

Evaluation of particle removal efficiency of filters in high temperature sulfuric acid using 30 nm liquid particle counter - Tomoyuki Takakura

Shuichi Tsuzuki

tomoyuki_takakura@ap.pall.com / shuichi_tsuzuki@ap.pall.com

Nihon Pall Ltd.

46, Kasuminosato, Ami-machi, Inashiki-gun, Ibaraki 300-0315 Japan

Phone: +81-80-1274-0578 Fax: +81-29-889-1957

Keywords: filtration, particle removal efficiency, liquid particle counter, sulfuric acid

INTRODUCTION

Since the scale of semiconductor devices are continuously reducing, the control level of size and numbers of particles are also becoming stricter during the manufacturing process; the role of filtration is of great importance for the control of particle level. Thus, it is a critical issue to use an appropriate filter in each process tool. A criterion for selecting an appropriate filter is the removal rating, which claims the size of particles to be removed by the filter. The rating of the filters used for semiconductor device manufacturing is performed in the deionized water (DIW) at ambient temperature [1]. In the actual manufacturing process, however, the filters are used in various chemical and temperature, and in such condition, it is empirically known that removal efficiency of the filters differs from that in the standard atmosphere (i.e. DIW at ambient temperature). Thus, it is important to know the actual particle removal efficiency (PRE) in the actual chemical. In the semiconductor cleaning process, high temperature sulfuric acid is commonly-used chemical, and there are some studies on PRE evaluation of filters in the chemical: One is in 120 °C sulfuric acid using a liquid particle counter (LPC) which can detect 60 nm and larger particles [2], and another is in 150 °C sulfuric acid using a LPC which can detect 40 nm and larger [3]. However, the measurement ranges of these LPCs are coarser than the filter rating used for the leading-edge semiconductor processes (< 20 nm), and finer measurement range would be preferred. In this study, we conducted PRE evaluation of filters in high temperature sulfuric acid using a LPC with sensitivity of 30 nm which is the currently finest one available in the chemical, and discussed the effect of the measurement range difference on PRE. Also, an effect of flow rate on the PRE was studied.

EXPERIMENTAL

Test system

The chemical recirculation line described in Figure 1 was used as the test system. In this line, 96% sulfuric acid (electronic grade) was recirculated. The filtration temperature was set to 90 °C, because this is a typical condition in the single wafer cleaning system. The solution

in which the particles were dispersed (i.e. challenge solution) was added to the chemical bath using the metering pump. After that, the particles in the line were measured by the LPC through the sampling lines placed at the upstream and the downstream of the test filter. RION KS-19F, which has sensitivity of 30 nm was used as the LPC; two different measurement ranges, > 30 nm and > 40 nm were employed in this measurement. One LPC was utilized for both upstream and downstream measurements performing challenge test twice; the first for downstream and the second for upstream. For the challenge solution, alumina nanoparticle (Sigma-Aldrich, < 50 nm) was dispersed in DIW. As depicted in Figure 1, even though the sulfuric acid was recirculated, the filtration is effectively single pass due to the clean-up filter placed downstream of the test filter. A 12 nm-rating polytetrafluoroethylene (PTFE) membrane filter was employed as the clean-up filter throughout the tests. Finally, the particle removal efficiency of the test filter was calculated by the following expression:

$$PRE = 100 \times (Count_{up} - Count_{down}) / Count_{up}, \quad \dots (1)$$

where $Count_{up}$ is the particle count monitored at the upstream line of the test filter and $Count_{down}$ is the one at the downstream line.

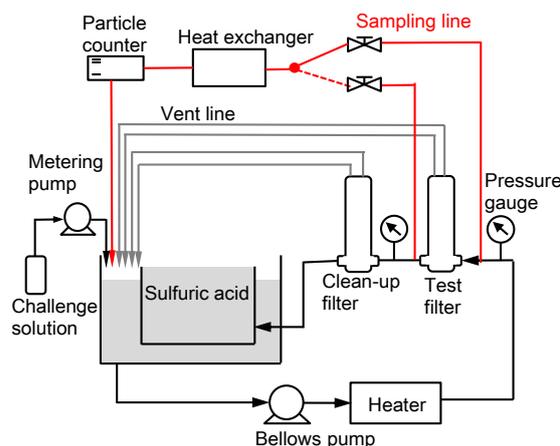


Figure 1. Test line for particle removal efficiency evaluation of filters in high temperature sulfuric acid.

