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Progress in optimization of transition metal cation chromatography and its application to analysis of silicon wafer contamination

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ABSTRACT

Methods are reported which yield sensitive semi-quantitative analysis of transition metal contaminants on silicon wafers. An effective extracting solution is proposed together with compatible concentrators and two eluent (column and post-column) chemistry combinations to measure ppt (10^{12}) concentrations and surface densities extending into the 10^{10} atoms per cm^2 range. Possible applications include numerous steps in wafer and integrated circuit manufacture as well as other solid-surface analysis.

INTRODUCTION

Silicon wafers are the building blocks upon which integrated circuits are formed. The production of these wafers involves poly-crystal silicon manufacture, single crystal growth, slicing, lapping, edge grinding, heat treatment, polishing, final cleaning and packaging. At every step, purity is a key issue, since the intentional dopants which govern the semiconducting properties are typically present in the ppb^a range. Other impurities must generally be controlled at still lower levels. Certain metals such as Cu, Fe and Ni are of particular concern because of the speed with which they enter and move through silicon during heat treatments and their detrimental effects on electrical and defect properties once there. We have utilized a number of sensitive techniques for the study of these contaminants including total reflection X-ray fluorescence (TXRF), secondary-ion mass spectroscopy (SIMS) and ion chromatography (IC). Among these options, IC offers a cost-effective method for rapid, in-house testing and process control. It also is complementary to the other methods in that it samples all surface and edges of the wafers rather than localized, generally front-side-only areas.

This paper will present improvements over prior transition metal methods [1–6] for this type of work. The process development has necessarily been done simultaneously with regular analytical work so that the final solutions are probably not fully optimized.

^a Throughout this article, the American billion (10^9) is meant.

EXPERIMENTAL

Auxiliary equipment

Silicon, in the presence of air and moisture, rapidly forms a native oxide layer of approximately 1 nm thickness. Indeed, the traditional cleaning processes [7] incorporate oxidative baths prior to the final rinse and spin dry in order to yield a stable surface. Any foreign elements incorporated into this oxide are potential contaminants of the silicon or the silicon dioxide layers formed in later processing. Thus an effective method for studying the wafer surface must include a means of digesting this SiO_2 layer. HF is the traditional solvent in this case and the one used here. Additional additives to this digestion-extraction solution have been investigated and are reported below.

Cells for the wafer extraction process have been fabricated from PTFE polymer sheets backed by stainless steel as shown in Fig. 1. The requirements were (1) chemical inertness and purity, (2) a maximum wafer surface to liquid volume ratio consistent with (a) ready access of the liquid to all surfaces and (b) the machinability of PTFE, (3) approximately 60 ml liquid volume and (4) a design which accepts whole wafers. Each of the standard wafer diameters, 100, 125, 150 and 200 mm, therefore has its own cell designed to accept four, three, two and one wafer, respectively. The edges of the multiple-wafer cells are grooved to maintain separation of the wafers while several raised points formed in the sidewalls serve this purpose for the single-wafer, 200-mm cell. Fig. 1 illustrates the four wafer, 100-mm cells. Drain and fill ports are machined into the bottom and top of each cell. The top includes an O-ring seal (not shown) so that the liquid can be forced out and through the concentrator column by gas pressure rather than pumping at this critical point. Conversion from impurity concentration in the liquid to surface concentration on the wafers is a geometrical calculation; 1 ppb corresponds to roughly $1 \cdot 10^{12}$ atoms per cm^2 .

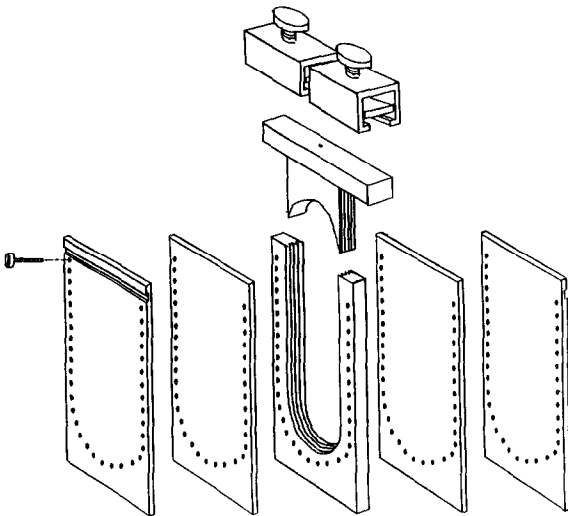


Fig. 1. Exploded view of cell for extraction of contaminants from wafer surfaces. The U-shaped piece, its cap and neighboring plates are PTFE and form the cell walls. The outer plates are stainless steel and the cap clamps are aluminum and stainless.

