Particle Removal from Silicon Wafer Surface in Wet Cleaning Process

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Abstract—Particle removal from silicon wafer surfaces was studied using acid and alkaline solutions employed in wet cleaning processes found in semiconductor manufacturing. It has been demonstrated that the alkaline solutions are superior to the acid solutions in terms of particle removal efficiency. The particle removal mechanism in the alkaline solutions has been confirmed as follows: the solutions etch the wafer surfaces to lift off particles, and the particles are then electrically repelled from the wafer surfaces. It has been determined experimentally that an etch rate of 0.25 nm/min or more is required to lift off the particles adsorbed on the wafer surfaces. The etch rate of NH₄OH-H₂O₂-H₂O solution is 0.3 nm/min when the mixing ratio is set at 0.05:1:5 (NH₄OH:H₂O₂:H₂O). With this mixing ratio, the surface smoothness of the wafers is maintained at initial level. It is therefore possible to reduce the NH₄OH content in NH₄OH-H₂O₂-H₂O solution to 1/20 of the conventional level.

In addition, it has been confirmed that when the pH value of NH₄OH-H₂O₂-H₂O solution becomes higher, polystyrene latex spheres and natural organic particles are oxidized with their surface turning into a gel and their shape changing. The particle removal efficiency has been demonstrated to be degraded by the oxidation of organic particles. The oxidation of organic particles becomes significant as the NH₄OH content in NH₄OH-H₂O₂-H₂O solution rises above 0.1:1:5 (pH is over 9.1).

These experimental results suggest that the mixing ratio of NH₄OH-H₂O₂-H₂O solution should be set at 0.05:1:5. This mixing ratio is effective in maintaining both particle removal efficiency and surface smoothness of the wafers.

I. INTRODUCTION

Wet cleaning technology remains essential to remove contaminants on silicon wafer surfaces as semiconductor devices are pursuing higher levels of integration and higher resolution patterns [1]. The RCA cleaning process presented in 1970 by Kern and Poutinen [2] is still employed across the world as a wet cleaning technology to remove contaminants from the wafer surfaces. Although NH₄OH-H₂O₂-H₂O solution in the RCA cleaning process is considered very effective in removing particles [3], its particle removal mechanism has not yet been fully understood.

Meanwhile the mechanism of particle adsorption from solution to the wafer surfaces is now being actively studied from the perspective of colloid chemistry [4]-[11]. It is reported that ionic strength in solutions and zeta potential of particles are very important factors of particle adsorption onto the wafer surfaces.

In the study reported in this article, the mechanism to remove particles adsorbed on the wafer surfaces has been investigated based on the mechanism of particle adsorption onto the wafer surfaces. In particle removal experiments, artificially contaminated CZ (Czochralski method) and FZ (Float zone purification method) wafers have been cleaned with both acid and alkaline solutions employed in the wet cleaning processes. It has been demonstrated that the alkaline solutions are superior to the acid solutions in terms of particle removal efficiency. It has been considered that particles are electrically repelled from the wafer surfaces due to the negative zeta potential of most particles in the alkaline solutions [11].

In addition to the studies from the colloid chemistry viewpoint, we considered it important to examine etching of the wafer surfaces caused by the alkaline solutions. For this purpose, the relation between etch rate and particle removal efficiency has been studied, using CZ and FZ wafers. Moreover, by employing polystyrene latex spheres to represent organic materials, the oxidation process of particles in NH₄OH-H₂O₂-H₂O solution was investigated to find out the relation between degree of oxidation and particle removal efficiency. As a result, it has been shown that the NH₄OH content in NH₄OH-H₂O₂-H₂O solution should be reduced to 1/20 of the conventional level to optimize particle removal efficiency. The remainder of this article will describe the details of the experimental process and the results.

II. EXPERIMENT

Five-in CZ (1, 0, 0) wafers are used in the particle adsorption experiments. Native oxide is first removed from the wafer surfaces in a 0.5% HF solution. The wafers are then immersed for ten min in various solutions seeded with particles, and they are then rinsed and dried. After native oxide has formed on the wafer surfaces, it is again removed in a 0.5% HF solution, and they are then rinsed and dried.

