Analytical Technique Compares Dopants in Fab Air and on Wafers

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Wafer surface cleanliness is a critical concern in the manufacture of ULSI IC products[1,2]. Particles and trace metallic impurities such as sodium, iron, copper, calcium, zinc and nickel from airborne particulates, reactors, chemicals or ultrapure water (UPW) are well covered by the literature. However, not all airborne contamination originates from particles. There is increasing concern with the adsorption of volatile contaminants onto wafer surfaces. For example, undesired adsorption of volatile boron and/or phosphorus compounds on wafer surfaces is harmful and has been noted.[3-5] A SEMATECH publication[6] shows boron contamination of thin film transistors yielded a doping level of $37x10^{10}$ atoms/cm^2 for a 15-min. exposure to cleanroom ambient. Phosphorus contamination of ~$3x10^{13}$ atoms/cm^2 has caused up to a 15% yield loss at a major fab.[7]

At a Glance

Not all wafer surface contamination originates from airborne particles. The adsorption of volatile contaminants such as boron and phosphorus compounds onto surfaces is a serious concern. Droplet scanning ICP-MS is a useful analytical method to measure surface concentrations of these contaminants.

The origin of boron in cleanrooms is well understood and believed to come primarily from the borosilicate glass in HEPA filters.[8,9] When air containing HF vapor passes through borosilicate glass media of HEPA filter, the gaseous boron compound (e.g., BF_3) is extracted into the cleanroom. It was found that the lightly doped n-type layer on the wafer surface was counter-doped by p-type dopant of boron from cleanroom air.[3] Unintentional phosphorus doping of wafers due to organophosphorus in the cleanroom ambient also has been reported.[10] The major phosphorus contaminant from HEPA filters was identified as triethyl phosphate (TEP), which was traced to the sealant used in adhering the filter media to their support modules.[7,11]

Techniques for measuring boron and phosphorus on wafer surfaces have included secondary ion mass spectrometry (SIMS), inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography mass spectrometry (GC-MS). When using SIMS, a thin layer of polysilicon is usually deposited on the wafer surface to cover the original surface to prevent subsequent contamination. Also, the effects of SIMS non-linear ion yield are minimized.[3,12] The encapsulated interface is then measured. However, the lack of matched standard(s) for instrument calibration makes surface contamination difficult to quantify. GC-MS, on the other hand, is usually suitable only for organic compounds (e.g., organophosphorus).

This article describes the use of a droplet-scanning pre-concentration technique, followed by ICP-MS measurement of boron and phosphorus. With a witness wafer protocol, the technique can provide quantitative contamination information about boron and phosphorus on the wafer surface with detection limits in the range of 3-6x10^{10} atoms/cm^2. The analysis process is simple and reliable because it uses NIST standard solutions for calibration.

Air monitoring and wafer analysis

We used two types of air samplers to collect cleanroom air. The sampler for inorganics was a module-based system consisting of a pump, filter, flow controller and electrical controls. Air was drawn through an aqueous solution for a specified number of hours. The extracted boron and phosphorus were then identified and quantified using ICP-MS and ion chromatography. The sampler for organics consists of pumps and sampling tubes that contain appropriate adsorbents to trap and concentrate organic compounds. These tubes are analyzed by TD-GC-MS (Thermal Desorption Gas Chromatography Mass Spectrometry).[13]

Based on the previous study, a typical range of boron found in semiconductor cleanrooms was 20 to

150 ng/m^3 air. The exact form of boron compounds was uncertain. They could be very small particles or gaseous compounds (e.g., BF_3). Using ion chromatography phosphorus as phosphate was found to be below the detection limit of 40 ng/m^3 air in most fabs.[13,14] As a comparison, the same procedures were used to measure the boron and phosphorus content in a class 100 cleanroom before exposing the witness wafers. Boron concentration was 100 ng/m^3 air. Phosphorus (as phosphate) concentration was below the detection limit, similar to that from most fabs. Prior to use, we pre-cleaned bare silicon wafers (witness wafers) to remove organics and metals and stored them in a nitrogen glove box(>98% N_2). We subjected all wafers to a droplet-scanning pre-concentration technique, placing a small droplet of a diluted acid solution (e.g., HF) on the wafer surface.

