Controlling Wafer Contamination Using Automated On-Line Metrology during Wet Chemical Cleaning

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Abstract. The capabilities of a trace contamination analyzer are discussed and demonstrated. This analytical tool utilizes an electrospray, time-of-flight mass spectrometer (ES-TOF-MS) for fully automated on-line monitoring of wafer cleaning solutions. The analyzer provides rich information on metallic, anionic, cationic, elemental, and organic species through its ability to provide harsh (elemental) and soft (molecular) ionization under both positive and negative modes. It is designed to meet semiconductor process control and yield management needs for the ever increasing complex new chemistries present in wafer fabrication.

INTRODUCTION

Sub-micron device technologies are highly sensitive to chemical impurities which may be present during wafer cleaning. Metallic contamination is a major source of performance failure in IC devices including increased p-n junction leakage, degradation of gate oxide breakdown voltage and reduced carrier lifetime. As critical device geometries continue to shrink below 0.13 µm, strict control of contaminants in wet chemical cleaning baths to ppt (parts per trillion) levels has become increasingly necessary.

In a 1999 publication, Shive et. al., discussed the benefits of on-line monitoring for metallics in wafer cleaning processes [1]. In that paper, a key assumption was that there was a relationship between the amount of metal on a wafer and the amount of metal in the last cleaning solution in which the wafer was immersed. In general this is true, however not in a simple fashion. Work by Helms [2], Poliak and Gupta et. al. [3] and others have demonstrated that the amount of contamination deposited on the wafer is a strong function of the specific contamination mechanisms involved, the process chemistry in the particular process step and the wafer treatment in prior steps.

There are literally hundreds of papers postulating contamination mechanisms as a function of the contaminant and the process chemistry involved. However most of these results are based on measurements made in the laboratory environment and may or may not simulate manufacturing process conditions. To this day there is only limited understanding of what is actually happening in the wet baths in the process line and how this impacts the yield and performance of the final product. We give a couple of examples that discuss potential contamination mechanisms for Cu and Fe to illustrate the complexity of the models that have been proposed.

It has been shown that Cu ions present in aqueous HF solution adsorb on Si wafer surface in the form of reduced metallic particles [4]. This electrochemical process can be expressed by the chemical equation:

$$2Cu^{2+} + Si + 6HF \leftrightarrow 2Cu + SiF_6^{2-} + 6H^+.$$  

As a result, measurements of UPW (ultrapure water) as a final rinse may not establish a correlation between Cu in the final UPW rinse solution to that on the wafer surface. Cu may be on the wafer surface, but it may not be detectable in the final rinse bath.

Mouche et. al. studied the mechanism of metallic impurity deposition on silicon substrates by dipping wafers in solutions [5]. They found that the number of Fe particles deposited on the wafer surface increased according to the increase of Fe concentration in SC-1 bath (0.5:1:5, T=70°C). This was confirmed by two experiments: particle counts by light scattering and characterization of the deposited particles by x-ray microanalysis. Because of the presence of Fe(OH)₃ (solid) in SC-1, it was believed that the precipitation of iron hydroxide Fe(OH)₃ physically absorbed on the wafer surface. Helms [2] also showed a correlation between the Fe contamination in SC-1 bath and on the wafer. SC-1 bath concentrations ranging from 100 ppt
to 1 ppb leads to surface concentrations of $10^{11}$ to $10^{12}$ atoms/cm$^2$. The results are similar to that reported by Mouche et al. [5]. However Helms [2] points out that Fe transfer to the wafer surface reaches a saturation point in SC1 solutions containing greater than 1000 ppt Fe contamination.

The International Technology Roadmap for Semiconductors (ITRS), 2001 Edition [6] highlights the critical need for better understanding of contamination and yield correlation as devices scale below the 65nm process node. This is discussed in Table 88 titled “Yield Enhancement Difficult Challenges” and the specific wording is as follows:

“Correlation of Impurity Level to Yield – Methodology for employment and correlation of fluid/gas types to yield of a standard test structure/product. Establish an employment methodology for each material type. Define a standard test for yield/parametric effect.”

