Management of Extreme Trace Analysis of Metal on Silicon Wafer Surfaces

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In order to analyze the trace metals at the level of 10^8-10^9 atoms/cm^2 on the silicon wafers, it is important to control the analytical environment, water and chemicals, and to clean and to handle carefully the analytical equipments and implements. These notes lead to decrease the contamination in the original acid solution that is used to collect metals in it. Some metals slightly contaminated in the original acid solution analyzed by ICP-MS for about three years were controlled within the range of 1－25 wt·ppt in our experiments. The detection limits of each metal for 8-inch silicon wafers are 3×10^8 - 1×10^9 atoms/cm^2. The intensity analyzed by ICP-MS for each metal tended to decrease to 80% with increasing the concentration of Si matrix more than 50 wt·ppm , while that by GF-AAS recorded virtually the same . The recovery rates for each metal except Cu were at least 95% for original concentration levels of $10^{10}-10^{12}$atoms/cm^2. The recovery rate of Cu was 80 – 90%.

1. Introduction

The demand for cleanliness with regard to silicon wafers and their processing environment is becoming severer as the integration level of LSI continues to increase. A silicon wafer can be contaminated by exposed to the environment, which includes the equipment, workers, and clean room air during the LSI fabrication process. The result may cause surface contamination by metals and organic compounds in addition to particles. Among these forms of contamination, metal contaminants are especially serious since it decreases recombination lifetimes[1] and negatively influences the device characteristics; accordingly, analytical methods with a high sensitivity of metals are required. To accurately analyze metal contaminants on silicon wafer surfaces, it is important to properly control the analytical environment, measurement equipment and implements such as pipette, messcylinder, messflask and beaker. The demanded analytical sensibility is 10^8-10^9 atoms/cm^2 in the surface concentration in the case of 0.1 μm LSIs[2]. This report demonstrates a management method required for the quantitative analysis of trace metals at the level of 10^8-10^9 atoms/cm^2 on silicon wafer surfaces .

2.Analysis of silicon wafer surface contamination

1) Preparation method for the silicon wafer surface

Vapor phase decomposition (VPD) method[3,4] and direct acid droplet decomposition (DADD) method[5] are widely used as methods of separation and recovery of metal contaminants from the silicon wafer surfaces. Both of these methods decompose the silicon oxide film present on the surface using hydrofluoric-based acids. The metal contaminants present on the surface, in the inside and at the interface of the oxide film are collected in the resulting mixture of silicate hexafluoride and water. When the oxide film decomposed with hydrofluoric acid, the surface of silicon wafer turns from hydrophilic to hydrophobic. 0.1 ml of the original acid solution that is used to collect metals are dropped on the silicon wafer and the droplet is scanned over the surface. The metals are concentrated into the droplet. The original acid solution can be prepared suitable for the each metal element by mixing hydrofluoric acid and hydrogen peroxide in the appropriate proportions. The recovered solution that is collected metals in the original acid solution can be analyzed using a high sensitivity analytical method such as graphite furnace atomic absorption spectroscopy (GF-AAS) or inductively coupled plasma mass spectrometry (ICP-MS) .

2) Influence of Si matrix on metal element detection limits

The recovered solution contains both the analyte metals and Si matrix. The Si matrix can be removed as a fluoride by the elevated-temperature process in the graphite furnace if the recovered solution is analyzed using GF-AAS[6]. Care is needed when using ICP-MS, because the appearance intensities of metals decrease when highly concentrated Si coexists in the same recovered solution[7]; the nebulizer and the interface are partly stuffed up, and the actual intensities of metals consequently decrease. As an example, scanning an 8-inch silicon wafer with a native oxide film with 0.1 ml of the original acid solution, yields a recovered solution containing about 300 wt・ppm of Si. The Si concentration increases with the oxide film thickness.

The solution contained 5 wt・ppb of Na, Fe, Ni and Cu was analyzed by ICP-MS when Si coexisted from 0 to 500 wt・ppm in the same solution. Figure 1 shows the relative intensities for the Si concentration measured by ICP-MS. Figure 2 shows the same relation by GF-AAS analysis. The relative intensity of each metal measured by

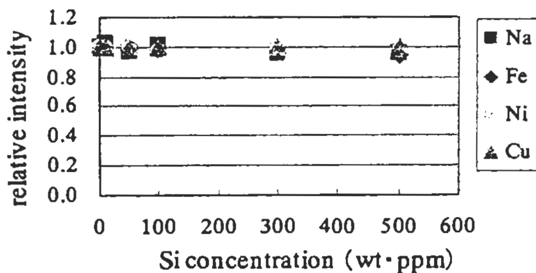

Fig.2. The relative intensity of each metal for the Si concentration analyzed by GF-AAS

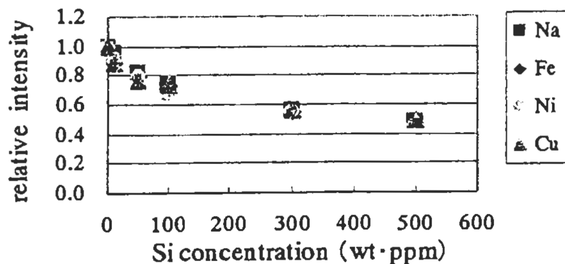

Fig.1. The relative intensity of each metal for the Si concentration analyzed by ICP-MS

ICP-MS decreases to about 0.8 at 50 wt・ppm Si concentration, and falls further as the Si concentration increases. GF-AAS, on the other hand, recorded virtually the same intensities although the Si concentration increases. The standard addition method is effective in the case of ICP-MS analysis for revising decrease of the intensities of metals by Si matrix.

