Collection Efficiency of Metallic Contaminants on Si Wafer by Vapor-Phase Decomposition-Droplet Collection

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The collection efficiency of metallic contaminants on four different types of silicon wafers was investigated. P, p⁺, n and n⁺-type polished silicon wafers were used for the substrate, and 14 metallic elements (Na, Mg, Al, K, Ca, Cr, Fe, Mn, Co, Ni, Cu, Zn, Mo and Ti) were contaminated on silicon wafer surface. Vapor-phase decomposition-droplet collection (VPD-DC) was employed as the sample preparation procedure. For the collecting solution, HNO₃, HF and a mixture of HF and H₂O₂ were used, respectively. A liquid droplet collecting metallic contaminants during VPD-DC was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). As a result, it was found that HNO₃ and HF were not suitable for collecting Cu. Copper was not collected completely in HNO₃ and HF. A mixture of HF and H₂O₂ is the most effective to collect all of the tested metallic elements, regardless of the dopant concentration and type of substrate.

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Introduction

Metallic contaminants on a wafer surface have been known to be a major source of performance failure in IC devices by increasing the p-n junction leakage, degradation of the oxide breakdown voltage and deteriorating the carrier lifetime.¹ With shrinking device geometries, the tolerance level of metallic contaminants is becoming more stringent. It has been reported that metallic contamination on a silicon surface needs to be suppressed to less than 1×10^{10} atoms/cm² to manufacture a 64-Mbit DRAM in order to prevent the above-mentioned failures.² According to device development and an estimation of the research organization, this level should be down to 1×10^9 atoms/cm² in the future. With this tendency, analytical techniques used to measure ultratrace metallic contaminants on a silicon surface have also been developed.

One of the most prevalent techniques used for measuring metallic contaminants is VPD-DC (vapor phase decomposition-droplet collection). During the VPD procedure, the wafer is exposed to hydrogen fluoride vapor in a closed container to decompose the surface oxide layer. The decomposition reaction of silicon oxide by hydrogen fluoride vapor is expressed by

Metallic contaminants remain on the wafer surface after the decomposition of silicon oxide. In the DC procedure, these metallic contaminants are collected into a small amount of ultra-high-purity liquid droplets by scanning the wafer surface. A liquid droplet prepared by VPD-DC is analyzed by different trace-element analysis techniques, such as atomic absorption spectrometry (VPD-AAS),³⁻⁷ inductively coupled plasma-mass spectrometry (VPD-ICP-MS)^{5,8-10} and total reflection X-ray fluorescence (VPD-TXRF).^{4,11-13}

DC is a procedure used to collect and preconcentrate all

impurities into liquid droplets. The composition of the collecting solution as well as the chemistry of the collected contaminants determine the collection efficiency. Morinaga *et al.* have reported that metallic contaminants deposit on a silicon wafer surface in a wet process depending on the type of metal element, the type of solution and the type of substrate.¹⁴ Therefore, a chemical reaction of metal at the silicon surface during VPD-DC can influence the collection efficiency of a metallic contaminant. However, there have been few reports concerning the collection efficiency of the VPD-DC procedure.

In this experiment, the collection efficiency of VPD-DC sample preparation was investigated for 14 elements (Na, Mg, Al, K, Ca, Cr, Fe, Mn, Co, Ni, Cu, Zn, Mo and Ti) on four types of silicon wafers. Standard solutions containing 7 elements in each solution were intentionally contaminated on a silicon wafer surface. The contaminated area was scanned with various collecting solutions in the VPD-DC procedure and a droplet containing metallic contaminants, collected from the silicon wafer surface, was measured by ICP-MS. The collection efficiency was determined as the ratio of the collected metallic concentration to the initial contamination concentration.

Experimental

Reagents and samples

Metal standard solutions (1000 µg/mL, High Purity Standards, Charleston, SC, USA) of 14 elements were used for intentional contamination. A multielement stock solution (1 µg/mL of each element) was prepared by mixing single-element standard solutions (1000 µg/mL each). Standard solutions for contamination were further prepared by diluting a multielement stock solution with 2% HNO₃ solution. HNO₃ (55%), HF (38%) and H₂O₂ (35%) of high-purity solutions (TAMAPURE AA-10, Tama Chemicals Co., Kanagawa, Japan) were used in all of the experiments. Details on the concentration of the

Table 1 Concentrations of the collecting solutions used in the experiments

HNO ₃ , %	HF/ppm	Mixture of HF and H ₂ O ₂	
		HF, %	H ₂ O ₂ , %
0.1	50	0.02	1
0.5	200	0.2	1
1	1000	2	1
2	5000		

