm. The thermal cracking of the precursor molecules is initialized by a uniformly heated graphite susceptor using six infrared lamps within the reactor chamber. The susceptor was firstly baked out at a high temperature of 800 °C to desorb molecules that could eventually influence the experiments and was kept uncoated during the experiments. To stick to actual growth conditions within the reactor chamber the substrate was rotated with 50 – 70 rpm, which is applied to ensure homogeneous growth of the III/Vs. Also the partial pressure of DTBAA was kept in a range from 2.5•10⁻³ to 2.6•10⁻² mbar which is suitable to incorporate a sufficient amount of N into GaAs in a realistic growth experiment.

The thermal decomposition of DTBAA and UDMHy was monitored by an FT quadrupole ion trap mass spectrometer (FTQIT) from Carl Zeiss SMT GmbH. The FTQIT showed high sensitivity by detection of a pptV of B₂H₆ in H₂ within a fast single shot measurement (~3 s) [8]. This new setup is very promising for in-situ gas phase and growth interaction analysis during MOVPE without disturbing the growth process itself and has been successfully applied for decomposition analysis of tertiarybutylarsine (TBAs) which has been described in detail in [9].

The FTQIT is connected with a bypass system to the MOVPE reactor. The bypass is operated under stable gas flow and pressure conditions, similar to the pressure in the reactor. The analyte is collected right above the middle of the susceptor with a quartz crystal nozzle and carried into the bypass system. For analysis a small gas volume of analyte is pulsed by an atomic layer deposition valve directly into the QIT of the mass spectrometer. Therefore, in comparison to set ups used in the past, no expensive pressure reduction stages are needed [10]. The quadrupole of the trap consists of a top, a bottom and a ring electrode. The analyte is first ionized by electron ionization (EI) with 70 eV and the created ions are then captured by an oscillating electric field which is applied to the ring electrode in the mass spectrometer. The applied field is oscillating in the radio frequency (RF) range with a used RF-voltage between 80 and 400 V which is adjusted accordingly to the measured mass range. The resulting motions of the ions within the FTQIT 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 fast Fourier transformation (FFT) of the detected damped image current. Due to the FFT technique the overall recording time for a single mass spectrum is below 2 s, which enables real time analysis, a high data point density and good statistics. The setup is furthermore suitable to remove a selected range of mass over charge ratios (m/z) from the trap by using stored waveform inverse Fourier transform (SWIFT) to enable ultra-high resolution measurements [8,11]. During the decomposition analysis the susceptor temperature was varied from room temperature (20 °C) up to 800 °C. Due to the distance of the nozzle to the susceptor, the effective temperature of the collected gas phase was determined by correlation of the TBAs decomposition results [9] with data from [12].

3. Results and discussion

In this paper the thermal decomposition pathways of DTBAA (205 u) have been investigated by an extremely sensitive (pptV-level) and very fast (< 2s) FT quadrupole ion trap mass spectrometer from Carl Zeiss SMT GmbH which was used inline in a metalorganic vapor phase epitaxy (MOVPE) system. In figure 1 the mass spectra of DTBAA measured at low temperature with a supplied partial pressure of 2.5\times10^{-3} mbar DTBAA are shown. The applied radio frequency voltage (RF) was kept at an amplitude of 200 V. Due to electron ionization (EI) with 70 eV the analyte is cracked into many fragments which can be seen in figure 1 a). Only a small portion of the DTBAA molecules has not been cracked, resulting in a small detected intensity at 205 u. All further peaks can be related to fragments of the DTBAA molecule itself. Figure 1 b) shows a mass spectrum detected using the same partial pressure, temperature, reactor pressure but with changed conditions within the FTQIT. For this and the following measurements a reduced filament current in the electron gun, a reduced ionization time and a reduced time between gas inlet and ionization of the analyte have been used. Under these conditions, no fragmentation of the captured DTBAA molecules is observed and only one peak around 205 u arises. These seemingly more sensitive ionization conditions are also very similar to the ones observed in the case of TBAs (134 u) [9] and seem to be valid for all investigated group V precursors. In contrast it was up to now not possible to find similar conditions for group III precursors. At a gas phase temperature of 175 °C the DTBAA molecule is already partly decomposed due to the supplied thermal energy which is shown in figure 2. In the low mass range NH\(_3\) (17 u) was detected by the used FTQIT at 18 u due to the formation of NH\(_4^+\) (18 u) within the mass spectrometer. This protonation reaction was confirmed by the measurement of an ammonia test gas that was directly supplied to the mass spectrometer which resulted in the detection of NH\(_4^+\) under the chosen conditions. Under the EI conditions used in figure 1 a) the NH\(_3\) test gas showed an expected fragmentation of the molecule into NH\(_2\) (16 u), NH (15 u) and N (14 u). NH\(_3\) is the product of aminyl radicals (NH\(_2^+\)) that are formed during the decomposition of the DTBAA molecule. Details on NH\(_2^+\) formation will be discussed later. Furthermore, formation of alkyl groups around 40 u and 42 u which most likely can be attributed to formation of Propyne (40 u) and Propene (42 u) were detected. These fragments can be attributed to EI induced fragmentation of Isobutane (58 u) and Isobutene (56 u). This was checked by investigations of appropriate test gases. The Isobutane test gas showed under the FTQIT settings used in figure 1 a) an expected electron ionization spectrum which can be found in [13]. Under the FTQIT settings of figure 1 b) the Isobutane fragmented partly into Propyne and Propene. In contrast only Propyne was detected as a fragment for the electron induced cracking of the Isobutene test gas. One can therefore attribute the detected Propene intensity in figure 1 and 2 to thermally induced formation of Isobutane and the Propyne intensity to formation of Isobutane as well as Isobutene.