Historically, wafer contamination has been measured and controlled in two ways: (1) off-line periodic testing of samples from wet station process baths using an approved laboratory [7,8]; (2) or by the examination of residues on test wafers which have been exposed to process solutions using either TXRF (total reflection x-ray fluorescence) or VPD-ICP/MS (vapor phase decomposition-inductively coupled plasma/mass spectrometry) [8,9].

Although it is possible to perform TXRF at the process line, TXRF’s inability to detect critical light elements such as Na, B and Al at trace contamination levels means that the results are not sufficient for comprehensive detection and control of process contamination. Off-line lab or VPD-ICP/MS measurement is still required if these critical species are to be measured. Also, the analysis area measured by TXRF, approximately from 0.5 to 0.8 cm$^2$, may also not be representative of the contamination across the entire wafer surface unless full wafer scans are performed [9]. However, these full wafer scans take many hours.

VPD-ICP/MS has excellent detection limits for all key elements on the wafer surface. It does measure the cumulative contamination across the entire wafer surface unless special local area methods are used. As in TXRF unpatterned test wafers are required.

The cost of both TXRF and VPD-ICP/MS measurements are relatively high since they require unpatterned test wafers that occupy valuable production wafer slots. This problem will get significantly worse with the conversion to the 300 mm wafer size.

Off-line chemical analysis is severely compromised as a process control tool by the long turn-around times ranging from hours to days and the inherent risk that contamination may be introduced during manual sampling from a cleaning bath. The accuracy of results and the time in which they become available is critical since a single contamination excursion in a 300 mm fab can cost upwards of $5 million per day in scrap wafers alone. This does not include the additional expertise, testing and labor required to troubleshoot and resolve contamination problems and to ultimately disposition the affected material. This estimate also ignores the potential delay in time to market, lost revenues, idle capacity, and the cost of recovering and re-qualifying contaminated equipment.

There is only limited understanding of the correlation between contamination in the process bath, contamination which is deposited on the surface of test wafers and the actual impact on device yields, performance and reliability problems. The overall complexity of the wafer process creates a large part of this problem, however the larger roadblocks are the uncertainties due to sampling artifacts and the high costs associated with the off-line and test wafer techniques discussed here. These costs and uncertainties are major barriers in obtaining statistically valid process chemistry data for correlation to process performance parameters. We would submit that the in-line measurement of process chemistry will lead to major progress in the understanding of contamination, its sources and yield correlation, particularly if it can be done cost-effectively with statistically valid basis.

We first announced a new in process mass spectrometry tool that has been designed to address this measurement need last year [10]. In this paper we present the results of the first trace contamination measurement results.

**IPMS TCA TECHNOLOGY**

In this paper, the capabilities of an in-process mass spectrometry trace contamination analyzer (IPMS TCA) will be discussed. This tool was specifically designed to enable real-time on-line quantitative measurement of contamination present in wet station process baths as well as other process chemistries [11,12]. Wet process measurement results are presented including
those obtained during the first on-line application in a manufacturing fab. For a more detailed discussion of the IPMS TCA design and its operational features, please see Ref. 11 from the proceedings of this conference.

In summary the IPMS TCA capability includes automated sample extraction, sample preparation and analysis. The sample preparation system includes dilution capability and a mixing module for the introduction of isotopic calibration standards.

The TCA automatically samples wet station process solutions via a narrow sample probe mounted vertically on the inside edge of the bath. The tip of the probe extends below the surface of the liquid. It draws 2 mL of sample into a reservoir through vacuum suction. After closing a valve to the bath, pressurized nitrogen gas is used to transport the sample through a fully encapped HP Plus Teflon tube to the TCA system. The TCA can be located up to 30 meters away from the wet station that is being sampled and incorporates five sample extraction and preparation modules so that up to five wet baths can be sampled simultaneously.