Evaluation of the particle counter

In general, count of LPC is not proportional to the actual concentration of particles in the higher concentration due to coincidence loss of the LPC. In order to ensure that there is no coincidence loss in this test, we investigated the relation before the PRE evaluation. In this evaluation, the same configuration as Figure 1 was employed; a filter only for this evaluation was placed at the position of “Test filter”. The procedure was as follows: First, the particle count at the upstream line was continuously monitored on the system as Figure 1 and confirmed the background level of the count. Second, certain concentration of challenge solution was added to the line and the count was monitored, then the challenge was stopped. Third, after confirming the count is back to the background, other concentration of the solution was added to the line; this step was repeated several times. Finally, the actual concentration of the solution and the corresponding particle count was plotted for each concentration of the solution.

Evaluation of particle removal efficiency

After the preparation written above, PRE of five kinds of polytetrafluoroethylene (PTFE) membrane filters were evaluated in 90 °C 96% sulfuric acid. The PRE was calculated for two different measurement ranges, > 30 nm and > 40 nm. Table 1 summarizes the overall condition of this evaluation. First, one each of Filter A ~ E was evaluated at 10 L/min. For the Filter A, PRE in room temperature (RT) deionized water (DIW) at 15 L/min was also evaluated with the same procedure after the evaluation in 90 °C 96% sulfuric acid to investigate the effect of difference in chemical on PRE. Second, in order to investigate an effect of flow rate on PRE, another Filter A was evaluated at 15 L/min in 90 °C 96% sulfuric acid, then compared with the data at 10 L/min.

Table 1. Summary of the PRE evaluation condition.

| Item | Condition |
|----------------------|--|
| Test line | Chemical recirculation line |
| Fluid | 96% H ₂ SO ₄ |
| Temperature | 90 °C |
| Challenge particle | Alumina nanoparticle (Sigma-Aldrich, < 50 nm) |
| Particle measurement | Liquid particle counter (RION KS-19F, > 30 nm) |
| Test filter | Pall PTFE membrane filters (Filter A ~ E) |

RESULTS AND DISCUSSION

Evaluation of the particle counter

Figure 2 shows particle count data of the LPC for various concentrations of the challenge solution. Both > 30 nm- and > 40 nm-count are shown. In the lower particle concentration range, the particle count of the LPC linearly increases along with the actual concentration. In the higher concentration, however, the particle count gradually deviates from the linear relation. This tendency is more significant for finer range. Considering this result, the particle concentration less than 0.2 ppb was adopted for all the tests in this paper.

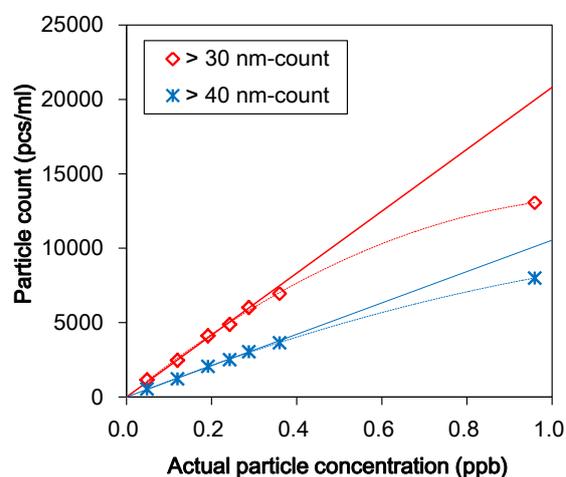


Figure 2. Relationship between the challenge concentration and the particle count. The particle counter is RION KS-19F; > 30 nm and > 40 nm-count are shown.

Evaluation of particle removal efficiency

Figure 3 shows the results of PREs in 90 °C 96% sulfuric acid measured at > 30 nm and > 40 nm ranges. At > 40 nm range, the PREs were 95 ~ 99%; the difference among each filter is not significant. In contrast, at > 30 nm range, the PREs decreased to 83 ~ 94%, and the difference among each filter is more significant. These results indicate that particle counter measurement at smaller size (i.e. > 30 nm) significantly improve our ability to detect the filters' PRE differences. Additionally, PRE for the Filter A in RT DIW shown in Figure 4 was greater than 99.5% for both measurement ranges. This result is reasonable because the removal rating of Filter A is 12 nm. But the method is not adequate for accurate evaluation of the 12 nm-rate filter in RT DIW in light of resolution. In contrast, the PRE deteriorates in 90 °C 96% sulfuric acid compared to the condition for the filter rating, thus the fine range (> 30 nm) of the LPC can evaluate the filter performance though the range is coarser than the filter rating. There are several possible causes for this deterioration. In liquid filtration system, PRE is affected by interactions among chemical, particles, and filter membrane. Temperature dependence of

expansion coefficient of the PTFE membrane may also affect the stability and structure of the membrane morphology. Further investigations will explore these possibilities and mitigation of the reduced PRE in high temperature sulfuric acid.