In contrast detection of Isobutane, tertiarybutyl radical (57 u) and Isobutene can be attributed to the thermal decomposition of the tertiarybutyl groups attached to the molecule. Formation of Isobutane and tertiarybutyl radical indicate a radical decomposition of the As-C bond. This radical decomposition leads to formation of tertiarybutyl radicals, that can react with H radicals or H\(_2\) present in the system to form
Isobutane which is schematically shown in reaction (R1). H radicals would only be present, if they are formed during the decomposition of DTBAA or within the mass spectrometer due to EI.

\[
\begin{array}{c}
\begin{array}{c}
\text{As} \\
\text{NH}_2
\end{array} \\
\text{radical}
\end{array} 
\begin{array}{c}
\text{As} \\
\text{NH}_2
\end{array} + 2\text{H}^+ 
\begin{array}{c}
\text{Isobutane}
\end{array}
\]

DTBAA  \quad \text{tertiarybutyl radical}  \quad \text{Isobutane} \quad (R1)

Isobutane can also be the result of an intramolecular coupling reaction (R1b). This reaction was predicted by DFT calculations for the DTBAA molecule and has also been shown for other metalorganic precursors like TBAs [12,14].

\[
\begin{array}{c}
\begin{array}{c}
\text{As} \\
\text{NH}_2
\end{array} \\
\text{Intramolecular coupling}
\end{array} 
\begin{array}{c}
\text{As} \\
\text{H}_2\text{N}
\end{array} 
\begin{array}{c}
\text{Isobutane}
\end{array} 
\begin{array}{c}
\text{TBIA}
\end{array}
\]

DTBAA  \quad \text{Intramolecular coupling}  \quad \text{Isobutane}  \quad \text{TBIA} \quad (R1b)

Formation of Isobutene indicates a second available decomposition pathway occurring through β-H-elimination of one or both tertiarybutyl groups. During β-H-elimination one of the Cβ-H bond of one C atom in β position is interacting with the As orbitals. This leads to the formation of a C=C double bond which is shown in reaction (R2).

\[
\begin{array}{c}
\begin{array}{c}
\text{As} \\
\text{NH}_2
\end{array} \\
\text{β-H-elimin.}
\end{array} 
\begin{array}{c}
\text{Isobutene}
\end{array} 
\begin{array}{c}
\text{As} \\
\text{NH}_2
\end{array}
\]

DTBAA  \quad \text{Isobutene} \quad (R2)

Additionally, a further broad peak around 195 u is detected within the mass spectrum. This can most likely be attributed to a ditertiarybutylarsine molecule (DTBAs - 190 u) since for higher masses a mass offset is present at the given RF voltage of 200 V, that can be removed by adjusting the RF voltage to a higher value of 300 – 400 V within a second measurement. Due to the higher amplitude of the electric field higher masses will be preferably trapped which results in a better sensitivity of the FTQIT in this mass range. The DTBAs could be a result of a radical cleavage of the N-As bond of DTBAA. At the chosen temperature the parent molecule is still not completely decomposed and under the settings used detected around 210 u with the same mass offset as the DTBA molecule.