Five inch CZ (1, 0, 0) and four-in FZ (1, 0, 0) wafers are used in the cleaning experiments to study particle removal. The wafers are artificially contaminated employing the following contaminant sources: particles naturally slurring in city water for typical particles in liquid phase, particles naturally slurring in ambient atmosphere outside of the cleanroom for typical particles in gaseous phase,
SiO₂ spheres of 0.3 µm and 1.0 µm in diameter as typical inorganic particles, and polystyrene latex spheres of 0.506 µm in diameter as typical organic particles. The wafers are contaminated by exposure to the ambient atmosphere outside of the cleanroom. By these procedures, wafers having a total of 5000–10 000 defects, classifies as either haze (<0.5 µm) or particles (>0.5 µm) on their surfaces are prepared for cleaning experiments.

These wafers are cleaned in the following chemicals.

a) NH₄OH-H₂O₂-H₂O solution: 29%NH₄OH:30% H₂O₂:H₂O = x:1:5 at 80°C;
b) TMAH(tetramethylammonium hydroxide)-H₂O₂- H₂O solution: 2.38% or 20% TMAH:30% H₂O₂: H₂O = x:y:z at 80°C;
c) H₂SO₄-H₂O solution: 97%H₂SO₄:30%H₂O₂ = 4:1 at around 120°C;
d) HCl-H₂O₂-H₂O solution: 36%HCl:30%H₂O₂:H₂O = 1:1:6 at 80-90°C;
e) HF-H₂O₂-H₂O solution [12], [13]: 50%HF:30% H₂O₂:H₂O = 1:33:66 at 25°C;
f) H₂O₂-H₂O solution: 30%H₂O₂:H₂O = 1:5 at 80°C.

In the H₂SO₄-H₂O₂ solution, the wafers are immersed for five min. In all other solutions, the wafers are immersed for ten min. Following the chemical cleaning, the wafers are rinsed with ultrapure water for ten minutes. In order to avoid particle contamination during the drying process of the wafers, the native oxide formed during the chemical cleaning is removed in a 0.5% HF solution. After removing the native oxide, the wafers are again rinsed with ultrapure water for ten min. Cleaning effect is evaluated by particle removal efficiency. The particle removal efficiency is evaluated by calculating the ratio of the particle counts before and after cleaning.

Particle counts on all wafers are evaluated using an Aerona WIS-100 wafer inspection system. The WIS-100 classifies detect size as particles (>0.5 µm) and haze (<0.5 µm). Before the experiments, the WIS-100 is calibrated with a relative standard wafer. Initial particle counts, before the experiments, are less than 50 per wafer.

The above experimental procedure is manually performed at a wet station. As for the material of construction of the bath, the HF cleaning and the ultrapure water rinsing use PFA baths while the other chemical cleanings use quartz baths. PFA carriers are used for immersing the wafers into the bath and transporting them from one bath to another. Chemicals used in these tests are all of ULSI-grade and low particle concentration.

III. RESULTS AND DISCUSSION
A. Solution pH

Fig. 1 shows the relationship between the solution pH and the number of particles adsorbed on the wafer surfaces. 10% vol. of city water is added to each test solution. The solution pH is adjusted by HCl with H₂O₂ or H₂SO₄ in acidic solutions, and it is adjusted by NH₄OH with H₂O₂ or TMAH with H₂O₂ in alkaline solutions. Maximum particle adsorption is observed in the low pH solutions, and the number of adsorbed particles is reduced with the increase of solution pH. Fig. 2 also shows the well known effect of pH on the zeta potential of a Fe₂O₃ particle [6]. It can be seen that the Figs. 1 and 2 curves match almost exactly. It has been reported that the number of adsorbed SiO₂ spheres or polystyrene latex spheres on the wafer surfaces is reduced with the increase of solution pH as shown in Fig. 1 [9]-[11].

Generally, the zeta potential of most particles is considered to be negative in alkaline solutions. In particular, the zeta potential of metal oxide particles is positive in acidic solutions and negative in alkaline solutions in accordance with the following equations from colloid chemistry [14], [15].

Low pH: \[ M - OH + H^+ \rightarrow M - OH_2^+ + OH^- \]

High pH: \[ M - OH + H^+ + OH^- \rightarrow M - OH^- + H^- + OH^- \]

In addition, it is reported that both hydrophilic (covered with oxide film) and hydrophobic (bare silicon surface) wafers exhibit a negative surface charge in water [4], [5].