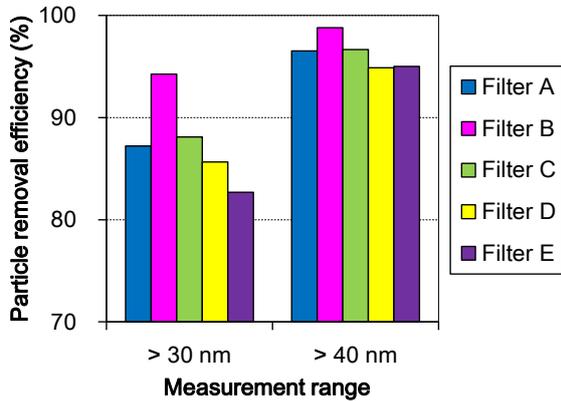


Figure 3. Results of PRE evaluation in 90 °C sulfuric acid using the LPC. PREs were calculated in two different measurement ranges (i.e. > 30 nm and > 40 nm) for each filter. One each of Filter A ~ E was evaluated. The flow rate was 10 L/min for all the filters in this figure.

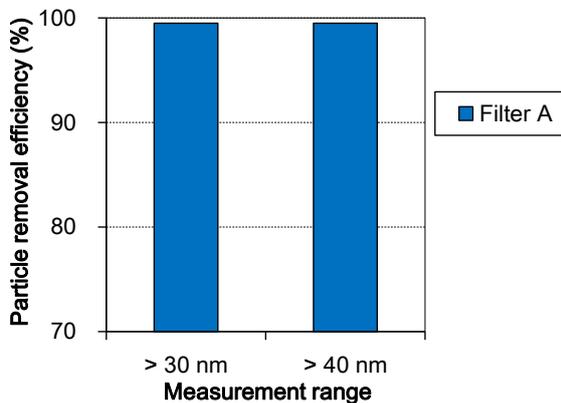


Figure 4. Results of PRE evaluation for the Filter A in RT DIW using the LPC. This test was performed after the test in Figure 3. PRE was calculated in two different measurement ranges (i.e. > 30 nm and > 40 nm). The filter showed > 99.5% in PRE for both measurement ranges. The flow rate was 15 L/min.

In order to see flow rate dependence of PRE in 90 °C sulfuric acid, results for two Filter A at 10 and 15 L/min respectively are shown in Figure 5. As shown in the figure, the PREs at 10 and 15 L/min are comparable. In general, if a filter has adsorption effect in its filtration mechanism, the PRE tends to become lower in higher filtration speed [4]. Thus, the results show that adsorption effect is not expected to be significant in this flow rate range.

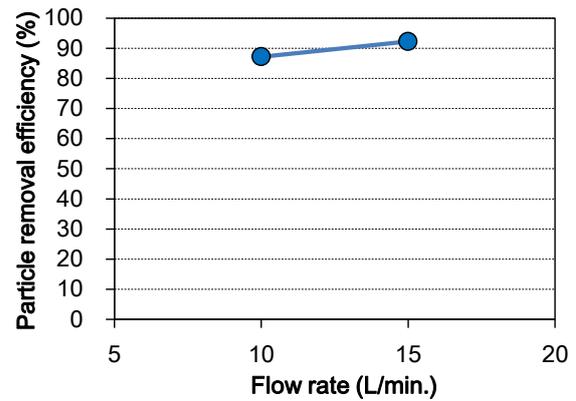


Figure 5. Results of PRE evaluation for two Filter A at 10 and 15 L/min in 90 °C sulfuric acid. The data at 10 L/min is excerpted from Figure 3.

