Changes in Particle Removal Efficiency of PTFE Membrane Filters in High Temperature Sulfuric Acid

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The scale of semiconductor devices is continuously shrinking. This increases the need to control both the size and number of particles present in the manufacturing process. Filtration is of great importance for controlling the particle level. One filter selection criterion is the removal rating, which claims the size of particles to be removed by the filter. The filter rating method used for semiconductor device manufacturing is typically performed in deionized water (DIW) at ambient temperature [1]. In the actual manufacturing process, however, the filters are used in a variety of chemicals and at various temperatures. In such cases, it is empirically known that removal efficiency of the filters differs from that in the standard DIW and ambient temperature test conditions. 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 a commonly used chemical, and there are some studies on PRE evaluation of filters in the chemical. Previous studies evaluated particles in high temperature sulfuric acid using liquid particle counters (LPCs) with measurement of particles in the > 40 and > 60 nm ranges [2, 3]. However, the measurement ranges of these LPCs are coarser than the filter rating used for the leading-edge semiconductor processes (< 20 nm). A finer measurement range would be preferred. In this study, an evaluation of PRE of filters in high temperature sulfuric acid using a LPC with sensitivity of 30 nm was conducted.

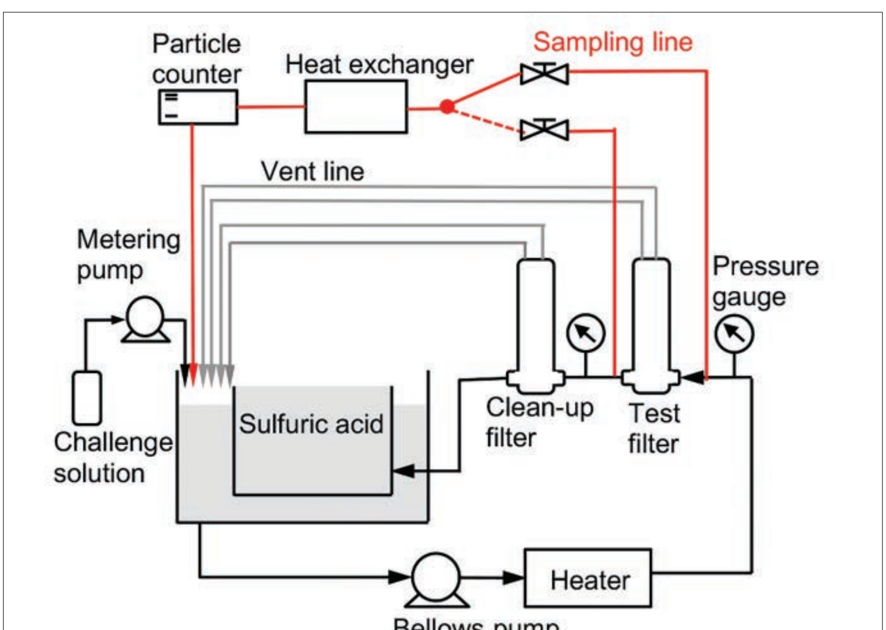

Figure 1. Test line for particle removal efficiency evaluation of filters in high temperature sulfuric acid.

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. For the challenge solution, alumina nanoparticles (Sigma-Aldrich*, < 50 nm) were dispersed in DIW and added to the chemical bath using a metering pump. 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. A 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 the challenge test twice. The first was for downstream and the second for upstream. As depicted in Figure 1, the sulfuric acid was recirculated, but single pass was substantively realized for the challenge particle due to the cleanup filter set at the downstream side of the

Item	Condition
Test line	Chemical recirculation line
Fluid	96% H_2SO_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)

Table 1. Summary of the PRE evaluation conditions

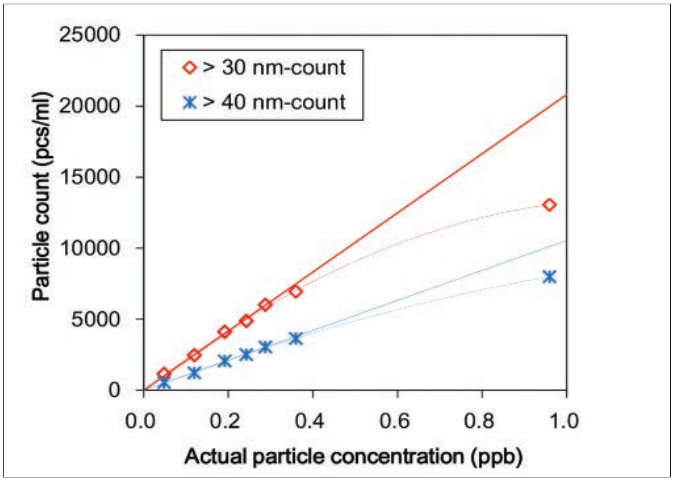

Figure 2. The relationship between the challenge concentration and the particle count. The particle counter is RION KS-19F; > 30 nm and > 40 nm-count are shown.

test filter. Finally, the particle removal efficiency of the test filter was calculated by the following expression:

PRE = 100 × ($Count_{up}$ - $Count_{down}$) / $Count_{up}$, … (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.

