Insight into semiconductor processes by a novel Fourier-Transform ion trap

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Introduction

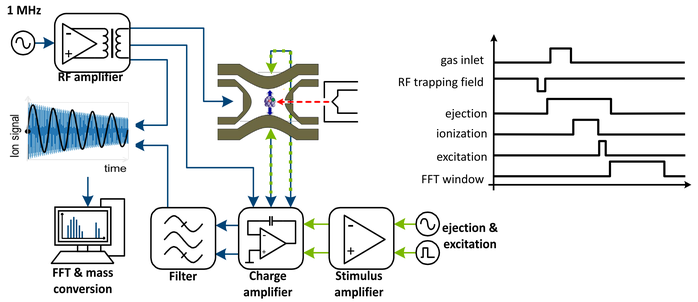
Semiconductor manufacturing has an growing demand for in-line process control metrology as the pressure on cost efficiency and quality is steadily increasing. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. When issues with chamber healthiness or first-wafer effects occur, which are caused by the chamber conditions and not by plasma processes, OES cannot be used, because there are no light emitting species. OES is also limited in sensitivity, therefore it is e.g. not suitable for small open area etch for the emerging advanced transistor devices.

Applications in different semiconductor manufacturing process steps are shown here, e.g., first wafer effects in wafer etching, outgassing issues in backend etch or understanding the decomposition and fragmentation of new MetalOrganic Vapor Phase Epitaxy (MOVPE) precursors. Apart from etch processes, a MOVPE process was investigated. MOVPE is used in e.g. LED or solar cell manufacturing. Tertiarybutylarsine (TBA) together with Triethylgallium (TEGa) are promising new precursors for III/V semiconductors. Their deposition chemistry, leading to Gallium Arsenide, is not fully understood yet.

Samples were taken from the gas phase, either directly from the chamber or between chamber turbo and backing pump. This gas is pulsed into the iTrap by an ALD valve for each measurement. Ionization takes place by Electron Ionization (EI). After ionization, matrix ions can be ejected from the trap to increase the ability to detect compounds with lower abundance in a large amount of matrix ions. This is done by Stored Waveform Inverse Fourier-Transform (SWIFT). The repetition rate of the pulsed measurements is approx. 1 Hz.

Experimental Setup

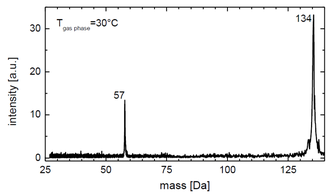
The iTrap is based on a compact Fourier Transform quadrupole ion trap mass spectrometer. Schematic of the detection principle and the measurement sequence:



- **Non-corrosive**, highly robust even in aggressive matrices
- Excitation of certain ion species **increases sensitivity** even though a high amount of bulk gas molecules and other process gases is present
- Heating up to approx. **150°C** possible to exclude memory effects
- Inlet Pressures from **UHV to atmospheric pressure** possible

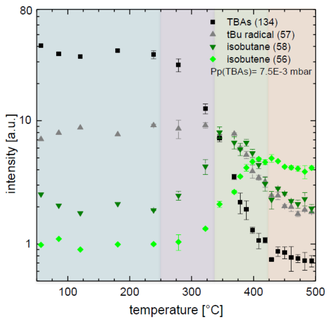
MOVPE:

Decomposition Investigations of Tertiarybutylarsine (TBAs)



Mass spectrum of TBAs at 30 °C with a TBAs partial pressure of 7.5E-3 mbar

m/z 134 = TBAs
m/z 57 = tBu group



Reactor pressure: 50 mbar
Partial pressure TBAs: 1E-2 mbar

- no thermal decomposition
- just TBAs and tBu radicals due to EI fragmentation
- Isobutene/isobutane nearly at noise level

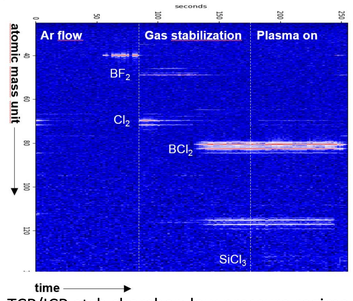
- thermal decomposition of TBAs intitiated
- radical decomposition mechanism (increasing tBu radical signal)

