Analytic Methods for ALD Technologies

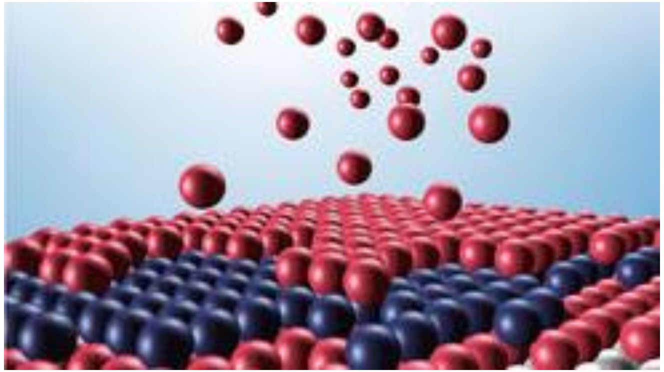
An in-depth look at mass spectrometry for the characterisation of ALD Processes

Dr Dane Walker
Technical Marketing Manager
Hiden Analytical Ltd

Introduction

What is ALD?

- **Atomic Precision:** ALD enables the deposition of materials with atomic layer precision, allowing for the growth of films with exact thickness and composition control.
- **Surface Chemistry:** Utilises self-limiting chemical reactions between gas phase precursor molecules and the substrate surface, ensuring uniform coverage even on complex geometries.
- **Cyclic Process:** Involves repeated cycles of precursor adsorption, purge, reaction, and another purge to build films one atomic layer at a time.
- **Wide Material Range:** Compatible with a broad range of materials, including oxides, sulphides, nitrides, and metals, making it highly versatile for various applications.
- **Temperature Control:** Can be conducted at temperatures ranging from below 100°C to over 300°C, accommodating temperature-sensitive substrates.



The ALD Process

The ALD process consists of repeated cycles of self-limiting chemical reactions between gaseous precursor molecules and a surface.

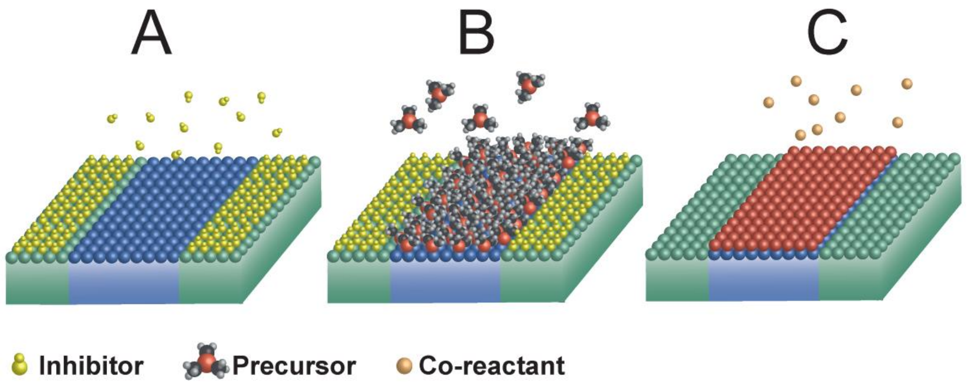
Precursor Adsorption: A precursor gas is introduced into the chamber and adsorbs onto the substrate's surface.

Purge: The chamber is purged with an inert gas to remove excess precursor.

Reaction: A second reactant is introduced, reacting with the adsorbed layer to form a monolayer.

Second Purge: The chamber is purged again to remove reaction byproducts and unreacted reactant, preparing the surface for the next cycle.

Process control and monitoring is critical.



Merkx et al., Chem. Mater. 2020, 32, 3335−3345

Application Examples

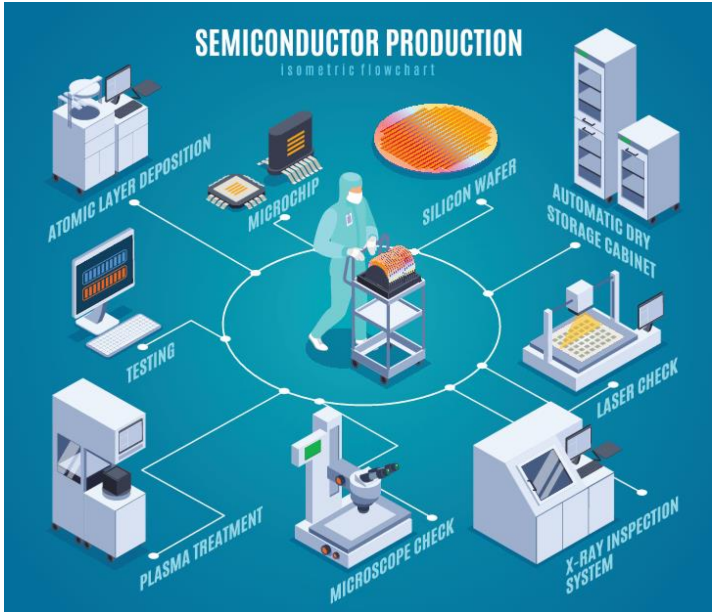
- **Semiconductor Devices:** Critical for manufacturing advanced semiconductor devices, including gate dielectrics, and memory devices where precise thickness control is essential for device performance.

