Particle reduction in high temperature sulfuric acid using PTFE membrane filter and low pulsation bellows pump

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***Abstract* — In order to reduce particles in the chemicals used for the semiconductor wafer cleaning processes, it is important to remove generated particles by filtration technology as well as to reduce particle generation from each part of the cleaning tool. We applied a newly developed bellows pump with low pulsation to 90 °C sulfuric acid, and evaluated the effect of the pulsation on the particle level downstream of the pump and particle removal efficiency of 5 nm-rated PTFE membrane filters in the chemical. Pressure pulsation behavior was compared between a conventional bellows pump and the low pulsation pump, and it was confirmed that the low pulsation pump effectively reduced the peak-to-peak value of pressure fluctuation. In addition, the particle level downstream of the pump drastically decreased for the low pulsation pump compared to the conventional pump. On the other hand, the results of particle challenge tests indicated that the filters' particle removal efficiency was unchanged regardless of the pump used. As a result, the particle level downstream of the filter when using the low pulsation pump became lower compared to that using the conventional pump. In conclusion, the low pulsation pump and the 5 nm-rated PTFE membrane filter are a good combination to effectively reduce particles in 90 °C sulfuric acid.**

Keywords* — *filter, particle removal efficiency, bellows pump, pulsation, sulfuric acid

I. INTRODUCTION

Reducing particles in chemicals used in the semiconductor manufacturing processes is important for improving yield of the semiconductor devices. As the feature size of the semiconductor devices decreases, control level of contaminant in the chemicals is becoming increasingly stringent. In order to reduce particles, it is critical to prevent particles from being generated at various parts (e.g., valves, tubes, pumps, etc.) and to effectively remove particles generated in the line by filters. Bellows pumps are commonly used in cleaning tools, and it is possible for them to generate particles due to their pressure pulsation. In addition, it is reported that the performance of filters is affected by pulsation of the pump used [1]. For these reasons, Nippon Pillar has developed a new bellows pump which reduces pulsation. In this work, in order to reduce particles in a chemical in a cleaning tool, we evaluated the newly developed bellows pump with low pulsation to examine how pulsation affects particle generation and the filter's particle removal efficiency (PRE). High temperature sulfuric acid, which is a commonly used chemical in semiconductor manufacturing, was adopted for this evaluation, since its high viscosity would enhance the effect of pulsation on particle generation and filter performance.

II. EXPERIMENTAL

A. *Measurement of pump pulsation, and the particle count downstream of the pump*

All the evaluation was performed using a chemical recirculation system shown in Fig. 1. Electronic grade 96% sulfuric acid was recirculated at 90 °C in this line.

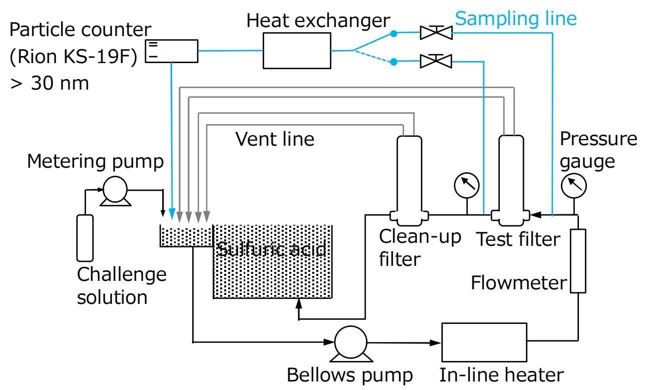

Fig. 1. Schematic of chemical recirculation system used for evaluation of filters and bellows pumps in 90 °C sulfuric acid.

Two bellows pumps were evaluated: A conventional (i.e. normal pulsation) bellows pump (PE-40HBH, Nippon Pillar) and a low pulsation bellows pump (PRS-50M, Nippon Pillar). In the conventional bellows pump, two bellows (left and right) are interconnected, and thus discharge of fluid is performed by each bellows alternately. The low pulsation bellows pump, on the other hand, controls two bellows individually; this system makes it possible to overlap discharges of fluid by the left and right bellows. As a result, pulsation by each discharge can cancel each other, resulting in low pulsation. Fig. 2 shows an example of pulsation of conventional and newly developed pump in water. The low pulsation pump can drastically reduce peak-to-peak value of pulsation.

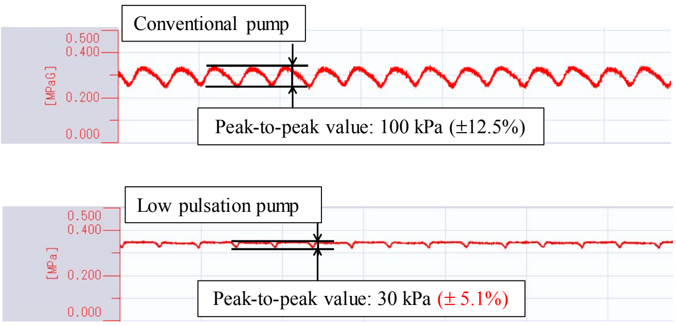

Fig. 2. An example of pulsation of a conventional and a newly developed pump in water. The pressure for discharge is around 0.3 MPa for each data.

