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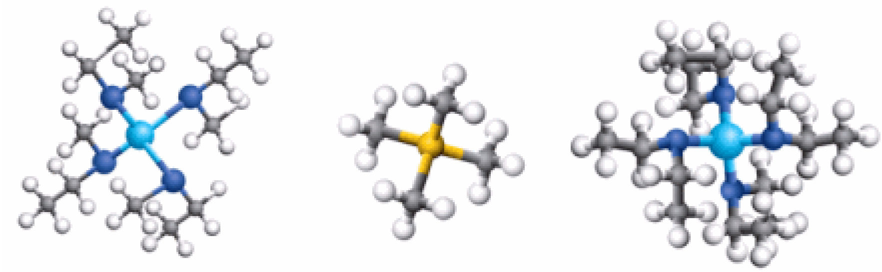
Are Your Precursor Analyses Accurate?

The Trouble with Hafnium Precursors

By Dr. Phil Clancy and Dr. Scott Anderson



Some organometallic precursors provide challenging problems for the analysis of trace metals by ICP-MS. Trace metal analysis by conventional methods can easily yield incorrect results, allowing the trace metals to remain undiscovered until films are produced on wafer. At that point, serious questions will come from the fab engineer. If proper testing and quantification methods are not developed, the initial certificates of analyses that demonstrate material quality will be incorrect and the actual contaminants can impact yield on the processed wafers. Because of these issues, Balazs has developed new methods for analysis of these compounds that are proven to be repeatable and reliable in spite of the measurement complexities.

The particular compounds are the hafnium based compounds, TDMAH (tetrakis (dimethylamino)hafnium), TEMAH (tetrakis(ethylmethylamino)hafnium), TDEAH (tetrakis (diethylamino)hafnium) and $HfCl_4$ (hafnium tetrachloride). These substances are volatile, water reactive, and air sensitive. Analytical difficulties are encountered because these compounds contain 38-56% hafnium by mass, as well as high concentrations of several contaminant metals including zirconium, titanium, aluminum, and others. These major contaminants range up to 2000 ppm in the original source material. Potential problems include sample preparation, determination of a realistic method detection limit (MDL), and mass interferences in the mass spectrometer.

Sample Preparation

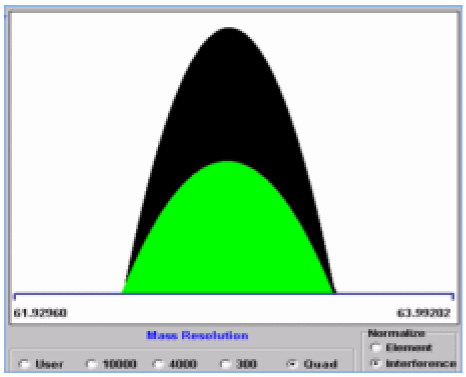
A typical sample preparation with difficult matrices will employ evaporation to remove the matrix and leave behind only trace metal contamination. This trace metallic residue can be redissolved in a clean acid solution that hopefully leads to a straight-forward analysis. For these hafnium compounds however, some of the metal contaminants also exist as volatile molecular species and are lost, even at room temperature, during evaporation. As a result, these volatile metal species will not be accurately quantified in the subsequent analysis. An evaporation technique may provide a nice low contamination value for a COA, but the real contamination will show itself in the final film. Balazs understands these volatile contaminants and has developed proper sample preparation techniques to ensure accurate results for both the COA and contamination in the final film.

Method Detection Limit Determination

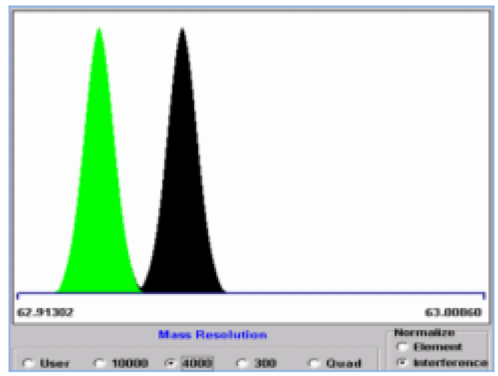
A common practice to determine the MDL is to analyze replicates of the sample and standards to produce a statistically generated MDL. However, this type of calculated MDL can very easily provide an unrealistic low MDL that is not “real.” Balazs takes another approach to elicit customer confidence in its detection limit values. By performing spike analyses while also considering element volatility, Balazs provides confidence in low level detection limits where recoveries must fall in an acceptable 75% - 125% range. By generating reporting limits in this way, Balazs clearly demonstrates a superior methodology at the lowest possible detection limit. Upon review of the data, clients can clearly understand the validity and have assurance in the data.

ICP-MS Interferences

Severe mass interferences in the ICP-MS can also be encountered in the analysis of the hafnium precursor compounds. Interferences are caused by species such as Hf^{2+} and HfO^{+} that are formed in the plasma of the ICP-MS. Zr and Ti contaminants may also form doubly charged species and oxides and adducts that are troublesome. Hafnium and zirconium consist of five major isotopes, while titanium consists of four. Each of these isotopes can exist in sufficient concentrations to be problematic with the accurate measurement of target contamination elements and cause false positive errors. If the analysis is carried out using a quadrupole ICP-MS with only unit mass resolution, these mass interferences are a major problem. Using a high resolution ICP-MS, most of the interfering mass signals can be separated from analyte signals, but in some cases it is still necessary to select alternative, less abundant isotopes for quantitation. Balazs has analyzed these compounds with different types of Mass Spectrometers and understands the mass interferences that are formed and the masses at which they cause problems. Experience with sample preparation issues, ICP-MS interferences and access to a state-of-the-art analytical instrumentation, coupled with R&D analytical chemists have proved critical for the reliable analysis of Hf precursor compounds.



Mass Resolution of a quadrupole ICP-MS is not adequate to separate the interference from the analyte response.



High Resolution ICP-MS is adequate to resolve the overlap seen on a quadrupole ICP-MS

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