After transfer into the automated TCA sample preparation system, the sample is mixed with enriched isotopes, equilibrated, introduced into the electrospray ionizer and the time-of-flight mass spectrometer (ES-TOF-MS). Quantitative analysis is completed using isotope dilution mass spectrometry (IDMS) and speciated isotope dilution mass spectrometry (SIDMS) methodologies [12-16].

The TCA system is fully clean room compatible, runs under computer control including sample extraction and preparation and interfaces with standard fab data systems. The fundamental nature of TOF-MS is similar to that of other mass spectrometers in that it utilizes electric and/or magnetic fields to separate charged species in space by their mass-to-charge ratio (m/z). The TOF-MS has an average 2000 M/ΔM resolution power and is presently configured to operate in a mass range from 18 to 230 m/z in positive ion mode (cations). The system allows accurate mass measurements, resulting in precise determination of the intact molecular and/or atomic components of the sample. Traditionally each elemental measurement is quantified by comparison to a calibration curve that has been generated by the measurement of standard solutions. Under normal operating conditions, a mass spectrometer instrument has significant inherent “drifts” which cause unpredictable changes in signal intensity over relatively short periods of time. This presents the need for frequent recalibration using standard solutions between unknown runs and subsequent adjustment of the calibration curve. In contrast to this, the TCA uses IDMS and SIDMS methods to correct for spectrometer instabilities as well as matrix effects. This enables accurate automated and unattended quantitative measurement of wet bath contamination levels and other process chemistries.

The TCA provides identification and quantitative measurement of metallic, anionic, cationic, elemental, and organic species present in semiconductor process solutions. Molecular information is preserved through use of the unique electrospray ionization system that is able to perform either “soft ionization” of molecular species for complete chemistry analysis or “harsh” elemental ionization for improved detection limits. The change from one mode to another is accomplished by simple computer controlled adjustment of electrospray parameters. No operator intervention is required.

In the IDMS method, an enriched isotope solution is prepared and mixed with the natural isotopes in the sample solution. Because the ratio of enriched isotope to natural isotopes does not change during the measurement, the calculation of concentrations can now be completed comparing signal intensities in the mass spectrum vs. comparison to a calibration curve generated using system standards. Specifically, poly-isotopes are quantified using IDMS with the formula shown below where $C_s$ is the element concentration in sample solution:

$$\text{Ratio} = \frac{(A_s C_s V_s + A_{sp} C_{sp} V_{sp})}{(B_s C_s V_s + B_{sp} C_{sp} V_{sp})}$$

Where:
- $A_s$ = Fraction of isotope A in sample (natural)
- $B_s$ = Fraction of isotope B in sample (natural)
- $A_{sp}$ = Fraction of isotope A in spike (altered)
- $B_{sp}$ = Fraction of isotope B in spike (altered)
- $C_s$ = Concentration of element in sample
- $C_{sp}$ = Concentration of element in spike
- $V_s$ = Volume of the sample
- $V_{sp}$ = Volume of the spike

Quantification of mono-isotopic elements such as $^{27}\text{Al}$, $^{23}\text{Na}$, and $^{59}\text{Co}$ relies on ratio methods applying spikes of elements with neighboring mass to determine their
concentrations. For example, $^{25}\text{Mg}$ is used for the quantification of sodium $^{23}\text{Na}$, and aluminum $^{27}\text{Al}$; $^{62}\text{Ni}$ is used for the quantification of cobalt $^{59}\text{Co}$. Figure 1 shows the quantification of mono-isotope $^{59}\text{Co}$ at various concentrations by use of a $^{62}\text{Ni}$ internal standard. These results were generated by measuring ultra pure water (UPW) spiked with a NIST multi-element traceable “stock” solution at blank, 200 ppt, 500 ppt and 1000 ppt concentrations. In the next section, we will show measurement results for other mono-isotopic elements present in the multi-element standard.

