



Effect of Plasma Parameters on the Analysis of Semiconductor Process Chemicals by ICP-MS

Introduction

The manufacturing processes of semiconductor devices require a variety of chemicals which must be ultrapure because the presence of impurities degrades the performance of the resultant devices. Impurity levels in these chemicals are usually determined by ICP-MS because of its ability to perform low-level analyses. Unfortunately, some important analytes, such as potassium, calcium, and iron are present at parts-per-trillion levels and suffer from plasma-generated polyatomic interferences. As a result, determination of these elements is difficult.

For the past several years, cool plasma has been used to reduce these interferences. With this technique, the energy of the plasma is lowered, thereby minimizing the formation of species with higher ionization potentials, such as Ar, ArH, and ArO. Yet elements with lower ionization potentials (e.g., K, Ca, and Fe) are effectively ionized. In this way, the plasma-based interferences on K, Ca, and Fe are reduced, and these analytes can be determined at low levels. However, drawbacks to the cool plasma technique exist, mainly because of the lower plasma energy. Due to the fact that some important analytes have high ionization potentials (e.g., boron and zinc) or strong bond energies with oxygen (e.g., titanium and tungsten), the lower plasma energy of cool plasma prohibits their ionization or decomposition and therefore, analysis. As a result, these

analytes must be analyzed separately with a hotter, more energetic plasma.

Another problem with cool plasma is that analyte sensitivity is greatly affected by sample matrix and acid concentration. To overcome this limitation, the method of standard additions, matrix-matched calibration standards, or sample pre-treatment must be used for quantitation. Although acid content and matrix effects can be minimized through dilution, the very low analyte levels prohibit extensive dilutions.

The problems associated with cool plasma analysis can be circumvented by using Dynamic Reaction Cell™ (DRC™) ICP-MS. This technique uses a hot, high-energy plasma for all analytes. The DRC eliminates interferences by simultaneously employing two techniques: chemical resolution and Dynamic Bandpass Tuning (DBT). Chemical resolution involves the use of a gas within the DRC, which reacts with the interference to completely eliminate it. At the same time, DBT is applied. DBT provides both a high mass cutoff and a low mass cutoff to define a precise mass bandpass window inside the DRC. The mass bandpass ejects all ions with masses outside the window, thus preventing the formation of new species that may interfere with the analytes.

This work explores the effects of plasma parameters on the analysis of chemicals important to semiconductor manufacturing processes.

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Experimental

Instrument Conditions

The instrument used in this work is the ELAN[®] DRC ICP-MS; operating conditions are shown in Table I.

Optimization of the instrumental parameters was performed using a 1- μ g/L multielement standard solution in 1% HNO₃. Once determined, all instrumental parameters remained constant throughout this work, with only the RF power being altered. However, for cool plasma operation, optimization of the nebulizer gas flow is usually required.

The analytes of interest and the mode in which they were run appear in Table II. Elements which do not suffer from interferences were determined without a reaction gas in the cell. This mode of analysis is known as standard mode and is the same as conventional ICP-MS analysis. Elements which suffer from interferences were run in the DRC mode, which refers to the cell being pressurized with a reactive gas, and the application of a DBT parameter. The gas flow and DBT parameters are determined using the ELAN DRC software. For all analyses, both standard mode and DRC mode elements were determined during a single measurement. The software automatically switches modes during an analysis; therefore, samples only need to be run one time, conserving sample and time.

Samples and Sample Preparation

The chemicals used in this work were 70% HNO₃ and 98% H₂SO₄ (Seastar Chemicals, Sidney, BC, CAN). Dilutions (when used) were made with 18.3 M Ω water (Millipore, Nepean, ONT, CAN). A 10-mg/L multielement PerkinElmer Pure[™] stock solution (PerkinElmer Instruments, Shelton, CT USA) was spiked into each sample to give a final concentration of 5 μ g/L. Relative sensitivity calculations were based on the sensitivities from a water blank and a 5- μ g/L standard solution in water. Internal standards were not used in this work.

Results

Nitric Acid (HNO₃)

For this study, a PFA nebulizer was used. This nebulizer generates small droplets and has a low sample uptake rate (0.25 mL/min). These characteristics result in accelerated droplet decomposition in the plasma.

