

Accurate Analysis of Precursor Compounds

Contamination in process materials can cause device failure and impact yield. But standard certificates of analysis (COAs) for new materials may not be as reliable as you think.

The purity of chemicals used to manufacture semiconductor devices is of critical importance to fab engineers. Contamination in process materials can cause device failure and impact yield. Because most fabs do not maintain the analytical instrumentation and expertise to test chemicals prior to use, they rely solely on the certificate of analysis (COA) supplied by the vendor for contaminant concentration in process chemicals. A typical COA contains information regarding the concentration of trace metals, for example, contained in a particular material lot, but has little or no quality assurance data to support the precision and accuracy of the measurements. The concentrations reported on the COA must simply be accepted at face value, with the assumption that the appropriate method development and validation have been performed, and that the measurements presented are truly the result of good laboratory practice.

For many process chemicals, particularly those that have been used in the marketplace for a long time, reliable procedures for analysis are in place, and COAs provided with delivered chemicals are generally reliable. However, with new and unique materials rapidly coming into use to meet the stringent demands of shrinking feature size, the analytical lab is under increasing pressure to test for contaminants in materials that are unfamiliar and novel. Traditional approaches that have proven reliable for conventional materials may not be suitable or adequate for the chemicals encountered today.

This article discusses the reliability of information contained in the COA, particularly with regard to trace metals analysis by inductively coupled plasma mass spectrometry (ICPMS). Analytical problems and potential pitfalls will be explored in the analysis of new precursor compounds used in chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes. The examples presented here are the result of years of method development and experimentation, and are offered in the hopes of calling attention to the possibility that COAs may not be accurate in all cases, especially in the case of new and different materials.

Hafnium precursor compounds

A class of materials that is receiving increasing attention is comprised of precursor compounds used to deposit hafnium. Hafnium oxide films are prom-

Table 1. Vapor Pressures of Hafnium Compounds

	TDEAH	TEMAH	TDMAH
70°C	0.04 Torr	0.3 Torr	1.9 Torr
100°C	0.4 Torr	1 Torr	3.4 Torr

ising candidates for high dielectric constant (high-k) gate oxides in CMOS and for the next generation of DRAM.¹ Hafnium oxide layers are typically formed by CVD or ALD, in which a hafnium precursor compound is introduced in the gas phase, and an ensuing chemical reaction is allowed to take place on the surface of the wafer. To be successfully used in production, potential precursor compounds must be reactive yet also possess sufficient stability to ensure safe handling, possess a suitable vapor pressure, and be pure enough so that the resulting film does not cause problems in the device (current leakage, threshold voltage shift, etc.).

Compounds such as tetrakis(diethylamido)hafnium (TDEAH), tetrakis(ethylmethylamido)hafnium (TEMAH) and tetrakis(dimethylamido)hafnium (TDMAH) have suitable physical and chemical properties useful in CVD and ALD, but their purity is often questionable because of contamination traceable to the minerals from which hafnium is originally refined. Hafnium sources vary, but final materials may contain high levels of zirconium (>1000 ppm), titanium and aluminum (400 ppb to 400 ppm).¹ Specifications for the hafnium materials are evolving as process needs are further understood, and these contamination concentrations will be driven lower. Already, specifications for trace metal concentrations similar to tetraethylorthosilicate (TEOS) at 1-10 ppb have been proposed, and methods are being developed to purify the hafnium compounds.

Development and purification of such new materials require the support of analytical methodology that is reli-

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Table 2. Samples With Or Without Evaporation

Analyzed After Evaporation		Analyzed Without Evaporation	
Element	TEMAH (ppb)	Element	TEMAH (ppb)
B	<DL	B	<DL
Ni	<DL	Ni	<DL
Cu	<DL	Cu	<DL
Zn	<DL	Zn	<DL
Ti	69	Ti	2694

Table 3. Isobaric Interferences in Quadrupole ICPMS

Element	Isotope (%)	Interference HfO	Isotope affected	Interference HfO ₂	Isotope affected	Interference Hf ²⁺	Isotope affected
Hf	174 (0.2)	190		206	²⁰⁶ Pb	87	
	176 (5.2)	192		207	²⁰⁷ Pb	88	⁸⁸ Sr
	177 (18.6)	193		208	²⁰⁸ Pb	88.5	
	178 (27.3)	194	¹⁹⁴ Pt	209	²⁰⁹ Bi	89	
	179 (13.6)	195	¹⁹⁵ Pt	210		89.5	
	180 (35.1)	196	¹⁹⁶ Pt	211		90	⁹⁰ Zr

able and sensitive in measuring concentrations of trace metal contaminants. The analytical method of choice uses ICPMS to make the final measurements because of the low detection limits theoretically offered by this technique. The hafnium precursor compounds, however, which contain 35-50% hafnium, present severe difficulties. Sample preparation is critical, since trace-level contaminants can easily be lost because of their volatility, resulting in an underestimation of the concentrations of some important contaminants. Difficulties have also been encountered in determining the method detection limit. Finally, both specific (isobaric) and non-specific (space charge) interferences in the mass spectrometer must be dealt with thoughtfully if accurate measurements are to be achieved. A great deal of effort and research is required on the part of the analytical laboratory to overcome these difficulties and produce reliable information for the COA.

