

Measurement of Trace Metallic Contaminants on Silicon Wafer Surfaces in Native and Dielectric Silicon Oxides by Vapor Phase Decomposition Flow Injection Inductively Coupled Plasma-Mass Spectrometry

János Fucskó, Samantha S. Tan, and Marjorie K. Balazs*

Balazs Analytical Laboratory, Sunnyvale, California 94089

ABSTRACT

A highly sensitive multielement analytical method known as vapor phase decomposition flow injection inductively coupled plasma-mass spectrometry (ICP-MS) was developed and used to measure the concentration of trace metals on silicon wafer surfaces. The method uses hydrogen fluoride vapor to decompose and release metal contaminants from a surface oxide. These trace metals are then collected by scanning a small drop of dilute acid solution throughout the wafer surface. Trace metals in the solution are measured by ICP-MS using flow injection (FI) sample introduction. Potentially, 60 elements can be measured with detection limits ranging from 10^8 to 10^{11} atom/cm². Typical surface concentrations of trace metals on silicon wafers with native oxides and dielectric oxides were measured and presented.

The removal and control of metallic contaminants on silicon wafers is an important aspect of wafer and semiconductor device manufacturing.¹ Metallic contaminants cause deterioration in the performance and yield of semiconductor devices.^{2,3} During high temperature processes, metals diffuse rapidly into silicon substrates and cause undesirable changes in electrical characteristics. In ULSI manufacturing, very low surface concentration of metals in the range of 10^{10} to 10^{11} atom/cm² or lower is required. This metal contamination level corresponds to less than 0.001% of a monolayer coverage on a wafer surface.

Currently, metal impurities on silicon wafers are measured predominately by surface analytical techniques such as total reflection x-ray fluorescence spectroscopy (TXRF) and secondary ion mass spectrometry (SIMS).⁴⁻⁶ The advantage of these techniques is that these are nondestructive techniques, do not require sample preparation, and they allow on-line or near-line measurements.³ These techniques have relatively good sensitivity with detection limits in the range of 10^9 to 10^{12} atom/cm². Traditional TXRF technique has poor sensitivity ($>10^{13}$ atom/cm²) for some important low mass elements such as B, Na, Mg, K, and Al.⁸ In addition, background interferences inhibit the measurement of other elements such as W and Fe at usefully low detection limits. Also, the accurate quantitation is difficult due to the lack of representative reference standards.

Furthermore, both SIMS and TXRF techniques measure only a very small area of the wafer and evaluate only the top 20 to 30 Å layer of the wafer surface which limits their application for measuring metal contaminants in dielectric oxide layers with greater thickness.

Another sensitive method currently used for metal analysis on silicon wafers is based on the use of graphite furnace atomic absorption spectroscopy (GFAAS).¹⁰⁻¹⁸ In this technique, a silicon oxide layer is decomposed by HF vapor and the metal impurity on a silicon wafer is collected into a very small volume of solution and analyzed for one element at a time by GFAAS. Detection limits achieved are in the range of 10^9 to 10^{11} atom/cm². The main disadvantage of this method is that only one element can be analyzed at a time since each element requires different parameter adjustments and sometimes different matrix modifiers. Consequently, analysis by GFAAS is time consuming and not practical. The advantages of this method are that the results obtained are accurate and low mass elements such as Al, Na, Mg, and K can be determined down to 10^{10} atom/cm².

Here, a multielement instrument, the ICP-MS is used for the determination of trace metals on silicon wafers.¹⁹ This

method overcomes the main disadvantage of the GFAAS because it can analyze many elements rapidly. Trace metals are collected from a wafer with native oxide or dielectric oxide layer using HF vapor phase decomposition (VPD) method. To achieve low detection limits, a flow injection sample introduction is used to measure very small sample volumes. A multitude of trace metals are determined by this method, however, the study was focussed primarily on the six most critical elements in a semiconductor processing environment (Al, Cr, Cu, Fe, Ni, and Na).