Water purity

The water supply to our laboratory utilizes reverse osmosis/deionization treatment which produces 18 M Ω water with less than 15 ppb total organic carbon. Nevertheless, column lifetimes on the order of weeks have been common using this water. Tests using water from sources with point-of-use final purification systems have indicated that water was a major factor in the problem. In an effort to improve the water a four-bowl Milli-Q point-of-use purification system was first tested. This yielded improved but still limited lifetimes. A Milli-Q UV Plus system was then installed and, with the other changes described below, has led to very satisfactory column lifetimes and background levels.

Progress toward a stable method

All of this work has involved the use of a concentrator cartridge to enhance sensitivity. This concentrator must be stable and non-contaminating in the presence of the extracting acid. This has necessitated the use of a polymer-based packing material and the avoidance of all metal parts such as the frits which are frequently used in concentrators. Both Waters and Dionex cation concentrator packings have been used successfully in this function.

Following excellent initial results with the Waters TSK column and ethylenediamine plus citric acid eluent, water-related column degradation soon became evident. Tailing of the Cu peak was the initial symptom followed by disappearance of this peak and tailing of other peaks. A number of packings and guard column arrangements were tried, always with more or less limited success until the water supply was improved with the installation of the Milli-Q UV Plus system. With this system the degradation of a Spherisorb ODS-5 column then in use was slowed but not stopped. The Dionex HPIC-CS5 polymer-based column has now given seven months of service without problems. The Waters TSK column has not been tested with this water supply.

The present system

The current system starts with the PTFE extraction cells. These are filled with a solution of 18.9 mM HF, 50 mM HCl and 4.9 mM H₂O₂ (see discussion below). The entire cell assembly is subjected to ultrasonic excitation and two 11-ml samples are taken to provide background data. The wafers are then added and the cell refilled from the same reservoir. The Si native oxide is dissolved within approximately 15 min with further ultrasonic agitation, and two more samples are taken. Concentration is accomplished by forcing these samples through a Dionex TCC-1 trace cation concentrator using approximately 45 p.s.i. nitrogen pressure on the cell. Flow switching at this point is handled by a Rheodyne inert switching valve (Model 90910).

Separation occurs on a Dionex HPIC-CS5 column with eluent composition of 3 mM pyridine-2,6-dicarboxylic acid (PDCA), 4.3 mM LiOH, 2 mM Na₂SO₄ and 25 mM NaCl [8]. The eluent is driven by a Wescan inert pump and membrane pulsation suppressor operating at 1 ml/min. Post-column derivatization utilizes a solution of 1 mM 4-(2-pyridylazo)resorcinol (PAR) and 3 M NH₄OH, (adjusted to pH 11 with acetic acid) flowing at 0.6 ml/min from a Waters reagent delivery module. Detection is via a Waters 484 UV-VIS detector operating at 520 nm. This method is referred to elsewhere in this paper as method 1. Data handling and valve switching are under the

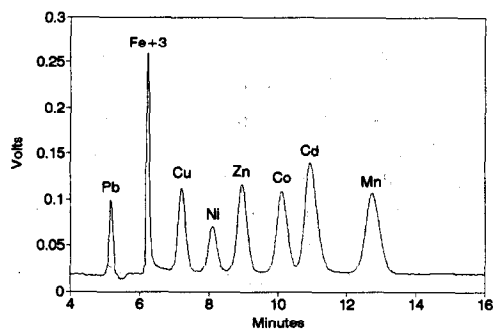


Fig. 2. Chromatogram for a 5-ppb multiple standard (except Cd and Pb at 20 ppb) using method 1.

control of Waters Maxima software and an NEC Powermate computer. A typical chromatogram using this system is shown in Fig. 2.

