Very sensitive real-time inline process mass spectrometer based on FFT Ion Trap Technique

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Abstract— **In this work, we introduce a new, very fast and extremely sensitive inline process mass spectrometry technique based on Fourier-Transform 3D-Quadrupole Ion Trap technology. With this new technology, we have successfully detected sub-ppbV AsH_3 and single digit pptV B_2H_6 dopants in H_2 process gases within seconds. Real-time inline measurement at a CVD chamber showed that our technology was capable to detect reaction products, contaminations on the wafer holder and dopant memory effects in real-time. In contrast to typical residual gas analyzers, our new 3D-Quadrupole Ion Trap did not show mass discrimination with increasing m/z–ratio and was therefore capable to detect large molecules with very low concentrations.**

Keywords—Ion Trap mass spectrometer; FFT; inline; real-time; pptV sensitivity; fast; robust.

I. Introduction

ITRS technology roadmap requires real-time inline "point of use" control of process gas compositions and contaminations with very high sensitivity [1]. Up to now, most of the real-time process gas analysis were carried out with differentially pumped Residual Gas Analyzers (RGA) which are based on the linear quadrupole mass filtering technique. However, the sensitivity of this technology is limited by the dynamic range of the secondary electron multiplying detector and its strong sensitivity loss with increasing m/z–ratio. For generating a complete mass spectrum, the RGA has to scan masses which usually takes a few minutes. Therefore, a real-time detection of multiple gas species is nearly impossible. Furthermore, typical RGA's are usually equipped with sensitive secondary electron multipliers and electron detectors which can be eroded by aggressive process gases such as chlorine, fluorine or hydrogen. As a result, RGA's, if used as a real-time inline monitoring device, will suffer from degradation and life-time problems.

We introduce a new process mass spectrometry technique based on Fourier-Transform 3D-Quadrupole Ion Trap technology which is more appropriate for real-time inline process analysis. With this new technology, we have achieved very fast measurements down to extremely low detection limits within seconds. Due to the absence of electron multiplier and fragile electron/ion detectors, our mass analyzer is, by concept, unaffected by typical aggressive process gases in the semiconductor manufacturing environment. Furthermore, our device is robust against temporal pressure bursts up to a few hundred mbar. Therefore, a direct installation of our mass spectrometer to the process chamber via a simple gas regulation valve without complicated and expensive pressure reduction stages is possible.

II. Fourier-Transform 3D-Quadrupole Ion Trap Technology

The 3D-Quadrupole Ion Trap mass spectrometer (iTrap®) of Carl ZEISS SMT GmbH is installed in a vacuum chamber (11,4cm x 11,4cm x 11,4cm) equipped with an Atomic Layer Deposition (ALD) valve for pulsed process gas sample injection (pulse duration ~ 50ms). This ALD valve can serve as an interface between the mass spectrometer and the customer process chamber which may have a process pressure up to a few hundred mbar. Vacuum in the iTrap® chamber is generated by a turbo molecular pump which maintains a low working pressure during the measurements. A schematic drawing of the iTrap® system together with its peripheries is shown in Fig. 1. The ion trap analyzer itself is equipped with an integrated electron gun which ionizes the pulse injected process gas species inside the ion trap with 70eV energy. By applying a radio frequency to the ring electrode of the ion trap, mass selective ion accumulation and in-phase mass dependent ion oscillations can be achieved. By using a highly sophisticated signal compensation concept, selective ion excitation technique and advanced low-noise charge amplifiers, the very small mirror current (in fA) on the upper and lower electrodes of the ion trap induced by the oscillating ion population in the ion trap can be electrically measured without using any separate particle detector. The corresponding mass spectrum is finally obtained by Fourier transformation. The working principle of the iTrap® electronics is shown in Fig. 2. This approach is a non-destructive measuring concept which allows for a) highly linear ion measurement and excitation, b) very fast and highly sensitive broadband measurements, c) selective ion manipulation for dynamic range enhancement, d) high mass resolution for ion identification and e) omission of degradable electron/ion detectors [2], [3], [4]. The relatively moderate footprint of the iTrap® system also allows the installation of the device onto typical semiconductor processing chambers as close as possible so that inline real-time process analysis can be achieved.

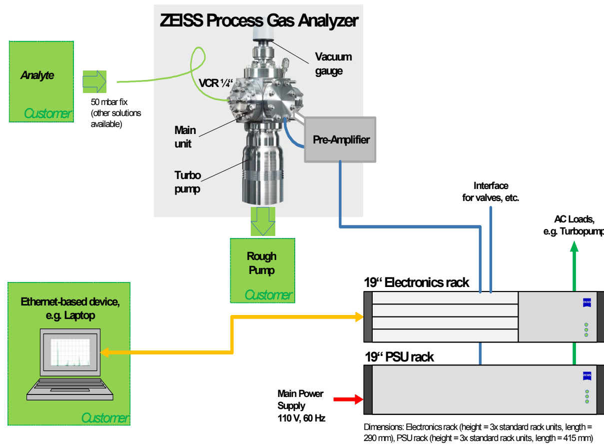

Fig. 1. Schematic drawing of the iTrap® system of Carl Zeiss SMT GmbH together with its peripheries.

