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Metal Contamination caused by Ion Implanters

by

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5.1d Metal Contamination Caused by Ion Implanters

5.1d.1 Introduction

Ion implantation, like all reactor processes, exposes the wafers to metallic contamination. There are several possible sources of these contaminants in an ion implanter [96a]. The obvious ones are the wafer loading mechanism, the process of pumpdown and venting of the loading chamber. These are easily detected using a plain test wafer [95a]. However, while using the high flux ion beam, several more sources of contamination exist which include the ion source, sputtered dopants or metals originating from the beam line, components in the ion implanter, wafer fixtures and the sputtered materials. Additionally, there may be interfering species present in the beam to begin with [96b]. Furthermore, other sources of contamination include wafer mounting devices, and heat sinks which may contaminate the back side of the wafer [96c].

Measuring the type and quantity of metallic contamination that occurs during the ion implantation step has generally been limited to measuring surface contamination using VPD-ICP-MS, VPD-TXRF, or SIMS. These measurements do reveal that metallic contamination on the surface can be significant (see Table 1).

Table 1. Surface Metallic Contamination After Ion Implantation

Element	Concentration Range ($1x10^{10}$ atoms/cm^2)
Aluminum	100 - 10,000
Iron	10 - 100
Chromium	1 - 10
Nickel	1 - 10
Titanium	10 - 100

More importantly however, are the metallic atoms that are implanted into the silicon itself during ion implantation. Since these metals are a part of the silicon itself and in very low concentration, the ability to accurately measure these contaminants was not possible until the early 90's [97]. A procedure was developed based on an already existing procedure that was being used to measure dopants in BPSG. This procedure developed in 1968 involved the dissolving of the oxide in a drop of hydrofluoric acid, collecting the drop and measuring the dopants it contained.

Knowing that the implantation of metals in a thick oxide is essentially the same as that in silicon (see Figure 1). A wafer that contained a thick oxide was subjected to ion implantation, stripped of its oxide, chemically treated and measured by ICP-MS. From the concentration of the metals found, the quantity of the metals implanted in a substrate could be determined.

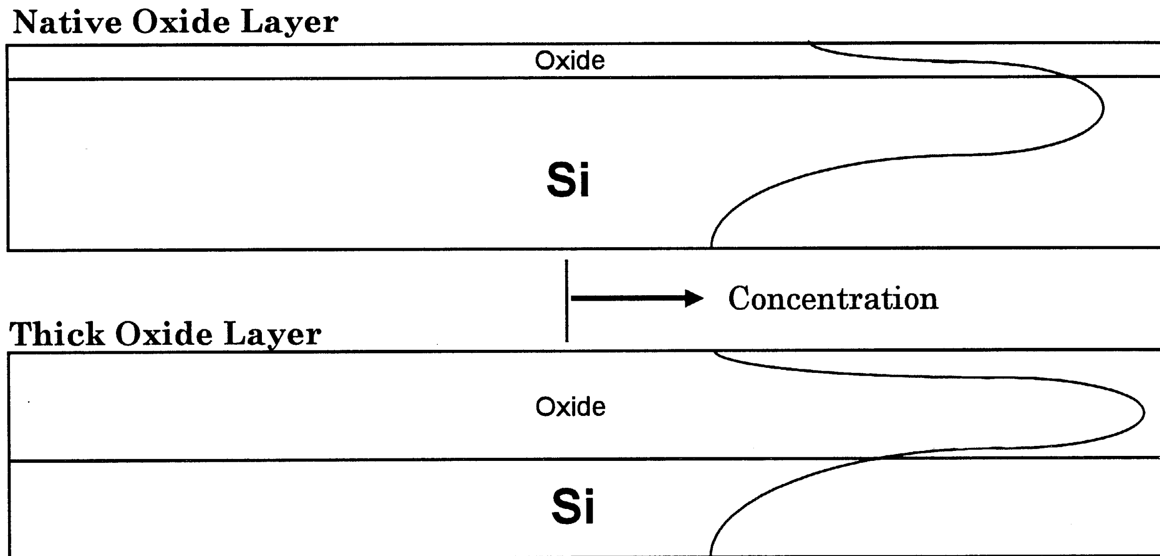

Figure 1. Concentration Profiles After Ion Implantation in Silicon and Silicon Dioxides.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was the analytical instrument of choice due to its sensitivity, superior elemental resolution and ability to quantitatively measure metals in solution. This instrument also can easily be standardized using NIST standards. The measurements are therefore accurate. For example, sixty-eight metals, Lithium to Uranium can be detected at very low levels (1E9-1E7 atoms/cm^2 depending on the metal.) Routinely, thirty metals are measured. For more sensitive work, five to nine metals are measured.

