

Systematic Investigations of Electron Ionization Fragmentation patterns of selected MOCVD precursors: Source temperature and electron energy dependence



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Introduction

Metal Organic Chemical Vapor Deposition (MOCVD) compounds are frequently used in semiconductor manufacturing such as Chemical Vapor Deposition (CVD) or Atomic Layer Deposition (ALD) processes.

Mass spectrometry for process development and process control currently gains increasing attention. Most prominently classical electron ionization (EI) is employed.

Trimethylaluminum (TMAI) is one of the most commonly used MOCVD precursor materials. A 70 eV EI mass spectrum is available in the NIST database and is used as reference in this work. EI Spectra for other materials, e.g. di-tert-butylsilane (DTBSi), however, as well as many other MOCVD compounds are not available in the NIST database [1].

Of particular interest of this work are two major questions:

1. As MOCVD compounds are inherently thermally unstable, the extent of thermal degradation in the EI source is investigated.
2. Threshold EI has the advantage of generating less congested mass spectra, however at the expense of a) significant loss of sensitivity and b) strong sensitivity dependence on minor electron energy changes. The fragmentation behavior is thus studied in detail to find out whether or not 70 eV EI mass spectrometry is applicable to MOCVD monitoring.

In future work, the results for various MOCVD compounds will be used to establish a corresponding mass spectral database.

Methods

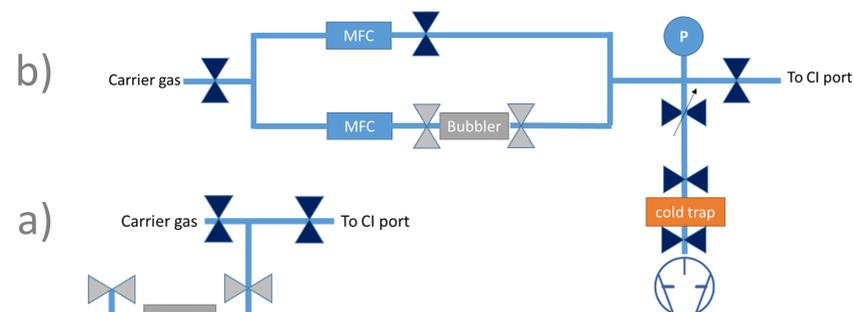
Mass spectrometer:

Thermo Finnigan MAT 95 XS double focusing sector field mass spectrometer equipped with an EI source providing adjustable electron energies and source temperatures.

Chemicals:

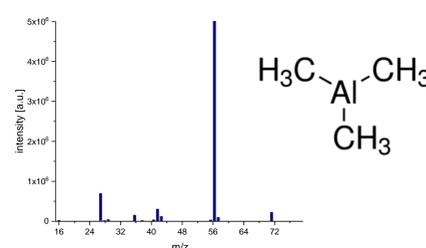
Trimethylaluminum (TMAI) and Di-tert-butylsilane (DTBSi) are purchased in ALD grade purity from Dockweiler Chemicals (Marburg, Germany)
Argon 5.0 (Messer Industriegase GmbH, Bad Soden, Germany) is used as carrier gas

Experimental Setup

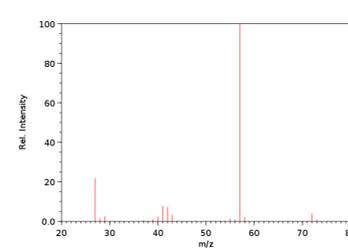


Trimethylaluminum (TMAI)

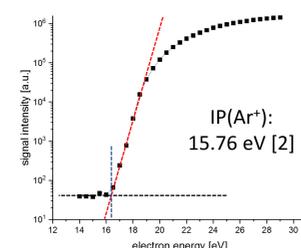
Measured 70 eV EI mass spectrum



70 eV NIST reference spectrum

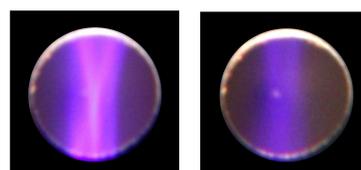


Argon reference data



- The instrument electron energy scale is affected by several ion source parameter settings of the MAT 95 instrument including pusher and draw out electrode potentials.
- The settings are significantly different for optimum instrument performance (see photographs below).
- Thus Argon was used as internal calibrant in all measurements (cf. left figure).
- The instrument scale is shifted by about +0.6 eV in the low energy range (5 – 20 eV).