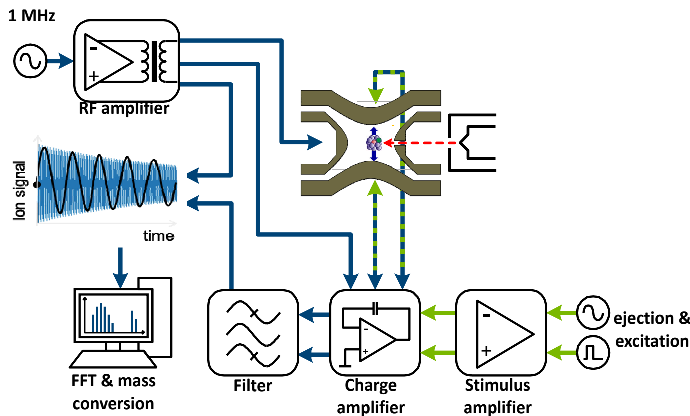

Fig. 2. The working principle of the iTrap® technology.

III. Evaluations of the iTrap® Technology Performance

In order to explore the performance of the iTrap® technology, a) benchmarking experiment with a typical RGA, b) detection-limit evaluations by measuring extremely low concentrations of n-type and p-type dopants in H_2 carrier gas and c) real-time inline process gas measurements at a CVD chamber during GaN epitaxy were carried out.

A. Benchmarking between iTrap® and typical RGA

RGA's based on the linear quadrupole mass filtering technique are usually used for real-time process gas analysis in semiconductor processes. Due to its limited mass resolution, low speed and sensitivity loss with increasing m/z–ratio, the RGA technology is by far a compromise solution with less satisfaction.

Therefore, a benchmarking experiment between iTrap® and a state of the art RGA in the light of mass resolution, measuring speed of an entire mass spectrum (30 amu to 200 amu) and sensitivity at higher masses was carried out. During our experiment, the Zeiss iTrap® mass spectrometer and a typical RGA were mounted simultaneously onto a ultra-high vacuum chamber for photo-resist outgassing investigation. During the measurement, both of the analyzers were running and the vacuum pressure was around $1x10^{-7}$ mbar. A clean quartz plate coated with a pre-baked photo-resist together with a lubricant-contaminated O-ring were loaded into the chamber as test samples. In Fig. 3(a) and Fig. 3(b), the mass spectra of the organic outgassing of the samples measured by the two technologies are shown, respectively.

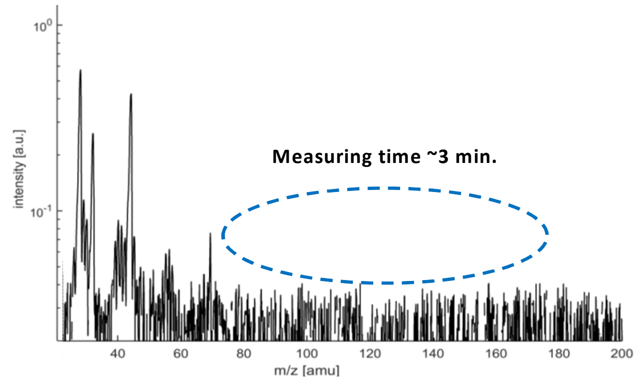

Fig. 3(a). RGA mass spectrum of organic outgassing of a photo-resist plus a lubricant-contaminated O-ring. Signals from the contaminated O-ring (above 80 amu) was missing due to mass discrimination with increasing m/z–ratio in RGA. Measuring time for the entire spectrum was around 3 minutes.

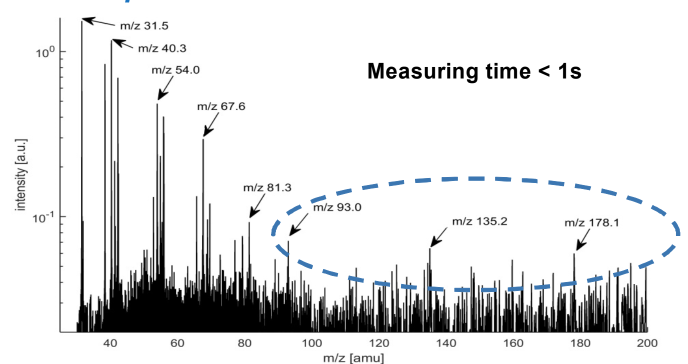

Fig. 3(b). iTrap® mass spectrum of organic outgassing of a photo-resist plus a lubricant-contaminated O-ring. Signals from the contaminated O-ring (above 80 amu) could be detected. Measuring time for the entire was less than 1 sec..

