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<td>IEEE Transactions on Semiconductor Manufacturing</td>
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doi: 10.1109/66.29672
Particle-Free Wafer Cleaning and Drying Technology

H. MISHIMA, T. YASUI, T. MIZUNIWA, M. ABE, AND T. OHMI, MEMBER, IEEE

Abstract—Wet chemical processes occupy a very important position in ULSI fabrication technologies. With increasing pattern densities of ULSI devices, a contamination-free cleaning and drying system has been increasingly required. For removing particulate contaminants from silicon wafers by chemical solution treatment, it has been found that the NH$_4$OH-H$_2$O$_2$ solution is excellent and the ratio of NH$_4$OH in the solution can be reduced down to 1/10 of the standard ratio while keeping high removal efficiency. By decreasing the NH$_4$OH content, a wafer damage which appears as a so-called haze during the NH$_4$OH-H$_2$O$_2$ treatment will be reduced. And for drying, in order to establish a particle-free wafer drying system, the particle generation-free isopropanol (IPA) vapor drying system has been developed. By eliminating all possible particle generation sources from the drying system, ultraclean wafer drying equipment has been realized. A number of technical items to be controlled have been thoroughly investigated. As a result, three technical items were found to seriously influence surface cleanliness after drying: the water content in IPA, temperature distribution around wafers, and the IPA vapor velocity. The optimum drying conditions in which high quality of wafer surface cleanliness can be realized were confirmed experimentally.

I. INTRODUCTION

Complete elimination of all possible impurities from semiconductor processing environments is very important for realizing ULSI devices of submicrometer to lower submicrometer feature sizes [1]. It is obvious that residual contaminants on wafer surfaces should be remarkably decreased with an accompanying increase in pattern densities. Because the particulate contamination on wafer surfaces mainly cause device failures, particle-free wet chemical processes are required for obtaining high yield and reliability for semiconductor fabrication. Generally, wet chemical processes can be classified as cleaning and/or etching processes using ultrapure water and chemicals and a drying process to remove water from wafer surfaces.

It has been shown that hydrogen peroxide solutions have an ability to remove organic and metallic contamination from silicon surfaces [2], [3], but the cleaning efficiency of particulate contamination has not yet been investigated quantitatively.

A wafer drying technique is indispensably carried out after rinsing with ultrapure water. The drying process is required to completely eliminate water from wafer surfaces without spontaneous drying and any residue of contaminants. A vapor drying technique using isopropanol (IPA) has the capability to satisfy these severe requirements [4].

The influence of the particulate contamination on silicon surface cleaning as investigated by comparing the cleaning efficiency of various cleaning methods. And, in order to achieve a particle-free drying system, IPA vapor drying equipment in which particle generation is completely eliminated in the drying area, was developed, and factors which affected wafer surface cleanliness were investigated.

II. EXPERIMENT

A. Cleaning Experiment

Wafer cleaning experiments were performed on artificially contaminated wafers. Polystyrene latex spheres having a diameter of 0.43 μm and silica latex spheres having a diameter of 0.5 μm were employed as organic and inorganic artificial particulate contaminants, respectively. Silicon wafers used for tests were 3-inches in diameter and (1, 0, 0) oriented p-type (6-8 Ω-cm) or n-type (3-5 Ω-cm). Latex suspensions containing 7 × 10$^5$-7 × 10$^{10}$ particles/ml were diluted to 10$^7$-10$^9$ particles/ml, and dropped onto the wafer surfaces, and then spun dry. By this procedure, wafers each having 500-2000 particles on its surface were prepared for cleaning tests.

The wafer surfaces were observed using a scanning electron microscope (SEM). Particle counts on wafers were evaluated using an Aerconca WIS-100 wafer inspection system. The WIS-100 classifies defect sizes to particles (over 0.5 μm) and a so-called haze (below 0.5 μm). Before the experiments, the WIS-100 was calibrated with a relative standard wafer.

After adhering the particles on the wafers, an initial particle count was performed for each wafer. Then, at least ten wafers were subjected to each cleaning sequence, and a second count was performed. Cleaning efficiency was evaluated by calculating the ratio of second and first measurements. The average of those ratios was reported as the cleaning efficiency.