Sample preparation

One approach to overcoming severe matrix effects caused by the very high levels of hafnium is to remove the hafnium compound by evaporation prior to sample analysis, a practice successfully used in the analysis of other materials for COAs in the semiconductor industry. The vapor pressures of TDEAH, TEMAH and TDMAH are sufficiently high so that evaporation under a stream of an inert gas can be accomplished in a reasonably short time (1-2 hr) at moderate temperatures (Table 1). The inherent assumption is that the trace metal impurities are not volatile, and will be left behind as a residue while the bulk of the sample matrix is removed by evaporation. The residue can then be redissolved in a suitable acid mixture and analyzed directly.

Our laboratory tested this approach and found that important contaminants not normally thought of as volatile if present as their salts were lost as the sample matrix was evaporated. Table 2 contains data from a sample of TEMAH that was prepared for analysis by evaporation; this is compared with the same sample prepared without evaporation. The data shows that the sample prepared without evaporation contains ~2700 ppb of titanium, but apparently much titanium is lost during the evaporation process. It was concluded that certain contaminants exist as volatile molecular species similar to the hafnium compound itself, and evaporation of TEMAH results in the loss of important contaminants.

Measurements show that the boiling points of TEMAH and the titanium analog tetrakis(ethylmethylamido)titanium (TEMAT) at a pressure of 0.1 Torr differ by only 1°C.² Any titanium present in the sample as TEMAT would certainly be lost

along with TEMAH during evaporation. It is clear from the data that evaporation should not be used as a preparatory step in the analysis. If the data in Table 2 was represented on two different COAs, the data with titanium at 69 ppb would most certainly be preferred, but unfortunately would also be incorrect and could lead to titanium contamination and process problems.

Determining the method detection limit

The method detection limit (MDL) used for reporting data should be realistic and actually reflect concentrations that the analytical method can detect with a given level of certainty. Spiked samples prepared at 5× the MDL should be measurable, and recoveries should fall between 75 and 125%. The laboratory must exercise great care in establishing MDLs, because with compounds such as the hafnium precursors, mass interferences and matrix effects can lead to problems, and calculated MDLs based on analysis of replicates cannot always be validated through the analysis of spiked samples.

A laboratory practice for determining the MDL that is widely used in the semiconductor and other industries is to analyze several unspiked replicates of a sample at an appropriate dilution, and calculate the standard deviation (SD) of the measurements for each analyte.³ By multiplying the SD by a t-factor and then dividing by the sensitivity of the instrument (counts/ppb for ICPMS), one arrives at the MDL. This procedure provides useful data in some instances, but can also lead to unrealistically low MDLs that cannot be validated through the analysis of spiked samples. The choice of an inappropriate dilution, for example, can lead to an incorrect value of the calculated MDL. Calculated MDLs should always be validated through the analysis of spiked samples to make sure that acceptable recoveries are achievable at the dilution selected for the MDL study.

Isobaric interferences

Isobaric interferences in ICPMS are caused by charged species (ions) within the plasma with the same (nominal) mass-to-charge (m/z) ratio as a target analyte, thus producing a false positive response. A classic example encountered in standard quadrupole ICPMS is the argon ion (Ar⁺), derived from the plasma gas, at m/z 40, which causes a positive interference in the measurement of ⁴⁰Ca. Various schemes have been devised and incorporated into the design of modern quadrupole ICPMS instruments to remove isobaric interferences produced by plasma gases and their molecular ionic derivatives. Collision cells and reaction cells pressurized with gases such as ammonia have been shown to successfully re-

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move molecular ions derived from plasma gases through collision, reaction and/or charge exchange. Alternatively, the analyst can select other isotopes of the target analytes for quantitation that are less affected by molecular ions generated within the plasma. In the case of calcium, however, the isotope at m/z 40 is by far the most abundant, and allows for much greater sensitivity provided the isobaric interference from the Ar^+ can be removed.

In the case of the hafnium precursor compounds, one must deal with a source of isobaric interferences other than those derived from the plasma gas. The very large amount (35-50%) of hafnium contained in the original compound causes major interference problems caused by the formation of Hf^{2+} , HfO^+ , HfO_2^+ , $HfOH^+$, etc. The isotope of hafnium at mass 180, for example, forms a doubly charged ion (Hf^{2+}) at m/z 90 that produces a strong isobaric interference in the measurement of ^{90}Zr .

Hafnium has five major isotopes, each of which forms similar species. In addition, hafnium precursor compounds often contain large amounts of zirconium (five isotopes) and titanium (five isotopes) derived from the source material that can contribute to problems with isobaric interferences. Table 3 lists the major ionic species formed from hafnium and the potential isobaric interferences that may be encountered.