The measuring time for the entire mass spectrum (30 amu to 200 amu) in the case of RGA was around 3 mins, whereas in the case of iTrap® it was less than 1 sec. This extremely high

measuring speed of iTrap® allows the user to obtain "true" real-time broad band process gas mass spectrum and process information which RGA cannot provide within such a short time.

Both spectra showed typical outgassing patterns of the photo-resist under 70eV ionization with mass fragmentation period of 14 amu ($-CH_2-$). However, the mass resolution of the iTrap® spectrum was extremely high ($m/\Delta m > 10000$), whereas the mass signals of the RGA were very broad. This high mass resolution of iTrap® is particularly useful for the identification and differentiation of advanced organic photo-resist molecules with overlapping mass fragmentation periods in the mass spectra.

Detailed investigation of the two spectra also revealed that the iTrap® mass spectrum contained extra features at masses above 80 amu whereas the RGA spectrum showed no signals in this mass region. These spectral features in the iTrap® mass spectrum are believed to be related to the lubricant-contaminated O-ring. Lubricants are usually strong poisons for semiconductor processes, and they contain long-chain organic molecules with high boiling points. Therefore, mass signals coming from these molecules are usually quite weak and are located in the higher mass region. Due to its sensitivity loss with increasing m/z–ratio, typical RGA can hardly detect such less volatile long-chain molecules. The iTrap® technology does not have any sensitivity loss with increasing m/z–ratio due to its linear measuring principle. Therefore, it is obvious that iTrap® is a more suitable device for real-time process contamination control especially if large organic molecules come into play.

B. Detection of AsH_3 and B_2H_6 concentrations in the pptV regime

AsH_3 and B_2H_6 are common n- and p-type doping precursors for Si layers in epitaxy processes. A very sensitive measurement of these precursors in the process gas in real-time may enable the user to control the dopant levels in the process chamber precisely. As a result, a more reproducible run-to-run doping level can be achieved. Furthermore, a very sensitive dopant detection in the process chamber also provides information about unwanted dopant memory effects and allow the user to execute predictive process chamber cleaning.

In the present experiment, a very low concentration of AsH_3 (1 ppbV) and B_2H_6 (2 pptV) were introduced into a 1 bar ultra- pure H_2 process gas flow respectively and measured with the iTrap® mass spectrometer. The iTrap® mass spectra in Fig. 4(a) and Fig. 4(b) impressively showed that iTrap® could measure sub-ppbV level AsH_3 and single digit pptV level B_2H_6 with a very good S/N-ratio. The measuring time of the spectra was around 3 to 5 seconds. These spectra were all recorded in the so-called one-short mode where no signal averaging nor integration were done during the measurements or data analysis. We believe that if spectral averaging or integration were applied, an even higher sensitivity below 1 pptV could have been achieved.

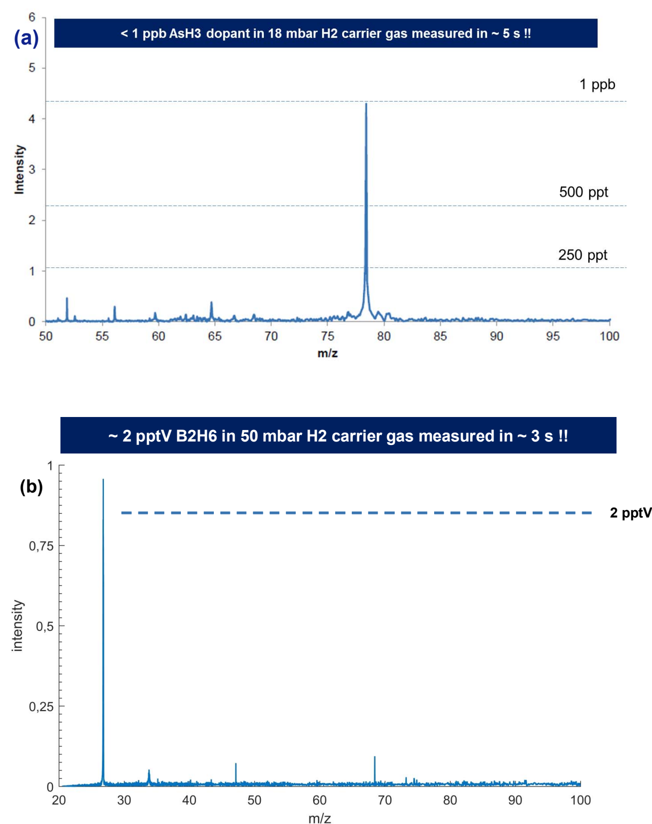

Fig. 4. *iTrap®* Mass spectrum showing (a) sub-ppbV level of AsH_3 and (b) single-digit pptV B_2H_6 in H_2 carrier gas flow. The measuring time was around 3 to 5 sec. The spectra were recorded in the so-called one-short mode where no signal averaging nor integration were applied.