The cleaning sequence examined was carried out with five kinds of solutions:

A) H$_2$SO$_4$-H$_2$O$_2$ solution (4 parts 98-percent H$_2$SO$_4$, 1 part 30-percent H$_2$O$_2$);

B) NH$_4$OH-H$_2$O$_2$ solution (1 part 30-percent NH$_4$OH, 1 part H$_2$O$_2$, 5 parts H$_2$O at 80°-90°C);
C) dilute-HF solution (1 part 49-percent HF, 100 parts H₂O at 23°-25°C);
D) HCl-H₂O₂-H₂O (1 part 35-percent HCl, 1 part H₂O₂, 6 parts H₂O at 80°-90°C); and
E) NH₄OH-H₂O₂-H₂O solution (0.25 parts NH₄OH, 1 part H₂O₂, 5 parts H₂O at 80°-90°C).

Immersion time in each of the cleaning solutions is 10 min except for the dilute-HF solution. The time for immersion in dilute-HF is 1 min. After immersion into the solutions, the wafers were rinsed for 10 min in ultrapure water and then spun dry. Chemicals used in these tests are all of electronic grade and low particle levels [5]-[7]. The particle counts of those over 0.5-μm diameter size in the chemicals were below 20 counts/ml or less. The quality of ultrapure water was 18.24 MΩ-cm in resistivity, 5 ppb in total organic carbon (TOC), 2-3 ppb in silica concentration, and 0.3 count/ml in particle counts of those over 0.2-μm diameter size [8]. All equipment used for the wafer cleaning and rinsing were made of either Teflon-PFA or quartz glass. The cleaning and rinsing processes were manually performed in a wet station.

B. Drying Equipment

Fig. 1 shows a schematic diagram of the newly developed wafer drying system. This system consists of an IPA heating and chilling system, a wafer transport system, an IPA liquid delivery system, and a fan filter unit. The IPA liquid in the chamber is indirectly heated by the bottom heater. The evaporated IPA vapor is condensed by the chiller placed at the top inside of the chamber. Condensed IPA liquid is recycled. To make this system particle-generation free, all materials in the chamber in contact with IPA vapor and/or liquid such as the vaporizing chamber and the chiller were made of 316L stainless steel. All internal surfaces were precisely buffed by a mechanical polishing and a chemical treatment [9]. In the IPA delivery system, IPA liquid is fed from the stainless steel vessel through the Teflon membrane filter having pore size of 0.1 μm and then sent to the chamber. To avoid the particle generation from the tubes, the electro-polished 316L stainless steel tubes were employed. The wafer transport system is automatically operated in obedience to the sequences. To prevent particle contamination during wafer transport, the moving portions of the system are kept away from the wafers as far as possible. Clean air is passed through an ULPA filter and is streamed with the vertical and laminar flow to keep the high quality of cleanliness in wafer transport spaces.

Wafers which have diameters of 3, 4, and 5 in were cleaned with chemicals and ultrapure water as described above. After rinsing, the wafers were immersed into the vapor zone for 5 min. During the wafer drying operation, the wafers were set above the receiver in the vapor zone and any condensed IPA containing water was immediately taken out from the chamber through the receiver. After drying, the wafers were taken out from the chamber using the automatic transportation robot.

The cleanliness of the wafer surfaces was evaluated using either the WIS-100 or an optical microscope. The particle counts in the IPA liquid and in clean air were measured by a HIAC/ROYCO particle counter and a light scattering particle counter which detects the 0.17-μm diameter particles, respectively.

III. RESULTS AND DISCUSSION

A. Cleaning

1. Comparison of Particle Removal Efficiency: Fig. 2 shows the particle removal efficiency of the five cleaning solutions for polystyrene latex spheres. The H₂SO₄-H₂O₂ and the NH₄OH-H₂O₂ solutions with the low NH₄OH content were found to have a high removal efficiency for both organic particles and haze. The other cleaning solutions were also effective for removing particles. It should be noticed that only the NH₄OH-H₂O₂ solution of the standard ratio reported by Kern and Puotinen [2] showed an increase in haze formation. This is due to an irregular etching of wafer surfaces during cleaning as described later.