![FIGURE 1. Quantification of mono-isotopic element Co solutions at blank, 200ppt, 500ppt and 1000 ppt concentrations by using $^{62}\text{Ni}$ as an internal standard (UPW). The vertical axis is concentration in ppb.](image1)

**TCA MEASUREMENT OF METALLIC CONTAMINATION**

In order to characterize the performance of the TCA in trace contamination analysis over a broad range of elements, measurements were conducted on UPW containing NIST traceable multi-element solutions diluted to concentrations of 100, 50, and 20 ppt. The UPW used in the dilution was produced by a Nanopure purification system. During analysis each sample was spiked with appropriate amounts of enriched isotopes ($^{25}\text{Mg}$, $^{41}\text{K}$, $^{44}\text{Ca}$, $^{46}\text{Ti}$, $^{53}\text{Cr}$, $^{57}\text{Fe}$, $^{62}\text{Ni}$, $^{65}\text{Cu}$, $^{68}\text{Zn}$, $^{122}\text{Sn}$, $^{136}\text{Ba}$, and $^{206}\text{Pb}$) for IDMS quantification.

![FIGURE 2. Mass spectrum of 100 ppt NIST traceable solution with the TCA operated in positive “harsh” ionization mode.](image2)

Figure 2 presents the typical spectrum obtained for the 100 ppt level solution. The TCA was operated in positive “harsh” ionization mode in this analysis. Because of the high mass resolution of the TOF-MS, the elemental peaks, such as Ni, Zn and Cu, are clearly resolved from the adjacent organic peaks. Figure 3 shows the average quantitation results for the three solutions (100ppt, 50ppt and 20 ppt). Elements present can be quantified at the 100 ppt level, independently of whether they are poly-isotopic or mono-isotopic. Some elements can also be quantified at lower concentrations, *i.e.*, 50 ppt and 20 ppt. Missing data in Figure 3 occur where the species cannot be measured with sufficient accuracy under current measurement conditions.

![FIGURE 3. TCA analyses of ultrapure water (UPW) spiked with NIST standard “stock” solution to 20, 50 and 100 ppt. Quantification performed Isotope Dilution Mass Spectrometry (IDMS).](image3)
The quality of the facility and the UPW used in this work were major limitations in our ability to perform successful quantification at the lower levels for a number of species. A high background concentration of Ca was observed in the 100 ppt analysis. The contamination source is unknown but believed to be human or facility related.

In another series of measurements, SC-1 (NH4OH:H2O2:H2O=1:1:5) and DHF (dilute HF, 1:50) solutions were prepared with 100 and 200 ppt concentration levels using the same methods as described above. The results are presented in Figures 4 and 5.

FIGURE 4. TCA analyses of SC-1 spiked with NIST standard “stock” solution to 100, and 200 ppt levels. Quantification performed by IDMS.

FIGURE 5. TCA analyses of DHF spiked with NIST standard “stock” solution to 100, and 200 ppt levels. Quantification performed by IDMS.

The error bars shown in Figures 3 to 5 are calculated using the following formula:

\[
\mu = X \pm t\sigma/(n)^{1/2}
\]

where

\(\mu = \) analytical results;

\(X = \) average of three measurements;

\(t = \) student’s “t” values at 95% confidence intervals = 4.3

\(\sigma = \) standard deviation of the measurements

\(n = \) numbers of measurements

Work is underway to optimize system detection limits and measure ultimate performance under conditions that are not limited by the current tool environment and UPW water purity.

ON-LINE MEASUREMENT OF PROCESS CHEMISTRY USING TCA

A TCA has been installed in a production wafer fab to provide on-line monitoring of wet station chemical baths. As first verification of on-line performance, the TCA was used to measure a serious of spiked UPW, SC-1 and DHF solutions. The results are compared against those of the lab ICP/MS used by the fab. Figure 6 shows a comparison of results between TCA and ICP/MS in a 200ppt (0.2ppb) multielement DHF solution. The results from TCA represent the average of 60 continuous measurements and those for the ICP/MS 3-4 measurements. The number of samples that can be sent for lab ICP/MS measurement was limited by time and cost constraints.