Evaluation of particle removal efficiency

After the initial preparation noted, five different 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.

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 the finer range. Considering this result, the particle concentration of less than 0.2 ppb was adopted for all the tests in this study.

Evaluation of particle removal efficiency

Figure 3. 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 the finer measurement range (i.e., > 30 nm) significantly improves the resolution of the measurement. Additionally, PRE for the Filter A in RT DIW shown in Figure 4 was greater

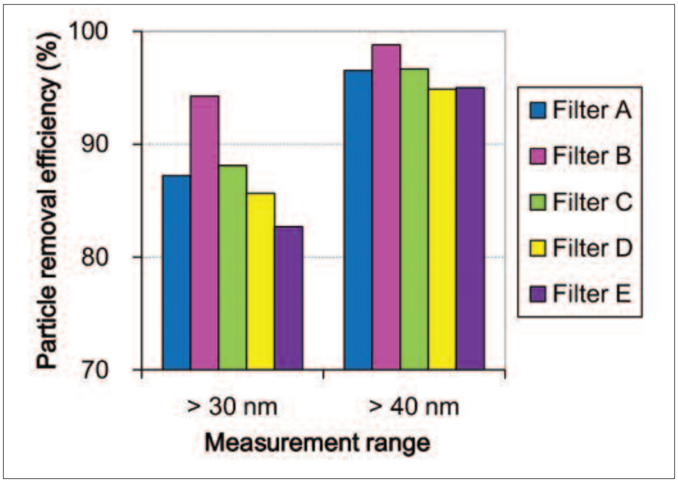

Figure 3. The results of PRE evaluation in 90 °C sulfuric acid using the LPC. PREs were calculated in two different measurement ranges (i.e., > 30 nm and > 40 nm) for each filter. One each of Filter A ~ E was evaluated. The flow rate was 10 L/min for all the filters in this figure.

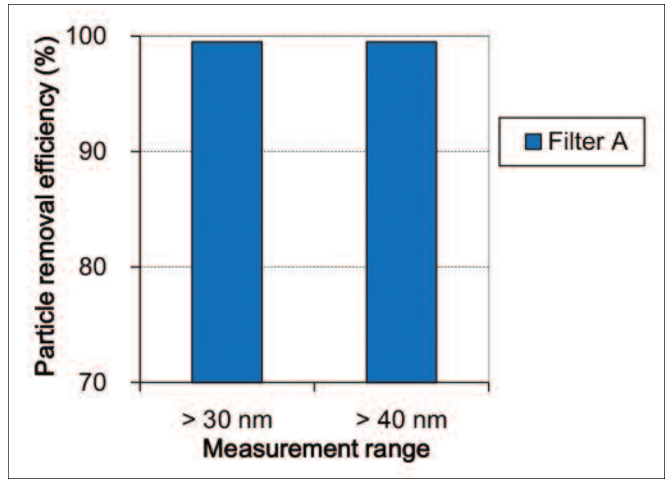

Figure 4. The results of PRE evaluation for the Filter A in RT DIW using the LPC. This test was performed after the test in Figure 3. PRE was calculated in two different measurement ranges (i.e., > 30 nm and > 40 nm). The filter showed > 99.5% in PRE for both measurement ranges. The flow rate was 15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

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 standard condition for the filter rating. The fine range (> 30 nm) of the LPC can evaluate the filter performance even 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 the filter membrane. Temperature dependence of the 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.

CONCLUSION

PRE evaluation of several kinds of PTFE membrane filters in 90 °C, 96% sulfuric acid using a LPC with sensitivity of 30 nm was 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 finer measurement range (i.e., > 30 nm) significantly improves the resolution of the measurement and highlights the performance differences of each filter. After the evaluation, PRE in standard test conditions of RT DIW was conducted for one filter (Filter A, removal rating: 12 nm). The filter showed PRE of > 99.5% for both > 30 and > 40 nm ranges. Based on this, the PRE decrease in 90 °C, 96% sulfuric acid was demonstrated. The effects of different flow rates on retention and on bath clean up speed were also conducted. Results can be found in the complete study listed below [4].

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