C. Real-time inline measurement at a CVD chamber during GaN epitaxy

GaN is a state of the art compound semiconducting material for the manufacturing of visible LEDs. In recent years, this new material has also been proved to be a key substance for the production of high power and high speed electronics [5]. For all these applications, GaN epitaxial layers have to be grown onto SiC or sapphire substrates by MOCVD or MBE processes.

Therefore, in order to demonstrate the real-time inline capability of iTrap® with a state of the art semiconductor manufacturing process, the mass spectrometer was integrated into the exhaust of an AIXTRON® G3 MOCVD chamber in which a GaN epitaxial growth was running. During the epitaxy, N_2, H_2, $Ga(CH_3)_3$ and NH_3 precursors were directed into the chamber. The temperature and the pressure of the process were around 1000°C and 100mbar, respectively. No dopant precursors were intentionally introduced into the process chamber during the growth. Fig 5 showed a real time spectrum of the epitaxial process. The measuring time was in the range of a few seconds.

This spectrum shows peak 1 & peak 2 which were identified by a previous experiment as gas species related to susceptor contamination outgassing. Peak 3 to peak 6 are believed to be gas phase reaction products which can either be related to the GaN formation (peak 3 & peak 4) or to particle formation in the gas flow (peak 5) or to adduct formation in the gas phase (peak 6) [6]. By tracing the behavior or variation of these peaks with time, the user will be able to obtain more real-time insight about the cleanliness of the susceptor, the efficiency of the dissociation/reaction processes of the precursors and the critical particle formation process in the MOCVD chamber. In this way, susceptor contamination can be under control, process drifts can be corrected and subsequently process yield can be increased. Two further peaks (peak 7 & peak 8) could also be observed in the spectrum. These peaks can be identified as Cp_2Mg (Biscyclopentadienyl-magnesium) related molecules. Cp_2Mg is a typical p-type dopant for GaN LED production. Although no Cp_2Mg was intentionally introduced into the process chamber during our growth, trace of Cp_2Mg is usually expected in nearly all GaN epitaxy chamber due to the large memory effect of Cp_2Mg. Therefore, in order to maintain a stable electrical performance of the GaN LED's, MOCVD chambers have to be cleaned regularly to remove this memory effect. Real-time inline iTrap® measurements can thus provide the user information about the unintentional dopant level of the process chamber and assistance for defining chamber cleaning intervals.

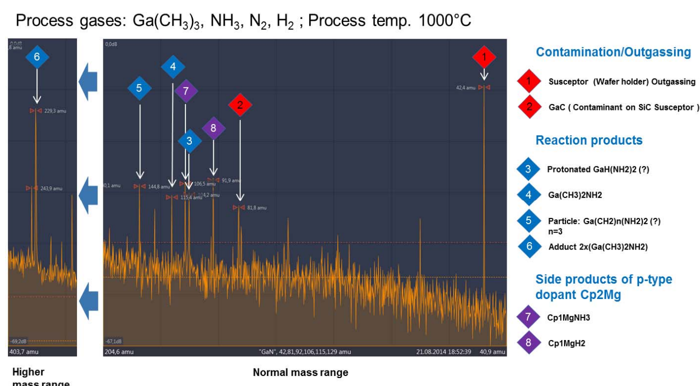

Fig 5 Real-time *iTrap®* mass spectrum recorded at the exhaust of a AIXTRON G3 MOCVD chamber during GaN growth process (100mbar). Peaks related to susceptor outgassing, gas phase reactions, particle formation and dopant memory effects could be observed.

IV. Conclusion

The mass spectrometer iTrap® of ZEISS has successfully demonstrated superior performances against typical RGA. In contrast to RGA, iTrap® does not have any sensitivity loss with increasing m/z–ratio. Therefore, it is believed that iTrap® is a more suitable device for real-time process contamination control especially if larger organic molecules are involved.

We also have successfully shown that iTrap® can detect sub-ppbV AsH_3 and single digit pptV B_2H_6 dopants in H_2 process gas within seconds. These results proved that our new technology is a good candidate as dopant monitor in epitaxy process chambers. Real-time inline measurement at a CVD chamber during GaN growth showed that iTrap® is capable to detect reaction products, contaminations on the wafer susceptor and dopant memory effects in real-time. These results demonstrate that iTrap® is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Acknowledgment

The authors would like to thank the continuous scientific and engineering support of the research groups " Physical & Theoretical Chemistry" and " Sensor Technology & Measurement technology system" of the University Wuppertal, Germany.

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