FIGURE 6 A comparison of analytical results between TCA and ICP/MS in 200ppt DHF solution

Figure 7 shows the first measurement results of an SC1 bath being used to process production wafers. This trend plot illustrates the volume of on-line data that can be cost-effectively achieved in a few hours (concentrations of select elements in the SC-1 bath are plotted against time in hours). In this case, one single production SC-1 bath is being sampled for 15 elements
simultaneously and 3 elements are shown in the trend plot. Up to five baths could have been sampled at one-fifth the frequency per bath. The rate of quantitative measurement is approximately 5 complete multi-element analysis results per hour. These results demonstrate the volume of quantitative measurement data that can be routinely and cost-effectively generated in just a few hours. These results also demonstrate the potential for statistically valid process control decisions based on actual process chemistry.

The chelate additions also improve SC-1 bath stability by minimizing the metal catalyzed decomposition of hydrogen peroxide. One of the commercial chelating agents, such as Titriplex (ethylene-diamine-tetra-acetic acid, EDTA) is commonly used for this purpose.

The TCA enables quantitative analysis of the process chemistry present in standard cleaning processes as well as these modified approaches. It is anticipated that the additional process chemistry information will speed up development and implementation of these new and improved cleaning processes.

FIGURE 7. Cu, Ni and Mn concentrations vs. time in hours in a production SC-1 bath

POTENTIAL APPLICATIONS: TCA ANALYSIS OF ORGANIC SPECIES AND ELEMENTAL SPECIATION IN WET CLEAN PROCESSES

The semiconductor industry is in the process of investigating more environmentally friendly and cost-effective cleaning chemistries. One approach is the use of highly diluted versions of existing cleaning solutions such as modified SC-1 (NH₄OH:H₂O₂:H₂O). In these new versions of SC1, the relative concentration of solution components is changed from 1:1:5 to 1:4:20 or even more extremely to 1:2:80. Combinations of anionic and non-anionic surfactants, as well as chelating agents [17-19] are added in an attempt to maintain cleaning effectiveness. Surfactants enable more effective particle removal and the addition of chelating agents can prevent metal precipitation/re-precipitation on the silicon wafer surface. These changes are also used to enable the elimination of the usual SC-2 clean that normally follows the standard SC-1 clean.

For example, “soft ionization” TCA analyses was used to identify the molecular species present in a SC-1 solution with the addition of 1 ppm of the surfactant CH₃(CH₂)₇SO₃Na, as shown in Figure 8. The mass spectra of surfactant C₇F₁₅CO₂H in BOE (buffered oxide etch) and a chelating agent EDTA, are shown in Figures 9 and 10, respectively. The two Cu

FIGURE 8. Spectrum of 1 ppm of the surfactant CH₃(CH₂)₇SO₃Na in SC-1 solution; TCA operated in soft ionization and negative mode.

FIGURE 9. Spectrum of 1 ppm surfactant C₇F₁₅CO₂H in BOE solution (300x dilution); TCA operated in soft ionization and negative mode.
species present in the BOE case, Figure 9, are from an unknown source. The spectrum in Figure 10 shows organic species with $^{12}\text{C}$ or $^{13}\text{C}$ combined with various Fe isotopes, i.e. $^{56}\text{Fe}$, $^{58}\text{Fe}$ and $^{57}\text{Fe}$.

FIGURE 10. Spectrum of Ferric EDTA, TCA operated in soft ionization and negative mode.