- **Photovoltaics:** Used to deposit thin films for solar cells, improving energy conversion efficiency through enhanced light absorption and electron transport layers.

- **Protective Coatings:** Applied for corrosion resistance or barrier layers on metals and polymers, extending the life of components in harsh environments.

- **Optical Applications:** Enables the creation of anti-reflective coatings for lenses and mirrors, and precise optical filters for sensors and cameras.

- **Medical Implants:** Deposits biocompatible materials on medical implants, enhancing their compatibility and longevity within the human body.



Challenges in ALD

Uniformity and Repeatability Issues

Precision Demand: Achieving uniform film thickness across complex 3D structures and large substrates is challenging, which is critical for device performance.

Process Sensitivity: Minor variations in process parameters (e.g., temperature, precursor flow rate) can lead to significant inconsistencies, affecting repeatability.

Contamination and Defect Control

Source Purity: Impurities in precursors or carrier gases can lead to inclusion of unwanted elements, affecting film properties.

Environmental Control: Maintaining ultra-clean process environments is crucial to prevent particulate contamination that can create defects in the films.

Need for In-situ Process Monitoring and Analytics

Real-time Feedback: Continuous monitoring is essential for detecting deviations in the process, allowing for immediate corrections to ensure quality.

Process Analytics

Process Analytics for ALD

Purpose: Utilise data from ALD operations to optimize performance and quality.

Techniques: Spectroscopy, mass spectrometry, and sensors for real-time parameter monitoring (temperature, pressure, precursor flow).

The Role of Real-Time Monitoring

Specialised systems, equipped with mass spectrometers allow for real time monitoring of species.

Immediate Adjustments: Detects deviations, allowing for quick corrections to process parameters.

Efficiency & Quality: Identifies opportunities for process improvement, enhancing yield and maintaining high-quality output.

Typical Inlet system for Process Analytics

Vacuum Process Gas Analysers

Analyse processes with high dynamic range operating at pressures >10^{-4} mbar it is necessary to pump the RGA with its own vacuum system and sampling connection

Sampling connection optimised to maintain fast response time and maximum sensitivity

Typical system, like the **Hiden HPR-30** uses an orifice inserted into the process chamber with a high conductance path from orifice to **RGA**

Re-entrant orifice provides for fast response, high sensitivity sampling

High conductance sampling path provides for residual gas analysis when the chamber is at less than 10^{-3} mbar, or at base vacuum

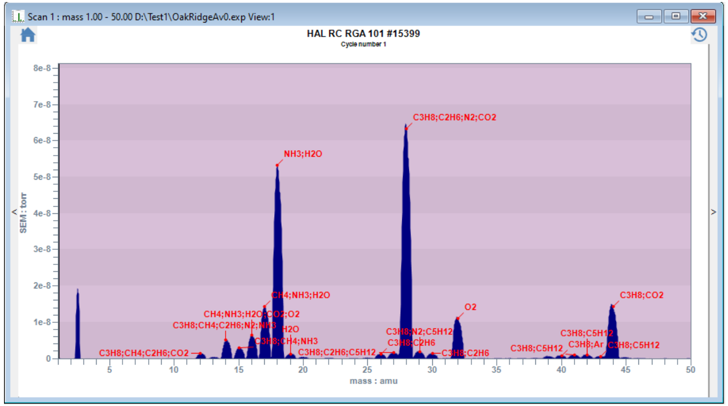
Re-entrant orifice is **custom designed** for special process monitoring requirements, for both process chamber configuration and process pressure

For monitoring gas composition and contaminants in sputtering, CVD, ALD, MOCVD,PECVD, PVD, evaporation, and optical coatings.

Real Time Monitoring

Enhancing ALD with real time monitoring

Predictive Maintenance: Forecasts equipment issues, reducing downtime.
Quality Assurance: Check that the deposited layer meets exacting standards, crucial for demanding applications.



The Future of ALD with Analytics

Innovation Driver: Facilitates the exploration of new materials and the refinement of processes, driving advancements in ALD technology.