Experimental

Sample preparation by HF vapor phase decomposition of an oxide layer.—Operating in a class 10 cleanroom environment, one or more wafers were loaded into a specially constructed VPD box containing a reservoir with HF solution. After a few minutes, the box was saturated with moist

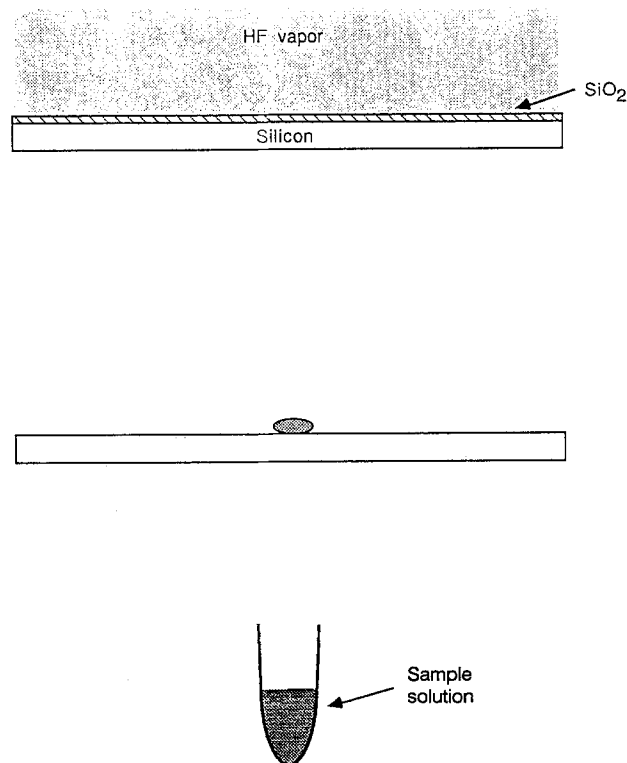


Fig. 1. Schematic diagram of the collection of trace metals from a bare silicon wafer by HF vapor phase decomposition method.

* Electrochemical Society Active Member.

Fig. 2. Schematic diagram of the setup for flow injection ICP-MS.