Simulation on filtration performance on the actual cleaning tool

In the actual wafer cleaning system, a typical setup of a filter is like the configuration as Figure 6. In such system, the time dependence of number of particles in the tank is described as follows [5]:

$$C = C_i \times \exp(-QEt/V), \quad \dots (2)$$

where C is the particle level of the chemical tank, C_i is the initial particle level, V is the chemical volume in the line, Q is the flow rate of the line, E is the PRE of the filter, and t is the elapsed time from the initial state. Expression (2) indicates that the speed of particle removal depends not only on PRE but also on flow rate. Figure 7 is a simulation result of particle removal in the tank. In this simulation, PRE of 90% and flow rate of 10 and 15 L/min are employed as the experimental data in the 90 °C 96% sulfuric acid. Also, a result for 100% PRE at 10 L/min was added for comparison. The results show the higher flow rate condition has notably quicker particle rinse-up speed, and the effect is more significant than the difference of PRE in this range.

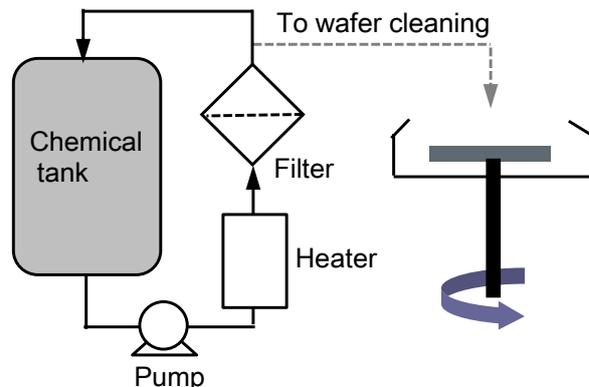


Figure 6. A sketch of the system employed for filtration of high temperature sulfuric acid in single wafer cleaning tool.

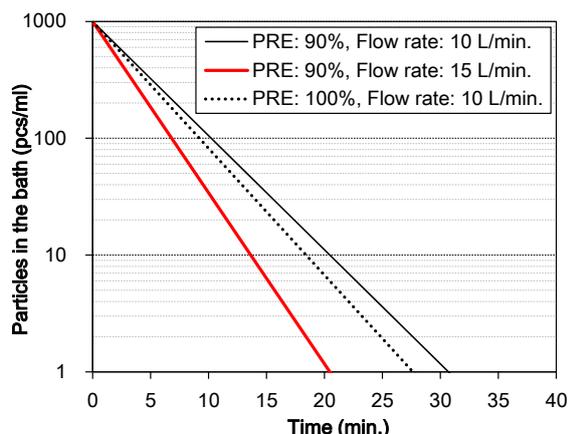


Figure 7. Simulation results of particle levels on the system described in Figure 6. The effect of PRE and flow rate difference on the particle rinse-up time is depicted. The expression (2) is used for the calculation. The following assumption is applied: $C_i = 1000$ pcs/mL, $V = 40$ L.

CONCLUSION

PRE evaluation of several kinds of PTFE membrane filters in 90 °C 96% sulfuric acid using a LPC with sensitivity of 30 nm were performed. In the chemical, the PREs of five PTFE filters were in the range of 95 ~ 99% for > 40 nm range and 83 ~ 94% for > 30 nm range at 10 L/min. Thus, it is indicated that the particle counter measurement at smaller particle size (i.e. > 30 nm) significantly improves ability to detect differences in filters' PRE. After the evaluation, PRE in RT DIW which is identical to the condition in filter rating was also evaluated for one filter (Filter A, removal rating: 12 nm), and the filter showed PRE of > 99.5% for both over 30 and 40 nm ranges. Based on this, the PRE is deteriorated in 90 °C 96% sulfuric acid compared to the condition for the filter rating. Also, the result that the PREs at 10 and 15 L/min in 90 °C 96% sulfuric acid were comparable each other indicates adsorption is not expected to be significant in the filtration condition. In such cases, it was simulated that filtration in higher flow rate notably improves the particle rinse-up speed in the actual wafer cleaning system.

REFERENCES

- [1] T. Mizuno *et al.*, IEEE transactions on semiconductor manufacturing Vol. 22, No. 4, 2009, pp.452-461.
- [2] T. Nagafuchi *et al.*, Solid State Phenomena Vols. 145-146, 2009, pp.69-72.
- [3] T. Takakura *et al.*, Proceedings of The 60th JSAP Spring Meeting, 2013, 28P-G8-14.
- [4] T. Umeda *et al.*, Proceedings of SPIE Vol. 9051 90511G, 2014.
- [5] M. Nose *et al.*, ISSM 2007, YE-P-070.