Fig. 3 shows the same relation between the cleaning efficiency and cleaning methods using wafers with the adhered silica latex spheres. The two NH₄OH-H₂O₂ and the dilute-HF solutions were found to obtain a high removal efficiency for both inorganic particles and haze. In this case, an increase in the haze density was not observed for the standard NH₄OH-H₂O₂ solution. On the other hand, the acid oxidizing solutions such as the H₂SO₄-H₂O₂ and the HCl-H₂O₂ solutions had low removal efficiencies, because they had no etching reaction for silicon.

From these results, the particle removal mechanism of the latices is presumed as follows. In the polystyrene latex spheres, it is presumed that removal mechanisms from silicon are an oxidizing degradation for the H₂SO₄-H₂O₂ solution, and the lift-off effect due to a slight etching of a native oxide on silicon for the NH₄OH-H₂O₂ solutions. In the case of the silica latex spheres, the dilute-HF solution dissolves both an oxide film on silicon and the latex simultaneously, and the NH₄OH-H₂O₂ solution slightly etches both wafer surfaces and the latex. Consequently, these solutions having the etching ability for silicon compounds revealed high cleaning efficiencies. It is highly
important that even the NH$_4$OH–H$_2$O$_2$ solution with low NH$_4$OH content has high cleaning efficiencies equal to that of the standard ratio.

Experimental results mentioned above show that the NH$_4$OH–H$_2$O$_2$ solutions have higher removal efficiencies for any particulate contaminants.

2. Haze Increase: As shown in Figs. 2 and 3, wafer cleaning with the NH$_4$OH–H$_2$O$_2$ solution has an excellent efficiency for removing the particulate contamination. However, this is due to the mechanism producing a slight silicon etching reaction, so that wafer surface roughness has a possibly to be increased in the NH$_4$OH–H$_2$O$_2$ cleaning procedure.

Fig. 4 shows the results of the repeating test alternating the NH$_4$OH–H$_2$O$_2$–H$_2$O (1:1:5 part by volume) cleaning and the dilute-HF etching by using the same wafers. It is seen from this figure that the haze increased in both treatments, particularly with the NH$_4$OH–H$_2$O$_2$ solution cleaning. An increase in haze was observed after several treatments with the NH$_4$OH–H$_2$O$_2$ solution. After the NH$_4$OH–H$_2$O$_2$ treatments, the haze count went up to several thousands per wafer.

Fig. 5 shows the beam spot of the scattering light reflected on the wafer used in Fig. 4 from an optical microscopy, where one treatment consists of the NH$_4$OH–H$_2$O$_2$ cleaning and the dilute-HF treatment. There was no existence of a scattering light on no-treatment wafers. However, the intensity of a scattering light became stronger with an increase in treatment times. This indicates that an increase in the haze was caused by roughing the silicon surface but not by adhering particles on it. Although such an increase in the haze count is not always reproducible, it is a serious problem for obtaining
high reliability of cleaning processes and damage-free silicon surfaces, particularly for very shallow source and drain junctions in very fine pattern ULSI.

3. Cleaning Efficiency of the NH$_4$OH–H$_2$O$_2$ Solution with Low NH$_4$OH Content: As mentioned above, we have shown that the cleaning with the NH$_4$OH–H$_2$O$_2$ solution is excellent for removing particulate contaminants but it sometimes causes surface roughness by the irregular etching. Furthermore, it has been confirmed experimentally that the particle removal efficiencies of the NH$_4$OH–H$_2$O$_2$ solution is kept at the same level even when the NH$_4$OH–H$_2$O$_2$ content in that solution is decreased to some extent.

Figs. 7 and 8 show the particle removing capability of the NH$_4$OH–H$_2$O$_2$ solutions for various NH$_4$OH contents by using polystyrene and silica latices, respectively, where the residual particle number on the wafer is illustrated as a function of NH$_4$OH contents. Here, absorbed particle number is about 10,000 before this cleaning procedure. It is worthwhile to note in Figs. 7 and 8 that the particle removal efficiency is improved by a factor of two order without accompanying any increase of haze density when the NH$_4$OH content is decreased less than a half of conventional content. This excellent particle removing capability is guaranteed in NH$_4$OH content ranging from 0.1 to 0.5 of conventional content.

B. Drying

1. Cleanliness Evaluation of Drying System: In order to realize a particle-free wafer drying technique using high purity IPA, the authors have developed a particle generation-free drying system. The IPA vapor drying system and the factors which affected the cleanliness of the wafer surface are described as follows.