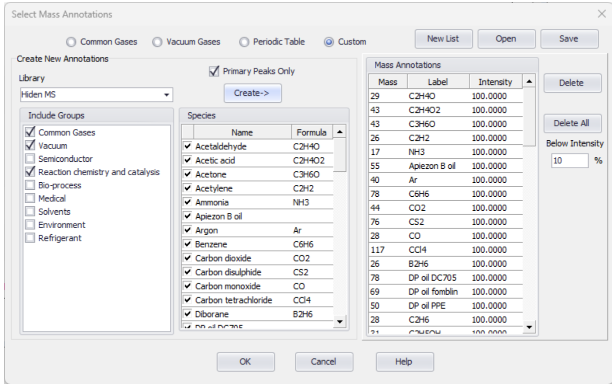
HIDEN ANALYTICAL

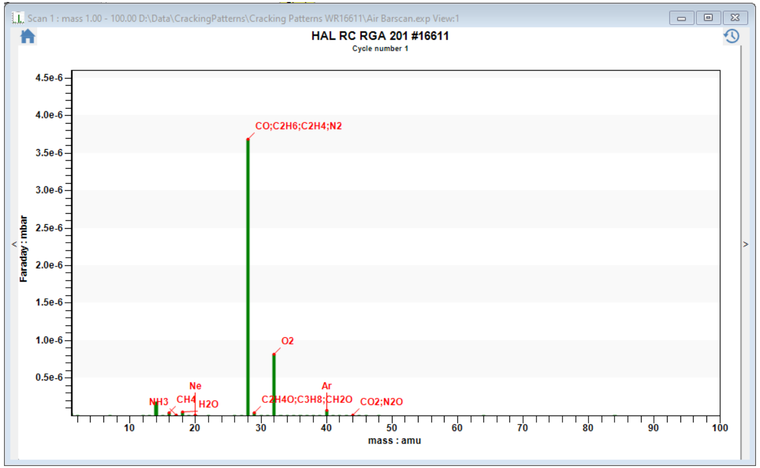
Residual Gas Analysis - RGA

Residual Gas Analysis (RGA) – A diagnostic technique using Quadrupole Mass Spectrometry to directly quantify species in the process chamber environment.

RGA Data – Mass spectra give a “vacuum fingerprint” of all species in the ALD chamber. Initial scans are used for leak checking and chamber contamination.

Process Optimisation – Identifying species in the process allows users to fine tune process conditions



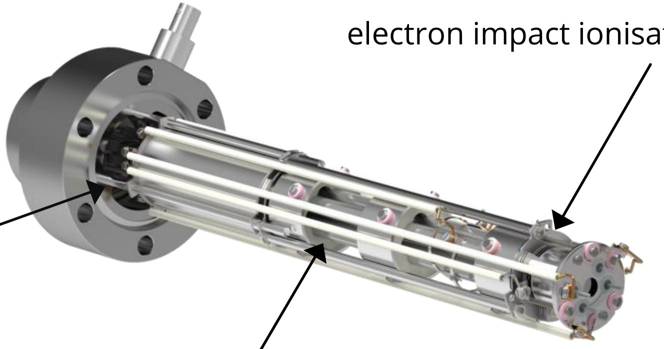


Integral RGA for high precision measurements

Ionisation Takes place at the ionisation source

RF/ DC filtering A combination of RF and DC fields applied to the quadrupole mass filter allows specified ions to travel to the detector

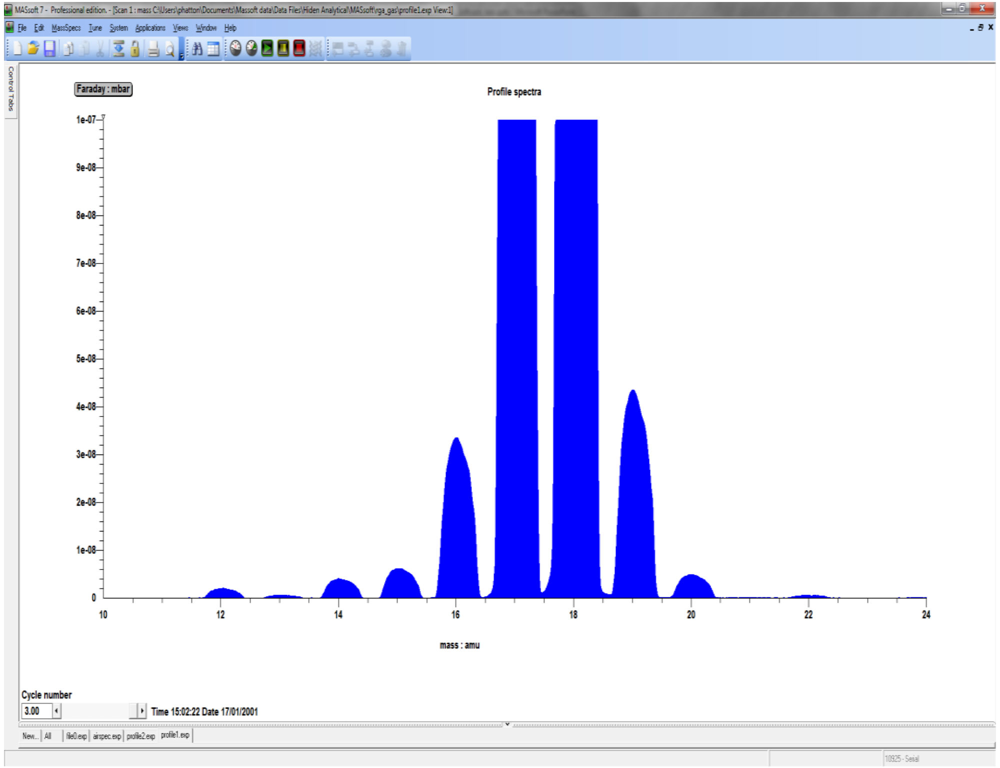
Detector A dual faraday/electron multiplier detector allows detection of ions to 3 x 10^{-16} mbar



Typical RGA Scans

Fingerprint Scan: A typical scan to give a "vacuum fingerprint" of the system. Quantifies species present – can be run at any time in the process.