The droplet is rolled (or scanned) in a reproducible pattern throughout the wafer surface to ensure a complete collection of trace amounts of contamination materials. The droplet is then manually pipetted onto a sample container. A second drop of diluted HF is used to scan the wafer surface again to complete the collection of contaminants. The two solutions are combined into a sample container and analyzed by ICP-MS.

Spike recovery verification

Spike recovery studies were done to verify the accuracy of the drop scan/ICP-MS method by placing, scanning and measuring known amounts of boron and phosphorus on the wafer surfaces. We prepared solutions of inorganic boron and phosphorus for spike recovery by a serial dilution with diluted nitric acid from stock solutions of 5 mg/mL boron (NIST 3107) and 10 mg/mL phosphorus (NIST 3139a). Solutions were spiked on surfaces of 200 mm wafers at various surface concentrations of boron and phosphorus (Table). All wafers were spiked and dried under >98% nitrogen. Three replicates for each spiking level were prepared. Wafers were cleaned with diluted HF as controlled blanks. For organic spike recovery studies, solutions of organic phosphorus (TEP) were prepared by a serial dilution with acetone from stock solutions and spiked on the surface of a 200 mm wafer. As with the inorganic samples, triplicates were prepared. Using a class 10 HEPA environment, the wafers were spiked and dried within two minutes to prevent contamination from the HEPA filters. We used wafers spiked with acetone as controlled blanks. The droplet scanning and analytical procedure of spiking wafer was the same as for witness wafers.

Percent Recoveries of Boron and Phosphorus

Inorganic Boron		Inorganic Phosphorus		Organic Phosphorus (TEP)	
Spike Levels atoms/cm^2	Spike Recovery (%)	Spike Levels atoms/cm^2	Spike Recovery (%)	Spike Levels atoms/cm^2	Spike Recovery (%)
$35x10^{10}$	87	$12x10^{10}$	55	$10x10^{10}$	57
$80x10^{10}$	92	$31x10^{10}$	83	$21x10^{10}$	82
$170x10^{10}$	96	$62x10^{10}$	94	—	—
	MDL= $3x10^{10}$		MDL= $6x10^{10}$		

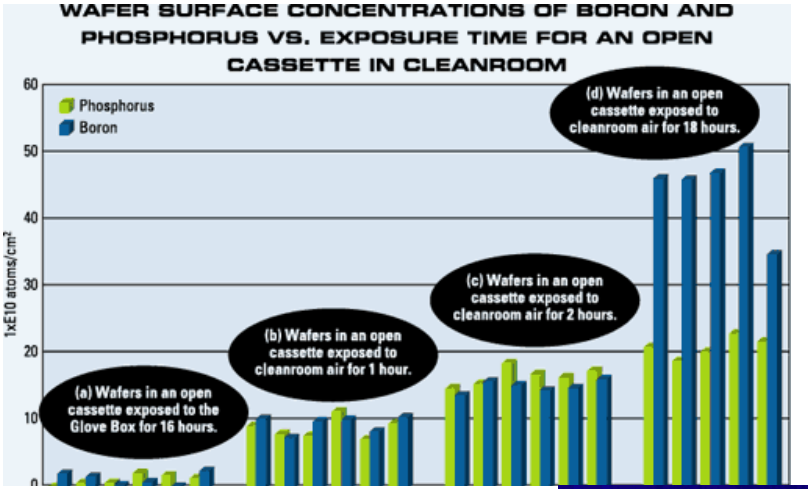
Recoveries are calculated based on the concentration of collected solution and the amount of spiked solution. Recoveries of inorganic boron and phosphorus were found to be >80% when spiking concentrations were at about 5-10 times the method detection limit (MDL) (Table), indicating the validity of boron and phosphorus analysis (inorganic forms) at very low levels. TEP recovery was >80% at the spiking level of $21x10^{10}$ atoms/cm^2. The low level spike recovery by the droplet-scanning ICP-MS technique demonstrates an alternative for analyzing trace TEP, although a much more detailed investigation is needed for other organophosphorus compounds.

