Novel Applications of Gas-Phase Analytical Methods to Semiconductor Process Emissions

Brian Goolsby and Victor H. Vartanian

Motorola, Semiconductor Products Sector
3501 Ed Bluestein Blvd.
M/D K10
Physical Analysis Laboratory
Austin, TX 78721

Abstract. The semiconductor industry currently faces technical challenges in transistor design as traditional materials used for decades are being driven to their physical limits. High-k materials (k>7 for Si3N4) are being developed as gate oxides for sub 100 nm MOSFETs to prevent electron tunneling between source and drain. Organometallic precursors under consideration could produce hazardous byproducts. Low-k materials (k<3.9 for SiO2) are being developed as insulators or barriers in the dielectric stack to reduce RC time delays and cross talk between adjacent conductors. Precursors containing carbon or fluorine may increase the emission of CF4 during chamber cleans. Heavily doped polysilicon or metals currently in use as gate electrodes may be replaced with metals or metal oxides having greater corrosion resistance or other advantageous properties. All of these new materials must be characterized from the standpoint of process byproduct emissions and abatement performance. Gas-phase analysis is critical to the safe and timely incorporation of these novel materials. Several new applications of Fourier transform infra-red spectroscopy (FTIR) are presented, including techniques being applied to address some of the current challenges facing the semiconductor industry. This report describes the characterization of various chemical vapor deposition (CVD) processes. Applications of gas-phase analytical methods to process optimization are also described.

INTRODUCTION

Traditional scaling techniques used for shrinking semiconductor devices are reaching a critical state. A consequence of making all parts of a chip smaller, as described in Moore’s law, is that circuit components are also placed closer together, posing serious electrical problems for common semiconductor materials [1]. In an effort to create materials that display the desired physical properties at smaller dimensions, a large number of chemicals, or “precursors” are being studied in chemical vapor deposition (CVD) processes [2]. Along with these new precursor molecules arises the need to characterize the processes that utilize them. Thorough characterization will speed their acceptance and integration by providing process windows with respect to film growth rates, purity levels, by-products, and compatibility with substrates, which helps in decision-making about tool throughput, abatement, environmental, health, and safety (EHS) and infrastructure impacts, as well as appropriate process control mechanisms.

While post-processing metrology provides a wealth of information, real-time monitoring with gas-phase analytical instruments provides the most thorough picture of what happens in the process chamber. For example, the identification and quantification of gaseous CVD reaction by-products can not be accomplished by measuring a film on a wafer. Furthermore, characterization of components in a CVD chamber’s exhaust makes it possible to fine-tune recipes to minimize potentially harmful emissions, thus reducing safety and environmental concerns. This includes the emission of gases that have a high
global warming potential (GWP), which the semiconductor industry has made a commitment to reduce. The same analytical techniques used to characterize a CVD process can be used to determine the effectiveness of a particular point-of-use (POU) abatement device.

Extractive Fourier transform infrared (FTIR) spectroscopy has tremendous utility as an analytical technique in semiconductor process characterization. Some compelling features include its ability to quantify a wide range of analyte concentrations, uniquely identify numerous gas-phase organic or inorganic compounds, and provide rapid analysis relative to the time-scale of most processes. In addition, the technique is transparent to normal tool operation, and can be implemented well downstream of a process chamber, typically sampling just after the roughing pump. While FTIR is by no means a novel technique, it is under-utilized for on-tool applications and real-time data collection for process development. Several new applications of extractive FTIR to recent advances in semiconductor processing are presented herein.

ADVANCED PROCESSES

Low-k CVD

The chemical vapor deposition of several low-k films containing Si, C, O, and H in various stoichiometric ratios has been characterized with FTIR. The spectrum in Figure 1 shows an example of this application. Note that several bands indicative of absorbance by hydrocarbon reaction by-products can be identified using this spectrum, and the utilization efficiency of the precursor material, used to make the film, can be measured.

![FTIR spectra collected during CVD of a low-k film using a silicon and hydrocarbon precursor. The spectra (from top to bottom) represent the precursor only, the deposition process in progress, and the chamber clean run immediately after the deposition.](image)

In addition to CVD, the chamber clean step after deposition of a low-k film has been a major focus for improvement. Recipe optimization to decrease NF3 use has been accomplished through the testing of numerous recipes designed to better utilize the reactive fluorine species. FTIR is an ideal tool for this application because it provides not only an endpoint marker, but also an emissions profile, which can be integrated to determine the global warming impact of a particular recipe. This property is a function of a molecule’s ability to absorb infrared radiation as well as its atmospheric lifetime. An example of this is shown in Figure 2, where spectra from two different clean recipes are compared. The optimized recipe has much lower CF4 output, cutting its overall fluorocarbon emissions significantly.

