Application Note

Applications of Quadrupole Mass Spectrometry in Atomic Layer Deposition

PROBLEM Atomic Layer Deposition (ALD) processes have become an important technology in semiconductor device manufacturing over the past two decades. ALD processes use sequential surface reactions between an adsorbed monolayer of one reactant on a substrate surface and a gas phase co-reactant to produce a very uniform layer of solid film. The thickness of the film is determined by the number of cycles of adsorption/reaction in the process.

In order to achieve consistent process quality, the process and chamber condition and the stability and composition of the gas pulses in these processes must be closely monitored. Any sensors that are analyzing the process gas composition must be able to detect contaminants and undesired byproducts down to very low concentrations at pressures ranging between high vacuum and atmospheric pressure, depending on the ALD process type.

BACKGROUND

QMS/RGAs

The performance and reliability of Quadrupole Mass Spectrometers (QMS) [1] have improved significantly in recent years and this has led to an increase in their use as Residual Gas Analyzers (RGAs) in semiconductor manufacturing processes. RGAs identify and quantify the chemical composition of a gas sample and QMS-based RGAs offer distinct advantages. They have very high sensitivity and wide dynamic range which enables detection of a broad spectrum of molecular and atomic species. The fast gas sampling, high scanning speeds, and high time resolution of QMS/RGA instruments are important characteristics for analyzing processes such as ALD that have quickly changing gas compositions. As well, with appropriate gas inlet configurations, a QMS/RGA can analyze gas streams up to atmospheric pressure.

A QMS/RGA analyzes a gas sample by first ionizing and fragmenting the molecules in the gas stream, then separating and detecting the ions by mass/charge (m/e) ratio. Figure 1 shows the different components of a QMS/RGA. It consists of an ion source (ionizer plus ion accelerator), a source slit, a quadrupole mass filter composed of four parallel metal rods arranged as shown in Figure 1, an exit slit, and an ion detector. Different methods may be used to ionize the sample, including electron impact ionization, chemical ionization, and laser ionization, with electron-impact ionization being the most common. In electron impact ionization, electrons emitted by a hot filament are accelerated and impact incoming molecules and atoms to create positive ions:

$$A_xB_y + e^- \longrightarrow A_xB_y^+ + 2e^-$$

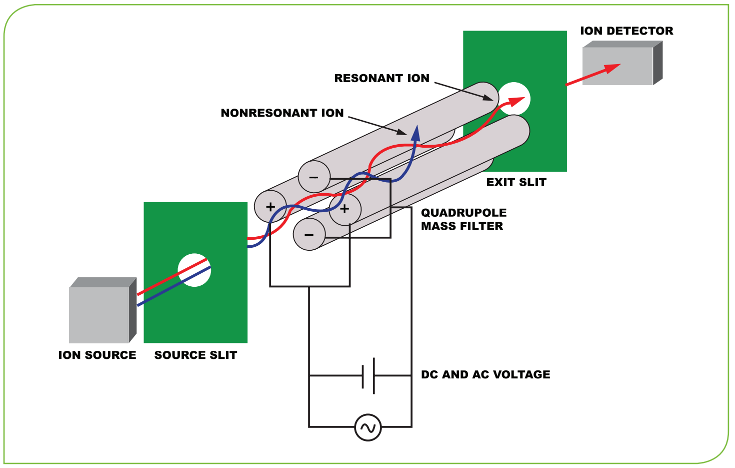

Figure 1:
The component parts of a quadrupole mass spectrometer.