Experimental instrumentation

The instrument used in this study was a Perkin Elmer Sciex Elan 6000 ICP-MS. The sample introduction system was an HF-resistant torch assembly with a microconcentric nebulizer (CETAC Technology, Neb.). Standard solutions of boron and phosphorus for calibrating the instrument were prepared from 10 ppm single stock solutions (NIST) using 18.2 MW ultrapure water and diluted nitric acid. The ICP-MS was optimized for hot plasma operation as per the manufacturer's recommendation.

Wafers' air exposure

To obtain controlled blanks and MDL, wafers were recleaned and scanned in the nitrogen glove box. Over a three-day period, 14 wafers were measured to determine the concentration and MDL for boron and phosphorus. At three times the standard deviation, the MDLs were found to be $3x10^{10}$ atoms/cm^2 for boron and $6x10^{10}$ atoms/cm^2 for phosphorus.

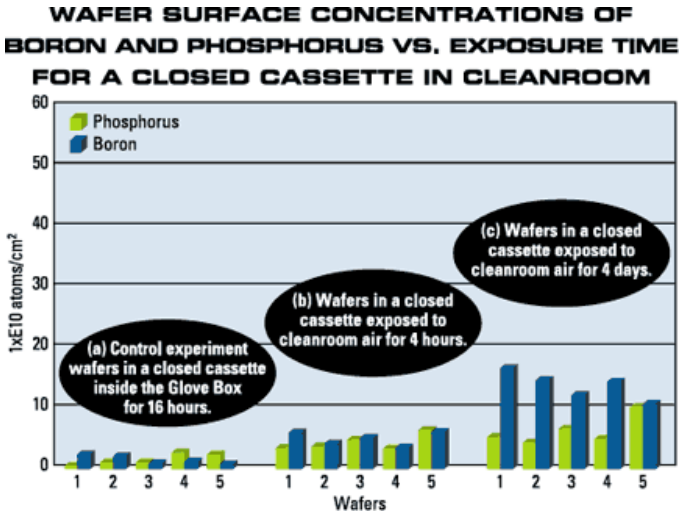


1. Wafers were placed vertically in an open cassette (a) inside the glove box (98% nitrogen) for 16 hours; (b) exposed to cleanroom air for 1 hour; (c) exposed to cleanroom air for 2 hours; and (d) exposed to cleanroom air for 18 hours. Each bar represents analysis of a wafer.

We then exposed wafers to cleanroom air and compared against controls for boron and phosphorus contamination. Figure 1(a) shows the results of a 16-hour study. Contamination increased continuously over time in the cleanroom, but not in the nitrogen glove box.

When six wafers with equal spacing of 3 cm were placed vertically in an open 25 wafer-cassette box and exposed to cleanroom air for one hour, average surface concentrations of boron and phosphorus were about $9x10^{10}$ and $10x10^{10}$ atoms/cm^2 (Fig. 1(b)). When the same wafers were exposed to cleanroom air for two hours, average surface concentrations of boron and phosphorus were $15x10^{10}$ and $17x10^{10}$ atoms/cm^2 (Fig. 1(c)). For an exposure time of 18 hours, concentrations of boron and phosphorus increased to $40x10^{10}$ and $20x10^{10}$ atoms/cm^2 (Fig. 1(d)). In this cleanroom's case, phosphorus concentration increased at a slower rate than boron.