Table 2 Operating conditions for the ICP-MS

Plasma condition	Normal (Cold)
RF power	1100 W (600 W)
RF frequency	40.68 MHz
Nebulizer type	MCN 6000
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	1.2 L/min (1.2 L/min)
Nebulizer gas flow rate	0.95 L/min (1.18 L/min)
Sample uptake rate	94 µL/min
Sampler cone	Pt (1.1 mm)
Skimmer cone	Pt (0.9 mm)
Quadrupole chamber	~ 1 × 10 ⁻⁵ Torr
Operating pressure	
Quadrupole scan mode	Peak hopping
Ion lens voltage	Dynamic (Fixed)
Dwell time/mass	50 ms
Number of sweeps	30
Number of replicates	10
Integration time/mass	1500 ms
Detector	ETP/AF210J

collecting solutions are listed in Table 1.

Samples were divided into four groups with their type. Boron-doped wafers with a diameter of 200 mm were p type (resistivity 9 – 12 Ω cm) and p⁺ type (resistivity 0.01 – 0.02 Ω cm). An N-type wafer was a lightly phosphorous-doped wafer with a diameter of 150 mm and a resistivity 5 – 20 Ω cm. An N⁺-type wafer was a heavily antimony doped wafer with a diameter of 150 mm and a resistivity 0.008 – 0.025 Ω cm. All of the wafers were single-side polished and cleaned with modified RCA cleaning.

Instrument and apparatus

A liquid droplet containing metallic contaminants collected from a silicon surface was analyzed by an ICP-MS (Elan 6000, Perkin Elmer, Norwalk, CT, USA) equipped with a micro-concentric nebulizer. The mass spectrometer was used in a peak-hopping mode. ICP was operated under a cool plasma condition for K, Ca and Fe and under the typical condition for all other elements. The operating conditions for the ICP-MS are listed in Table 2.

A schematic diagram of the apparatus for contamination is shown in Fig. 1. The apparatus has four walls made with Teflon, and the top and bottom are open. An IR lamp is placed inside a Teflon box. Contamination using this apparatus was carried out in a class-1 clean bench settled in a class-100 clean environment.

Procedure

All of the wafers were treated as a hydrophobic surface by VPD prior to use, and were mounted on the top of an apparatus

Fig. 1 Schematic diagram of the assembly used for the contamination and drying of metallic contaminants on a silicon surface.

located in the clean bench. Each 1 mL of standard solutions (1 ng/mL of each element) was dropped at a different location on the polished wafer surface (Fig. 1). The standard solution for contamination was divided into two groups: group I was a mixture of Na, Mg, Al, K, Ca, Cr and Fe; group II contained Mn, Co, Ni, Cu, Zn, Mo and Ti. One milliliter of a 2% HNO₃, blank solution containing no impurity was also dropped on the wafer surface to check for any unintentional contamination from the environment. Then, an IR lamp was illuminated any solution on the wafer surface dried. The contaminated wafer was cooled in air and placed in a closed container filled with HF vapor for 3 min. Each contaminated spot was then scanned with 1 mL of various collecting solutions for 3 min. The collected droplet was measured by ICP-MS. All of the experiments were carried out in a class-100 clean room.

Results and Discussion

Collection efficiency by HNO₃

Figure 2 shows the collection efficiency of metallic contaminants on four types of silicon wafers by HNO₃. Thirteen elements, except for Cu, were effectively collected regardless of the concentration of HNO₃. The Cu collection efficiency was less than 90% for all of the studied concentrations of HNO₃; there was a big difference depending on the type of substrate. The Cu collection efficiency on p, n, and n⁺-type silicon wafer surfaces increased as the concentration of HNO₃ was increased, while that on a p⁺-type wafer was almost constant regardless of the HNO₃ concentration. This result is considered to have been caused by a difference in the boron doping concentration.

The following discussion concerning the difference in the Cu collection efficiency on the p⁺-type silicon surface is based on the band model reported by Seidel *et al.*¹⁵ According to their band model, the width of the space-charge layer on the silicon surface is shrunk sharply because of a high concentration of boron. This leads to an equivalent narrowing of the potential well, which cannot confine the electrons injected into the conduction band by the oxidation step (Eq. (2)). These injected electrons are, therefore, forced to tunnel through the space-charge layer into a deeper region of crystal. Due to the very large hole concentration, they have a high probability of recombination with holes from the valence band.

The reaction in which silicon in an aqueous solution releases electrons can be expressed by

where E^0 is the standard redox potential.