EI source photographs



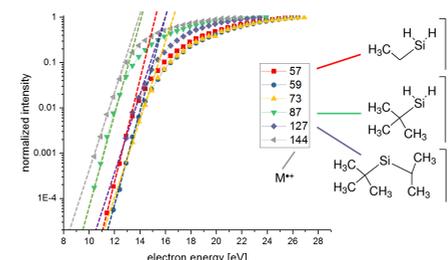
- The ion source block of the MAT 95 instrument was retrofitted with an optical window. The photographs on the left show the afterglow of electronically excited N₂⁺ ions. The electron beam enters from the top and exits at the bottom.
- Left: 70 V electron acceleration voltage, pusher -120 V, extractor -20 V.
- Right: 20 V electron acceleration voltage, pusher +100 V, extractor -20 V.
- (For illustration purpose only)

Measurement procedure

- If applicable (i.e., the MOCVD compound has sufficiently high room temperature vapor pressure) the headspace is introduced directly via the CI (Chemical ionization) gas port into the EI source of the sector field instrument (figure left, a).
- For low vapor pressure compounds, the set-up as depicted in the figure on the left, b) is used; in this case the Argon carrier gas is saturated with the MOCVD compound via aspiration.
- At constant ion source temperature of 300°C the electron energy is varied from 5 eV to 30 eV and at selected electron energies the ion source temperature is varied from 150 to 300 °C.
- Argon is used for the calibration of the instrument electron energy scale to absolute ionization and appearance potentials, respectively.
- Ionization potential for Argon: Ar⁺ 15.76 eV [2].

Di-tert-butylsilane (DTBSi)

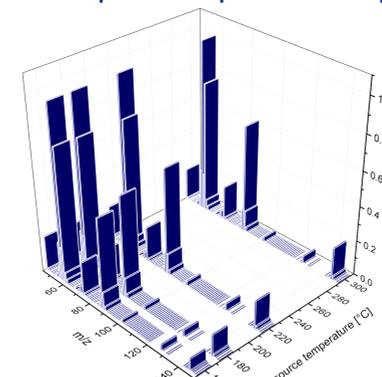
Appearance potential measurements



Top: Electron energy resolved data for the molecular ion and selected fragments of DTBSi. 144 Th (M⁺): 8.5 eV; 87 Th: 9.5 eV; 57 Th: 11 eV. Uncertainty: ± 0.5 eV.

Right: Electron energy resolved mass spectra of DTBSi. At electron energies ≤ 15 eV, the molecular ion and the fragment at 87 Th are of similar magnitude; the fragment at 57 Th is not observed. However, at 70 eV, the sensitivity for (M⁺) is at least two orders of magnitude higher.

Source temperature dependent mass spectra



Left: 70 eV EI mass spectra of DTBSi at different EI source block temperatures.

The relative intensities hardly change with temperature; thus significant thermal degradation in the ion source is excluded.

Conclusions

- For both selected MOCVD compounds electron energy and ion source temperature dependent measurements were successfully carried out.
- The instrument electron energy scale is calibrated to the absolute energy scale using the Ar⁺ signal.
- Despite the intrinsic thermal fragility of MOCVD compounds, elevated ion source temperatures did not lead to significantly increased compound degradation.
- For the two compounds investigated, 70 eV EI is favorably used for monitoring as the molecular ion is detected with sufficiently high abundance. Thus, signal fluctuations with small electron energies are negligible and at the same time maximum sensitivity (ion yield) is obtained.
- It remains to be shown whether or not the (expected) gain of the molecular ion intensity - at the expense of large loss in sensitivity - at lower electron energies is favorably exploitable in the respective fields of application.

Outlook

- TMAI and DTBSi were used a) as proof of principle for the measurement approach b) to assess the qualification of the mass spectrometric system used for the study, and c) to train the secure handling of such substances in MS experiments. This knowledge will be used to refine the compound delivery to the ion source of the mass spectrometer.
- Additional MOCVD compounds will be investigated to create a corresponding EI mass spectral database.

Literature

1. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, retrieved June 1, 2019.
2. Rosenstock, H.M., Draxl, K., Steiner, B.W., Herron, J.T. "Energetics of gaseous ions"; J Phys Chem Ref Data 1977, 6, 1-485.
3. Fass, R.A., Kendall, S.G.; "Appearance Potential Measurements by Mass Spectrometry"; J Chem Edu 1971, 48, 545 – 547.

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