Furthermore, a high intensity of Ammonia (NH₃) is detected. It is assumed that Ammonia is formed due to a radical decomposition reaction (R3) of the N-As bond within the DTBAA molecule under the formation of an aminyl radical (NH₂•) and DTBAs• (189 u). Due to the available H radicals both radicals are expected to be detected as Ammonia and DTBAs in the FTQIT respectively.

In contrast to the main proposed reaction pathways in [5], whose initial steps are depicted as reaction (R1b) and (R2), radical decomposition of the N-As bond was not treated in the gas phase decomposition calculations. Our findings support that a direct cleavage of the N-As bond must be energetically accessible and highly probable under the applied conditions. This decomposition process is shown as reaction (R3).
The formation of aminyl radicals (NH$_2$•) during the decomposition of DTBAA could explain the up to 40 times higher reported Nitrogen incorporation efficiency using DTBAA at low temperatures compared to the one using UDMHy (60 u) [5,15]. The formed aminyl radicals (NH$_2$•) should be highly reactive if they are near to a surface and are likely to be incorporated. At higher temperatures formation and desorption of NH$_3$ from the surface should become more probable. This explains the observed exponential decay of N incorporation with increasing growth temperature reported in [5].

Reaction (R4) shows a proposed decomposition pathway including formation of Isobutane and Isobutene resulting in incorporation of As and desorption of NH$_3$ which can be detected by the FTQIT in the experiment. Therefore, this decomposition reaction would fully explain our measured reaction products.

In Figure 3 a) the detected intensities are plotted against the gas phase temperature within the reactor chamber of the MOVPE system. The DTBAA starts to drop to half of the intensity around $T_{\text{decomp}} = (160 \pm 10)$ °C. The decomposition temperature $T_{\text{decomp}}$ is comparably low to the one of the conventionally used N source UDMH$_2$ that decomposes at $T_{\text{decomp}} = 420$ °C which was determined by mass spectrometric investigations [4] and can be confirmed by our studies within the same reactor system (figure 4). The low decomposition temperature makes DTBAA very suitable for growth of dilute nitrides which are typically grown at comparably low temperatures and has been proven for growth of Ga(N,As), (Ga,In)(N,As) and Ga(N,As,Sb) on GaAs [5,7,15]. It has also been shown that DTBAA is capable of growing Ga(N,As) with just the addition of triethylgallium (TEGa). This makes DTBAA very promising for future applications, especially at comparably low temperatures.

Furthermore, the reaction barriers for DTBAA decomposition reactions were determined by DFT calculations. The reaction barrier for β-H-elimination at 400 °C into Isobutene (R2) was determined with 266 kJ/mol compared to a reaction barrier of 257 kJ/mol for the formation of Isobutane by radical decomposition (R1b). Since both reaction barriers are quite similar the kinetically most favorable reaction is β-H-elimination which exhibits a lower Gibbs reaction energy of -62.7 kJ/mol compared to -38.9 kJ/mol for (R1b) [5].

These findings can be compared to the detected intensities of Isobutane (radical reaction pathway) and Isobutene (β-H-elimination) within our measurement. Firstly, the activation energy of (266 ± 57) kJ/mol determined from our data fits within the error the proposed reaction barrier and will be shown and discussed at the end of the paper in figure 4.

In our data the signal intensity of Isobutane (radical reaction pathway) remains higher than the one of Isobutene (β-hydrogen elimination). This shows a higher probability for the radical decomposition pathway of the tertiarybutyl groups from the molecule compared to β-hydrogen elimination. This is somehow contradicting with the determined Gibbs reaction energies. But we do observe a drop of the Isobutane intensity to nearly half of its value around 300 °C in our measurement. An explanation could be that the
radical decomposition of one of the two tertiarybutyl groups is hindered or less favorable at higher temperatures. Also there is hardly no difference in temperature at which decomposition into Isobutane and Isobutene sets in. The temperature determination of the gas phase in our experiment might not be sufficient to distinguish between the proposed minor difference of reaction barriers for the formation of Isobutane and Isobutene in [5].

A very likewise behavior of a tertiarybutyl group attached to an As atom has also been observed for TBAs molecule. Theoretical and experimental results of TBAs decomposition have shown a temperature difference between the set in of radical decomposition and β-hydrogen elimination which becomes the main decomposition pathway at higher temperatures [9,12,16,17]. This supports the idea of the less favorable radical decomposition of one of the tertiarybutyl groups attached to the DTBAA molecule and supports the relevance of the β-hydrogen elimination.