The ionization process produces both parent ions (the original molecule with a positive charge) and positively charged molecular fragments; the fragmentation pattern acts as a fingerprint that helps in identifying the chemical species present in the sample. The ions created in this manner are accelerated using electric fields and directed through a slit into the quadrupole mass filter. The mass filter consists of four parallel metal rods arranged as shown in Figure 1. The applied voltages influence the trajectory of the ions coming through the source slit and passing along the central channel formed by the four rods. For a given combination of DC and AC voltage, only ions having a specific m/e ratio (known as resonant ions) have a trajectory that takes them through the mass filter and the exit slit. Ions having any other m/e value (non-resonant ions) will have a trajectory that causes them to impact the quadrupole rods and thus fail to pass through the exit slit. Once through the exit slit, the selected ions are detected, typically by a Faraday plate or secondary electron multiplier. By sweeping the voltages on the rods, it is possible to select for different values of m/e that will pass through the exit slit. The quadrupole/exit slit combination "filters" the ions created in the source, allowing only ions with a selected m/e to pass. The detector produces an electrical signal proportional to the number of ions of the selected m/e that strike it. All molecular and atomic components in the sample gas can be analyzed in a single scan of the possible voltages and the results of the analysis are displayed as a mass spectrum (plot of detector peak intensity vs. m/e).

Atomic Layer Deposition (ALD) and QMS/RGA

Atomic Layer Deposition (ALD, [2] [3]) is an advanced deposition technology that deposits thin films one-monolayer-at-a-time, as shown in Figure 2. ALD reaction chemistries may be driven by either thermal or plasma activation and ALD processes have been developed that operate between vacuum and atmospheric pressure. ALD has several advantages over conventional CVD for thin film deposition in semiconductor device manufacturing.

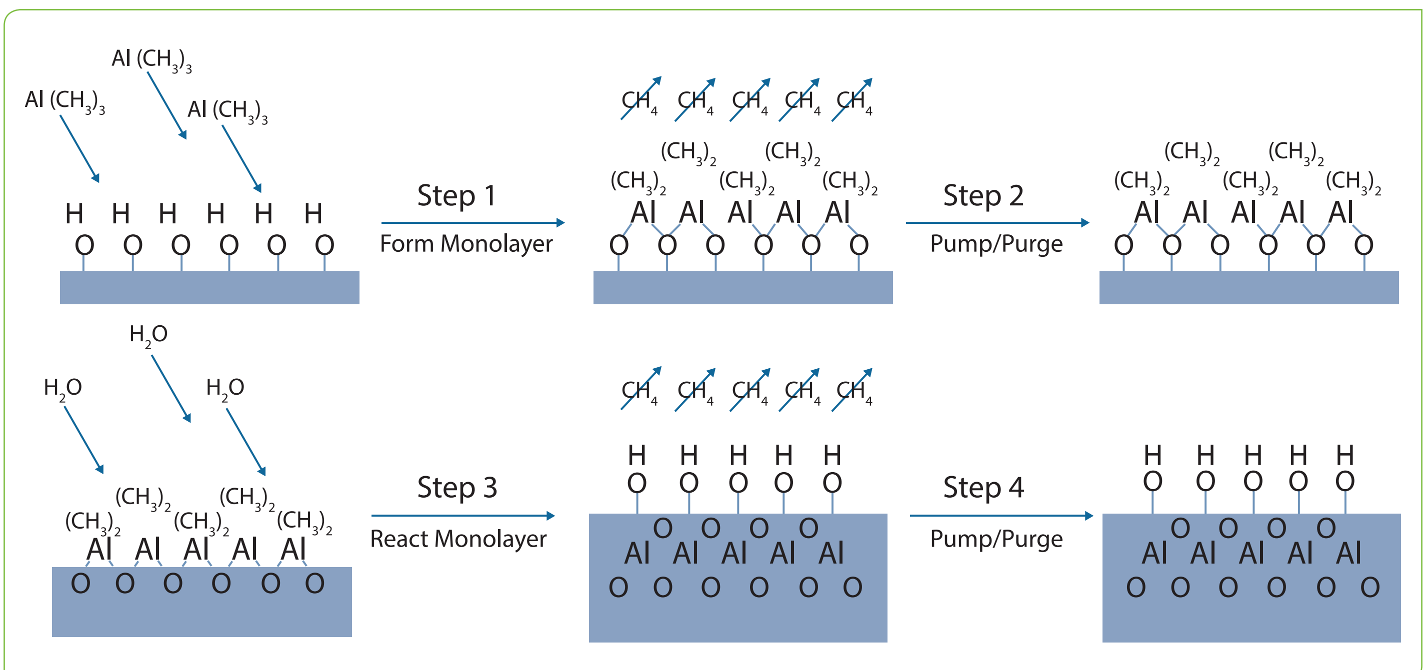

Figure 2:
An atomic layer deposition process for deposition of Al_2O_3 layers.