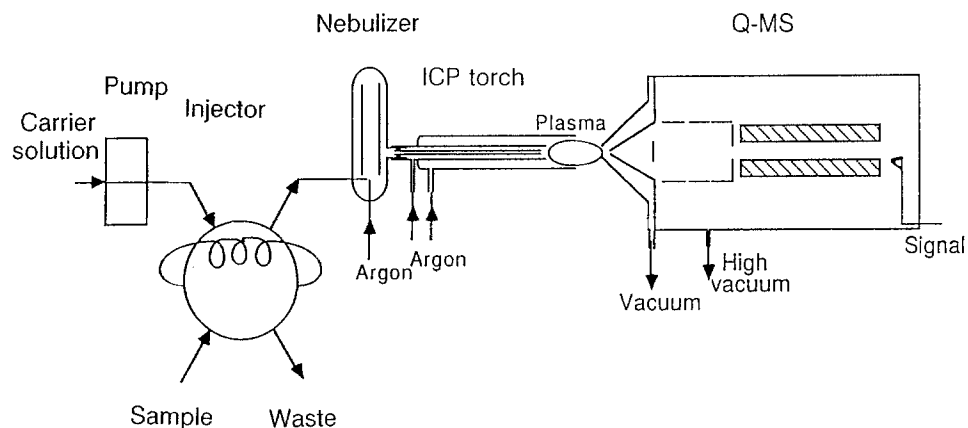
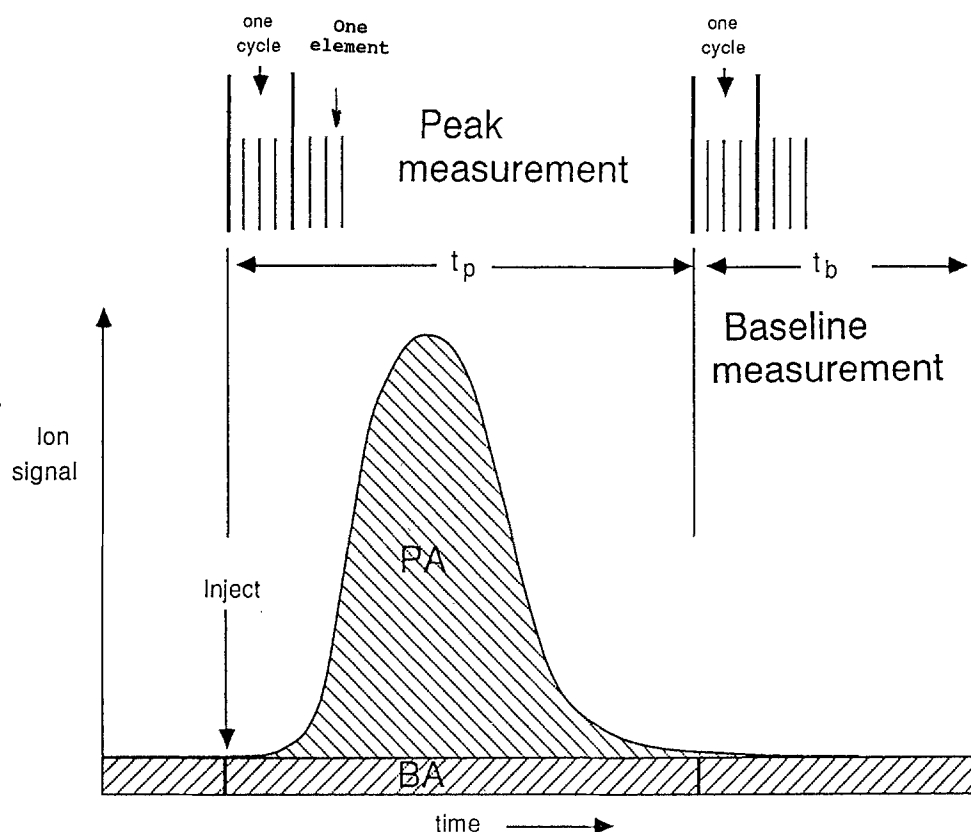
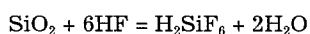


Fig. 3. The ICP-MS transient signal.



HF vapor and the reaction with the silicon oxide layer was initiated (Fig. 1). The exposure time of the wafers is dependent on the thickness of the oxide layer. Native oxides of 15–30 Å thickness are decomposed completely in about 20 min. However, decomposition time can range from 3 to 12 h for thermal or CVD silicon oxide layers with thicknesses of 2,000–10,000 Å. The HF vapor reacts with the silicon oxide following the equation



This procedure was similar to that described by Shiraiwa *et al.*^{11,12} After the decomposition of the oxide layer, the silicon wafer surface becomes hydrophobic. A small drop of a dilute acid solution, (*e.g.*, HF) was added to the wafer surface. The drop of acid was rolled carefully in a reproducible pattern throughout the wafer surface to ensure complete recovery of trace metals. After this step, the drop was removed by a pipette and transferred to a small sample tube for analysis by flow injection ICP-MS.

To achieve low analysis blanks, each apparatus and piece of equipment used in the process was pre-cleaned carefully before use. Ultrapure chemical reagents used in the process were analyzed and verified by ICP-MS to have concentra-

tions of less than 0.5 ppb for every analyte. Ultrapure de-ionized water used for cleaning also was analyzed and verified by ICP-MS to contain less than 0.1 ppb for each analyte.