Figure 3 b) shows the detected intensities of further decomposition products. As mentioned above Propyne and Propene can be attributed to fragmentation of DTBAA due to electron ionization. At very high masses bisDTBAA (393 u) has been detected. In the synthesis DTBAA is distilled for purification. During this process bisDTBAA can form due to a condensation reaction under abstraction of Ammonia (NH₃). This possibility has been shown for the Antimony analog [18]. bisDTBAA dissolves within the DTBAA precursor and was detected within the FTQIT. The bisDTBAA intensity starts to drop even before DTBAA is decomposed, while the intensities of DTBAA and DTBAs slightly increases. Therefore, the bisDTBAA seems to decompose into radicals of DTBAA as well as DTBAs that can react with the present H⁺ radicals to form DTBAA and DTBAs respectively. In addition, the bisDTBAA is fully decomposed around the same temperature like in the case for DTBAA. Since the decomposition of the condensation product results in the formation of DTBAA no negative effect on the N incorporation of the precursor is expected. The corresponding growth experiments on Ga(N,As) exhibit no influence of the bisDTBAA on the incorporation mechanism [5]. The DTBAs intensity increases further and remains present up to a temperature of 250 °C. At this temperature the DTBAs seemingly becomes unstable and decomposes. As shown in reaction (R4) it is likely to form Isobutane and Isobutene by radical cleavage and β-H-elimination of the As-C bonds respectively.

No further decomposition products including As have been observed within the FTQIT. The remaining As might form As₂ or As₄ and could adsorb on available surfaces within the reactor which is visible as black coating of the liner as well as in the line to the mass spectrometer. Therefore, they are not likely to be detected within our FTQIT setup if they are formed during decomposition of the DTBAA.

Decomposition temperatures of DTBAA on the bare graphite susceptor is compared to the decomposition of TBAs, UDMHy and DTBAA on an introduced 2 inch GaAs (001) surface in figure 4. For all precursors the decomposition temperature was determined by tracking the intensity of the mother molecule peak, which fits to findings from literature for TBAs (T_decomp = (350 ± 10) °C) and UDMHy (T_decomp = (440 ± 10) °C) [5, 6, 16]. Seemingly, the conventionally used As and N precursors decomposes at higher temperatures compared to the novel As and N source DTBAA. By introducing a 2 inch GaAs (001) surface into the reactor system a slight decrease of T_decomp from (160 ± 10) °C to (150 ± 10) °C was observed. This shows to some extent a catalytic effect of an actual growth surface on the DTBAA decomposition. Nevertheless, the accuracy of the temperature and the influence of the measurement setup has to be kept in mind for stating a significant surface effect. The comparably low decomposition temperature of DTBAA shows further the advantage of DTBAA over the currently used precursors, when looking for high N incorporation and enabling growth of devices at low temperatures by MOVPE. Especially metastable alloys that are able to be grown in molecular beam epitaxy (MBE) at lower temperatures might become accessible in MOVPE. The currently used precursors for MOVPE are decomposition limited in the temperature range used for these devices.
Figure 5 shows an Arrhenius plot created out of the breakdown curve of DTBAA out of figure 4. Evaluation of the slope allows the determination of the pre-exponential attempt frequency factor $A$ as well as the activation energy of the decomposition reaction. The activation energy of the DTBAA decomposition is determined to $(2.75 \pm 0.6) \text{ eV}$ which corresponds to $(266 \pm 57) \text{ kJ/mol}$. This fits to the proposed reaction barriers from DFT calculations within the literature and their determined activation energy ($E_A \approx 2.5 \text{ eV}$) of the temperature dependent N incorporation data [5]. From the reversed slope of the NH$_3$ signal in the Arrhenius plot of our data an identical activation energy of $(2.72 \pm 0.4) \text{ eV}$ is determined. This supports the assumption that the aminyl radical (NH$_2$•) measured as NH$_3$ signal is directly related to the N incorporation into dilute nitrides like Ga(N,As) during growth with DTBAA and explains the incorporation efficiency at low temperatures.