Relating these observations to the results shown in Fig. 1, it is believed that both the wafer surfaces and the zeta potential of particles exhibit a negative charge in alkaline solutions. As a result, the wafer surface and particles are presumed to be electrically repulsive in alkaline solutions. This indicates that alkaline solutions are beneficial for removing particles from the wafer surfaces.

B. Wafer Cleaning by Alkaline Solutions

The RCA cleaning method [2], which is one of the major wet silicon wafer cleaning methods, employs a
NH₂OH-H₂O₂-H₂O solution as the alkaline solution. The NH₂OH-H₂O₂-H₂O solution usually employs the mixing ratio of 1:1:5 (NH₂OH:H₂O₂:H₂O). Fig. 3 shows the relationship between the various NH₂OH contents in NH₂OH-H₂O₂-H₂O solution and the solution pH. As shown in Fig. 3, the pH value of the 1:1:5 solution is 9.9 at 80°C. However, the results shown in Figs. 1 and 2 indicate that the NH₂OH content in NH₂OH-H₂O₂-H₂O solution can be reduced if it is to be used exclusively for particle removal.

Fig. 4 shows the relationship between the pH value of the cleaning solutions and their particle removal efficiency when the NH₂OH content in NH₂OH-H₂O₂-H₂O solution is varied as follows: 0.001:1:5, 0.01:1:5, 0.05:1:5, 0.1:1:5, 0.25:1:5, 0.5:1:5, and 1:1:5. In this experiment, five in. CZ (1,0,0) wafers are used. Fig. 5 shows the results of the same experiment as Fig. 4, except that it uses four inch FZ (1,0,0) wafers. Fig. 6 shows the relationship between the pH value of the cleaning solutions and their particle removal efficiency when the TMAH-H₂O₂-H₂O solution is used instead of the NH₂OH-H₂O₂-H₂O solution. The TMAH content in TMAH-H₂O₂-H₂O solution is varied as follows: 0.1:1:5, 1:1:5, 4:1:0, 9:1:0 (using 2.38% TMAH), and 2:1:4, 4:1:2 (using 20% TMAH). Five inch CZ (1,0,0) wafers are used in this experiment.

Before the cleaning experiments, each wafer is contaminated with city water particles, SiO₂ spheres, polystyrene latex spheres, and ambient atmosphere particles. As for the cleaning, the following sequence is employed:

a) Immersion into NH₂OH-H₂O₂-H₂O solution or TMAH-H₂O₂-H₂O solution for 10 min at 80°C;
b) Ultrapure water rinsing for 5 min at 25°C;
c) Immersion into hot ultrapure water for 10 min at 80-90°C;
d) Ultrapure water rinsing for 10 min at 25°C;
e) Immersion into 0.5% HF solution for 1 min at 25°C;
f) Ultrapure water rinsing for 10 min at 25°C.

As can be seen in Figs. 4-6, the particle removal efficiency goes up in most cases as the pH value of the cleaning solution increases. However, the particle removal efficiency of polystyrene latex spheres and ambient atmosphere particles is not improved even when the pH value increases. These two cases will be discussed later. The experimental results shown in Figs. 4-6 indicate that the electrical repulsion generated between the wafer sur-
faces and particles in alkaline solutions is by itself not sufficiently effective to remove the particles adsorbed on the wafer surfaces.

Fig. 7 illustrates the etch rate on the wafer surfaces using the NH₄OH solution and the TMAH solution. Fig. 7 also illustrates the etch rate on the wafer surfaces using the NH₄OH-H₂O₂-H₂O solution and the TMAH-H₂O₂-H₂O solution. To determine the etch rate, half of the wafer surface is masked with an oxide film and then the wafers are immersed in the alkaline solutions at 80°C. After removing the oxide film, the step on the wafer surfaces generated by etching is measured with a Dectak 3030ST Surface Analyzing System to determine the etch rate. The etch rate on the wafer surfaces is considerably lowered when H₂O₂ is added. However, it is true that the wafer surfaces are etched even in the solutions with H₂O₂ added. The etch rate goes up whether or not H₂O₂ is added as the pH value increases.