Instrumentation.—The instrument used in this study is a Perkin Elmer Sciex Elan 500 ICP-MS retrofitted with Elan 5000 software. The sample introduction system is an HF resistant torch assembly with a cross-flow pneumatic nebulizer. Recently, a CETAC 5000 ultrasonic nebulizer was installed to achieve better detection limit for most elements, including Fe. Before this upgrade Fe was measured by GFAA, because of background interferences from ArO^+ signal. A Teflon injection valve was installed to enable the manual injection of a small volume of sample. A schematic of the system is shown in Fig. 2.

A Perkin Elmer AAS Model 2380 with a HGA 400 graphite furnace attachment was used for comparison of concentration of some critical elements with ICP-MS results.

Concentration calibration of the ICP-MS and GFAAS was performed using multielement standard solutions prepared from NIST standards which contained the same acid concentration as the sample being analyzed. The concen-

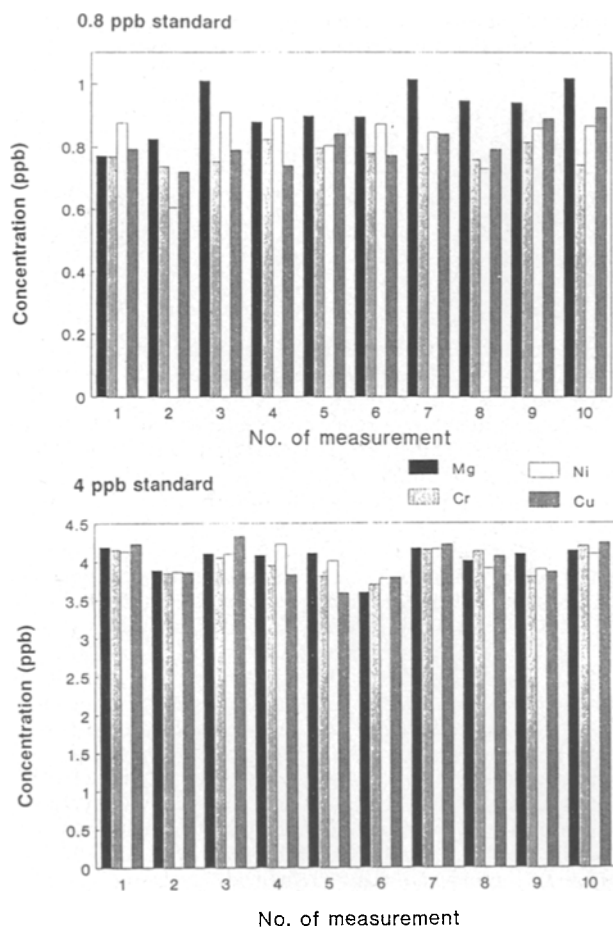


Fig. 4. Precision of data obtained by FI-ICP-MS for an 0.8 ppb standard and a 4.0 ppb standard over a 6-h period.

trations of trace metals in the sample solution were converted to atom/cm² for evaluation of bare wafers and to parts per million (µg/g) for evaluation of a dielectric oxide layer.

Data acquisition.—Data from the ICP-MS were acquired through the graphic mode of the Elan 5000 software. For each element, the dwell time and number of points measured per mass unit were optimized in the procedure. The injection frequency for one sample for one to seven elements was set at 2 min. The transient ion signal obtained and its data integration is shown schematically in Fig. 3.

Since the standard Elan software did not support the evaluation of a transient signal, a data processing program was written for this purpose in QuickBasic. Data acquired from the ICP-MS were converted into an ASCII format and evaluated by this customized program. The data array was cut into two-minute periods, each of them representing one injected sample. The signal of each element then was inte-

Table II. Recovery of trace metals on 6-inch bare wafers by HF vapor-phase decomposition method.