Note that an anomalous rise was seen for the result of ICP-MS although no metals present; the intensity of the ^{63}Cu increased with Si concentration, as shown in Fig. 3. This effect is thought to be due to the interaction of several interference peaks of M/z=63 such as SiFO and $SiH_2O \cdot OH$ including Si. It would appear that when Cu is analyzed by ICP-MS which is not so good mass-resolution, the use of the ^{65}Cu is appropriate.

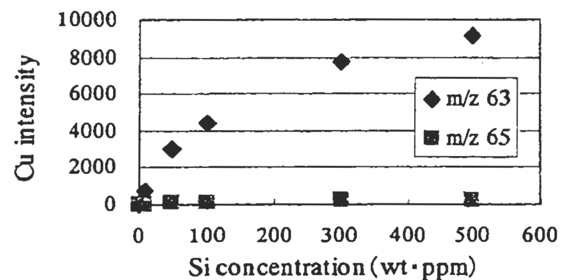

Fig.3. The defference in the intensity of ^{63}Cu and ^{65}Cu with increasing Si concentration

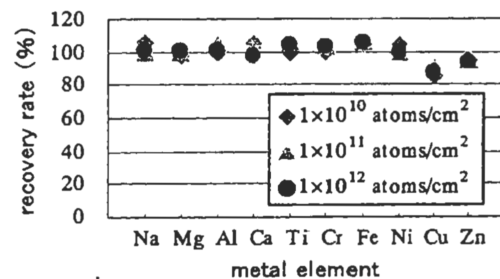

Fig.4. Recovery rate

3) Metal recovery rate

We tested the recovery rates for each metal using ICP-MS. At first, standard wafers that the surface area densities of each metal were 1×10^{10} atoms/cm^2, 1×10^{11} atoms/cm^2 and 1×10^{12} atoms/cm^2 were prepared by dropping the known concentration solution of each metal. Next each contaminated metal was separated and collected from the wafer surface, and analyzed. Figure 4 shows the recovery rate for each metal. The recovery rates for each metal except Cu were at least 95% for original concentration levels of 10^{10}–10^{12}atoms/cm^2. The rate for Cu of which ionization

series was lower than Si was 80−90% using the original acid solution of hydrofluoric acid and hydrogen peroxide aqueous solution.

4) Contamination of the original acid solution

It goes without saying that the original acid solution should be completely free of metal contaminants. In practice, however, some trace amounts of contaminants are always present. Figure 5 shows the fluctuation of the concentration of some metals slightly contaminated in the original acid solution analyzed by ICP-MS for about three years. The calibration curve was drawn at every analysis by the measurement of the standard solution with known concentrations of metals. The composition of the standard solution was equal to that of the original acid solution. We adopted the background equivalent concentration (BEC) value, as a detection limit, which was the intersection of the calibration curve and the horizontal-axis. The detection limits of the metals fluctuate within the range of 10 to 25 wt·ppt for Na, 1 to 15 wt·ppt for Al, 5 to 25 wt·ppt Fe, 1 to 5 wt·ppt for Ni and 1 to 7 wt·ppt for Cu. These fluctuations are thought to be caused by the interference with mass spectrum of ICP-MS and the condition of equipment in addition to the contamination of environment, deionized water, chemicals and implements.

It is important to decrease the contamination in the original acid solution in order to improve the detection limits. The preventive method includes the care of contamination from operators and in handling the implements such as beaker, pipette, messcylinder, messflask and wafer tray. Cleaning and controlling the analytical equipment was also required. The implements were usually dipped in the acid solution and were thoroughly rinsed in deionized water just before use. The implements that were thought be contaminated were returned to acid solution after pre-cleaning. Sufficient acid solution was passed through the sample injection system of the ICP-MS in order to suppress memory effects and unexpected contamination. The measurement started after the contamination levels were less than detection limits of the metals as shown in Fig. 5. Optimum tuning was always carried out in order to suppress the formation of ArO ion or ArC ion since their molecular weights equal those of Fe or Cr. It was also important not to adhere gross contamination to the implements and the equipment during operation. Use of clean glove and mask was effective for protection.