RESULTS AND DISCUSSION

Improvements to standard methods

The paper of Yan and Schwedt [9] suggested several means of increasing the sensitivity above that of the standard methods. These have been investigated and the positive results incorporated into the methods discussed. Data are presented here supporting their efficacy.

Increasing the PAR concentration to 1 mM from the recommended 0.2 mM yields the results shown in Fig. 3 for the present system. A pH near 11 is needed to stabilize the PAR at this concentration. This solution can be held for a week under a nitrogen atmosphere. The operating point of 1 mM was chosen in order to maximize the Ni response with little loss elsewhere.

The following improvements were found to be effective for a modified Waters Method SMTE-708 [10] (Nova-Pak C_{18} column with 100 mM tartaric acid, 2 mM octanesulfonate and 10% acetonitrile adjusted to pH of 3.05 with NaOH). First, the addition of 10 ft. of 1/16 in. diameter PTFE tubing held at 60°C following introduction of the post-column reagents increases the sensitivity of most of the detectable elements. Fe^{2+} , in particular, yields a factor of 10 larger signal. Other elements show fractional improvements. Second, Zn-EDTA (the $ZnNa_2$ salt of ethylenediaminetetraacetic acid) at 0.13 mM concentration in the post-column reaction solution enables the alkaline earth ions Ca and Mg to be detected. It also increases the sensitivity for Pb by a factor of 2. The optimum wavelength for detection in this case is 490 nm. In this method Fe^{3+} elutes in the void volume and is not quantitatively detected. This method is referred to here as method 2. A 10-ppb chromatogram is shown in Fig. 4. We have not yet returned to this method following the water improvement in order to test its stability.

Only the PAR increase is effective for method 1. Increased post-column temperature reduces sensitivity in this case while Ca and Fe^{3+} elute simultaneously.

Optimization of the digestion-extraction solution

The minimum HF concentration in the solution used to sample contaminants

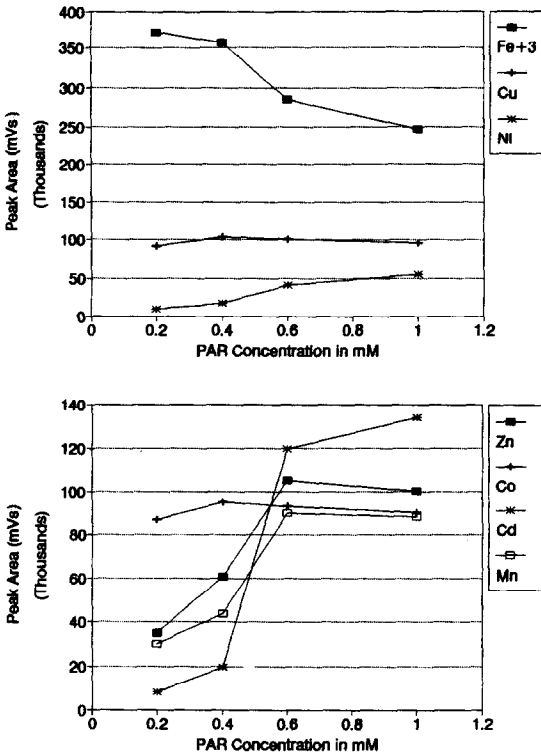


Fig. 3. Effect of PAR concentration on peak area response to a 1.5-ppb multiple standard.

from the wafers is limited by the need for a reasonable time to dissolve the native oxide. This solution does not yield high recovery and detection of the elements on those surfaces. In addition, the iron on the surface may be divided between valence 2 and 3 states, with quite different sensitivities to the two states. Since this valence information is secondary for the present purpose, Fe is converted entirely to the more sensitive 3+ state by the addition of H₂O₂ at the 4.9 mM level for method 1.