Figure 1 shows relative sensitivities for potassium in 1% - 30% HNO₃ acquired with cool plasma, normal plasma, and hot plasma conditions (800 W, 1280 W, and 1600 W, respectively). From this data, it is evident that the potassium signal is much more stable with increasing acid content under hot

Table I. Operating Conditions for ELAN DRC ICP-MS

Parameter/System	Setting/Type
Nebulizer	PFA Micro Flow Concentric (ESI, Inc. Omaha, NE, USA)
Sample Uptake Rate	0.25 mL/min
Spray Chamber	PFA Scott Double Pass (ESI, Inc., Omaha, NE, USA)
Injector	Sapphire, 1.8 mm i.d. (ESI, Inc. Omaha, NE, USA)
Sampling Cone	Pt (1.1 mm orifice) (PerkinElmer P/N WE01-4815)
Skimmer Cone	Pt (0.9 mm orifice) (PerkinElmer P/N WE01-4816)
RF Power	800, 1280, 1600 W
Plasma Gas Flow	16 L/min
Nebulizer Gas Flow	0.90 – 0.95 L/min
Reaction Gas	Ammonia (99.999%, Matheson Gas Products, Mississauga, ONT, Canada)

Table II. Analytes and Measurement Mode

Analytes	Measurement Mode
Na, Al, Cu, Zn	Standard (without reaction gas)
K, Ca, Fe	DRC (with reaction gas)