Wafer ID	Surface concentration ($\times 10^{10}$ atom/cm ²)			Recovery (%)
	Spike	Recovered	Blank	
Aluminum				
1	12.6	13.0	0.76	89
2	23.5	23.0	4.1	90
3	44.7	43.6	0.38	94
			Avg = 1.78	
Chromium				
1	6.54	6.44	<0.2	99
2	12.2	11.0	<0.2	90
3	23.2	22.8	<0.2	98
			Avg = <0.2	
Copper				
1	5.41	0.24	<0.1	4.4
2	10.1	<0.2	<0.1	<2.0
3	19.2	1.59	<0.1	8.3
			Avg = <0.1	
Nickel				
1	5.67	6.07	<0.1	107
2	10.6	9.78	0.2	92
3	20.1	20.1	<0.1	100
			Avg = <0.1	
Iron-by GFAAS				
1	10.8	12.0	—	103
2	22.1	25.8	0.6	113
3	29.5	32.9	1.1	109
			Avg = 0.85	
Sodium				
1	17.9	21.2	1.90	87
2	33.4	37.9	8.57	96
3	63.5	67.7	6.60	98
			Avg = 5.69	

grated both at the peak portion and at the baseline portion. The normalized baseline integral (BA) was subtracted from the peak integral. The baseline subtracted peak area was the analytical signal (PA), which was linear to the analyte concentration within the working range.

Results and Discussion

Precision of data obtained by flow injection ICP-MS.—To evaluate the precision of the results obtained by flow injection ICP-MS, a standard solution was injected periodically over 6 h and then analyzed for four elements. The elements analyzed were Mg, Cr, Ni, and Cu. Figure 4 shows the data obtained for a 0.8 and a 4.0 ppb standard. The precision obtained for a 0.8 ppb standard was $\pm 15\%$ and for a 4.0 ppb standard solution was $\pm 8\%$. These concentrations were chosen because they represent the actual concentration ranges of trace metals in a solution obtained from a wafer after the VPD step. These concentrations translate to surface concentrations of about 10^{10} - 10^{11} atom/cm² on a 6-inch wafer.

Recovery of trace metals from bare silicon wafer.—To verify this new method, the removal of trace metals from a silicon wafer surface must be shown to be quantitative and

Table I. Surface concentration of trace metals on 6-inch wafers by ICP-MS.

Wafer ID	Surface concentration ($\times 10^{10}$ atom/cm ²)					
	Al	Cr	Cu	Ni	Fe	Na
1	77	<0.2	<0.2	<0.2	<2	12
2	76	0.7	<0.2	<0.2	<2	9
3	83	<0.2	<0.2	<0.2	<2	10
4	84	<0.2	1.5	<0.2	<2	9
5	82	0.4	<0.2	<0.2	<2	15
6	82	<0.2	<0.2	<0.2	<2	13
Average	81 \pm 3	<0.2	<0.2	<0.2	<2	11 \pm 2
B1	0.8	<0.2	<0.2	<0.2	—	1.9
B2	4.2	<0.2	<0.2	<0.2	<2	8.6
B3	0.4	<0.2	<0.2	<0.2	<2	6.6
Average	1.8 \pm 2.1	<0.2	<0.2	<0.2	<2	5.7 \pm 3.4

Table III. Detection limits of trace metals by VPD-FI-ICP-MS on 6-inch wafers.

Elements		Surface concentration ($\times 10^{10}$ atom/cm ²)			
		Pneumatic	Nebulizer	Ultrasonic	Nebulizer
		Optimized single element detection limit	Typical detection limit	Optimized single element detection limit	Typical detection limit
Aluminum	Al	1.1	3	0.4	0.5
Chromium	Cr	0.1	0.3	0.1	0.3
Cobalt	Co	0.05	0.1	0.0033	0.009
Iron	Fe	1 ^a	2 ^a	2	2
Lead	Pb	0.05	0.1	0.01	0.015
Magnesium	Mg	— ^b	— ^b	0.1	0.2
Manganese	Mn	0.1	0.2	0.03	0.05
Nickel	Ni	0.07	0.2	0.02	0.06
Potassium	K	— ^b	— ^b	4	4
Sodium	Na	1	5	0.4	1
Vanadium	V	0.02	0.05	0.03	0.08
Zinc	Zn	0.3	1	0.22	0.3

^a Measured by GFAA.^b Not measured.

reproducible. The verification method was to spike a silicon wafer with known amounts of trace metals and then to analyze the wafer using the described experimental procedure. Since wafers with known quantities of low level metallic concentrations were not available, this study was initiated with the measurement of a set of bare wafers for establishing baseline surface concentrations of metallic impurities and for determining a subtraction blank.