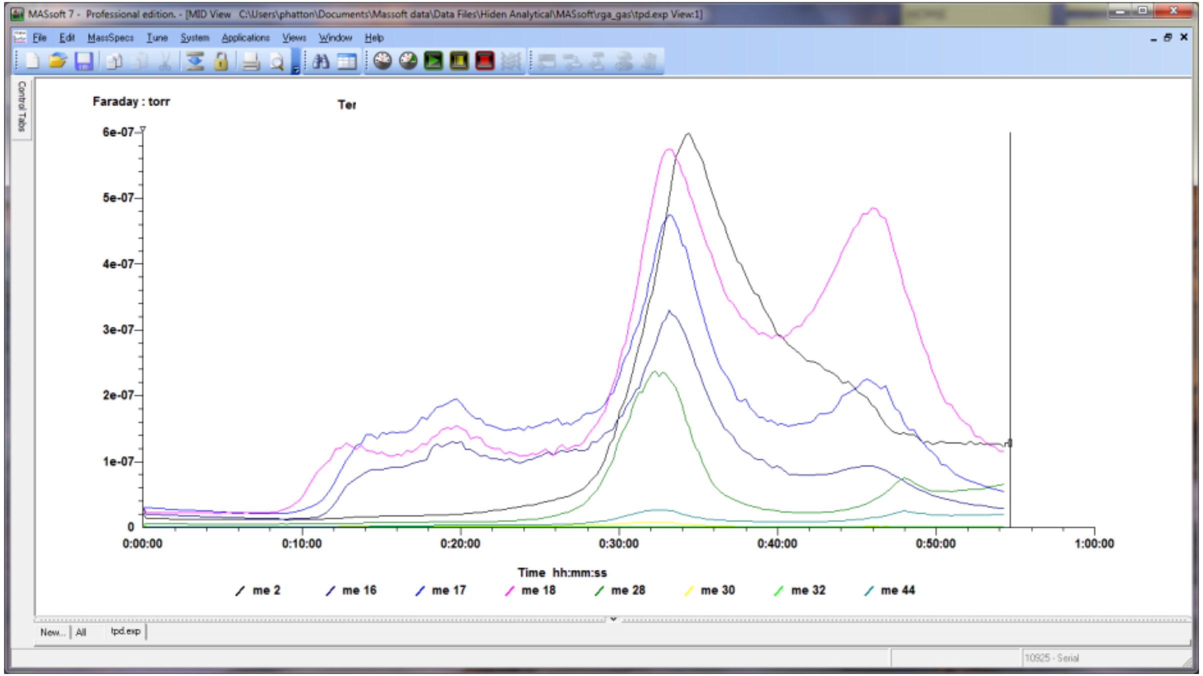
Leak Checking: A real time scan of one species, typically helium, used to check the leak tightness of the process chamber.



