Application of ICP-MS for Relating Metal Contamination on Wafers to Metal Sources and Levels

by

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ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) is an excellent tool for quantitative assessment (measurement) of metallic contamination in the production of semiconductor devices. It is suitable for determining metal concentrations on bare silicon wafers, as well as in many dielectric, metallic and metal oxide layers on a wafer. It is also suitable for analysis of liquids of all types. As a consequence, ICP-MS provides useful information on both the source and the levels of metallic contamination at virtually every processing step (see Table 1).

TABLE 1. Processes Where Metallics are Routinely Measured Using ICP-MS.

- Wafer cleaning, e.g., wet, dry, spray
- Oxidation, e.g., thermal, CVD, wet (steam)
- Other CVD Processes
- Photolithography
- Etching, e.g., wet chemical, plasma
- Ion Implantation
- Wafer Handling, e.g., metal tools
- Wafer Transportation, e.g., boxes, cassettes, conveyors
- Reactor Cleanliness
- Atmospheric Contamination
- Process Development

TECHNIQUE

The advantages of using ICP-MS procedures (rather than surface analysis procedures), come from the ability to standardize, accurately quantitate the analyses, do matrix matching, and provide highly accurate and sensitive measurements (down to 10^{7} atoms/cm^{2}) over a wide range of concentrations (six orders of magnitude). All of this is possible in a single measurement run of up to 72 elements. These advantages come from the inherent versatility of mass spectroscopy in general, coupled with a variety of sample preparation and front-end sample introduction techniques.

While techniques such as gettering can be used to manage metallic contamination on the wafer, as device geometrics go to 0.25 µm and 0.18 µm with very thin gate oxides (<50 Å), it becomes increasingly important that these sources of metal contamination are understood so that steps can be taken to eliminate them. ICP-MS techniques are a key tool in this process of contaminant elimination.

This laboratory, being proficient in the analysis of metal at very low level (0.1-10 ppt) in all liquid materials used in processing and most of the thin films produced, embarked on a program to relate sources of metallic contamination to contaminants found on wafer surfaces. While sampling and measuring the liquids involved in processing is relatively simple and straight-forward, procedures for measuring the various films, such as oxides, doped oxides, nitrides, metals, and organics needed to be developed.

Vapor Phase Decomposition (VPD) is a process that has been used to remove metals from bare wafer surfaces and to concentrate them in a small spot on the wafer or a small drop that is removed from the wafer for analysis by tools such as GFAAS, ICP-OES, and ICP-MS using ETV, FIA, MDX, FIA-USN or DIN nebulizers. There are, however, serious problems if VPD is used alone. They include:

- loss of volatile fluorides (B, As, etc.) see Table 2.
- precipitation of insoluble fluorides (La, etc.)

- inability to remove metals above silicon on the electromotive series (Cu, Au, Pt, etc.)
- slowness for thick dielectric films

TABLE 2. Volatile Metal Fluorides.

	MP°C	BP°C
BF_3	-129	-101
AsF_3	-6	51
GeF_4	-15	s@ -37
GeF_2	110	d@ 160
PF_3	-151	-101
PF_5	-94	-85
SiF_4	-90	s@ -96
CrF_3	1100	s@ 1100
CrF_4	-28	400

s=sublimes
d=decomposes

Other sample removal methods were needed. Two techniques were developed which are referred to as DSE (drop scan etching) and FDC (film desolation and concentration). In VPD, a small amount of pure water is used to pick up the soluble metal fluoride salts for subsequent analyses by ICP-MS. In DSE, the same technique is used, except that the small quantity of liquid referred to as a drop is specifically designed to dissolve metals (e.g., Cu) that do not form soluble fluoride salts. Frequently, nitric acid is used instead of pure water as the appropriate liquid.

For thick film oxides, nitrides or metals, VPD is too slow or even impractical. Consequently, the entire film and all metals are first dissolved in a relatively large quantity of a specific solution. This solution is then chemically processed and concentrated so that specific metals can be measured by ICP-MS.

APPLICATIONS

With sample collecting and processing procedures in place, it is now possible to measure a series of events to determine how they affect residual metallic contamination on wafers, especially for critical steps such as gate oxides. Since the gate oxide is so critical, cleaning has received considerable attention with the result of many papers being published on cleaning solutions, their specific chemistry, and steps.