Figure 2 shows a comparison of surface concentrations of boron and phosphorus with an increasing time of exposure to the cleanroom air; but the wafers were kept in a closed cassette box (edges not taped), under nitrogen. We then exposed the wafers to cleanroom air for four hours. Average surface concentrations of boron and phosphorus were about $4x10^{10}$ and $6x10^{10}$ atoms/cm^2 (Fig. 2(b)), which is close to the MDLs. However, when the wafers in the closed cassette box were exposed to cleanroom air for four days, average surface concentrations of boron and phosphorus were found to be about $14x10^{10}$ (boron) and $6x10^{10}$ (phosphorus) atoms/cm^2 (Fig. 2(c)). Contamination levels were reduced significantly when the wafers were kept inside a closed cassette box. Inert nitrogen protected them from cleanroom air, reducing the deposition probability of boron and phosphorus contaminants. A similar experiment was repeated using cleanroom adhesive tapes to seal the cassette box. No significant reduction of contamination was found. The slight contamination found on wafers from cassette boxes $14x10^{10}$ (boron) and $6x10^{10}$ (phosphorus) atoms/cm^2 was likely due to leaks. A better way to completely seal the cassette box is needed.



2. Wafers were placed vertically in a closed cassette (edge not taped) (a) inside the glove box (98% nitrogen) for 16 hours; (b) exposed to cleanroom air for 4 hours; (c) exposed to cleanroom air for 4 days. Each bar represents each analysis of wafer.

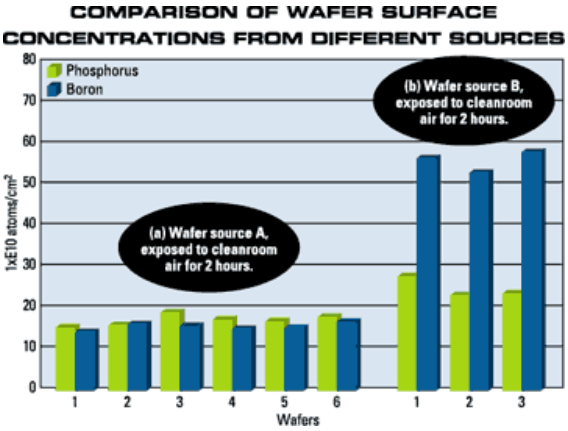
Prior to exposure, six wafers from source *A* and three from source *B* were re-cleaned twice with diluted HF, vertically placed in three open cassette boxes (three wafers per cassette box) and exposed to cleanroom air for two hours. There was a higher concentration of phosphorus found on source *B* wafer than source *A* (Fig. 3). The reason is unknown. It could be attributable to surface characteristics such as crystal orientation, roughness, surface termination, etc.

Conclusion

Droplet scanning ICP-MS is a highly sensitive analytical method, demonstrably useful to measure boron and phosphorus surface concentrations. With a witness wafer protocol, this technique can provide quantitative contamination information of boron and phosphorus on the wafer surface with detection limits as low as $3x10^{10}$ atoms/cm^2 for boron and $6x10^{10}$ atoms/cm^2 for phosphorus.

The longer the exposure time to cleanroom air, the higher the contamination. A cassette box can reduce the deposition possibility of surface contaminants because the nitrogen inside protects from cleanroom air. However, a better way to seal the cassette box is needed for complete wafer protection. Wafers from different sources may have different deposition rates of boron and

phosphorus when exposed to the same cleanroom air.



3. Wafers were placed vertically in an open cassette (a) 6 wafers from source *A* exposed to cleanroom air for 2 hours; (b) 3 wafers from source *B* exposed to cleanroom air for 2 hours. Each bar represents analysis of a wafer.

Although it seemed impractical in the past to remove boron or phosphorus from the cleanroom air[3], it has been recognized that contaminant n and p type dopants are a problem. Unless specific removal measures have been taken, the process engineers must assume boron or phosphorus contaminants exist in the cleanroom. Extensive attention has been focused on reducing or removing gaseous contaminants from cleanroom air. An ion exchange fiber has been used to remove boron contamination from cleanroom air.[15] Chemical filters such as activated carbon also have been investigated for removal of acid gas, basic gas and organic gas.[16] As IC feature size decreases, the requirement for controlling unwanted doping on wafer surfaces will become more and more critical. •

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