5.1.d2 Procedure:

Basically, the procedure involves depositing oxide on two or more wafers. All but one of these wafers (the control) are placed in the reactor for ion implantation. After implantation, all of the wafers, including the control are surface cleaned and rinsed with ultra pure water (UPW.) The oxide is stripped off the wafer using a mixture of dilute hydrofluoric (HF) and other acids. The resulting solution is placed into a tube and concentrated. During this step, the silicon is removed from the matrix. The resulting concentrate is then analyzed by ICP-MS (see Figure 2).

A 2000 Å thick oxide will have approximately 90% effectiveness for collecting implanted material in a high energy ion implanter. Thicker films will trap 100% of the implanted metals with 5000 Å being a maximum thickness.

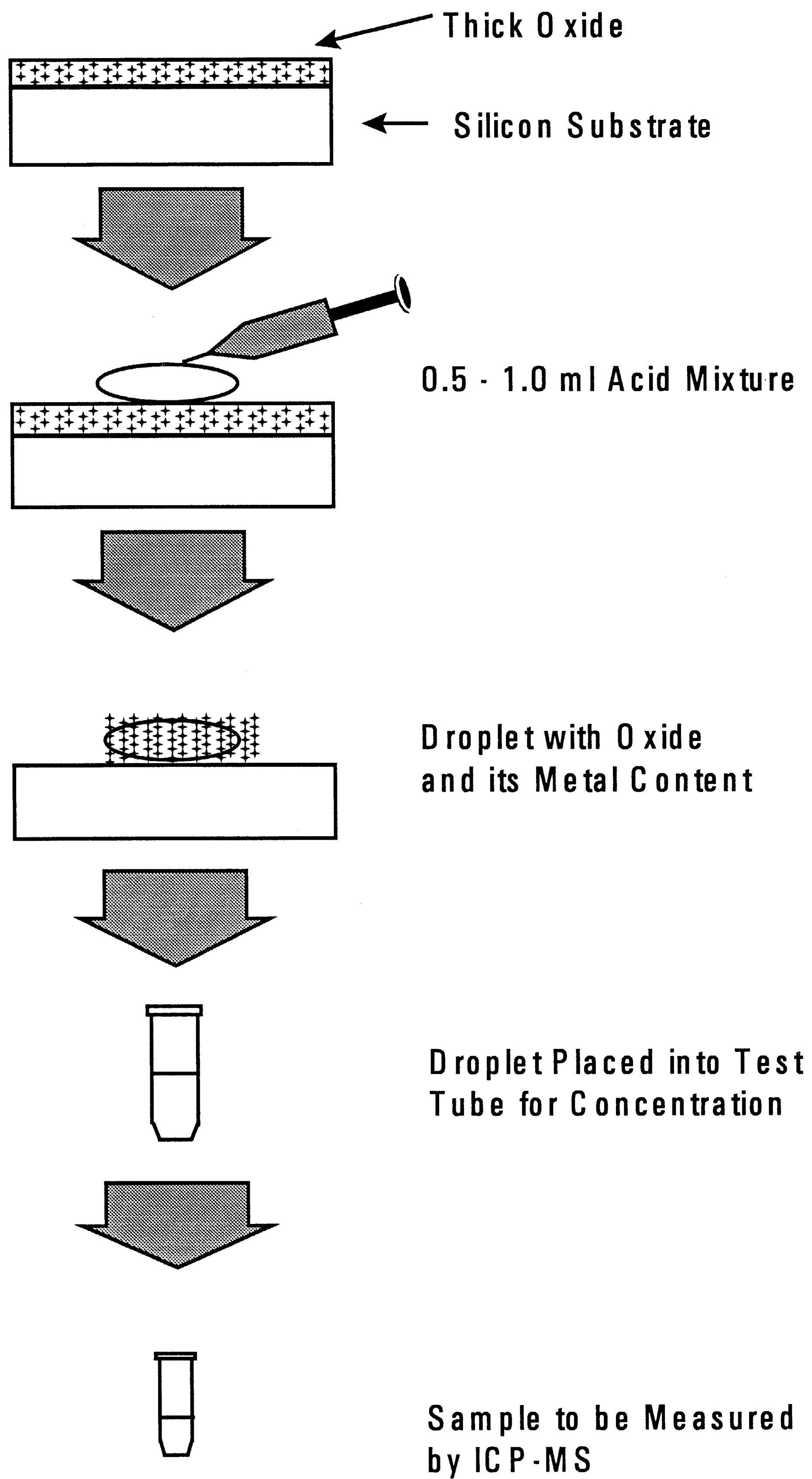

Figure 2. Drop Scan Procedure for Measuring Metals in a Thick Oxide

The analysis of numerous wafers from a variety of ion implanters using this technique has shown that the type of contamination found is consistent but the quantity varies significantly, The main metals found are aluminum, titanium, iron, chromium, nickel and tungsten in ranges from 10 - 10,000 atoms/cm^2 (see Table 2). A full measurement of thirty metals found in a specific set of wafers from an ion implanter using the technique described is shown in Table 3.