Table I shows the particle counts in wafer transport spaces just above the vaporizing chamber, when the wafer transport system was operated and stopped. It is evident that the particle counts over 0.17-µm diameter are less than 1 ft$^{-1}$ even in operation. Additionally, particle adhering on the wafer surfaces during the wafer transport process was also evaluated. No increase in particle counts were observed after 30 operations.

Fig. 9 shows the variation of particle counts in bottom IPA and condensed IPA before and after an 8-h vaporizing operation. Although particles in bottom IPA were concentrated, no concentration of particles in condensed IPA was observed even after an 8-h operation. The particle counts in condensed IPA were always less than one-tenth of that in bottom IPA. It is evident from these results...
that this IPA vapor drying system is composed so as not to generate particles.

2. Electrostatic Charging During Wet Chemical Processing: The electric potentials through cleaning to drying due to electrostatic charge are shown in Table II. This table shows the following two points. One is that the electrostatic charging after spin drying easily approaches -25 kV, while that after vapor drying is nearly ±0 kV. The second point is that the electrostatic charging after rinsing can be perfectly discharged to neutralize by vapor drying. It is confirmed that the IPA vapor drying technique is essentially excellent in the particulate contamination caused by electrostatic charging.

3. Results of Wafer Drying: A number of technical items which affect the cleanliness of wafer surfaces after drying were thoroughly investigated. As a result, three technical items have been revealed to be controlled during the drying operation. These important items were water content, temperature distribution of IPA, and the IPA vapor velocity. Effects of these items on the surface cleanliness are described as follows.

a. Water content: Fig. 10 shows the influence of the water content in IPA on the cleanliness of the wafer surface after drying. The defect count on wafers gradually increases with the increase in the water content to more than 2000 ppm. Although when the water content exceeds 5000 ppm, the defect count rapidly increases. Fig. 11 shows a photograph of the wafer surface dried under the water content of 27 000 ppm. A number of contaminant spots were observed near the periphery. These facts seem to be caused by the remaining residues of water on the wafer surfaces. Therefore, the water content in IPA should be always maintained at less than 2000 ppm during the drying process.

b. Heating system of IPA: IPA in the vaporizing chamber is heated by the bottom heater and the side wall heater, where the side wall heater is set to keep the side wall surface temperature at 130°C. In order to evaluate IPA vapor generation, bottom heater distribution is changed to two types, i.e., one is uniform distribution and the other is localized to about half area of IPA liquid vessel around the center. Table III shows the particle counts after IPA vapor drying for these two types of bottom heaters, where the input electric power to these two bottom heaters is kept at the same level. The particle counts on the wafer surface in uniform bottom heating are lesser than that in the localized bottom heater. This means that the entrainment caused by the boiling of IPA is directly polluting the wafer surfaces.

Consequently, IPA liquid should be vaporized by an entrainment-free heating system that is uniform heat of IPA liquid.

c. Velocity of IPA vapor: The amount of vapor in contact with wafers per unit time is corresponded to the rising up velocity of the IPA vapor. Table IV shows an example of the influence of the linear velocity of IPA vapor on the defect counts. The linear velocity was calculated by measuring an amount of condensed IPA per unit area. With an increase in the linear velocity, the defect
Wet chemical processes occupy a very important position in ULSI fabrication technologies. With the increase in pattern densities of ULSI devices, a contamination-free cleaning and drying system has been more and more realized.

For the removal of particulate contaminants from silicon wafers by the cleaning solutions, it has been demonstrated that the NH₄OH–H₂O₂ solution is excellent to remove particles and the content of NH₄OH in that solution must be reduced down to 1/2–1/10 of the conventional content to improve the particle removing capability by a factor of two order without any increase in surface roughness.

On the other hand, in order to establish the particle-free wafer drying system, the particle generation-free IPA vapor drying system has been developed. By eliminating all possible particle generation sources from the drying system, the ultraclean wafer drying equipment has been realized. Furthermore, we have thoroughly investigated a number of technical items to be controlled. As a result, three technical items, i.e., the water content in IPA, the IPA heating system, and the IPA vapor velocity, seriously influence the surface cleanliness after drying. At the same time, the optimum drying conditions in which the high quality of the surface cleanliness can be realized were determined.