Figs. 8-11 show the particle removal efficiency as a function of the etch rate when each wafer is contaminated with city water particles, SiO₂ spheres, polystyrene latex spheres, and ambient atmosphere particles. These figures are obtained from Figs. 4-6 in which the pH value is converted to the etch rate by the data shown in Fig. 7. The particle removal efficiency shows a rapid increase up to an etch rate of 0.25 nm/min. When the etch rate reaches 0.25 nm/min, the particle removal efficiency levels off. In order to remove particles adsorbed on the wafer surfaces by means of the alkaline solutions, the etching of the wafer surfaces is necessary in addition to the electrical repulsion effect described before. An etch rate of 0.25 nm/min is required to efficiently remove particles when the wafers are cleaned by the alkaline solutions for ten minutes. It is therefore possible to reduce the content of NH₄OH or TMAH until the etch rate on the wafer surface reaches 0.25 nm/min. When the mixing ratio of NH₄OH-H₂O₂-H₂O solution is 0.05:1:5, the etch rate of both CZ and FZ wafers reaches 0.3 nm/min. On the other hand, when the mixing ratio of TMAH-H₂O₂-H₂O solution is 9:1:0 (2.38 wt. % TMAH: H₂O₂: H₂O), the etch rate of the CZ wafer reaches 0.28 nm/min.

C. Particle Removal Mechanism

Table I shows the particle removal efficiency when acid solutions are used. Table II shows the particle removal efficiency when alkaline solutions of the NH₄OH-H₂O₂-H₂O solution and the TMAH-H₂O₂-H₂O solution are used. Among the acid solutions, the H₂SO₄-H₂O₂ solution exhibits very high particle removal efficiency. It is expected that the H₂SO₄-H₂O₂ solution oxidizes and decomposes the particles absorbed on the wafer surfaces due to its strong oxidizing force. In addition, the number of particles adsorbed on the wafer surfaces is limited in the H₂SO₄ solution as shown in Figs. 1 and 2. The H₂SO₄-H₂O₂ solution is believed to have a high particle removal efficiency because of the strong oxidizing force as well as the electrical state between the wafer surfaces and particles.
On the other hand, the particle removal efficiency of HF-H₂O₂-H₂O solution is low, even though the etch rate is very high at 0.42 nm/min as shown in Table I. This indicates that etching the wafer surface is by itself not an effective particle removal technique.

As shown in Table II, the alkaline solutions exhibit high particle removal efficiency for all of the examined methods. This is due to the electrical repulsion effect which is generated between the wafer surfaces and particles in the alkaline solutions as shown in Figs. 1 and 2, as well as the etching effect of the wafer surfaces in the alkaline solutions as shown in Figs. 8–11.

Fig. 12 illustrates the mechanisms to remove the particles adsorbed on the wafer surfaces. In the solutions with an extremely strong oxidizing force (such as the H₂SO₄-H₂O₂ solution), the particles adsorbed on the wafer surfaces are oxidized, decomposed, and dissolved into the solutions. On the other hand, in the alkaline solutions (such as the NH₄OH-H₂O₂-H₂O solution), the particles adsorbed on the wafer surfaces are lifted off when the surfaces are etched and then dislodged from the wafer surfaces by electrical repulsion. Alkaline solutions require both the etching of the wafer surfaces and the electrical repulsion to remove the particles. It is observed from Tables I and II that the alkaline solutions are superior to the acid solutions in terms of particle removal efficiency.

D. Surface Micro-Roughness

Fig. 13 shows the change of the surface micro-roughness on CZ and FZ wafers when the NH₄OH content in NH₄OH-H₂O₂-H₂O solution is varied. The surface micro-roughness is evaluated with a scanning tunneling microscope (STM). As shown in Fig. 13, the surface micro-roughness on the CZ wafers is degraded when the NH₄OH content in NH₄OH-H₂O₂-H₂O solution is set above 0.1:1:5. This correlates well with the change of the etch rate of the wafer surfaces when the wafers are immersed into the NH₄OH-H₂O₂-H₂O solution. On the other hand, the surface micro-roughness on the FZ wafers is not degraded. The reason for this lack of degradation is not precisely known.