In the experiment, a set of 6-inch bare wafers from the same lot was analyzed for six critical trace metals. The results obtained are shown in Table I; Cr, Cu, Ni, and Fe were not found above 2×10^{10} atom/cm² and for most wafers these elements were below their detection limits. In contrast, Al and Na were found at much higher concentrations, which on average were 81×10^{10} atom/cm² and 11×10^{10} atom/cm² respectively.

To establish a subtraction blank, three of these wafers were randomly selected and analyzed again with a second VPD step for the same trace metals. The results obtained also are presented in Table I with these wafers relabelled as B1, B2, and B3. From the table, we see that the concentration of Al was reduced drastically to an average of less than 2×10^{10} atom/cm². However, the Na concentration was not significantly different from its original level. This indicated a Na contamination at an average level of 6×10^{10} atom/cm², suggesting that the detection limit for Na was limited by the sample preparation step. In contrast, the ICP-MS instrument detection limit for Na at 0.1 ppb suggests that it would be possible to measure Na down to 10^9 atom/cm².

Based on this experiment the wafers were considered relatively clean after performing only one VPD step. Therefore, the remaining wafers were used for evaluating the recovery of trace metals from the wafer surface using the VPD process. The recovery studies were initiated by spiking the samples. One method of spiking the wafers is to distribute and dry a known volume of a standard solution

Table V. Comparison of trace metal concentrations in hydrogen peroxide solutions and on 6-inch bare wafers.

Element	Concentration hydrogen peroxide (ppb)		Surface concentration ($\times 10^{10}$ atom/cm ²)		
	Sample A	Sample B	Wafer A	Wafer B	
Aluminum	Al	22	2.6	580	92
Chromium	Cr	3.3	0.1	<1	<1
Iron	Fe	6.7	<2	82	<5
Nickel	Ni	2.6	<0.1	1.2	0.9
Sodium	Na	10	2.3	12	14

on the wafer. This method ensures that an accurately known amount of trace metals is deposited onto the silicon wafer surface.

Table II shows the recovery of six elements at three spike concentrations. The spike concentrations vary from 0.5×10^{11} to 6×10^{11} atom/cm². The percent recovery was computed by subtracting the average concentration from three blank wafers (B1, B2, and B3 from Table I) from the concentration of the spiked wafer and then dividing the value by the actual spike concentration. Subtraction of the average blank value was significant only for Na. There was good recovery (90 to 110%) for trace elements such as Al, Cr, Fe, Ni, and Na at all the concentrations studied.

However, for Cu, the recovery was poor and not reproducible. Previous studies, *e.g.*, Gupta *et al.*¹⁸ also had shown the same phenomenon. An explanation for this is that since Cu was more electropositive than silicon and hydrogen, the Cu ions were readily reduced and electroplated as metal on the silicon surface. Poor Cu recovery therefore would be expected since Cu metal does not dissolve in a dilute HF solution easily. However, 80 to 90% of Cu can be removed from the surface with a strong oxidizing chemical, as later studies showed. Similar studies showed 80 to 100% recoveries for trace metals such as Co, Ga, In, Ir, Mg, Mn, Rb, Ti, W, Zn, Sn, and V. However, poorer recoveries (<50%) were observed for Bi, Au, Hg, and La using the same sample preparation method.