4. Summary and Outlook

The thermal decomposition of DTBAA has been investigated by an extremely sensitive and very fast FT quadrupole ion trap (FTQIT) mass spectrometer from Carl Zeiss SMT GmbH which was used inline in a metalorganic vapor phase epitaxy (MOVPE) system. Due to fine adjustment of the ionization conditions within the FTQIT the typically observed fracturing by electron ionization with 70 eV was avoided leading to a straight forward interpretation of the measurement data. The temperature dependent breakdown curve of the investigated nitrogen and arsenic source DTBAA has shown different decomposition pathways. Production of Isobutane indicates radical decomposition of the As-C bonds within the molecule. Furthermore, formation of Isobutene showed $\beta$-hydrogen elimination of the tertiarybutyl groups attached to the molecule. Both decomposition reactions seem to be relevant over the whole investigated temperature range from the start of the decomposition up to 600 °C. The temperature at which the DTBAA intensity drops to 50 % was determined with $T_{\text{decomp}} = (160 \pm 10) \text{ °C}$. The decomposition temperature of DTBAA was found to be slightly reduced by introducing a 2 inch GaAs (001) wafer into the reactor which acts as a catalyst for the decomposition. Activation energies of the observed reactions were found to be in good agreement with the activation energies proposed in [5]. In addition to the proposed decomposition pathways radical cracking of the N-As bond within the molecule seems to be a possible reaction pathway resulting in a high intensity observed for Ammonia. The Ammonia signal is interpreted to be a reaction product of formed Aminyl radicals (NH$_2$•) which react on the way to the FTQIT with present H radicals in the system. This is further supported by the determined activation energy of 2.7 eV which fits well to the activation energies for N incorporation into Ga(N,As) [5]. Overall the comparably low decomposition temperature of DTBAA should make the precursor suitable for growth of dilute nitrides at low temperatures leading to high nitrogen incorporation efficiencies. Also only large alkyl groups have been detected during the decomposition. Therefore, and due to the absence of a direct C-N bond within the molecule the DTBAA should be suitable to reduce C incorporation into devices based on dilute nitrides.

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Declarations of Interest: none

Graphical Abstract:
Figure 1: DTBAA (205 u) mass spectra collected at a reactor temperature of 100 °C with a supply of 2.5×10⁻³ mbar DTBAA and an applied radio frequency with an amplitude of 200 V. All intensities have been normalized to the detected intensity of the most frequent fragment. a) Various fragmentation products by cracking of the DTBAA molecules during electron ionization (EI) with 70 eV. b) Sensitive ionization conditions occurred by applying a comparably low filament current, ionization time and waiting time between gas inlet and ionization in the FTQIT.
Figure 2: Mass spectrum of partly decomposed DTBAA (205 u) collected at a gas phase temperature of 175 °C with a supply of 2.5×10⁻³ mbar DTBAA and an applied radio frequency with an amplitude of 200 V. All intensities have been normalized to the detected intensity of the parent molecule peak of DTBAA from figure 1b).
Figure 3: a) Decomposition curve of DTBAA (205 u) and the main decomposition products Isobutane (C\textsubscript{4}H\textsubscript{10}, 58 u), tertiarybutyl radical (C\textsubscript{4}H\textsubscript{9}•, 57 u), Isobutene (C\textsubscript{4}H\textsubscript{8}, 56 u) and Aminyl radical (NH\textsubscript{2}•, 16 u) detected as Ammonia (NH\textsubscript{3}, 17 u). b) Decomposition curve of DTBAA and bisDTBAA (393 u) with further decomposition products DTBA\textsubscript{s} ((C\textsubscript{4}H\textsubscript{9})\textsubscript{2}AsH, 190 u), Propene (C\textsubscript{3}H\textsubscript{6}, 42 u) and Propyne (C\textsubscript{3}H\textsubscript{4}, 40 u).
Figure 4: Breakdown curve of DTBAA (205 u) on the bare graphite susceptor, of DTBAA on 2 inch GaAs (001) surface (81 cm²), of TBAs (134 u) and UDMHy (60 u) within the same reactor system on the bare graphite susceptor. The intersection points with the grey line indicate the decomposition temperature $T_{\text{decomp}}$ which is defined where the intensity drops to 50 %.

Figure 5: Arrhenius plot for the detected intensities of DTBAA (205 u) and Ammonia ($\text{NH}_3$, 17 u). Linear regression of the slopes allows the determination of the activation energy of the reactions as well as the pre exponential attempt frequency factor $A$. 

\[\begin{align*}
E_A^{\text{DTBAA}} &= (2.73 \pm 0.4) \text{ eV} \\
\ln(A) &= (73 \pm 9) \text{ 1/s}
\end{align*}\]
References