It has been demonstrated that the micro-roughness on the wafer surfaces greatly affects the electrical characteristics of the thin oxide film which is formed on it [11], [16], [17]. Therefore, the NH₄OH-H₂O₂-H₂O solution to be used for particle removal should adopt a mixing ratio which does not degrade the micro-roughness of the wafer surfaces. As shown in Figs. 8–11, the particle removal efficiency levels off when the etch rate exceeds 0.25 nm/min. Therefore, the mixing ratio of NH₄OH-H₂O₂-H₂O solution which exhibits the etch rate close to 0.25 nm/min is NH₄OH-H₂O₂-H₂O = 0.05:1:5. As shown in Fig. 13, the water surfaces is not degraded with this mixing ratio. In order to obtain both sufficient surface smoothness and sufficient particle removal efficiency, the NH₄OH content in NH₄OH-H₂O₂-H₂O solution should be reduced from the conventional level of 1:1:5-0.05:1:5.
E. Haze Increase in Hot Ultrapure Water Bath

Fig. 14 shows the particle removal efficiency as a function of cleaning solution pH. The wafers are contaminated with city water particles, SiO₂ spheres, polystyrene latex spheres, and ambient atmosphere particles. In this figure, the following cleaning sequence is employed:

a) Immersion into NH₄OH-H₂O₂-H₂O solution for 10 min at 80°C;

b) 

c) 

d) 

Fig. 8. The particle removal efficiency as a function of the etch rate when the wafers are contaminated with city water particles. NH₄OH-H₂O₂-H₂O solution and TMAH-H₂O₂-H₂O solution are used for cleaning.

Fig. 9. The particle removal efficiency as a function of the etch rate when the wafers are contaminated with SiO₂ spheres. NH₄OH-H₂O₂-H₂O solution and TMAH-H₂O₂-H₂O solution are used for cleaning.

Fig. 10. The particle removal efficiency as a function of the etch rate when the wafers are contaminated with the polystyrene latex spheres. NH₄OH-H₂O₂-H₂O solution and TMAH-H₂O₂-H₂O solution are used for cleaning.

Fig. 11. The particle removal efficiency as a function of the etch rate when the wafers were contaminated with ambient atmosphere particles (Enviro-Air). NH₄OH-H₂O₂-H₂O solution and TMAH-H₂O₂-H₂O solution are used for cleaning.
Particle on Water

In Alkaline Solution

Fig. 12. The mechanism of particle removal from the wafer surfaces.

Fig. 13. Relationship between the surface micro-roughness (Ra) on CZ wafers and the ratio of NH₄OH-H₂O₂-H₂O solution. Surface micro-roughness (Ra/10 min) is measured after 10 minutes immersion in the solution.

b) Immersion into hot ultrapure water for 10 min at 80-90°C;
c) Ultrapure water rinsing for 10 min at 25°C;
d) Immersion into 0.5% HF solution for 1 min at 25°C;
e) Ultrapure water rinsing for 10 min at 25°C.

Comparing with the cleaning sequence shown in the Fig. 4, the ultrapure water rinsing at 25°C between the NH₄OH-H₂O₂-H₂O cleaning and the hot ultrapure water cleaning is neglected. The particle removal efficiency is reduced as the pH value in the cleaning solution increases.

Mishima et al. have reported that the particle removal efficiency of the NH₄OH-H₂O₂-H₂O solution is reduced as the NH₄OH content in this cleaning solution increases [3]. This is because the wafer surfaces are roughened by the high pH NH₄OH-H₂O₂-H₂O solution and this roughness is reported as a haze.

Table III shows the pH value and the etch rate of the wafer surfaces in the NH₄OH-H₂O₂-H₂O solution bath and in the following hot ultrapure water bath when the above cleaning sequence is employed. In this experiment, PFA carriers are used when the wafers are immersed to the bath and transported from a bath to another. The reason the hot ultrapure water in the bath turned alkaline is that the NH₄OH solution is carried over to the hot ultrapure water bath from the NH₄OH-H₂O₂-H₂O bath by means of the wafers and the PFA carriers. As shown in Table III, the etch rate on the wafer surfaces in the hot ultrapure water bath is higher than that in the NH₄OH-H₂O₂-H₂O bath. This means the wafer surfaces become rougher more seriously in the hot ultrapure bath. The WIS-100 detects this roughness as a haze, so that the particle removal efficiency is degraded as the pH value increases when the above cleaning sequence is adopted. These results indicate that the particle removal efficiency is improved by the introduction of cold ultrapure water rinsing at 25°C between the NH₄OH-H₂O₂-H₂O cleaning and the hot ultrapure water cleaning.