An alternate approach to dealing with isobaric interferences is to analyze samples on a high-resolution magnetic sector ICPMS. While a quadrupole instrument with a resolution of ~ 0.75 amu cannot resolve $^{90}Zr^+$ from $^{180}Hf^{2+}$, a magnetic sector instrument

with mass resolution as high as 10,000 can resolve the two ions and measure them separately. Other isobaric interferences are more difficult to overcome. Hafnium hydride (HfH^+) at mass 180.95439 produces an interference in the measurement of the tantalum isotope at mass 180.94801, and a resolution of $\sim 30,000$ is required to resolve tantalum from hafnium and measure the tantalum ion. Not even a double-focusing high-resolution mass spectrometer has the mass resolution required to measure them separately.

Space charge effects

Even more troubling than isobaric interferences, which produce false-positive readings, is the signal suppression caused by space charge effects, which produce readings that have a large negative bias. Signal suppression can lead to reported concentrations on the COA that are much lower than the actual concentrations.

The space charge effect is a phenomenon that is observed when a sample containing a very high concentration of a matrix or concomitant element is analyzed by ICPMS.^{4,5} Unlike isobaric interferences, which are m/z -specific in nature, space charge effects are non-specific and manifest as a signal suppression for all measured masses. Signal suppression occurs when an abundant matrix element causes a large buildup of positive charge in the ion path just downstream from the plasma and upstream from the ion lens system. Simply put, there are too many ions in too small a space, and analyte ions are repelled in an axial direction, lost from the ion beam. Ultimately, fewer analyte ions pass through the ion

Table 4. Effect of Sample Dilution on Space-Charge-Induced Signal Suppression

Element	Dilution 3		Dilution 2		Dilution 1	
	TDEAH (ppb)	1000 ppb spike (% rec)	TDEAH (ppb)	500 ppb spike (% rec)	TDEAH (ppb)	500 ppb spike (% rec)
Na	262	92	115	93	1.9	16
Al	2992	92	526	60	84	5
Ca	293	93	5.2	63	0.9	8
Fe	1533	100	475	65	113	4

lens system and reach the ion detector, causing lower signal intensity. The reduced ion signal produces a negative bias with respect to the actual analyte concentration.

The analysis of hafnium precursor compounds carries a great potential for space charge interferences. The effect is pronounced with a matrix element of higher m/z . Heavier ions are repelled to a smaller extent because their forward momentum helps to counteract the radial influence of the electrostatic field. Thus, heavier ions tend to be concentrated in the axial region of the ion beam, and lighter ions tend to be repelled more strongly toward the outer region of the ion beam. Hafnium, with an average mass of 178.49, is a classic example of a matrix element that can produce strong space charge effects. The fact that the hafnium precursor compounds under study contain 35-50% hafnium by mass makes the space charge problem potentially more troublesome.

One way to show that space charge is at work is by sample dilution. The hafnium concentration in solution is reduced at successively higher dilutions, and space charge effects are also re-

duced. The effect of dilution on measured analyte concentrations is shown in Table 4, in which the same sample was analyzed along with a spike at three dilutions. Dilution 2 is a tenfold higher dilution than dilution 1, and dilution 3 is twentyfold higher than dilution 1. The analyte concentrations are drastically underestimated in dilutions 1 and 2 because of signal suppression. Poor spike recoveries are also evident in dilutions 1 and 2. Clearly, analyte concentrations can be severely underestimated unless space charge effects are taken into account. That being said, the data under the heading Dilution 1 looks far better on a COA than the data under the heading Dilution 3. This data could be placed on a COA because spike data is never placed on a COA. Dilution 1 data, however, is incorrect and could lead to contamination and yield problems if this data were used to choose material for a contamination-sensitive process.

It is apparent from Table 4 that appropriate dilution of samples is essential if accurate analyte concentrations are to be obtained, and only through the analysis of spiked samples can the appropriate dilution be

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determined. An unfortunate consequence of sample dilution, however, is elevation of the MDL. Some compromise is necessary if space charge effects are to be overcome.

Summary

The information contained in the COA is of critical importance to the process engi-

neer. It is the job of the analytical laboratory to make sure that this information is accurate, and that due diligence has been paid to potential problems, especially in the analysis of new and unfamiliar materials. In this article, we have attempted to illustrate the challenges that new materials may present using the hafnium precursor

compounds as an example. Generating MDLs for these compounds in conventional ways can result in problems for the process engineer if those detection limits do not take into account space charge effects and the simple idea of the detection limits actually having true meaning. The issue with titanium loss in sample preparation is quite important, since a simple evaporation to eliminate the sample matrix may provide a very low titanium value and an attractive COA for a customer, but the titanium (and other potential contaminants) actually contained in the precursor compound is truly present, and will end up in the final processed film. The low titanium value on the COA is misleading, and its presence in the deposited film can result in an adverse effect on yield.

In the end, the analysis of hafnium and other precursor compounds is not simple, and a naive approach can lead to data that is misleading and inaccurate on the COA. The importance of the analysis of spiked samples, particularly during method development, cannot be overemphasized. Production engineers should be aware of the possibility of questionable data on the COA, particularly with new materials, and should not hesitate to ask questions or request supporting data. **SI**

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