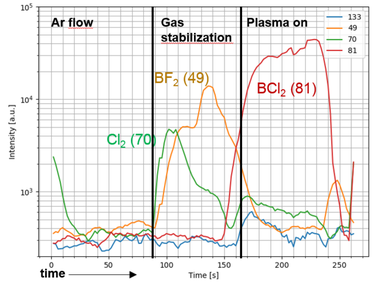
- at T_{gas} > 330°C decomposition due to β-h-elimination becomes the important process
- tBu signal decreases due to increasing β-h-elimination and decreasing TBAs level

- saturation at T_{gas} > 450°C
- no TBAs signal
- tBu signal tracked by isobutane

First Wafer Effect

Change of gas composition during gas stabilization step:
Fluorine is present from a cleaning step prior to etching. Fluorine radicals on chamber walls react with BCl_3 to BF_2. Before a first wafer of a batch is processed two cleaning steps are performed: Leads to **First Wafer Effect. Not detectable with OES**

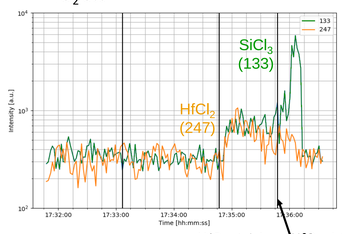




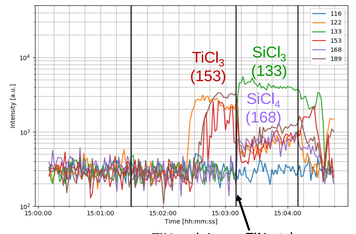
TCP/ICP etch chamber; low pressure regime (2-10 mT); BCl_3 etch; SiO_2 wafer
During gas stabilization and plasma etch steps BCl_3 (116/118Da) and Cl_2 (70/72 Da) mixed in Nitrogen were flown. In the cleaning step different gases, e.g. NF_3 and O_2, were used.

End Point Detection

HfO_2 etch



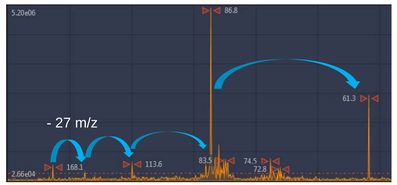
TiN etch



Heavy etch products are easily detectable. The increase of $SiCl_3$ in the Hf etch and the decrease of $TiCl_3$ in the TiN etch are suitable end point markers.

Outgassing and Chamber Health

Outgassing after processing of the wafer leads to observable contamination inside the backend etch chamber.



m/z 168 → 141 → 114 → 87

TiCAl4 → TiCAl3 → TiCAl2 → TiCAl

m/z 61 and m/z 75: TiCH bzw. TiAl

Signal distribution at m/z 87: TiF_2 and TiCl.

Changing the pressure or temperature during the ash step (removal of organic matter after the etch) reduces the outgassing of the wafer after the full process is completed significantly.

Conclusions

- iTrap allows study of etch reaction products as a function of pressure, concentration and previous cleaning steps
  - Correlation with etch rates enables ultrafast process optimization on the basis of real time iTrap data
- iTrap proves reaction of BCl_3 with F, presumably outgassing from chamber wall: Expected BCl_2 shows up only with delay.
  - As Plasma is off, this effect can not be investigated with OES
  - Risk of unwanted First Wafer Effects can be mitigated
  - Insight to the dealing with parts attached to the etch chamber and to the sampling line to the MS itself
- Heavy species like $SiCl_3$, $TiCl_3$, $SiCl_4$, $HfCl_2$ can be monitored, also in non-plasma conditions, whereas typical RGA's suffer from low sensitivity at high masses
- Processes in the time range of 10-30 s can be easily examined
- iTrap investigates TBAs decomposition in MOVPE reactor system

Literature

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