An example of applying these techniques is shown in Table 3, which describes the correlation between chemical purity and the concentration of metals on wafers dipped into these chemicals. The results illustrate the accumulative effects of metals like aluminum and iron whose insoluble metal oxides precipitate onto a wafer surface. Although SC2 should remove most of these metallic contaminants, any peroxide solution that didn't contain HCl or HF would not.

Table 4 shows another set of measurements comparing the cleaning efficiency of various solutions in removing metallic contamination. Wafers were purposely contaminated in a SC1 bath heavily spiked with 650 ppb of each metal shown. Subsequently, they were cleaned with three different cleaning solutions. The results illustrate that the SC2 and HF peroxide can remove most of the contaminating metals. However, as previously discussed, insoluble metal oxides such as Al, Fe, Sn, and Zn remain on the wafer in considerable quantities. Although hot dilute $HF/H_2O_2/H_2O$ does a significantly better job, concentrations of the 10^{10} atoms/cm^2 persist.

TABLE 3. Trace Metals in Two H_2O_2 Solutions and on Wafers Dipped into Them

Element	H_2O_2 [M] ppb		Wafer 10^{10} atoms/cm^2	
	A	B	A	B
Al	22	2.6	580	92
Cr	3.3	0.1	<1	<1
Fe	6.7	<2.0	82	<5
Ni	2.6	<0.1	1.2	0.9
Na	10	2.3	12	14

Determining metals in thick oxides such as initial oxide, fill oxide, spacers, intermetal dielectrics, or doped planarization or passivation films has become a routine activity at the lab. Table 5 depicts a study of thick film oxide and TEOS samples produced via different techniques and reactors. This Table is interesting in that it illustrates that reactors can contribute significant quantities of metallic contamination which will get dispersed in the etching bath. Also, it appears that TEOS can vary by lot or manufacturer.

Table 6 was compiled by evaluating numerous wafers for metallic contamination that had been through photoresist etching, ion implantation, and various wafer handling procedures. These data are presented as ranges of what has

been found to date utilizing data from several reactors and processes at different IC manufacturing sites. Of these, ion implantation studies are particularly interesting since what is measured as metallic contamination caught in a thick oxide test wafer is also what was implanted in the processed wafers. In this case, cleaning is of no help in removing these metals and thus, cleaning up the implanter becomes a real necessity.

When measuring metals in films, both recovery and sensitivity are important. Table 7, the Periodic Chart, contains recovery data by element. A recovery study is done by deliberately contaminating a clean wafer with known quantities of metals or metal salts and using a specific procedure to see what quantity was actually recovered. The percentages given are a measure of the amount of metal recovered versus the amount applied.

As is seen, recoveries are very good for most elements. Some exceptions are Cu, W, and Ag, which are above Si on the electromotive series. They require special treatment to remove them from the silicon wafer. However, Pt, Au, Hg and Bi cannot be recovered even when strong chemical treatment is used.

Different setups for both front-end injection systems and types of ICP-MS units (quadrapole or HR/Magnetic Sector) can result in very sensitive measurements down to 1×10^8 atoms/cm^2 for most elements, and 10^7 or 10^6 for some. Table 8 illustrates the differences in obtainable sensitivity for tin when it is measured as 1 of 30, 6, or 2 elements from a single 6-inch wafer. Oftentimes, a rough scan for 30 elements will be used for detecting unsuspected metallic contamination, whereas, 6-critical elements are most frequently measured to follow specific processes of cleaning. Only 1-3 elements are measured when a specific study is being done where the greatest sensitivity is desired.

SUMMARY

In summary, because of the ability to put wafer films into solution for very low level, accurate, and NIST traceable tests, it has now become possible to relate metallic contamination on wafers with sources of metallic contamination and to measure the efficiency of wafer cleaning processes. It is now possible to evaluate both liquid and wafer samples from any series of events to determine their metallic contamination. This capability has been accomplished by using different chemistry for metal removal and sample concentration, and by using multiple sample injection systems to enhance ICP-MS performance. Nearly all metals (Au, Pt, Pd, Hg, Te, Ru, and Bi are exceptions), can be analyzed accurately via these techniques.

