# Determination of Inorganic Species in the Solution Extracted from Cleanroom Gloves Used in Semiconductor Process

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Because the purity of process chemicals plays an important role in device reliability, the continuing increase in the scale of integration for semiconductor devices has led to the need for monitoring trace levels of ionic contaminants and particulates.[1,2] Accurate and reliable determination of ionic contaminants of process wafer becomes increasingly difficult as semiconductor feature sizes continue to decrease. The causes of wafer contamination and particle generation are too numerous and complex to be predicted, but it is known that the contaminants are mostly generated by the cleanroom, cleanroom personnel, process equipment, and the process itself.[3~7] To maximize cleanliness, engineers must consider all sources of possible contamination, including not only fixed contamination sources but also mobile sources, such as cleanroom gloves and other consumables. In cleanroom glove chemistry, a relationship between the cleanroom glove and the product surface cleanliness was known. Sample extraction followed by various testing methods, such as atomic absorption spectrometry (AAS), ion chromatography (IC), atomic emission spectrometry (AES), etc., has been traditionally used for the quantification of the contaminants.[8] A glove extraction procedure was described by Hartzell et al who discussed not only the procedures including the Soxhlet test but the transfer of glove contaminants to product wafers in detail. It is known that the results of extraction tests that measured metal and anionic contaminants on cleanroom gloves and the results of total reflection x-ray fluorescence (TXRF) analysis of wafer surfaces exposed to the gloves were correlated.[8]

Since the relationship between the cleanroom glove and the wafer contamination was proved in such contaminant-transfer studies, cleanroom gloves used in Korea semiconductor plant were sampled and the extracts were analyzed by IC, inductively coupled plasma (ICP)-AES and high resolution ICP-mass spectrometry (HR-ICP-MS) in this study. Analytical results are discussed in the view of wafer cleaning processes and expected to be used as a reference to control a sub micron Ultra Large Scale Integration (ULSI) process in the semiconductor industry or other areas of clean technologies.

## Experimental Section

**Sample preparation**. Polyethylene beakers and bottles were leached in 1 : 1 $HNO_3$ : deionized (D.I.) water for 1 week, followed by thorough rinsing with D.I. water. Each pair of glove sample was placed in the acid leached beakers covered with a Teflon watch glass and soaked in 100 mL of D.I. water for two days at room temperature. Polyethylene and latex gloves (manufactured by Correct Touch, Malaysia) were tested. Four samples were prepared for each type. Analysis blanks were prepared by the same method without gloves. The prepared samples were spiked with standard solutions and split into three portions and tested by ion chromatography (IC), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS). All extractions were performed in a class 10 laboratory.

**Instruments and operating conditions**. Scanning ICP-AES instrument employed in this study was a JY 138 model (Jovin-Yvon, France) with a high resolution nitrogen purged 1 m monochromator. This system is equipped with a 40.68 MHz generator with a demountable standard torch, including a sheath gas flow and a 1 m focal length of monochromator. A Meinhard C type nebulizer with a Scott type spray chamber was used for sample nebulization . The ICP-AES system was operated at 1.1 kW forward power with a coolant flow of 12 L/min, and a sample uptake rate of 3 mL/min with a peristaltic pump. The sheath gas flow wasn't used throughout this work. The ICP-AES was used to determine zinc, magnesium, calcium, and barium in the extract.

Metals below the detection limits of ICP-AES were determined by using a high resolution ICP-MS (HR-ICP-MS). The HR-ICP-MS employed in this study to detect ultra trace 11 metals was a Plasma Trace II (Micromass, UK), which features a double focusing sector mass analyzer with a ISIS nebulizer provided by VG Elemental (Winsford, UK). The spray chamber was maintained at 10 °C with a chiller. The optimized operating conditions are 1.35 kW of forward power, 15 L/min coolant gas flow, 2 L/min auxiliary gas flow, and 1 L/min aerosol gas flow rate. An electron multiplier was used for the mass analyzer detector. Operating conditions including resolution in HR-ICP-MS are listed in previous papers.[9]

The DX-300 (Dionex, USA) high performance ion chromatography (HPIC) with a conductivity detector was also used to determine some alkali cations and anions, such as nitrate, sulfate, sodium, potassium, etc. The flow rate of sodium carbonate eluent was 1.5 mL/min and injection volume was optimized at 100 μL.