The film thickness and composition can be controlled much more accurately over large areas and challenging surface structures. Furthermore, ALD processes are, in general, lower temperature processes than conventional CVD, making them more compatible with nanoscale dopant profiles and feature sizes. The unique self-limiting surface chemistry of ALD processes broadens the range of available precursors for thin film deposition processes and allows exact control of film stoichiometry, a characteristic that is very difficult or impossible using conventional CVD.

Trace contaminants in the process ambient can produce undesired gas and surface reactions that adversely affect the production of continuous and pinhole-free films by ALD processing. Therefore, ALD process ambient must be closely monitored during many of the ALD and ancillary process steps. Precursor gas supplies must be analyzed for contamination and supply stability. The process ambient must be checked for residual contamination to optimize process parameters such as the required purge time following exposure of the internal system components to moisture or to in situ cleaning. Leak detection is, of course, a constant requirement in these systems. Quadrupole mass spectrometry has a demonstrated utility as an ideal analytical tool for ALD processing and it has been used in many characterization studies of ALD processes. References [4], [5], and [6] provide representative studies showing how a QMS/RGA system can be employed for monitoring ALD process chemistry.

SOLUTION

MKS QMS/RGA Systems for ALD

A QMS/RGA employed as a process monitor for ALD has specific operational requirements. These are primarily centered on the need for high sensitivity and rapid gas sampling times that correlate the ALD cycle times with the scan frequency of the mass spectrometer. Typically, the acquisition time for a mass signal should be of the order of 1 – 3 milliseconds for QMS/RGA systems employed in ALD processes. The requirement for rapid gas sampling also means that process gas inlet of the QMS/RGA must be designed to minimize any potential for adsorption and desorption of the gas phase species in the process sample. Finally, rapid gas sampling must not impact the sensitivity of the QMS/RGA which must maintain detection limits well below 1 ppm for the expected contaminants.

MKS Instruments offers a variety of QMS/RGA systems that are well-suited for use in ALD process applications. These systems have important design features that ensure that they satisfy the exacting requirements of ALD process monitoring. Figure 3 shows a typical ALD sampling arrangement used with MKS QMS/RGA systems. Separate base pressure and process inlets, coupled with fast purging capability for the process line (via valves V2 and V4), enable both dual pressure range operation and high-speed sampling. As well, the wetted internal volume of the sampling system is kept low to further facilitate rapid sampling. Capillary systems may also be used. All components of process gas sampling system are temperature-controlled (20 - 190°C) to avoid both undesired reactions between the process gas and the component materials and adsorption/desorption of gas species on the wetted surfaces. MKS Instruments' fast-response UniBloc™ inlet valve operates with a dual pressure range to allow QMS/RGA sampling at both background and process pressures.

High sensitivity in the QMS/RGA analyzer is achieved using MKS Instruments' patented V-lens™ ion optics. V-lens technology uses double focusing ion optics to