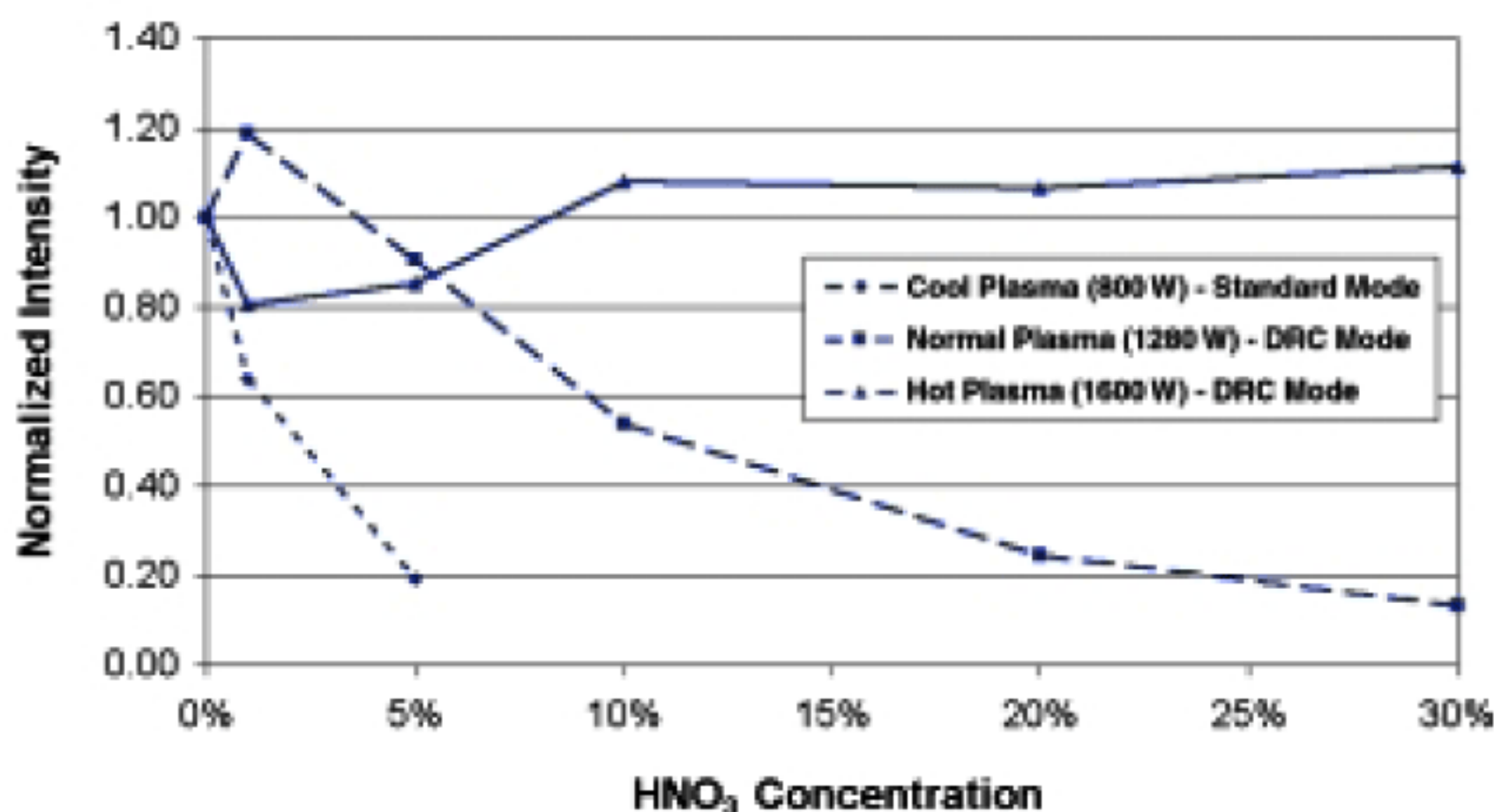


Figure 1. Relative sensitivity for potassium in various concentrations of HNO₃ at three different plasma powers (800 W, 1280 W, 1600 W).

plasma conditions than for the lower energy plasma. Figure 2 displays the same data for a number of elements. Clearly, with lower plasma energy, significant signal suppression occurs as the acid concentration increases. Cool plasma conditions show a significant suppression even in 5% HNO_3 , which limits the acid content of samples that can be analyzed using this technique. On the other hand, the data obtained using the ELAN DRC under hot plasma conditions in DRC mode show that this matrix suppression is greatly reduced. In fact, Figures 1 and 2 show that an RF power of 1600 W effectively eliminates matrix suppression.

These results clearly demonstrate that the effect of matrix concentration can be minimized by using a hotter plasma. Furthermore, the data also demonstrate that by using an RF power of 1600 W, a single, external calibration curve can be used for the determination of various concentrations. This eliminates the need for matrix-matched standards and the method of standard additions, which are required when cool plasma is used. In addition, as a result of only running a single calibration curve, a significant time-savings is accomplished during the analysis.

Sulfuric Acid (H_2SO_4)

The same instrumental conditions and tests used for HNO_3 were applied to H_2SO_4 . Figure 3 shows the effect of plasma power on the relative intensities of several elements in 1% and 5% H_2SO_4 . As seen with HNO_3 , the hotter, more energetic plasma proves to be more robust with higher acid concentrations, although there is still significant suppression at concentrations of 5% and above. However, this work does not explore how internal standards may reduce this effect.