Fig. 2 Collection efficiency of metallic contaminants on (a) p-type, (b) p⁺-type, (c) n-type and (d) n⁺-type silicon surfaces by HNO₃. Contaminated concentration: 1 ng of each element.

The reaction where Cu ion in a solution is reduced by accepting electrons can be expressed by the following oxidation/reduction reaction equation:

A comparison of the Cu collection efficiency on p-type and p⁺-type silicon surfaces is shown in Fig. 3. In the case of the p-type silicon surface, electrons released by the oxidation of silicon can give rise to a reduction of the Cu ion. The Cu collection efficiency thus decreased as the concentration of HNO₃ was decreased, because reduction of the Cu ion became dominant.

The Cu collection efficiency on a p⁺-type silicon surface can be explained based on the band model mentioned above. Electrons released by the oxidation of a silicon tunnel into the deeper region of crystal and recombine with holes. The reduction of Cu ion was restricted and the ionization of Cu was dominant in an oxidizing agent. Consequently, the Cu collection efficiency on the p⁺-type silicon surface was relatively good, even at a low concentration of HNO₃, compared to the result of other types of substrates.

The Cu collection efficiency on n and n⁺-type silicon surfaces was similar to the result for a p-type silicon surface. From this result, it is assumed that the collection of Cu on n and n⁺-type silicon surfaces was interfered by the reduction of Cu ion at a low concentration of HNO₃.

However, the Cu collection efficiency by HNO₃ was less than 90% on four types of silicon wafers. This means that a small amount of Cu remained on the wafer surface, and HNO₃ was not

Fig. 3 Model of the Cu collection efficiency for (a) lightly and (b) heavily boron doped wafers.

suitable to collect the Cu contaminant completely. The collection efficiency of some elements had deviations between 80–120% regardless of the HNO₃ concentration. These deviations are thought to be an experimental error caused by a poor sample treatment during intentional contamination, the drying process, and so on.

Collection efficiency by HF

The collection efficiency of metallic contaminants by an HF

Fig. 4 Collection efficiency of metallic contaminants on (a) p-type, (b) p⁺-type, (c) n-type and (d) n⁺-type silicon surfaces by HF. Contaminated concentration: 1 ng of each element.

solution is shown in Fig. 4. A similar result was found on four types of wafers. The collection efficiency of 13 elements was good, and that of Cu was less than 70%. It is thought that the collection of Cu was influenced by the reaction between silicon and HF. It is well known that Cu plates out on a silicon wafer surface in HF.^{16,17} SiO₂ of the silicon wafer surface is etched away by HF immediately. Cu contacts directly with bare silicon, resulting in an outplating of Cu. For this reason, some of the Cu contaminant remained on the silicon surface in HF. Therefore, the collection efficiency of Cu was reduced in HF.

Collection efficiency by a mixture of HF and H₂O₂

The collection efficiency of metallic contaminants by a mixture of HF and H₂O₂ is shown in Fig. 5. The concentration of H₂O₂ was 1% and the concentration of HF was changed from 0.02% to 2%. All of the metallic contaminants were collected effectively under all conditions. Moreover, there was no decrease in the Cu collection efficiency on p, n, and n⁺-type silicon surfaces. This is thought to have resulted because the oxidation of Cu was predominant in an H₂O₂-based mixture with a strong oxidizing agent, even when electrons released by the oxidation of silicon were supplied. It has been reported that a Cu contaminant was removed well in an HF/H₂O₂ cleaning solution.^{18,19} It has also been discussed that a high oxidation power and passivation of a silicon surface by H₂O₂ are essential for removing a Cu contaminant on a silicon surface. It is considered that Cu on the silicon surface was collected very effectively in a mixture of HF and H₂O₂ for the same reason.

Conclusions

The collection efficiency of metallic contaminants on four different types of silicon wafers was investigated when VPD-DC was employed as the sample-preparation procedure. Na, Mg, Al, K, Ca, Cr, Fe, Mn, Co, Ni, Cu, Zn, Mo and Ti were contaminated on p, p⁺, n and n⁺-type silicon wafer surfaces and collected into a collecting solution, which was HNO₃, HF and a mixture of HF and H₂O₂, respectively. The collection efficiency of 13 elements, except for Cu, was good in all of the studied collecting solutions. The collection efficiency of Cu was different, depending on the type of silicon wafer and collecting solution.