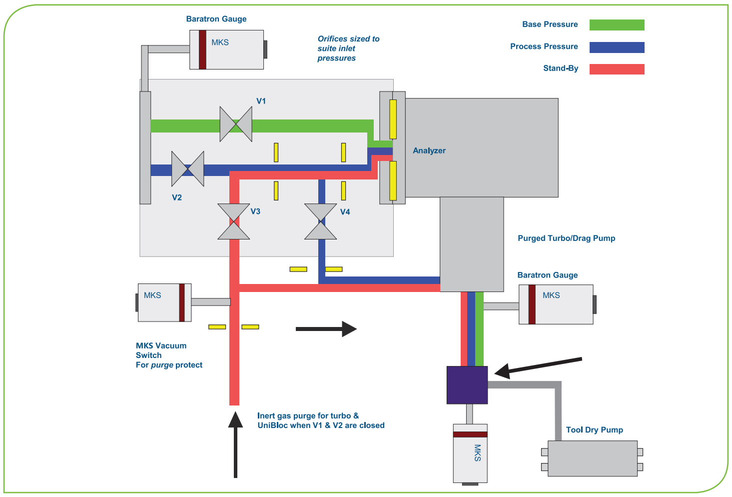

Figure 3:
A typical ALD process sampling configuration for use with MKS Instruments QMS/RGA systems.

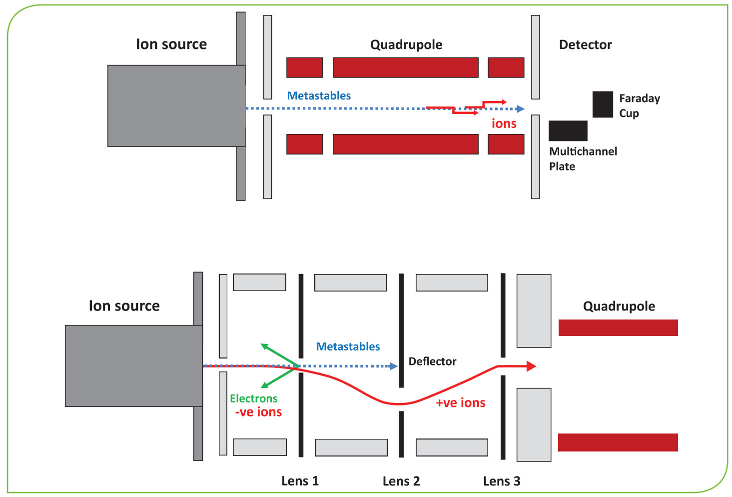

Figure 4:
Conventional ion optics (top) vs. MKS Instruments' V-lens™ ion optics (bottom).

block neutrals and metastable species from passing to the quadrupole while steering the positive ion beam into the quadrupole mass filter (Figure 4). V-lens technology significantly reduces background noise and enhances sensitivity in MKS QMS/RGAs, consistently producing limits of detection in the low ppb range. V-lens ion optics achieve these results even with gases that inherently produce large amounts of metastable species that would otherwise increase the baseline noise in a conventional QMS/RGA system.

QMS/RGA – ALD Applications

1. Aluminum Oxide Thermal ALD

Aluminum oxide ALD is a widely used process for creating dielectric isolating and passivation layers in semiconductor and solar cell manufacturing. It is a classic thermal ALD process, employing temperatures up to 300ºC. The deposition process uses the reaction chemistry shown in Equation (1):

$$Al(CH_3)_3 + 3H_2O \longrightarrow Al_2O_3 + 3CH_4$$

In this application study, QMS/RGA measurements were used to examine the stability of the pulsed reagent flow. Figure 5 shows the results of the QMS/RGA analysis. The analysis confirmed the stability of the TMA (trimethylaluminum, $Al(CH_3)_3$) supply during individual pulses and uncovered instabilities in the H_2O pulse behavior.

2. Titanium Nitride ALD

The ALD deposition process for titanium nitride films uses titanium tetrachloride and ammonia. It is a well characterized process that produces films with low resistivity, high-density and low levels of impurities. Titanium nitride films are required for example on metal electrode diffusion barriers or DRAM electrodes.

Figure 6 shows QMS/RGA analysis data for an ALD process that produced titanium nitride, Ti_3N_4, thin films according to Equation (2):

$$3TiCl_4 + 4NH_3 \longrightarrow Ti_3N_4 + 12HCl$$

The QMS/RGA trace in Figure 6 shows good responses of the dominant precursor signals for ammonia (Mass 17) and atomic titanium (Mass 48). Furthermore, the trace highlights various issues that exist in the precursor and pulse stability. Thus, this study demonstrates the value of in situ monitoring for the detection of equipment malfunctions.