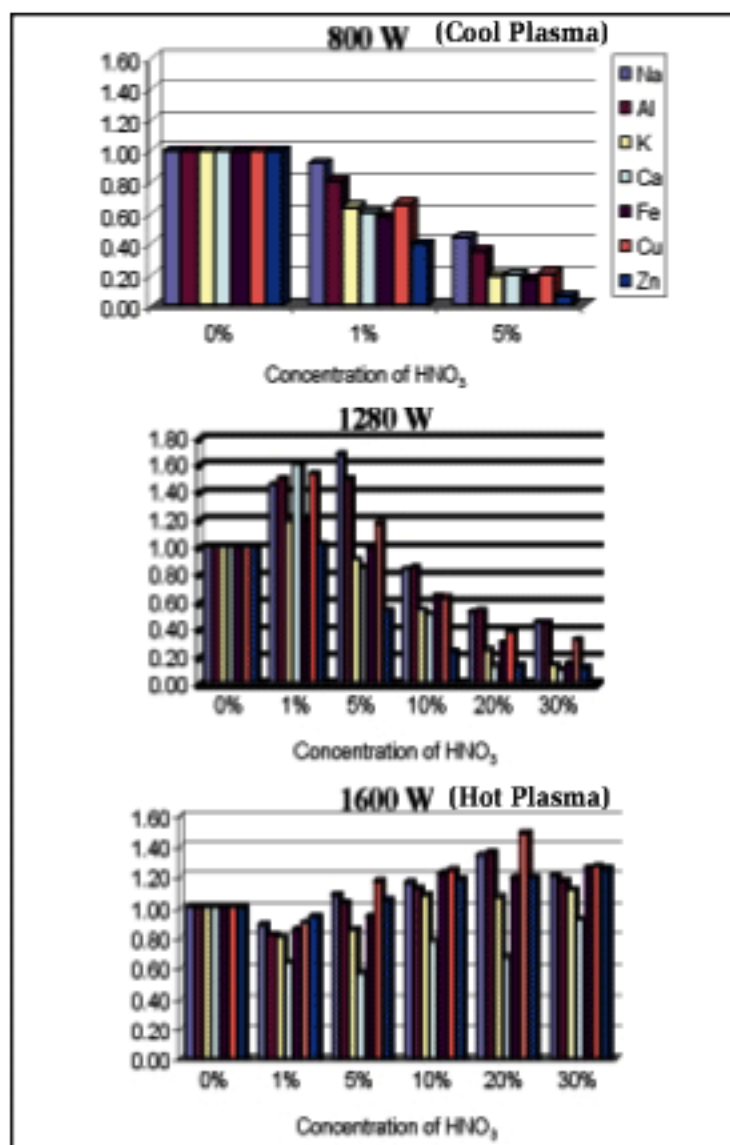


Figure 2. Relative sensitivities for several elements in various concentrations of HNO_3 at three different plasma powers (800 W, 1280 W, 1600 W).

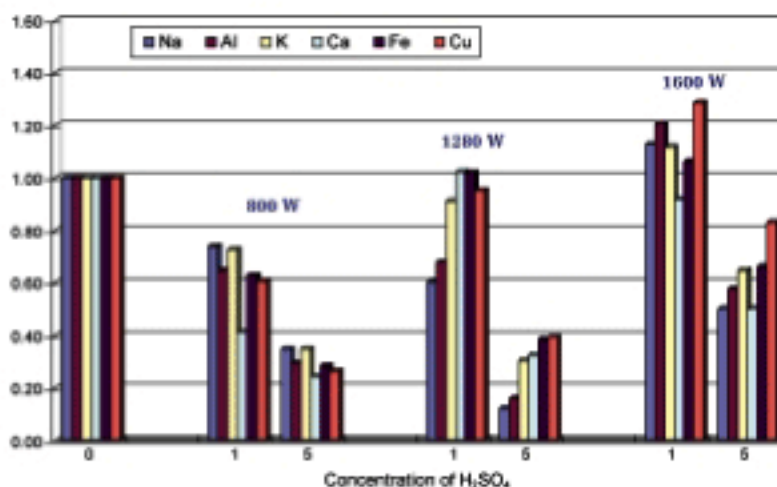


Figure 3. Relative sensitivities for several elements in various concentrations of H_2SO_4 at three RF power conditions: 800 W (cool plasma); 1280 W (normal plasma); 1600 W (hot plasma).

Conclusions

This work clearly shows the advantages of using a hot, energetic plasma with the ELAN DRC for the analysis of various acid matrices. By using hot plasma conditions, the relative sensitivities of analytes are minimally affected by acid concentration. The result of this observation is that one set of plasma conditions can be used to analyze a variety of samples of different acid concentrations. This characteristic is much different than the

cool plasma technique, which requires optimization for each different matrix composition, even of the same chemical. As a result, the ELAN DRC increases sample throughput and minimizes troublesome sample preparation procedures.

The ELAN DRC can routinely determine potassium, calcium, and iron impurities in semiconductor process chemicals using hot plasma conditions. These analyses can be performed since

interference removal is accomplished in the dynamic reaction cell through chemical resolution and the application of dynamic bandpass tuning. In addition, once the conditions are established for the DRC, they remain constant and are transferable from one instrument to another, unlike cool plasma which requires continuous adjustments for changes in plasma conditions. The ELAN DRC is the only ICP-MS with these unique capabilities.

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