## Results and Discussion

According to the contaminant-transfer study reported by Lee et al, a correlation exists between the analytical results of the extraction study and the wafer contamination.[3] Since total amount of transferred contaminants was several orders of magnitude smaller than that of the extracted from gloves, it is meaningful to determine the contaminants in the cleanroom gloves in order to predict possible contamination and select useful gloves depending on the purpose.

**Ion chromatography analysis**. Prominent contamination sources of cleanroom equipments and facilities can be classified into ions, particles, and some organics. Those are mostly generated by mobile contamination sources. Once equipments are contaminated, it is very difficult to eliminate the contaminants up to the ultra trace level even for aqueous soluble ions that are relatively easy to detect and control. In this study anions and alkali cations extracted from gloves were determined by high performance ion chromatography with a 5.9% RSD or less for 4 replicates. The analytical results are listed in Table 1. It was known that during the extraction, D.I. water will penetrate into the surface layers of the latex and polyethylene glove matrices and remove species within a three-dimensional region.

As shown in the table, the extracted anions from the latex glove surface are mainly chloride, nitrate, and sulfate, of which total concentration was about 0.84 mmol that was higher than that of cations. Total amount of alkali metals extracted from a pair, of latex gloves was less than 0.03 mmol and lithium wasnt detected from the extract. It means that other metal cation levels of the extract would be higher than alkali metals.

From the table it is obvious that the polyethylene glove extract was cleaner than the latex glove extract because total anion concentration of the former (about 0.02 mmol) is approximately one fortieth of that of the latter. But, a high transfer efficiency of polyethylene glove is expected from the analytical results of contaminant-transfer study, compared to that of latex glove.[8] Extracted chloride levels were higher than those of any other anions in the extract of polyethylene glove, and a similar trend was observed in the latex glove. As shown in the table, the extracted nitrate level was relatively very low, whereas the sodium level was even higher than that of latex glove. Chlorine of a latex glove was transferred about 200 times more efficiently to a silicon wafer than that of a polyethylene glove and potassium of polyethylene glove was rarely transferred to the wafer. [3] In this study the transfer efficiency of chloride was the same as that of potassium for a latex glove. Total amount of alkali metals extracted from a pair of polyethylene gloves was about 0.05 mmol that was higher than that from a pair of latex gloves. It should be emphasized that the most possible contaminant is a metal chloride if polyethylene gloves were used in the cleanroom. Fortunately the contaminants transferred from the gloves can be easily removed by washing with an aqueous solvent unless re-adsorption occurs, because most chloride, nitrate, and alkali metal salts observed in this experiment are known to be soluble in aqueous solvent.

**Determination of metals of the extract using ICP-AES and ICP-MS**. Because large amounts of anions from the extract were observed through HPIC, large amounts of metal impurities were expected to be present, too. They were determined by ICP-AES with a RSD of 5.4% or less for 4 replicate experiments. Metal impurities less than ppb level, such as Al, Mn, Ni, Be, etc, were determined by ICP-MS. The analytical results are listed in Table 2 for ICP-AES and Table 3 for ICP-MS.

As expected in ion chromatography the latex glove contained more metal contaminants than the polyethylene glove. From Table 2, a large amount of zinc was observed in both gloves, about $2\times10^{15}$ atoms/cm$^2$ for the latex glove and $8\times10^{13}$ atoms/cm$^2$ for the polyethylene glove. Alkaline earth metals, Mg and Ca which are very sensitive in ICP-AES were detected in the latex glove while $3.5\times10^{13}$ atoms/cm$^2$ of Ba was determined in the polyethylene glove. It is known that transfer efficiencies of Zn and Ca are similar in the latex glove, but the efficiency of Ca is about 50 times higher than that of Zn in the polyethylene glove.[3] Because the metals determined by ICP-AES tend to be in form of cation in water due to their low standard reduction potentials, they are possibly attached to the gloves as salts or oxides. Since all metal salts with major anions observed in ion chromatography are soluble in aqueous solutions except barium sulfate, they can be theoretically eliminated from silicon wafers by cleaning solutions, such as a mixture of ammonia and hydrogen peroxide or diluted acids in the semiconductor process. Of course several factors, such as re-adsorption, surface zeta potential, or other redox mechanisms should be considered in a real manufacturing process.