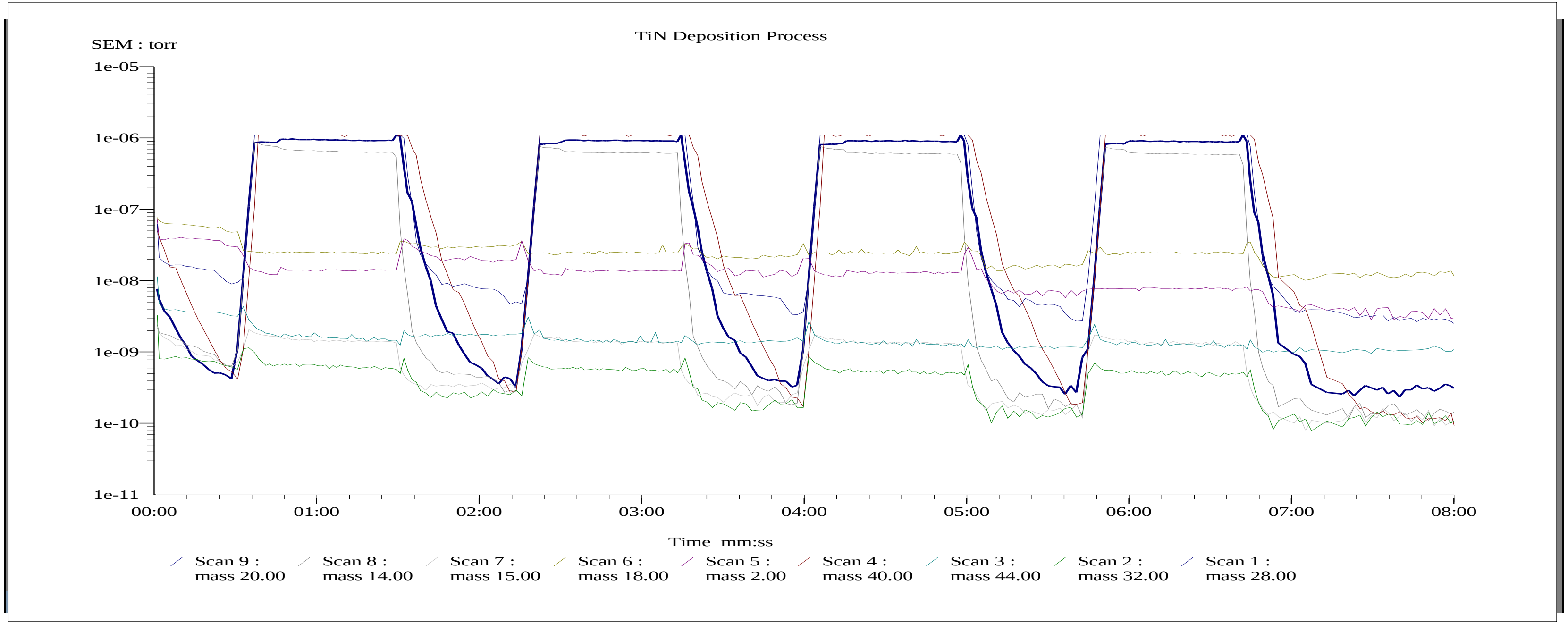
Typical RGA Scans

Precursor Quality: After the Precursor species are added to the chamber, scan to check precursor composition and check for impurities.

Reaction Monitoring: As deposition progresses, precursor and reactant species can be followed with respect to time, where changes in concentrations can be monitored, giving a direct insight into the deposition process.