![FTIR spectra collected during CVD of a low-k film using a silicon and hydrocarbon precursor. The spectra (from top to bottom) represent the precursor only, the deposition process in progress, and the chamber clean run immediately after the deposition.](image)
High-k Deposition

Atomic layer deposition (ALD) represents a major development in the ability to grow high-k dielectric films with good control of uniformity and composition. The growth of one monolayer at a time using ALD provides the control necessary to interleave different materials together even in very thin films. The extremely low quantity of chemical precursor consumed in an individual cycle, resulting in the growth of one atomic layer, is a benefit to process engineers but would be expected to pose a challenge for downstream detection of reaction byproducts. Figure 3 shows a series of measurements made with extractive FTIR, demonstrating the ability of this technique to resolve miniscule pulses from the tool’s chemical delivery system. The plot shows by-products (CH4 and HCl) from two different precursors being tracked, showing how the layers are interleaved. For example, one of the precursors, a metal chloride, is converted to HCl in a reaction at the wafer’s surface. The top line in Figure 3 shows how the quantity of HCl in the chamber effluent changes with each of 15 pulses. These types of data may also be used as a diagnostic for successful delivery of a precursor. Unexpected disappearance of one of the reaction by-products from the FTIR spectrum might indicate that the chemical ampoule is empty or that a delivery line is clogged.

Dielectric Etch of Via Patterns Using Unsaturated Fluorocarbons

In an effort to develop via etch chemistries with a reduced environmental impact, several unsaturated fluorocarbon (UFC) compounds were evaluated for global warming emissions and process performance on a medium density etch chamber for silicon oxide. A wide range of IR-absorbing perfluorocarbons can be identified using an FTIR spectrum from a dielectric etch process. A series of such spectra can then be used to calculate the global warming potential of the entire process.

The test processes and their emissions results are compared to a traditional, baseline (PFC) perfluorocompound-based process. For oxide etching, global warming emissions reduction as high as 88% were attained compared to a C3F8-based process, with similar process performance (etch rate and via profile) as determined by scanning electron microscopy (SEM) of the via cross-section [3]. In the C3F6 process, a large percentage of the total emissions (>50%) are due to unreacted C3F8, a high GWP feed gas. By simply switching to a more reactive, lower-GWP gas such as hexafluoro-1,3-butadiene, the emissions from unreacted feed gas are eliminated almost entirely. In addition the C4F6 process resulted in lower CHF3 emissions, which is likely due to lower photoresist erosion, as photoresist is the major source of hydrogen for the formation of CHF3. Results from several of the tested compounds are presented in Figure 4.

![FIGURE 3. Extractive FTIR sampling downstream of an ALD process’s exhaust pump is able to resolve byproducts from short pulses of two different precursors. Top line is HCl, lower is CH4.](image)

![FIGURE 4. Global warming potential (GWP) reductions relative to C3F8 in identical processes using 9 alternative gases. Lightly shaded bars represent the overall percent reduction; dark bars are normalized reduction based on etch depth.](image)

Etch Recipe Development for Novel Gate Electrodes

Ruthenium and ruthenium oxide have been proposed as metal oxide gate electrodes because they are thermally stable and resistant to corrosion, but as with most materials, there are process and integration
issues that must be addressed. Characterization of early process attempts can provide valuable data to this end. The chemical environment and plasma conditions during which the toxic byproduct ruthenium tetroxide (highly injurious to eyes, inflames mucous membranes, and causes respiratory distress) is formed, can be determined by FTIR [4]. A series of attempts were made to etch RuO₂ films with various plasma chemistries. The FTIR spectrum shown in Figure 5 was collected during an Ar/O₂ recipe, revealing the possible formation of RuO₄ for this test case.

FIGURE 5. FTIR spectrum collected during an attempt at etching RuO₂.

COMPLEMENTARY ANALYSIS TECHNIQUES

A thorough process picture requires quantitative techniques capable of identifying or measuring all by-products. This can not necessarily be achieved with just one technique. For example, ionized plasma species are short-lived, and thus more easily characterized in situ using optical emission spectroscopy (OES), while homoatomic dimers (N₂, O₂, etc.) are undetectable by typical FTIR spectroscopy. Strongly absorbing species in complex mixtures may overwhelm other features in an FTIR spectrum. For a critical gas such as fluorine (F₂), which is present in abundance in chamber clean processes, an alternative measurement technique is needed.

A commercially available fluorine chemical sensor (FCS) was exposed to exhaust from a CVD manufacturing tool during a cleaning process (data shown in Figure 6). This portable measurement device relies on fluorine’s photoemissive reaction with an organic substrate for operation, and it displayed ppb sensitivity, fast response, and no interferences from other species. The collected data were used in conjunction with quantitative FTIR data to generate a mass balance for the process.

FIGURE 6. Fluorine concentrations in tool exhaust measured by a fluorine chemical sensor (FCS) during a chamber clean.

CONCLUSIONS

Analytical systems on semiconductor processing tools provide real-time data that extends beyond simple endpointing. Characterization of mature processes can lead to a better understanding of potential environmental impacts, and in some cases, possible improvements can be identified. Moreover, the early learning provided by capable techniques such as FTIR can ease the development and integration of new materials, which are critical to the next generation of semiconductor devices.

ACKNOWLEDGMENTS

The authors gratefully acknowledge contributions to the preceding work by: Laurie Beu, Laura Mendicino, Dina Triyoso, Darrell Roan, and Terry Sparks of Motorola, Semiconductor Products Sector, APRDL. Simon Karecki, Ritwik Chatterjee*, and Rafael Reif of Massachusetts Institute of Technology. Curt Laush of URS Corp.

*Currently at Motorola.

REFERENCES