There are some areas that have not yet been explored that are now enabled by the TCA, such as the measurement of elemental speciation. For example, we know that many transition metals likely form complex compounds in SC-1 solution. This may also be true for metals in DHF solution. How do those metal complexes undergo absorption or desorption on the wafer surface? May equilibrium be species dependent? There remain open questions. Mori et. al [20] investigated the adsorption of Fe(III), Ni(II) and Zn(II) on wafer surface in SC-1 solution (1:1:5, T=80°C) and concluded that the main adsorption species was the dissolved neutral hydroxide complexes, i.e. \( \text{M(OH)}_n \), where \( \text{M} = \text{Fe, Ni, and Zn} \). This conclusion was based on the calculated distribution of hydroxide complexes as a function of pH. For example, in the calculation, Fe(III) forms Fe(OH)$_3$ (aq) in SC-1 solution at pH =10.6. The dissolved neutral hydroxide species is then adsorbed on the wafer surface, i.e. trapped inside the silicon oxide layer. This thin film Fe contamination (not Fe(OH)$_3$ particles) was confirmed by TXRF angle scan profiling. However, this conclusion is completely different from Mouche’s as discussed earlier [5]. Furthermore, based on another calculation, the total concentration of ammonia complexes of Ni(II), e.g. Ni(NH$_3$)$_2$$^{2+}$, Ni(NH$_3$)$_5$$^{2+}$ Ni(NH$_3$)$_6$$^{2+}$, ..., is $10^{10}$ times higher than hydroxide complexes, e.g. Ni(OH)$_2$$^{2-}$, Ni(OH)$_3$$^-$, Ni(OH)$_2$. Why do only the neutral hydroxide species deposit on the wafer surface? Why not ammonia complexes which are in much higher concentration? In addition, it has been known that the zeta potential of wafer surfaces is negative in a SC-1 solution with pH $\approx$10.6 [21]. Because of the attraction of opposite charges, the positive species such as Ni(NH$_3$)$_2$$^{2+}$ and Zn(NH$_3$)$_5$$^{2+}$ or Cu(NH$_3$)$_6$$^{2+}$ seem more likely to deposit on the negative wafer surface than neutral species do. The explanation that has been given [5] is that in SC1, the Cu ions are totally complexed by the ammonia molecules which can decrease their reactivity and mobility due to the steric factor; resulting in one more theoretical hypothesis and postulate for debate. These questions may be better answered by measuring the exact species present in the process chemistry as enabled by the IPMS TCA.

The detailed in-bath reactions associated with organic additives such as surfactants or chelating agents is also not understood. The theoretical hypotheses involve calculation of pKs, ionic strengths, and reactivities but soon this approach becomes very complicated and any conclusion based on the calculation is questionable. Although metallic contaminant analysis may remain a primary target in the bath chemistry measurement, the information provided by direct elemental speciation and species measurement and identification will enable a better understanding of the contamination mechanisms involved.

The bottom line of this discussion is that there is much that is unknown about process chemistry and the new cleaning approaches are generating additional complexity. Better understanding of the actual mechanisms present will lead to the design and successful implementation of more effective cleaning solutions.

CONCLUSIONS

We have demonstrated that the new IPMS TCA capability enables identification and quantification of metallic and organic species, both in cationic or anionic forms in wet clean process solutions. In this case we have applied this capability to UPW and standard BOE, SC-1, and DHF semiconductor process solutions. We have also shown organic and specie measurement capabilities in analytes of the relatively new dilute SC-1 chemistries which include surfactants and chelating agents.

The capabilities of the trace contamination analyzer (TCA) include operator unassisted
automated on-line operation. The tool provides real-time process chemistry measurements and has the capability to provide elemental and molecular species information.

It is expected that this new high volume cost-effective measurement capability will provide statistically valid process chemistry characterization and yield correlation for the first time. The tool produces real-time statistically valid process information that will enable excursion avoidance and required corrective action. Bath refresh or changeout requirements can be determined based on actual process chemistry and contamination levels as well as the need for unanticipated equipment preventative maintenance. Overall these capabilities will enable better and more cost-effective semiconductor process control and yield management.

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