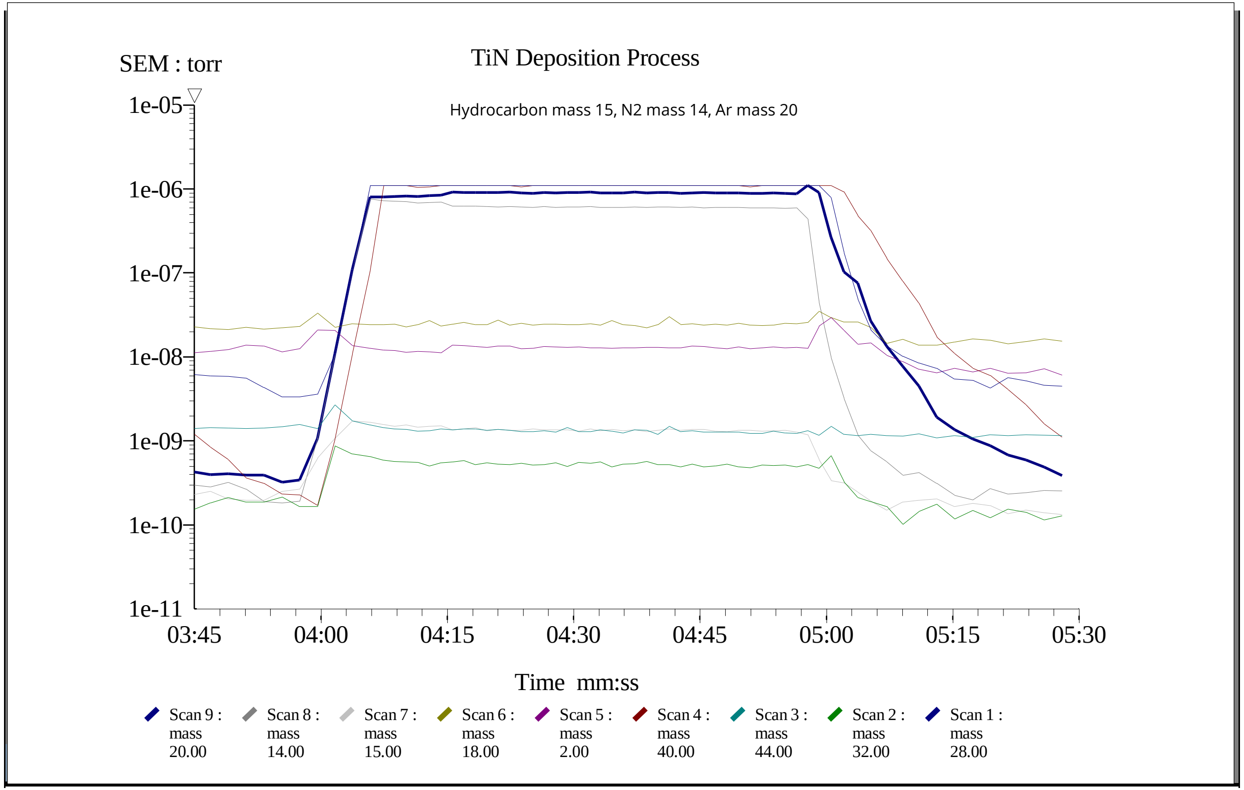
ALD Deposition Data examples



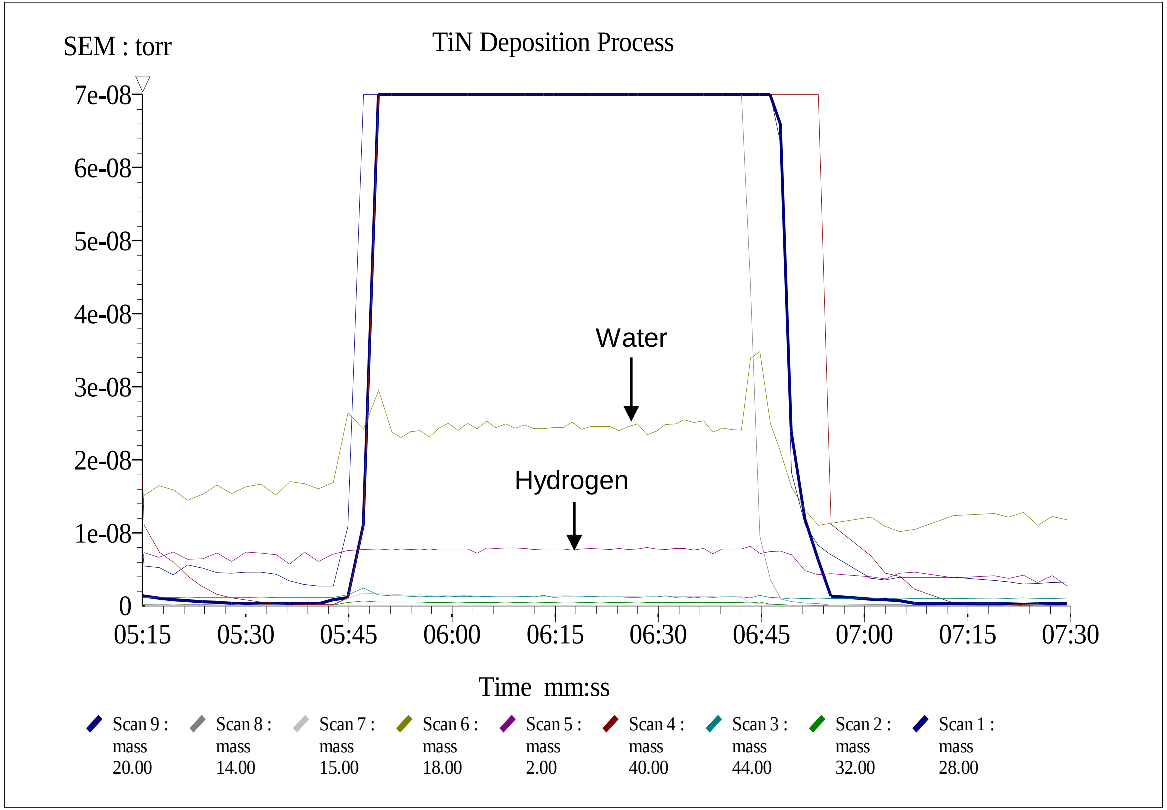
Trend Analysis of: water, hydrogen, hydrocarbons CO_2, Ar, N_2 in four titanium nitride deposition cycles.

TiN Deposition: A Wafer Cycle Profile

- TiN Process Endura PVD
- Reagent Gas Levels Monitored
- 8mbar process pressure
- Ultrapure Ti Target
- 60:40 N_2 to Ar