The particle removal efficiency of polystyrene latex spheres and ambient atmosphere particles shows the greater drop than that of city water and SiO₂ spheres when the above cleaning sequence is adopted.
TABLE III
THE pH VALUE AND THE ETCH RATE AT 80°C ON CZ WAFERS IN NH₄OH-
H₂O₂-H₂O BATH AND THE FOLLOWING HOT ULTRAPURE WATER BATH

<table>
<thead>
<tr>
<th>Rate</th>
<th>NH₄OH Bath</th>
<th>H₂O₂ Bath</th>
<th>Hot U.P.W Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>H</td>
<td>EtchRate (mm/min)</td>
</tr>
<tr>
<td>1:1:5</td>
<td>9.9</td>
<td>0.82</td>
<td>9.0</td>
</tr>
<tr>
<td>0.25:1:5</td>
<td>9.2</td>
<td>0.64</td>
<td>8.5</td>
</tr>
<tr>
<td>0.075:1:5</td>
<td>8.9</td>
<td>0.35</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Fig. 15. Influence of solution pH on the shape of 1.0 μm SiO₂ spheres by oxidation.

Fig. 16. Influence of solution pH on the shape of 1.866 μm polystyrene latex spheres by oxidation.

**F. Oxidation of Polystyrene Latex Spheres**

Fig. 15 shows the shapes of the SiO₂ spheres in each solution. In this experiment, the SiO₂ spheres of 1.0 μm in diameter are added to each solution at 80°C and then the solution is dropped onto the wafer surfaces after 10 minutes has passed. The pictures are taken after the droplet has dried. The inorganic particles of SiO₂ spheres maintain their original shape in each solution as shown in Fig. 15. Further the particle removal efficiency of Fig. 14 is similar to that of Fig. 4.

Fig. 16 shows the shapes of polystyrene latex spheres in each solution. The polystyrene latex spheres with a diameter of 1.866 μm are used in this experiment. When the pH value in the NH₄OH-H₂O₂-H₂O solution exceeds 9.3 (NH₄OH: H₂O₂: H₂O = 0.25: 1: 5), the organic particles of polystyrene latex spheres are oxidized and their surfaces turn into a gel, as shown in Fig. 16, resulting in the change of their shape.

It is believed that the polystyrene latex spheres adsorbed on the wafer surfaces are also oxidized during the NH₄OH-H₂O₂-H₂O cleaning. The decline of particle removal efficiency shown in Fig. 14 takes place when the pH value in the cleaning solution exceeds the specific level at which the shape of polystyrene latex spheres starts to be distorted. It is therefore possible that the shape and the surface condition of the particles have some effect on the capability of the solutions to remove those particles.

On the other hand, the particle removal efficiency of polystyrene latex spheres shown in Fig. 4, which includes the cold ultrapure water rinsing at 25°C between the NH₄OH-H₂O₂-H₂O cleaning and the hot ultrapure water cleaning, shows no degradation—even when the pH value exceeds 9.3. The reason for this lack of degradation is not clear. We suspect that the cold ultrapure water rinsing at 25°C following the NH₄OH-H₂O₂-H₂O cleaning has some effect on the capability to remove those oxidized particles.

However, whenever the pH value exceeds 11.1 using TMAH-H₂O₂-H₂O solution which includes the cold ultrapure water rinsing at 25°C following the TMAH-H₂O₂-H₂O solution shown in Fig. 6, the polystyrene latex spheres cannot be completely removed. Since the oxidizing power of H₂O₂ is enhanced as the pH value increases [18], we suspect that a great degree of oxidation of polystyrene latex spheres is caused by the higher pH of the TMAH-H₂O₂-H₂O solution.

**G. Ambient Atmosphere Particles Outside of the Cleanroom**

Fig. 17 shows the pictures of particles adsorbed on the wafer surfaces from ambient atmosphere particles outside of the cleanroom. These particles feature various shapes since they are existing in the natural environment. In addition, they are composed of various constituents including inorganic and organic materials.