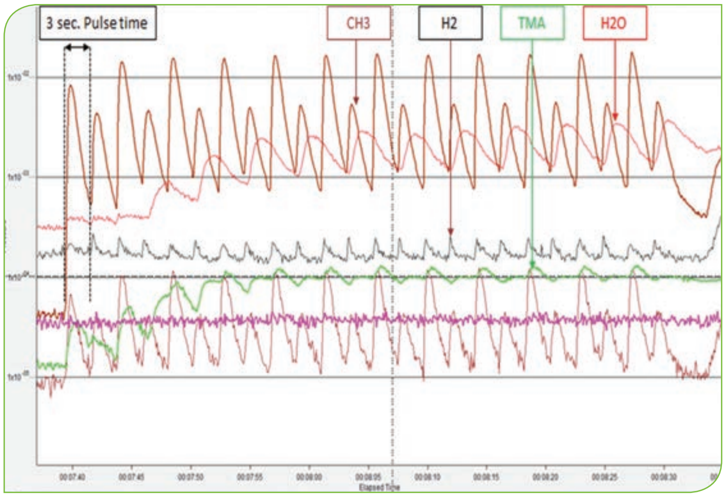

Figure 5:
QMS/RGA analysis of pulse stability in ALD Al_2O_3 process.

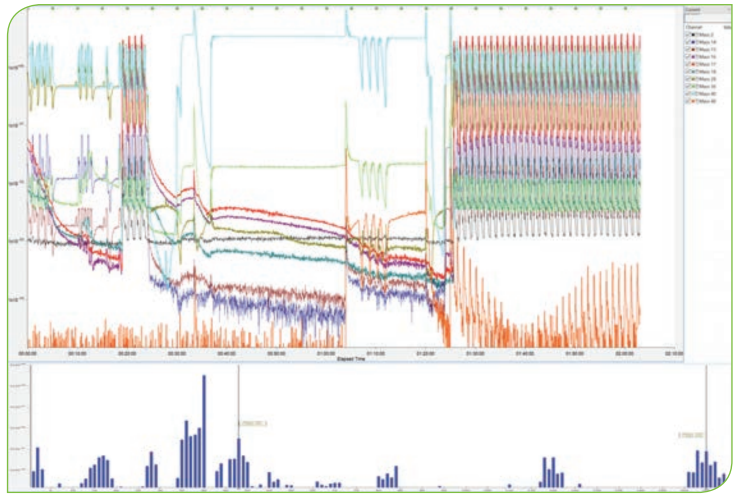

Figure 6:
QMS/RGA Analysis of titanium nitride ALD process.

3. Titanium Dioxide PE-ALD

Titanium dioxide (TiO_2) layers are used, for example, as high dielectric constant (high-k) films in DRAM manufacturing or as high-k gate oxide layers in FinFETs. ALD processing for TiO_2 films uses the organometallic compound tetrakis (dimethylamido)titanium (TDMAT), oxygen (O_2) or ozone (O_3), and plasma excitation to decompose the material once it is adsorbed on the substrate surface (Equation (3).

$$\mathbf{Ti[N(CH_3)_2]_4 + O_2 \longrightarrow TiO_2 + Byproducts}$$

Figure 7 shows QMS/RGA data for the TiO_2 ALD process. In this PE-ALD deposition, the QMS/RGA data showed that the chamber gas exchange characteristics were unlike those typically observed in thermal ALD. Due to the constant pressure conditions used in PE-ALD, the precursor supply pulse can't be monitored in a well-defined manner, as in thermal ALD. However, the data for mass peak 15 (CH_3) and mass peak 44 ($N(CH_3)_2$) confirm that the desired precursor saturation is being achieved during the single wafer deposition process.