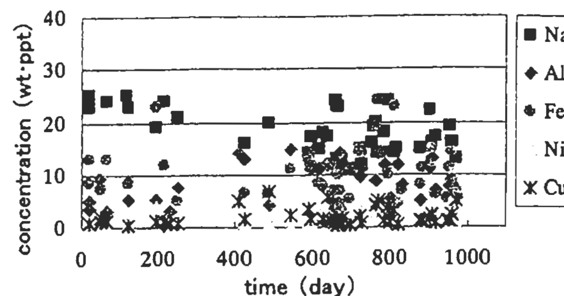

Fig.5. Fluctuation of the concentration of metals slightly contaminated in the original acid solution analyzed by ICP-MS

5) Detection limit

The detection limit is determined by impurity concentration in the original acid solution, volume of recovered solution analyzed, and the area of the silicon wafer. The impurity concentration of the recovered solution is an important factor. In the case of Fe, if the Fe concentration in the original acid solution is less than 5 wt·ppt, the detection limit of Fe on an 8-inch silicon wafer is 2×10^8 atoms/cm^2. On the other hand, the detection limit of Fe worsens to 1×10^9 atoms/cm^2 if the Fe concentration in the original acid solution is 25 wt·ppt, which is the highest value shown in Fig. 5. The guaranteed detection limit of Fe is 1×10^9 atoms/cm^2, when we take contamination into consideration during sample preparation, the stability of the analytical equipment, and the concentration of Si in the recovered solution.

Table1 The detection limits of metals on 8-inch silicon wafer analyzed by ICP-MS and GF-AAS (atoms/cm^2)

Metal elements	ICP-MS	GF-AAS
Na	3×10^9	1×10^9
Al	1×10^9	1×10^9
Cr	5×10^8	2×10^9
Fe	1×10^9	2×10^9
Ni	2×10^8	5×10^9
Cu	3×10^8	2×10^9

Detection limits of metals on an 8-inch wafer are shown in Table 1. The analyzed by ICP-MS detection limits are from 10^8 to 10^9 atoms/cm^2 for 1

ml of recovered solution. When only one element is analyzed, the detection limits shown in Table 1 become half since only 0.5 ml of recovered solution is needed for analysis. While GF-AAS is relatively poor sensitivity compared to ICP-MS, detection limits analyzed by GF-AAS on 8-inch wafer are not significantly lower than those by ICP-MS. This is because GF-AAS requires less volume of recovered solution.

GF-AAS analysis does not require dilution of the recovered solution in the case of the existence of the native oxide , since the measured intensities for metals do not decrease even in the presence of 500 wt・ppm of Si in the recovered solution, as mentioned in Sections 2. GF-AAS is superior to ICP-MS from the viewpoint that the presence of Si in the recovered solution has less impact on measurement sensitivity.

In order to improve the detection limit for Na, the original acid solution can be prepared by distilling deionized water in a non-boiling type distiller. This special acid solution improves the ICP-MS detection limit for Na to 2−5 wt・ppt from 10−25 wt・ppt, as shown in Fig. 6. Based on these values, the detection limit of Na on the 8-inch wafer are 1×10^8 − 3×10^8 atoms/cm^2, when the volume of recovered solution is 0.5 ml. The metal concentration is analyzed in accord with the order by varying the purity of deionized water and the sampling volume.

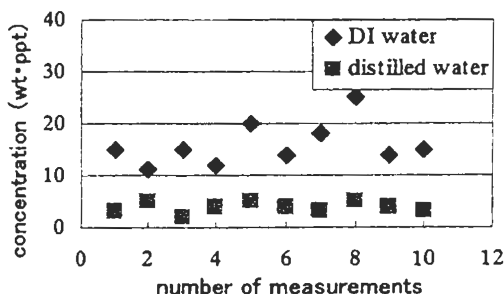

Fig. 6. Fluctuation of the analytical results of Na in the original acid solution made from DI water and from distilled water

3.Summary

The detection limits of metal impurities on the silicon wafers depend on the analytical environment, water, chemicals, and the conditions of analytical equipments and implements. The concentration of Si matrix that coexists in the recovered solution with high concentration and the recovery rate also affect the detection limits. The BEC values of various metals in the original acid solution that is used to collect contaminants were always measured from the viewpoints of managing the experiments. It is important to continue to keep the above ordinary experimental rules in order to analyze the trace metals at the level of 10^8-10^9 atoms/cm^2 on the silicon wafers. Metal contaminants in the original acid solution analyzed by ICP-MS for about three years were controlled within the range of 1 − 25 wt・ppt in our experiments. Consequently, the detection limits of metals to 3×10^8 -1×10^9 atoms/cm^2 on the 8-inch silicon wafer were being guaranteed.

Reference

[1] M. Itsumi ; *Appl. Phys. Lett.*, **63**, 1095 (1993).
[2] International Technology Roadmap for Semiconductors 2000 Update (2000).
[3] A. Shimazaki, H. Hiratsuka, Y. Matsushita and S.Yoshii ; Ext. Abst. 16th Conf. Solid State Device and Materials, Kobe, B-4-3, 281 (1984).
[4] Y. Tanizoe, S. Sumita, M. Sano, N. Fujino and T. Shibata ; *Bunseki Kagaku*, **38**, 177 (1989).
[5] S. Ariga ; Material Technology, **9**, 166 (1991).
[6] H. Matsunaga, M. Takenaka and N. Hirate ; *Bunseki*, 11, 76 (1997).
[7] H. Kawaguchi, T. Tanaka, T. Nakamura, M. morishita and A. Mizuike ; Anal. Sci., **3**, 305 (1988).