Fig. 4 presents the experimental result when the NH₄OH-H₂O₂-H₂O cleaning is applied to the particles shown in Fig. 17. As shown in Fig. 4, the particle removal efficiency varies to a great degree when the pH value of the cleaning solution exceeds 9.1. Based on the findings concerning the polystyrene latex spheres, it is postulated that the surface of the organic particles turns to a gel and their shape becomes distorted. Fig. 17 also shows pictures of the particles which remain on the wafer surfaces after the cleaning process. Most of the residual particles feature the distorted shapes. Some residual particles have experienced surface oxidation and have changed to a gel. Therefore, the mixing ratio of 0.05:1:5 (NH₄OH: H₂O₂: H₂O), which keeps the pH level below
Fig. 17. The adsorbed particles from ambient atmosphere outside of the cleanroom and their shape after high pH alkaline solution cleaning (NH₄OH·H₂O₂·H₂O = 1:1:5).

9. is preferable for removing the particles in actual manufacturing conditions.

IV. CONCLUSIONS

1) The mechanism for removing particles adsorbed on the wafer surfaces with the alkaline chemical plus H₂O₂ solution has been explained. The particles adsorbed on the wafer surfaces are first lifted off when the wafer surfaces are etched. These particles are then electrically repelled from the surfaces by the alkaline solution.

2) It has been demonstrated in the experiments that the etch rate required for the alkaline chemical plus H₂O₂ solution to remove the particles adsorbed on the wafer surfaces is more than 0.25 nm/min for both the CZ and FZ wafers. The etch rate of both the CZ and FZ wafers becomes 0.3 nm/min when the mixing ratio of NH₄OH·H₂O₂·H₂O solution is set at 0.05:1:5. This means the NH₄OH content in NH₄OH·H₂O₂·H₂O solution can be reduced to 1/20 of the conventional level of 1:1:5.

3) The experiments have revealed that the surface micro-roughness of CZ wafer is degraded when the NH₄OH content in NH₄OH·H₂O₂·H₂O solution is set above 0.1:1:5. On the other hand, the surface micro-roughness of FZ wafer is not degraded. The reason for the absence of degradation of the FZ wafer is unknown. However, when the mixing ratio of NH₄OH·H₂O₂·H₂O solution is set at 0.05:1:5, this degradation of the CZ wafer is not detected. It has therefore been determined that the mixing ratio of 0.05:1:5 is effective in maintaining both surface smoothness of the wafer and particle removal efficiency.

4) It has been confirmed that the CZ wafer surfaces become rough more seriously in the hot ultrapure water bath just after the NH₄OH·H₂O₂·H₂O cleaning, resulting in the increase of haze and the degradation of the particle removal efficiency. However, this degradation of the CZ wafer surfaces has been reduced by the introduction of the cold ultrapure water rinsing between the NH₄OH·H₂O₂·H₂O cleaning and the hot ultrapure water cleaning.

5) It has been revealed that the particle removal efficiency of polystyrene latex spheres adsorbed on the wafer surfaces becomes degraded because the spheres are oxidized in the alkaline chemical plus H₂O₂ solution. When the mixing ratio of the NH₄OH·H₂O₂·H₂O solution is set above 0.25:1:5 (pH: higher than 9.3), the surface of polystyrene latex spheres turns to a gel and their shape becomes distorted. The particle removal efficiency is reduced or levels off as this phenomenon proceeds. However, the artificial polystyrene latex spheres can be completely removed when the cold ultrapure water rinsing at 25°C is adopted between the NH₄OH·H₂O₂·H₂O cleaning and the hot ultrapure water cleaning.

6) The particle removal efficiency of ambient atmosphere particles adsorbed on the wafer surfaces becomes variable when the pH level of the alkaline chemical plus H₂O₂ increases. This phenomenon takes place when the mixing ratio of the NH₄OH·H₂O₂·H₂O solution is set above 0.1:1:5 (pH: higher than 9.1). Based on the findings concerning the polystyrene latex spheres, it is postulated that the surface of the organic materials turns to a gel and their shape becomes distorted. However, the particles in the natural environment cannot be fully removed by the simple modification of the rinsing process.

7) The above experimental results suggest that the mixing ratio of the NH₄OH·H₂O₂·H₂O solution employed in RCA cleaning process to remove particles should be set at 0.05:1:5 (NH₄OH·H₂O₂·H₂O). Furthermore, it is essential to introduce the cold ultrapure rinsing between the NH₄OH·H₂O₂·H₂O cleaning and the hot ultrapure water cleaning in order to obtain both sufficient particle removal efficiency and sufficient surface smoothness.

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