

## Decomposition behavior of III/V semiconductor precursor gases in a closed gas cell in-situ TEM holder observed by mass spectrometry

Maximilian Widemann<sup>1</sup>, David Krug<sup>2</sup>, Felix Gruber<sup>2</sup>, Andreas Beyer<sup>3</sup> and Kerstin Volz<sup>3</sup>

<sup>1</sup>Materials Science Centre and Department of Physics, Philipps University Marburg, Hans-Meerwein-Straße 6, Marburg, 35032, Germany, Marburg, Hessen, United States, <sup>2</sup>Materials Science Centre and Department of Physics, Philipps University Marburg, Hans-Meerwein-Straße 6, Marburg, 35032, Germany, United States, <sup>3</sup>Materials Science Centre and Department of Physics, Philipps University Marburg, Hans-Meerwein-Straße 6, Marburg, 35032, Germany, Germany

III/V semiconductor devices are used for many technological applications, e.g. LEDs, lasers and solar cells. A widely used fabrication process for these materials is metal organic vapor phase epitaxy (MOVPE), where metal organic precursor gases are supplied to a heated substrate. The precursor gases decompose thermally and the growth material adsorbs onto the crystalline substrate resulting in a layer by layer crystal growth. Mass spectrometry analysis of the gas phase in the MOVPE reactor is able to give detailed insights into the decomposition of the precursor gases, and thus into the growth process [1]. In-situ studies of the growth process promise an improvement of the performance of the fabricated materials, however direct observations of the crystal growth in conventional MOVPE reactors are challenging. In-situ (scanning) transmission electron microscopy ((S)TEM) allows the investigation of dynamic processes, which occur during growth of III/V semiconductors. Gas environmental cell and heating holders enable to supply gases while heating the sample so that conditions comparable to those during the MOVPE process can be realized in any microscope [2] and semiconductor growth can be performed. The comparability of such a micro reactor with a conventional one, however, still needs to be proven.

To this end, a commercially available Protochips in-situ system, equipped with a quadrupole mass spectrometer working with 70 eV electron ionization, has been modified to investigate the processes occurring during semiconductor growth. In order to allow the usage of toxic and pyrophoric gases, like the precursor gases used in MOVPE growth, a gas mixing system, an appropriate gas monitoring system as well as a gas scrubbing system have been added to the setup [3]. A double CS-corrected JEOL JEM 2200FS operating at 200 kV was used for the TEM observations. Investigated precursor gases are tertiarybutylphosphine (TBP) and trimethylgallium (TMGa), which are used for gallium phosphide growth at partial pressures between 10<sup>-1</sup> and 10<sup>-3</sup> hPa and a V/III ratio of around 10. Additionally, N<sub>2</sub> is used as carrier gas at pressures in the range of 102 hPa. Temperatures at which efficient decomposition takes place are expected to be above 450 °C [4].

We observe the thermal decomposition behavior of the precursor gases in the micrometer scaled TEM holder tip as well as the influence of the irradiating electron beam interacting with the gas volume.

Figure 1 and 2 show mass spectra at 750 °C and 900 °C of the thermal decomposition species of TBP. The spectra were recorded with a gas mixture of 99% nitrogen and 1% TBP with a total pressure of 100 hPa. They were background corrected and the contribution of the nitrogen and undecomposed TBP molecule signal was subtracted. Additionally, they were normalized to the phosphine peak intensity at 34 u and plotted to the same scale. In this way, only the signal of TBP decomposition species are visible and a comparison of their ratio is feasible. The experiment was performed without an impinging electron beam to see only the effect of temperature. Both spectra show intensities indicating the presence of phosphine (31 u to 34 u), and a changing ratio of isobutane and isobutene with varying temperature. Increasing the temperature from 750 °C to 900 °C especially reduces the intensity at 43 u, the base peak

position of isobutane, whereas the 39 u, 41 u and 56 u peaks, pertaining to isobutene, increase. Additionally, these findings give insight in the decomposition mechanisms. Isobutane is produced due to homolytic fission, whereas isobutene by beta-hydrogen elimination of TBP. The results show that the beta-hydrogen elimination becomes more favorable as decomposition mechanism for TBP with increasing temperature.