Contaminant Analysis



Zoom in on the process run data to reveal the primary process contaminants

Water at 0.1%

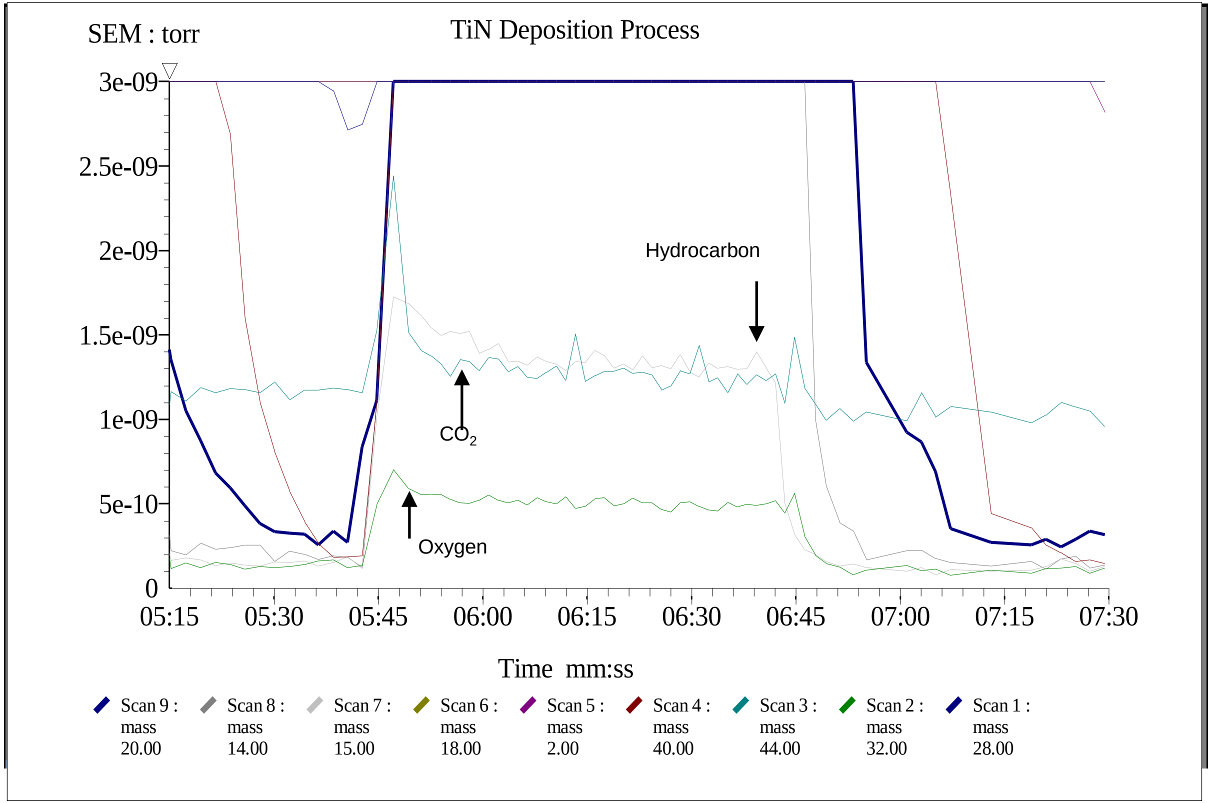
Hydrogen at 0.05%

Low Level Process Contaminants

Further zoom to examine **ppm level contaminants**

In process **hydrocarbon** background at 100ppm

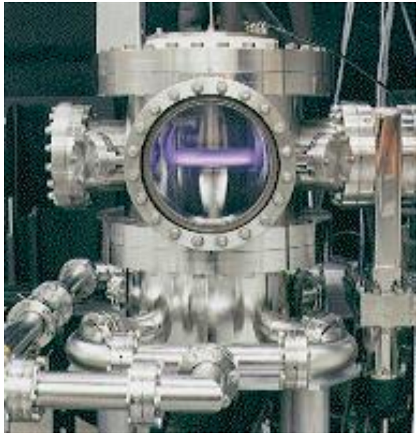
CO_2 at 120ppm

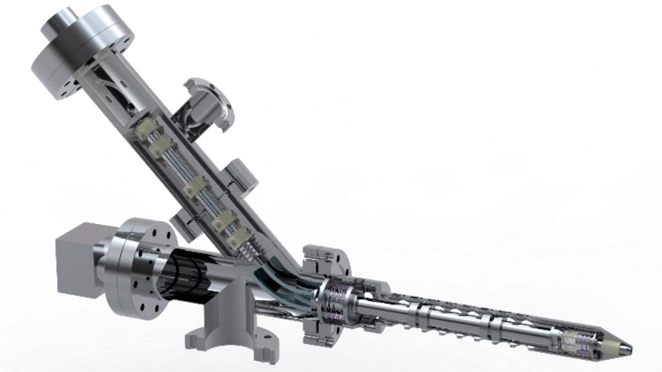


Special Cases – Plasma Assisted ALD (PA-ALD)

Enhanced ALD Technique: PA-ALD utilizes plasma to enhance the chemical reactions involved in the ALD process, enabling lower temperature operations and improved film properties.

Key Mechanism: The use of plasma generates reactive species (ions and radicals) that can achieve more efficient and sometimes chemically different surface reactions compared to thermal ALD processes.





Considerations and Challenges

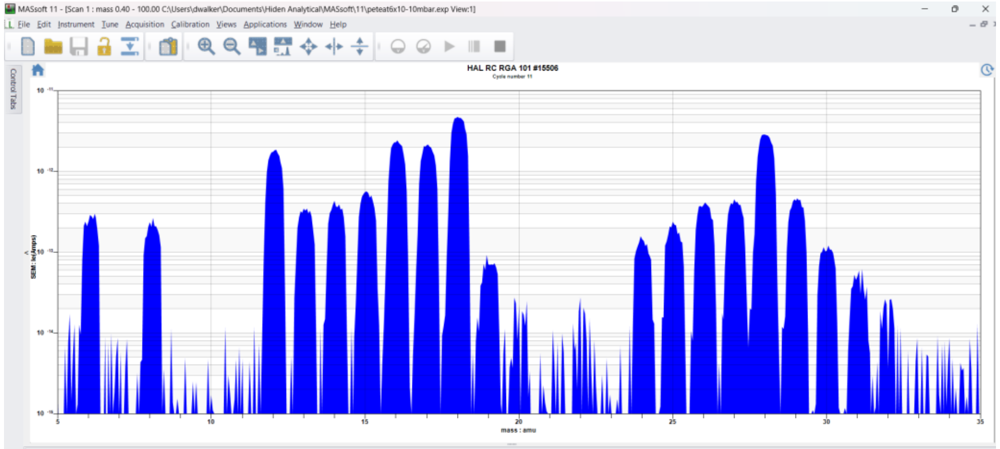
Ion Energy Control: Managing the energy of ions is crucial to prevent damage to the substrate and ensure the desired film characteristics.

Process Optimization: Requires careful optimization of plasma parameters to achieve the best results, including power, pressure, and gas composition.