Detection limits.—The method detection limits for various trace metals on a 6-inch wafer by ICP-MS are shown in Table III, using both pneumatic and ultrasonic nebulizer. The optimized detection limit was obtained by measuring only one element per one injection, whereas the typical detection limit was obtained by analyzing five or six elements per sample injection. In general, the optimized detection limits were lower by a factor of 2 to 4 for most elements, except elements such as Fe and K, which are affected by background interferences. For these elements, the longer integration time did not result in better detection limits. Both sets of detection limits were in the range of 10^8 to 10^9 atom/cm² except for Al, Na, and Fe. The reasons for the higher detection limits for these elements were the presence of traces of these metals in the ultrapure reagents and in the environment, and the use of an aluminum oxide injector tube for sample introduction. When the ultrasonic nebulizer is used to achieve better detection limits, it is even more important to minimize contamination from reagents and from the environment.

A survey of metal contaminants on wafers from various sources.—Bare wafers.—Trace metals on bare wafers from

Table IV. Surface concentration of metal contaminants on bare silicon wafers from different sources.

Source	Surface concentration ($\times 10^{10}$ atom/cm ²)							
	A	B	C	D	E	F (EPI)	G	H
Aluminum	470	270	88	32	27	<5	8	20
Sodium	22	10	54	43	28	<7	8	10
Chromium	<1	<1	<1	<1	<1	<0.4	<0.4	<0.4
Iron	58	16	15	5	2.8	<2	<5	<5
Nickel	2.0	1.6	—	—	—	<0.4	<0.4	<0.4
Zinc	—	—	<1	<1	<1	<1	<5	<5

Table VI. Typical concentration of metal contaminants in dielectric oxide films on silicon wafers from different sources.

Source	Concentration (ppm of oxide)					
	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

different sources were studied. The results obtained are listed in Table IV. The most common metal contaminants on bare wafers were Al, Fe, and Na. The lowest metal concentration was on an epitaxial silicon wafer which had its silicon layer deposited from a gas phase source. Epitaxial wafers are usually very clean since they are not exposed to wet processes. One major source of metal impurities is liquid processing chemicals.⁸ Al, Fe, and Na are typical contaminants found in most chemicals. An example of the contaminants found in a hydrogen peroxide solution used in a SC1 clean is shown in Table V. Two different grades of H₂O₂ were evaluated. Trace metal concentrations in the H₂O₂ samples were analyzed by ICP-MS and correlated with the surface metal concentration of wafers cleaned in each respective H₂O₂ bath. The data in Table V show that sample A had higher concentrations of trace metals than sample B. The Al and Fe concentration on wafer A cleaned in H₂O₂ sample A was 5 to 10 times higher than wafer B cleaned in H₂O₂ sample B. The concentration of trace metals in both H₂O₂ samples was relatively low and yet the concentration caused a dramatic difference in wafer surface concentration. Interestingly, no significant differences were observed for Na using the two H₂O₂ samples even though the Na concentrations were significantly different, suggesting that Na contamination was introduced by other sources.

Dielectric oxide films on wafer.—For wafers with thermal or CVD oxide layers, the sample solution may contain a significant amount of silicon. The presence of a high concentration of silicon causes background interference for certain elements and therefore must be eliminated from the solution. A solution containing a significant concentration of silicon and HF produces background molecular species such as SiO⁺, SiOH⁺, SiO₂⁺, SiF⁺, SiF₂⁺, SiF₃⁺, ArSi⁺, SiOF⁺, SiOHF⁺, and SiOF₂⁺ in the argon plasma. Interferences from the background species can occur with Ca, Ti, Ni, Cu, Zn, and Rb.

In contrast with dielectric oxide layers, the amount of silicon in the sample solution collected from a bare wafer was only 3 to 5 pm. The silicon at this concentration did not interfere significantly with the determination of trace metals of interest.

Typical concentrations of metal contaminants in dielectric oxide layers are shown in Table VI. The metal concentrations are presented in ppm and the thickness of each sample is provided also. Sample E is the cleanest oxide film that was generated from a TEOS source. Measurement of trace metals in these oxide layers is important because the results can be useful in solving practical process problems (e.g., changes in oxide breakdown voltages) and in the identification of contaminating sources.