Table 2. Range of Metal Contaminants Implanted into the Substrate

Element	**Concentration Range** (1x10^{10} atoms/cm^2)
Aluminum	10 - 10,000
Iron	10 - 10,000
Chromium	10 - 5,000
Nickel	10 - 5,000
Tungsten	0.1 - 50

These contaminants come from the tungsten filament and stainless steel and aluminum parts. The expanded full thirty metals analysis reveals that every minor metal in stainless steel can also be found in the implanted wafer. Even though the aluminum and tungsten represent the greatest amount of contamination, the quantities of molybdenum, zinc, tin, sodium and potassium are still significant and of concern. The amount of calcium and magnesium found although not as deleterious are still considerably higher than they should be. These materials may come from non-metallic components used in ion implanters. By using these data, operators have been able to reduce metallic contaminants to levels that are tolerable and do not cause serious damage to the substrate.

Table 3. High Energy Contamination (of oxide) in an Ion Implanter

Trace Metals in Oxide Film on 150mm Silicon Wafers
Concentration in 10^{10} atoms/cm^2

Element		Detection Limit	Sample #1	Sample #2	Control
Calcium	Ca	1.0	42	39	24
Potassium	K	0.2	18	12	8.5
Sodium	Na	0.5	22	14	16
Aluminum	Al	0.5	290	280	18
Iron	Fe	0.5	34	35	9.0
Chromium	Cr	0.5	4.7	3.0	0.8
Nickel	Ni	0.4	9.0	11	3.6
Zinc	Zn	0.2	18	17	19
Lithium	Li	0.1	*	*	*
Beryllium	Be	0.3	*	*	*
Magnesium	Mg	0.6	18	12	5.5
Vanadium	V	0.05	*	*	*
Manganese	Mn	0.1	0.6	0.2	1.0
Cobalt	Co	1.0	0.2	0.2	0.2
Gallium	Ga	0.02	*	*	*
Strontium	Sr	0.05	0.05	0.09	0.06
Zirconium	Zr	0.1	*	*	*
Molybdenum	Mo	0.1	0.3	0.1	*
Cadmium	Cd	0.02	*	*	*
Tin	Sn	0.05	1.1	0.2	1.2
Antimony	Sb	0.05	*	*	*
Barium	Ba	0.05	0.2	0.10	0.06
Titanium	Ti	0.8	236	45	*
Yttrium	Y	0.07	*	*	*
Rubidium	Rb	0.05	*	*	*
Indium	In	0.01	*	*	*
Cesium	Cs	0.005	*	*	*
Cerium	Ce	0.002	*	*	*
Thorium	Th	0.002	*	*	*
Uranium	U	0.002	*	*	*

* = None detected above the detection limit.

When using procedures of this type, it is important to do recovery studies. Since it is not possible to add known amounts of metals to a thick oxide, recovery studies were done on bare wafers. The ability to recover metals by using HF only is shown in Table 4. It is important to point out that copper can not be recovered by using HF alone. To recover copper a mixture of HF/H_2O_2 must be used to remove the oxide. With this mixture, 90% or better of the copper can be removed and measured.

5.1.d3 Summary

Although metallic contamination occurs in all reactors, those from the ion implantation process are the most severe since they are embedded in the silicon. The higher the concentration, the greater and more serious is the damage. By using the thick oxide collecting technique and accurate absolute analysis such as a standardized ICP-MS measurement, implanter performance can be measured for dopants and contaminants and the ion beam operation improved.

5.1.d4 References

[95a] M. K. Balazs and J. Fucsko, "Application of ICP-MS for Relating Metal Contamination on Wafers to Metal Sources and Levels, " NIST Poster Session, January 1995

[96a] H. Ryssel, M. Current and Z. Frey, " Contamination Control for Ion Implantation," in *Ion Implantation Science and Technology*, Ion Implantation Technology Co., Yorktown, NY, ed. J.F. Ziegler, Chapter 11-12, 1996

[96b] Op. cit., Chapter 11-12

[96c] Ibid., Chapter 11-12

[97] This procedure was developed at Balazs Analytical Laboratory and printed by permission.

Table 4. Recovery of Trace Metals on 6-inch Bare Wafers by HF (Surface Concentration x10^{10} atom/cm^2)

Wafer ID	Spike	Recovered	Blank	Recovery %
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	10.0	<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	