When HNO₃ was used as the collecting solution, Cu on the p⁺-type silicon surface was collected to near 90% in a low concentration of HNO₃, contrary to the results of the other three types of silicon wafers. This result is considered to have been caused by restricting the reduction of Cu ion. Electrons that were released by the oxidation of silicon tunnel into a deeper region of the crystal and recombine with holes of the p⁺-type silicon wafer. Therefore, the reduction of Cu ion was restricted and the ionization of Cu was dominant in an oxidizing agent. The Cu collection efficiency, however, was less than 90% on four types of silicon wafers in HNO₃. It is supposed that a small amount of Cu remains on the wafer surface in HNO₃, which is not suitable for collecting all of the Cu contaminant. The Cu collection efficiency by HF was less than 70% for four types of silicon wafers. HF is also not suitable for Cu collection due to

Fig. 5 Collection efficiency of metallic contaminants on p, p⁺, n and n⁺-type silicon surfaces by a mixture of HF and H₂O₂. Concentration of H₂O₂: 1%; contaminated concentration: 1 ng of each element.

the deposition of Cu in HF.

All of the elements including Cu were collected very effectively by a mixture of HF and H₂O₂. It is considered that the mixture of HF and H₂O₂ provided sufficient oxidation power to ionize the metallic contaminants and to prevent the deposition of Cu by generating a continuous oxide layer on the silicon surface. It turned out that the mixture of HF and H₂O₂ is the most effective way to collect metallic contaminants on a silicon wafer surface, regardless of the dopant concentration and the type of substrate.

References

1. W. Kern, in "Handbook of Semiconductor Wafer Cleaning Technology", ed. W. Kern, **1992**, Noyes Publications, Park Ridge, 8.
2. W. Kern, in "Handbook of Semiconductor Wafer Cleaning Technology", ed. W. Kern, **1992**, Noyes Publications, Park Ridge, 596.
3. H. Nagasawa and M. Enomoto, *Bunseki Kagaku*, **1997**, *46*, 375.
4. L. H. Hall, J. A. Sees, and B. L. Schmidt, *Surf. Interface Anal.*, **1996**, *24*, 511.
5. R. S. Hockett, in "Handbook of Semiconductor Wafer Cleaning Technology", ed. W. Kern, **1992**, Noyes Publications, Park Ridge, 584.
6. A. Shimazaki, H. Hiratsuka, Y. Matsushita, and S. Yoshii, Extended Abstracts of the 16th Conference on Solid State Devices and Materials, **1984**, 281.
7. Y. Tanizoe, S. Sumita, M. Sano, N. Fujino, and T. Shiraiwa, *Bunseki Kagaku*, **1989**, *34*, 177.
8. M. Takenaka, Y. Yamada, M. Hayashi, H. Omori, S. Ito, and A. Okada, *Bunseki Kagaku*, **1997**, *46*, 743.

9. G. Settembre and E. Debrah, *Micro*, **1998**, *16*, 79.
 10. K. Fujiwara, Y. Toumori, H. Mitsumata, M. Inada, and T. Nakahara, *Bunseki Kagaku*, **1999**, *48*, 681.
 11. M. Yamagami, M. Nonoguchi, T. Yamada, T. Shoji, T. Utaka, Y. Mori, S. Nomura, K. Taniguchi, H. Wakata, and S. Ikeda, *Bunseki Kagaku*, **1999**, *48*, 1005.
 12. R. S. Hockett, *Anal. Sci.*, **1995**, *11*, 511.
 13. S. Pahike, L. Kotz, T. Ehmann, P. Eichinger, and A. Huber, in "Proceedings of the Eighth International Symposium on Silicon Materials Science and Technology", ed. H. R. Huff, H. Ysuya, and U. Gösele, **1998**, ECS, San Diego, California, 1524 – 1540.
 14. H. Morinaga, M. Suyama, M. Nose, S. Verhaverbeke, and T. Ohmi, *IEICE TRANS. ELECTRON.*, **1996**, *E79C*, 343.
 15. H. Seidel, L. Csepregi, A. Heuberger, and H. Baumgartel, *J. Electrochem. Soc.*, **1993**, *137*, 3626.
 16. T. Ohmi, T. Imaoka, T. Kezuka, J. Takano, and M. Kogure, *J. Electrochem. Soc.*, **1993**, *140*, 811.
 17. H. Morinaga and T. Ohmi, in "Proceedings of the Fourth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing", ed. R. E. Novak and J. Ruzyllo, **1995**, ECS, Chicago, Illinois, 257 – 268.
 18. V. Bertagna, F. Rouelle, and M. Chemla, *Semicond. Sci. Technol.*, **1998**, *13*, 444.
 19. G. M. Choi, H. Morita, H. Morinaga, J. S. Kim, and T. Ohmi, in "Proceedings of the Sixth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing", ed. T. Hattori, R. E. Novak, and J. Ruzyllo, **1999**, ECS, Honolulu, 272 – 279.
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