Conclusion

A highly sensitive multielement analytical method, called vapor phase decomposition flow injection inductively coupled plasma-mass spectrometry (VPD-FI-ICP-MS) was developed and used to measure the concentration of trace metals on silicon wafer surfaces.

ICP-MS is a sensitive technique for rapidly analyzing trace metals on silicon wafer surfaces. Sample preparation methods using HF vapor-phase decomposition and sample evaporation were developed to collect trace metals from different types of silicon wafer surfaces. Very small volumes of analyte solution were analyzed by flow injection ICP-MS. Detection limits are typically in the range of 10⁸ to 10¹⁰ atom/cm². ICP-MS can serve as a reference technique for the calibration of surface analytical techniques, such as TXRF and SIMS in addition to offering an improved technique for measuring trace metals accurately and reproducibly.

Manuscript submitted Sept. 9, 1992; revised manuscript received Dec. 29, 1992.

The Balazs Analytical Laboratory assisted in meeting the publication costs of this article.

REFERENCES

- B. F. Phillips, D. C. Burkman, W. R. Schmidt, and C. A. Peterson, *J. Vac. Sci. Technol.*, **A1**, 646 (1983).
- R. Takizawa, T. Nakanishi, and A. Oshawa, *J. Appl. Phys.*, **62**, 4933 (1987).
- K. Honda, T. Nakanishi, A. Oshawa, and N. Toyokura, *ibid.*, **62**, 1960 (1987).
- T. J. Schaffner, *Surf. Interface Anal.*, **14**, 598 (1989).
- A. J. Swift, *Mater. Design*, **10** (1989).
- M. Grasserbauer and G. Stinger, *Fresenius, Z. Anal. Chem.*, **337**, 701 (1990).
- J. Fujimara and H. Yano, *This Journal*, **135**, 1195 (1988).
- O. J. Anttila, M. V. Tilli, M. Schaekers, and C. L. Claeys, *ibid.*, **139**, 1180 (1992).
- W. Hub and V. Penka, *Microcontamination '91*, Conference Proceedings, p. 266, San Jose, CA (1991).
- A. Shimazaki, H. Hiratsuka, Y. Matsushita, and S. Yoshii, *Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials*, Kobe, p. 281, 1984, Japan, Japan Society of Applied Physics.
- T. Shiraiwa, N. Fujino, S. Sunita, and Y. Tanizoe, in *ASTM Conference on Semiconductor Fabrication: Technology and Metrology*, Santa Clara, 1988, Proceeding ASTM No. STP 990 (1989).
- Y. Tanizoe, S. Sumita, M. Sano, N. Fujino, and T. Shiraiwa, *Bunseki Kagaku*, **38**, 177 (1989).
- A. Corradi, M. Domenici, and A. Guaglio, *J. Cryst. Growth*, **89**, 39 (1988).
- T. Shimono and M. Tsuji, at Advanced Wet Chemical Processing II, p. 49, 11th Workshop on ULSI Ultra Clean Technology, Tokyo, June 6, 1991.
- T. Shimono, M. Tsuji, M. Morita, and Y. Muramatsu, *Microcontamination '91*, Conference Proceedings, p. 544, San Jose, CA (1991).
- R. Poliak, R. Matthews, P. Gupta, M. Frost, and B. Triplett, *ibid.*, p. 511.
- H. C. Molenkopf and D. C. Gupta, *ibid.*, p. 577.
- P. Gupta, M. Van Horn, and M. Frost, in *Chemical Proceedings of Semiconductor Pure Water and Chemical Conference (SPWCC)*, p. 191, Santa Clara, CA (1992).
- S. Tan, J. Fucsko, and M. Balazs, Paper presented at the FACSS/Pacific Conference, Anaheim, CA, Oct. 6-11, 1991.