We demonstrate our findings on the thermal and electron beam induced decomposition behavior of III/V semiconductor precursor gases inside an in-situ closed gas cell TEM holder.

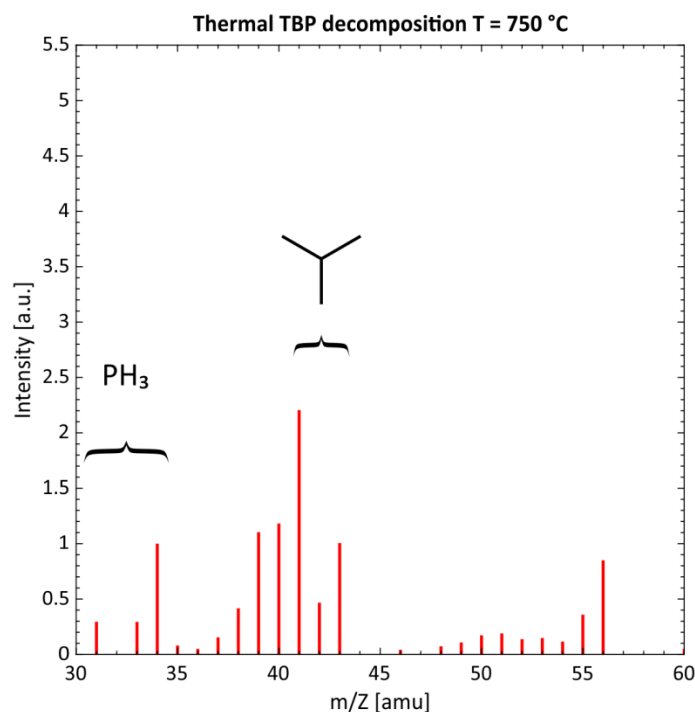


Figure 1. Mass spectrum of TBP decomposition species at 750 °C corrected with respect to the pure TBP and nitrogen intensities. The most dominant peak positions for phosphine and isobutane are indicated.

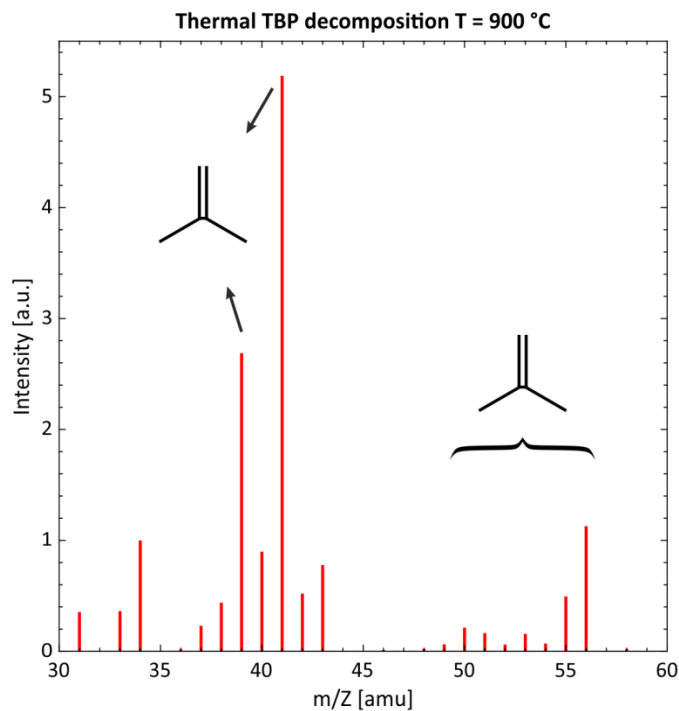


Figure 2. Mass spectrum of TBP decomposition species at 900 °C corrected with respect to the pure TBP and nitrogen intensities. Peak positions of isobutene peaks are indicated. Compared to the 750 °C spectrum the intensities of isobutane are decreased, whereas the one of isobutene are increased.

#### References

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