Elements, such as Al, Ni, Bi, Ag, etc, in sub ppb level were determined by high resolution ICP-MS, as shown in

**Table 2**. Analytical results of the extracted solution from cleanroom gloves using inductively coupled plasma atomic emission spectrometry (unit : ppb)

| Glove type | Zn | Mg | Ca | Ba |
|---|---|---|---|---|
| Latex | 10300 | 75.5 | 2730 | 3.0 |
| Polyethylene | 613 | 0.4 | 2.7 | 548 |

**Table 1**. Analytical Results of the extracted solution from cleanroom gloves using ion chromatography (unit: ppb)

| Glove type | $Na^+$ | $NH_4^+$ | $K^+$ | $Cl^-$ | $NO_2^-$ | $Br^-$ | $NO_3^-$ | $HPO_4^{2-}$ | $SO_4^{2-}$ | TMA-OH[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Latex | 76.3 | 261 | 470 | 28300 | 6.9 | 7.0 | 1710 | 6.1 | 827 | 37.5 |
| Poly-ethylene | 1075 | 4.9 | 6.9 | 618 | 1.0 | <0.1 | 3.0 | 2.0 | 233 | <0.05 |

[a] Tetramethylammonium hydroxide

**Table 3**. Analytical results of the extracted solution from cleanroom gloves using inductively coupled plasma mass spectrometry (unit : ppb)

| Elements | Latex glove | Polyethylene glove |
|---|---|---|
| $^{9}$Be | 0.025±1.7% | 0.024±0.48% |
| $^{27}$Al | 0.56±3.4% | * |
| $^{55}$Mn | 0.25±4.6% | * |
| $^{58}$Ni | 0.13±1.1% | 0.16±6.1% |
| $^{69}$Ga | 0.015±3.6% | 0.009±4.6% |
| $^{77}$Se | 0.68±5.4% | * |
| $^{85}$Rb | 0.15±1.5% | 0.064±0.7% |
| $^{88}$Sr | 0.12±10.4% | 1.86±3.2% |
| $^{107}$Ag | 0.017±2.5% | 0.017±1.0% |
| $^{111}$Cd | 0.014±10.3% | 0.12±0.4% |
| $^{209}$Bi | 0.098±0.25% | 0.098±0.2% |

*See text.

Table 3. Unlike Ba, Mg, Ca, and Zn mentioned above, Bi, Ag, and Se are required to be cautiously monitored in cleaning process of silicon wafers due to difficulties in cleaning away those elements. In this experiment Ag and Bi were detected in both gloves, but Se, Al, and Mn were not observed in the polyethylene glove. The detection limits for Se, Al, Mn were 10 ppt, 2.0 ppt, and 0.7 ppt, respectively. Although there are three isotopes of selenium in nature as m/e 76, 77 and 80, quantitative determination of Se requires high resolution in ICP-MS because of interference of $Ar_2^+$, $ArCl^+$, and $ArCa^+$. In this experiment the resolution for $^{77}$Se was set to be 8,000. Fortunately concentrations of those heavy elements were low enough to be ignored for the wafers in semiconductor process.

In result it was turned out that cleanroom gloves used in a semiconductor plant contained significant amount of $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Na^+$, Zn, Ba, and Ca. The presence of such a large amount of those elements on the surface of cleanroom gloves can largely produce a chance to contaminate wafers in the fabrication process. It is interesting to note that all the elements, except $Na^+$ and Ba, were extracted more from Latex gloves than from polyethylene gloves. The results indicate that the use of those gloves, especially Latex glove should be well controlled and the possible contaminants observed in this experiment should be monitored carefully in the manufacturing process. In addition, the use of HR-ICP-MS made it possible to determine and control heavy ultra trace elements, which were not paid attention in the process seriously.

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