Pressure fluctuation with time (pulsation) of each pump was measured by a pressure gauge (HPS-1/2-N, Surpass Industry Co., Ltd.) downstream of each pump in flow rate of 10 L/min. and 16 L/min. Pressure data under each condition was recorded every 100 msec. At the same time, the particle level downstream of the pumps was monitored by a liquid particle counter (LPC) with a sensitivity of 30 nm (KS-19F, RION) via the two sampling lines upstream and downstream of a test filter. A 5 nm-rated polytetrafluoroethylene (PTFE) membrane filter (XpressKleen^{TM} G2 KC filter, Pall) was used as the test filter.

B. *PRE of filter*

In the previous section, we described a procedure for particle counts upstream and downstream of the test filter. Applying these counts to the following expression, we may obtain the PRE of the test filter:

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

where $Count_{up}$ is the particle count monitored upstream line of the test filter and $Count_{down}$ is the one downstream line. However, the PRE calculated in this way is just a rough estimation and not necessarily accurate for the following reason: The number of particles in the actual chemical is generally low, and thus the particle count downstream of the filter is within the noise level of the LPC. When using LPCs, which utilize light scattering method, under these conditions, bubbles cannot be distinguished from actual particles, thereby affecting the LPC's particle count. Therefore, we decided to evaluate PRE of the filters using the two kinds of pumps by means of particle challenge test which intentionally causes test particles to flow into filters.

The two Pall 5 nm-rated PTFE filters after the evaluation written above were used as the test filters. In the previous studies, we have reported a PRE evaluation method in high temperature sulfuric acid [2, 3]. The same method was applied to evaluate the two filters used under the two bellows pumps as follows.

In the test system in Fig. 1, 90 °C sulfuric acid was recirculated at a flow rate of 16 L/min. As the test particle, alumina nanoparticle (Sigma-Aldrich, < 50 nm) dispersed in deionized water (i.e. challenge suspension) was prepared. The challenge suspension was added to the chemical bath using a metering pump. After that, the particles in the line were measured by the LPC through the sampling lines placed upstream and downstream of the test filter. One LPC was utilized for both upstream and downstream measurements performing the challenge test twice; the first for downstream and the second for upstream. In this test method, even though the sulfuric acid is recirculated, filtration is regarded as single pass due to the clean-up filter placed downstream of the test filter. Eventually, PRE of the test filters was calculated by the expression (1).

Firstly, each test filter was evaluated using each pump. Secondly, in order to confirm the possibility that the individual difference of the filter influenced the test results, the filter used for the conventional pump was also tested using the low pulsation pump.

III. Results and Discussions

A. *Measurement of pump pulsation, and the particle count downstream of the pump*

Fig. 3 shows pressure fluctuation with time at the downstream of each bellows pump (upstream of each test filter) in 90 °C sulfuric acid at 10 L/min. and 16 L/min. Pulsation of the newly developed pump is clearly reduced compared to that of the conventional pump. Table I shows peak-to-peak values of pressure fluctuation based on the data in Fig. 3. Peak-to-peak values of the conventional pump increase as the flow rate increases, however, those of the low pulsation pump do not increase even if the flow rate increases. Thus, pulsation is effectively reduced with higher flow rate for the low pulsation pump.

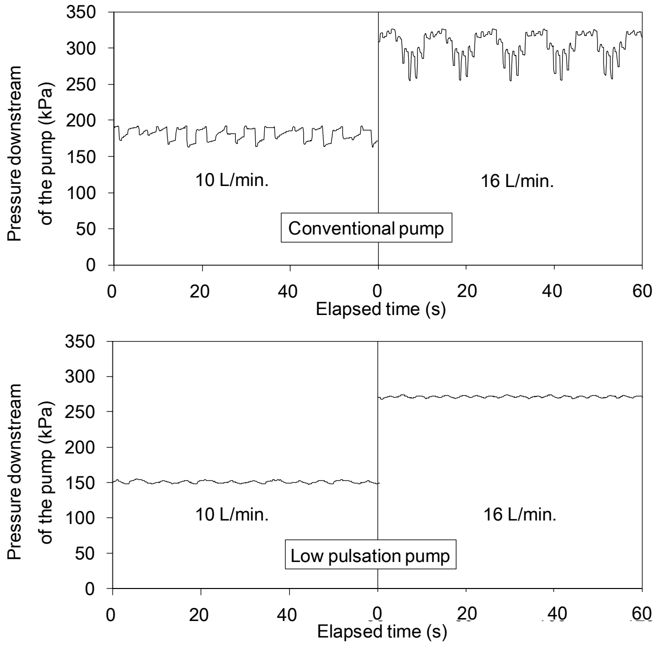

Fig. 3. Pressure fluctuation with time at the downstream of each bellows pump (upstream of each test filter) in 90 °C sulfuric acid.