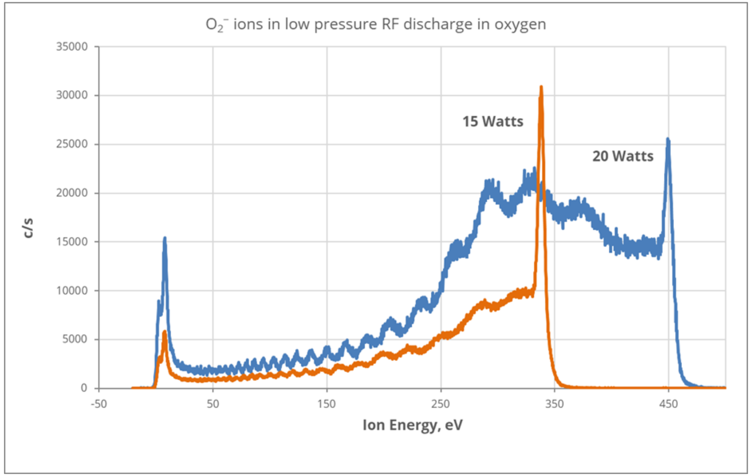
Plasma Assisted ALD (PA-ALD) – Typical Data

Combined Mass and Energy Analysis System: A unique MS system, tailored for energy resolved mass spectra.

The **Hiden Analytical EQP** system is tailored for mass and energy analysis of ions, neutrals and radicals in plasmas.



Vacuum Fingerprint Time averaged scans: +ve, -ve and neutral species scans.



Ion Energy Distribution Scans (IEDs)

Special Cases – Pulsed ALD

What is Pulsed ALD?

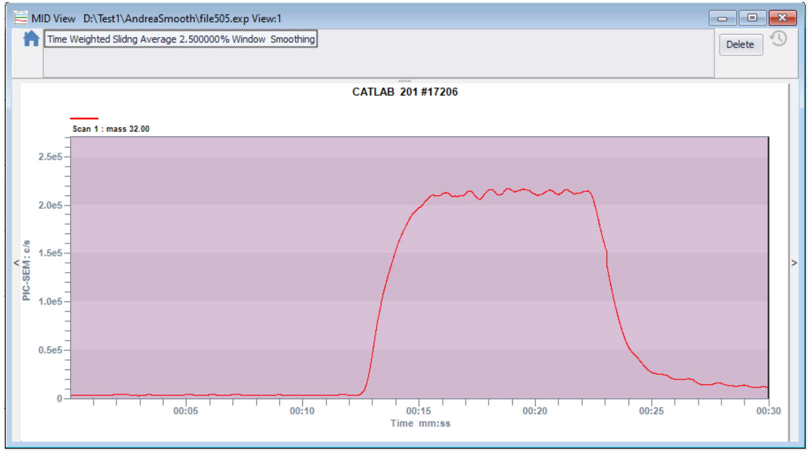
- A sophisticated variant of Atomic Layer Deposition that introduces chemical precursors in a pulsed, rather than continuous, manner.
- Enables atomic-scale precision in the deposition of thin films, crucial for advanced material fabrication.

Mechanism of Pulsed ALD

- Sequential exposure of the substrate to gas-phase precursors, each pulse followed by an inert gas purge to remove unreacted precursors and byproducts.
- Self-limiting reactions ensure a single atomic layer per cycle, enhancing uniformity and thickness control.

Advantages

- Compared to traditional ALD, pulsed ALD offers enhanced control over film thickness and material properties, increased deposition rates, and reduced precursor waste.



Example Applications

Microelectronics: Fabrication of gate oxides and insulating layers.
Photovoltaics: Coating of conductive oxides for solar cells.
Nanotechnology: Creation of ultra-thin coatings for nanoparticles.

Conclusions

ALD Processes can be optimised by characterisation methods such as Mass Spectrometry

Specialist Mass Spectrometry systems such as the Hiden HPR-30 allow for real time monitoring of processes over a range of pressures and conditions

For processes such as **PA-ALD and Pulsed ALD** Mass spectrometry systems such as the Hiden EQP allow for analysis of neutrals and ionn with options to analyse time resolved species in Pulsed ALD.

HIDEN ANALYTICAL

Recent Hiden Users

USA	UK/Europe	Asia Pacific
Applied Materials	Bosch	Canon
Axelis	IMEC	Hitachi Fundamental Res.
CVC/Veeco	Motorola	Hyundai
DuPont	Nortel Networks	LG Electronics
General Motors	Oxford Plasma Technology	NEC
IBM Research	Philips	Samsung
Lawrence Livermore	Rolls Royce	Sony Corporation
Motorola	SGS Thomson	TDK
NIST	Siemens	Tokyo Electron
Semetech	Surface Technology Systems	Toshiba

MOTOROLA ROLLS ROYCE Rolls-Royce® HITACHI BOSCH

HIDEN ANALYTICAL LTD

420 EUROPA BOULEVARD
WARRINGTON, WA5 7UN, UK
INFO@HIDEN.CO.UK
+44 (0)1925 445225