TABLE 4. Cleaning Efficiency Study — Contamination Measured on Wafer Surface (x 10^{10} atoms/cm^2)

	Starting Wafer	75°C SC2 Clean	25°C Dilute $HF:H_2O_2:H_2O$ Clean	72°C Dilute $HF:H_2O_2:H_2O$ Clean
Al	16,000	18.5	19.5	9
Fe	134	5.1	1.8	2.1
Sn	315	29.4	1.84	1.2
Pb	7.9	0.1	0.1	0.01
V	0.9	0.02	0.02	0.03
Zn	12.1	6.5	3.75	0.6
Ca	5	8.1	7	2

TABLE 5. Typical Concentration of Metal Contaminants in Dielectric Oxide Films on Silicon Wafers from Different Sources

	Concentration: ppm of oxide					
Source	A	B	C	D	E (TEOS)	F (TEOS)
Oxide Thickness Å	3000	3000	3000	6000	2000	8000
Aluminum	2.9	1.2	16	18	0.2	7.3
Sodium					<0.4	0.93
Chromium	1.2	0.53	6.9	0.63	<0.02	
Iron	4.6	4.4	12	3.0	<0.2	0.76
Nickel	2.3	0.68	4.5	0.56	<0.2	-
Copper	2.4	1.8	0.31	-	-	-
Manganese	-	-	-	0.11	-	-
Cobalt	-	-	-	0.01	-	-
Magnesium	-	-	-	-	-	0.66
Zinc	-	-	-	-	-	0.18
Zirconium	-	-	-	-	-	0.02

TABLE 6. Typical Concentrations of Trace Metals Found on Silicon Wafers after Different Processing Steps. Surface Concentrations (x 10^{10} atoms/cm^2)

Process	Na	Al	Ti	Cr	Fe	Ni	Zn	W
Photoresist Etching								
Low		10		1	10	1		
High	500	800		50	200	50		
Ion Implantation								
Low		50	10	10	10	10		2
High		10,000	1,000	5,000	10,000	5,000	100	500
Wafer Handling								
Low		10		1	5	1	5	
High		500		4,000	8,000	8,000	700	

TABLE 7. Recovery of Elements from Bare Silicon Wafers

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li 98%	4 Be 95%											5 B >90% +	6 C	7 N	8 O	9 F	10 Ne
11 Na 104%	12 Mg 98%											13 Al 98%	14 *Si	15 P	16 S	17 Cl	18 Ar
19 *K 100%	20 Ca 98%	21 Sc 98%	22 Ti 95%	23 V 98%	24 Cr 98%	25 Mn 102%	26 Fe 110%	27 Co 100%	28 Ni 98%	29 Cu 85%	30 Zn 104%	31 Ga 100%	32 Ge 94%	33 As <90% +	34 Se	35 Br	36 Kr
37 Rb 100%	38 Sr 98%	39 Y 101%	40 Zr 95%	41 Nb 82%	42 Mo 87%	43 Tc -	44 Ru 20-80%	45 Rh 15-80%	46 Pd 85%	47 Ag 84%	48 Cd 96%	49 In 99%	50 Sn 105%	51 Sb 95%	52 Te 20-80%	53 I	54 Xe
55 Cs 96%	56 Ba 95%	57-71 *La 40-94%	72 Hf 100%	73 Ta -	74 W 78%	75 Re -	76 Os -	77 Ir 78%	78 Pt 10-50%	79 Au 1-10%	80 Hg 25-70%	81 Tl 95%	82 Pb 101%	83 Bi 10-48%	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac **															

*	58 Ce 99%	59 Pr 96%	60 Nd 96%	61 Pm	62 Sm 97%	63 Eu 97%	64 Gd 100%	65 Tb 100%	66 Dy 100%	67 Ho	68 Er 100%	69 Tm 99%	70 Yb 99%	71 Lu 99%
**	90 Th 100%	91 Pa	92 U 100%	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

+Without VPD,
with solution strip technique

TABLE 8. Sensitivity of Tin in VPD Scans of Varying Sizes.

	When Part of a 30 Element Scan	When Part of a 6 Element Scan	When Part of a 2 Element Scan
Sensitivity (10^{10} atoms/cm^2) On 6" Wafer	0.25	0.1 to 0.2	0.01