TABLE I. SUMMARY OF PUMP PULSATION INTENSITY MEASUREMENTS OF EACH BELLOWS PUMP IN 90 °C SULFURIC ACID.

Flow Rate	Peak-to-peak value of pressure fluctuation (kPa)	
	Conventional bellows pump	Low pulsation bellows pump
10 L/min.	27	7
16 L/min.	72	6

Fig. 4 shows the particle counts upstream and downstream of the test filter when using each pump. Since the test filters remove particles in the chemical, the particle counts downstream are lower than those upstream. Comparing the two pumps, it can be seen that the low pulsation pump has lower counts at both upstream and downstream of the filter; the particle level downstream of the filter when using the low pulsation pump became lower by 30% compared to that using the conventional pump. These results indicate that the low pulsation pump effectively reduces particle shedding from the pump itself and/or the line.

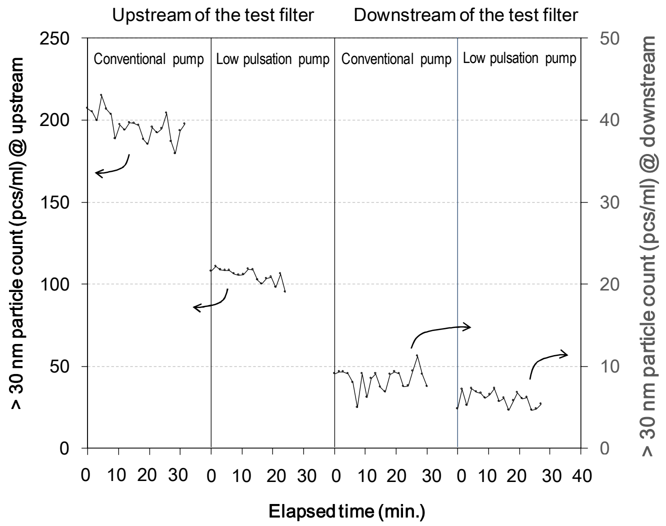

Fig. 4. Particle counts downstream (i.e. upstream and downstream of test filter) of each pump in 90 °C sulfuric acid. Flow rate was 16 L/min.

B. *PRE of filter*

Fig. 5 shows PRE of the filters when using each pump in 90 °C sulfuric acid. With either kind of the pumps, PREs of the filtration were over 90% and there was no significant difference between the two pumps. Thus, it can be concluded that this filter shows stable performance regardless of the magnitude of pump pulsation in this chemical. Litchy, *et al.* [1] have reported that filters' PRE deteriorates in the case of extremely high pulsation condition like a diaphragm pump. Our results differ from the previous report on the point; the reason would be that pulsation of bellows pumps is not as large as diaphragm pumps. Also, difference in the detailed configuration among filters may have caused the difference.

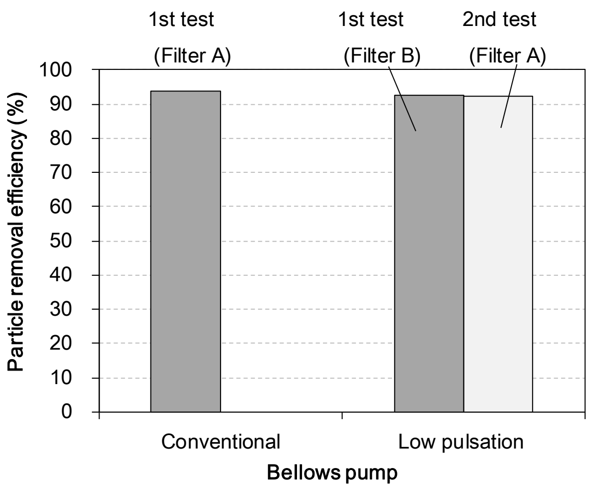

Fig. 5. Results of particle challenge tests in 90 °C sulfuric acid. Two 5-nm-rated PTFE filters (Filters A&B) were evaluated in the recirculation system with each different bellows pump. The flow rate was 16 L/min. Filter A firstly used for the conventional pump was also tested using the low pulsation pump.

IV. CONCLUSION

The newly developed bellows pump effectively reduced the peak-to-peak value of pressure fluctuation in 90 °C sulfuric acid. In addition, the particle level downstream of the pump drastically decreased for the low pulsation pump compared to the conventional pump. On the other hand, the results of particle challenge tests indicated that the filters' PRE was unchanged regardless of the pump used. As a result, the particle level downstream of the filter when using the low pulsation pump became lower by 30% compared to that using the conventional pump. In conclusion, the low pulsation pump and the 5 nm-rated PTFE membrane filter are a good combination to effectively reduce particles in 90 °C sulfuric acid. As our ultimate goal is zero particles in the chemicals used for the semiconductor wafer cleaning processes, we will develop filters of better PRE and aim to reduce particle generation from pumps further.

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