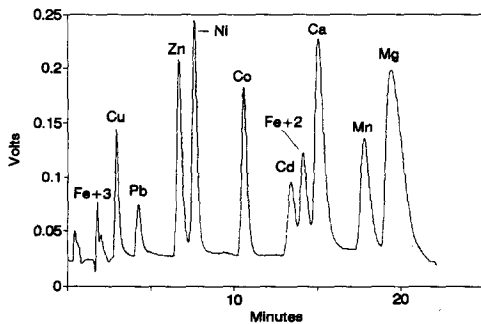


Fig. 4. Chromatogram for a 10-ppb multiple standard using method 2.

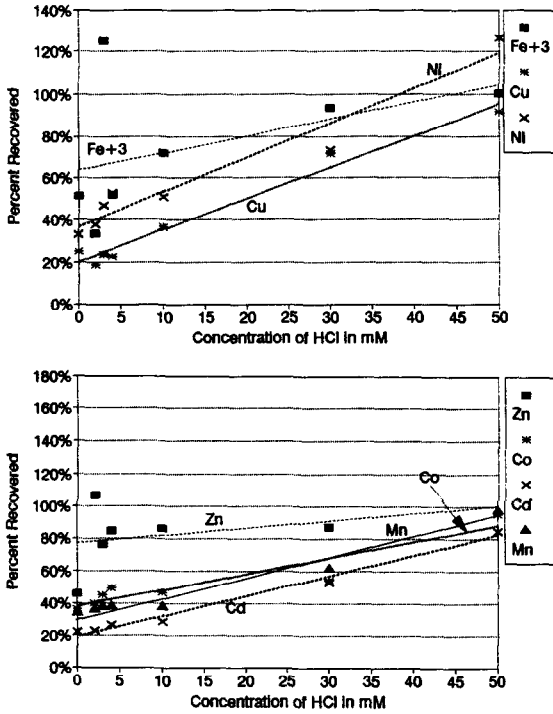


Fig. 5. Percentage recovery of intentional contamination at the 1.5-ppb level on a 100-mm wafer using method 1. In each case the system background reading measured prior to the introduction of the wafer has been subtracted. The straight lines are linear regressions to each set of data.

TABLE I

DETECTION LIMITS MEASURED FOR THE TWO COLUMNS AND CHEMISTRIES DISCUSSED

Signal-to-noise ratio = 3.

Ion	Method 1 ^a		Method 2 ^b		System background	
	ppb	1 · 10 ¹⁰ atoms/cm ²	ppb	1 · 10 ¹⁰ atoms/cm ²	ppb	1 · 10 ¹⁰ atoms/cm ²
Pb	0.30	7	0.20	5		
Fe ³⁺	0.02	2			3.20	300
Fe ²⁺	— ^c	— ^c	0.11	10		
Cu	0.06	5	0.08	6		
Ni	0.12	10	0.05	4		
Zn	0.06	5	0.05	4	0.43	35
Co	0.07	6	0.06	5		
Cd	0.20	17	0.15	13		
Mn	0.07	6	0.10	9		
Ca			0.05	6		
Mg			0.06	13		

^a PAR concentration, 1 mM; Zn-EDTA concentration, 0 mM; no reaction coil used.

^b PAR concentration, 1 mM; Zn-EDTA concentration, 0.13 mM; reaction coil used at 60°C.

^c Can be detected but is converted to Fe³⁺ with H₂O₂.

In order to improve the recovery and detection of the surface impurities, HCl has been added as mentioned earlier. The effect of this addition is shown in Fig. 5. Here the proper amount of dilute multiple standard to yield a 1.5-ppb solution of each of the elements in the cell has been placed on a wafer surface and allowed to dry. Such wafers were then placed in the cell containing the extraction solution with variable HCl concentration, and the resulting solution was analyzed. Zinc was approximately fully recovered in all cases but all of the other elements studied benefitted from the HCl addition. At higher levels of the metals the recovery was more complete even at low HCl concentration. For the cell without wafers, recovery was also complete except for Fe and Cd at approximately 65%. Thus the retained amounts are primarily associated with sites on the silicon wafers themselves.

Detection limits and background levels

Table I illustrates typical detection limits for the methods discussed above together with the surface concentration equivalents. The system backgrounds shown limit the practical detection limits for Fe and Zn to three times their standard deviation or approximately 3 and 0.4 ppb, respectively.

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