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# Decomposition Behavior of III/V Semiconductor Precursor Gases in *In-situ* TEM MOVPE Investigations Observed by Mass Spectrometry

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III/V semiconductor devices are used for many technological applications, e.g. LEDs, lasers and solar cells. A widely used fabrication process of 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 on the crystalline substrate resulting in a layer by layer growing crystal. Mass spectrometry analysis of the gas phase in the MOVPE reactor are able to give detailed insights into the decomposition of the precursor gases, and thus into the growth process [1]. However, structural investigations of the samples are usually carried out post growth, since there are only limited possibilities for investigations, which can be done during the growth procedure. Moreover, direct observations of the crystal growth in conventional MOVPE reactors are challenging. Though *in-situ* studies of the growth process promise an improvement of the performance of the fabricated materials. *In-situ* (scanning) transmission electron microscopy ((S)TEM) allows to investigate 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. However, the comparability of such a micro reactor with a conventional one needs to be proven. Especially the influence of the electron beam and the smaller dimension of the reactor on the thermal decomposition of the precursor gases are of interest.

To this end, a commercially available Protochips *in-situ* system, equipped with a quadrupole mass spectrometer, 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 $C_S$-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 GaP growth at partial pressures between $10^{-1}$ and $10^{-3}$ hPa and a V/III ratio of around 10. Additionally, $N_2$ is used as carrier gas at pressures in the range of $10^2$ hPa. Temperatures at which efficient decomposition takes place are expected to be in the range of 400 °C to 500 °C.

We observe the decomposition behavior of the precursor gases in the micro meter scaled holder tip geometry in a conventional TEM. Especially the thermal decomposition in dependence of the temperature which is realized in a volume of only thousands of cubic micrometers, and the irradiating electron beam interacting with the gas volume are investigated.

Figure 1 shows two mass spectra (MS) at room temperature (blue) and 1000 °C (orange) of a gas mixture of 99% nitrogen and 1% TBP with a total pressure of 400 hPa. They were normalized to the nitrogen peak at 14 amu. The experiment was performed without impinging electron beam to see only the temperature effect. The comparison of the MS reveals that the intensity of the TBP molecule at 90 amu decreases by 87%. This strong decrease at an elevated temperature demonstrates that, even in the small volume of the holder tip, precursor gases can be thermally decomposed by a high proportion. We will demonstrate our results on the decomposition behavior of the precursor gases by comparing MS with different gas mixtures, temperatures and beam doses.

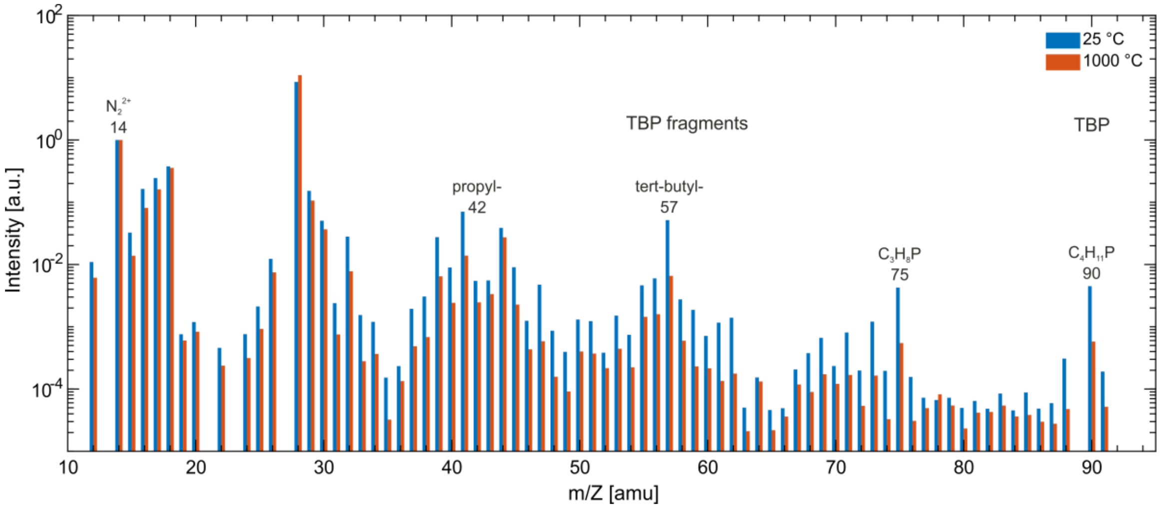


**Figure 1.** MS of 99% nitrogen and 1% TBP with a pressure of 400 hPa and different temperatures. Blue shows the MS at room temperature and orange at 1000 °C normalized to the nitrogen peak (14 amu). The MS at elevated temperature shows a TBP peak (90 amu) decreased by 87% caused by thermal decomposition of the molecule.

References

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