ACKNOWLEDGMENT

This work was performed in the Supercontrol Room in the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University.

REFERENCES


Hiroyuki Mishima was born in Fukuyama, Japan, on February 6, 1952. He received the B.S. and M.S. degrees in industrial chemistry from Okayama University, Okayama, Japan, in 1974 and 1976, respectively. In 1976, he joined Tokuyama Soda Co., Ltd., where he was engaged in the development of ion-exchange membrane systems and water treatment systems. From 1985 to 1988, he was a Visiting Researcher at Tohoku University where he was engaged in the research and development of wafer cleaning and drying systems. Mr. Mishima is a member of the Institute of Environmental Sciences.

Tomiharu Yasui was born in Yamaguchi, Japan, on January 1, 1948. He graduated from the electrical course of Nanyo Technical High School in 1966. In 1966, he joined Tokuyama Soda Co., Ltd. From 1966 to 1984, he was engaged in the development of a cleaning and drying system using solvents for the semiconductor process.

Tetsuo Mizuniwa received the B.S., M.S., and D.Sc. degrees in mineral processing engineering from Tohoku University, Sendai, Japan, in 1970, 1972, and 1978, respectively. In 1975, he joined Kurita Water Industries Ltd. where he has been engaged in the research and development of ultrapure water systems and analysis.

Mitsuo Abe received the B.S. degree in industrial chemistry from Chuoh University, Tokyo, Japan, in 1976. In 1976, he joined TOMCO MFG, Ltd., where he has been engaged in the research and development of vapor drying systems. He was a Researcher at Tohoku University from September 1986 to March 1988.

Tadahiro Ohmi (M’81) was born in Tokyo, Japan, on January 10, 1939. He received the B.S. and Ph.D. degrees in electrical engineering from Tokyo Institute of Technology, Tokyo, Japan, in 1961, 1963, and 1966, respectively. Prior to 1972, he served as a Research Associate in the Department of Electronics of Tokyo Institute of Technology, where he did research on Gunn diodes, velocity overshoot phenomena, multivalley diffusion and frequency limitation of negative differential mobility due to an electron transfer in the multivalleys, high field transport in semiconductors, unified theory of space-charge dynamics in negative differential mobility materials, Bloch oscillation induced negative mobility and Bloch oscillators, and dynamics in injection layers. He is presently a Professor in the Department of Electronics, Faculty of Engineering, Tohoku University. He is currently engaged in research on high performance ULSI, ultrahigh speed ULSI, current overshoot transistor LSI, HBT LSI and SOI on metal substrate, base store image sensor (BASIS), and high speed flat panel display, and advanced semiconductor process technologies, i.e., ultraclean technologies such as high quality oxidation, high quality metallization due to low kinetic energy particle bombardment, very low temperature Si epitaxy having simultaneous doping capability due to low kinetic energy particle bombardment, crystallinity control film growth technologies from single crystals, grain size controlled polysilicon and amorphous due to low kinetic energy particle bombardment, in situ wafer surface cleaning technologies due to low kinetic energy particle bombardment, highly selective CVD, highly selective RIE, high quality ion implantations having low temperature annealing capability, etc., based on the new concept supported by a newly developed ultraclean gas supply systems, ultrahigh vacuum compatible reaction chamber having a self-cleaning function, ultraclean wafer surface cleaning technology, etc. He is the author of 150 original papers and 150 patent applications. He received the Ichikawa Award in 1979 and the Teshima Award in 1987.

Dr. Ohmi is a member of the Institute of Electronics, Information, and Communication Engineers of Japan, the Institute of Electrical Engineers of Japan, the Japan Society of Applied Physics, and the ECS. He served as a Chairman of the Technical Group on Semiconductors and Semiconductor Devices of the Institute of Electronic and Communication Engineers of Japan for the 1985–1987 term and as Chairman of the Technical Group on Silicon Materials and Devices of the Institute of Electronic, Information, and Communication Engineers of Japan for the 1987–1988 term. He serves as a Chairman of the International Symposium on Power Semiconductor Devices and General Chairman of the Institute of Basic Semiconductor Technology Development (General Chairman of Ultraclean Society).