4. TiO_2 ALD Chamber Clean

QMS/RGA monitoring is also useful in monitoring and optimizing ALD chamber cleaning processes. In cleaning processes, it is important to have sufficiently long cleaning steps while simultaneously preventing an overclean that can damage chamber parts by exposing them to corrosive chemicals such as hydrogen fluoride. Figure 8 shows QMS/RGA data for a TiO_2 chamber clean that uses NF_3 as the etchant. The data clearly show the efficient and desired dissociation of NF_3 to produce abundant fluorine radicals (the effective cleaning reagent) in the system. However, a comparison of the data for the first and second clean shows that water is present during the first clean and absent in the second. QMS/RGA data thus confirmed that the remote plasma source was trapping some undesired water from its cooling system.

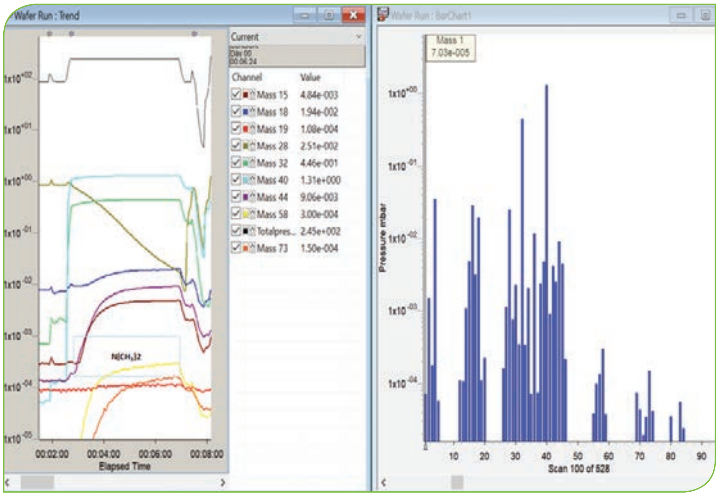

Figure 7:
QMS/RGA Analysis of titanium dioxide ALD process.

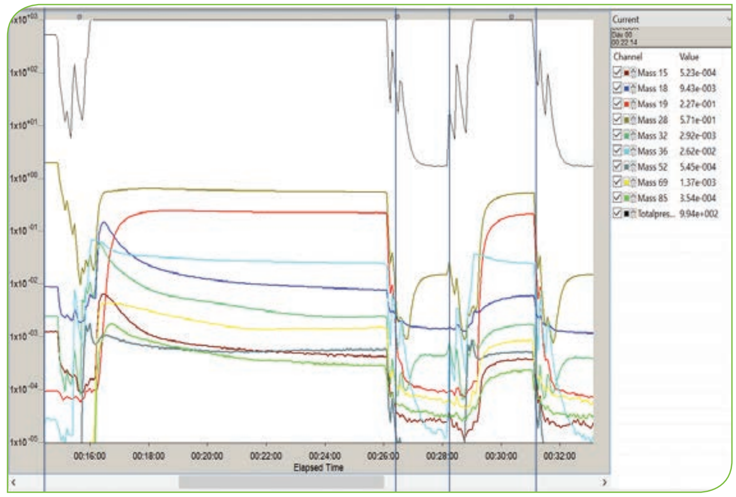

Figure 8:
QMS/RGA Analysis of titanium dioxide chamber cleaning process.

CONCLUSION

New innovations in QMS/RGA technology provide significant analytical benefits when this tool is used as a process monitor in Atomic Layer Deposition, Atomic Layer Etch, and ALD chamber cleaning applications. MKS Instruments' innovative ion source and ion optics technology provides significant improvements in the sensitivity of QMS/RGA systems, with typical detection limits in the low ppb range for species of interest in ALD, etch and cleaning. Also, with respect to system stability MKS provides robust and reliable QMS/RGA solutions for monitoring critical process chemistries on thermal ALD and Plasma Enhanced (PE) ALD processes.

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