Particle Monitoring in Liquids: Liquid Particle Counter

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Particle Monitoring in Liquids: Liquid Particle Counter

Abstract

To study the performance and characteristics of a liquidborne particle counter (LPC), we used a LPC to measure particle size distributions in water. Unlike normal light scattering LPC, the LPC used in this experiment was based on interferometry, and it could distinguish bubbles and particles. Therefore, instead of using a complex pressurized system, we used a simple vacuum sampling system.

The LPC was able to measure particles from 0.2µm to 0.5µm. Particles larger than 0.5µm were counted in the last size channel. The sizing accuracy of the LPC was evaluated by measuring the size distributions of PSL spheres in DI water. The three measured sizes were: 0.2µm, 0.3µm and 0.4µm. Results shows that the largest sizing error, which was 10%, happened for 0.2µm. For 0.3µm and 0.4µm PSL, the sizing was very accurate.

The LPC was calibrated using PSL in DI water. Because the response of LPC is a function of refractive index contrast, this effect should be accounted for when measuring particle/liquid system whose refractive index contrast is not the same as PSL/DI water.

Coincidence and saturation cause counting error when the particle concentration is high. We used the LPC to measure size distributions of a CMP slurry at different dilution ratios. It was found that when dilution was not high enough, the LPC was saturated and no particle was detected. When coincidence and saturation happened, the total detected particle concentration increased as dilution ratio increased. Then it approached constant.

Introduction:

Today, the air cleanliness in cleanrooms have been extensively studied and very well controlled. Therefore, airborne particulate contaminations from the cleanroom environment are no longer major problems. Now, the major sources of contaminations are personnel, processing equipments, and process liquids. Semiconductor processing usually requires use of strong acid, bases and oxidizers. These chemicals often contain
high levels of particles. Table 1 compares the typical particle concentrations of several contaminations sources [1]:

Table 1 Particle concentrations of several contamination sources [1]:

<table>
<thead>
<tr>
<th>Contamination source</th>
<th>Particle concentration (#/liter, &gt;0.5µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 10 cleanroom</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Process gases</td>
<td>&lt;10 (&gt;0.01µm)</td>
</tr>
<tr>
<td>DI water</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Bottled chemicals</td>
<td>&lt;100,000</td>
</tr>
</tbody>
</table>

Note that particle concentrations in reactive process liquids are orders of magnitudes higher than other sources. It is essential to monitor and control the contamination caused by the supposedly clean liquids.

Liquid laser particle counters (LPCs) are widely used in cleanrooms for monitoring the quality of DI water, process chemicals and chemical mechanical polishing (CMP) slurry. Commercial available liquid LPCs can detect particles in the range of 0.03µm to 5.0µm (PMS, Boulder, CO). There are several important issues need to be addressed when using an liquid LPC:

- **Sizing accuracy:** All LPCs define particle size in terms of the diameter of a sphere whose projected area is equivalent to that of the particle being measured. When the particle is not spherical, the reported size varies with the orientation of the particle in the LPC viewing volume. In addition, the lighting intensity of the laser beam is not uniform. Particles with the same size will have different response when they are illuminated by light of different intensity. Sizing error also occurs when the electronic circuit parameters drift from the original setting.

- **Counting accuracy:** As mentioned in Table 1, particle concentrations in some chemicals are pretty high. Two phenomena may cause severe counting errors: coincidence and electronic saturation. Coincidence happens when more than one particles simultaneous appear within the viewing volume. Saturation happens when the electronic pulse processing system is unable to detect and size individual pulse when the pulse rate exceeds the capability of that system to differentiate between successive pulses. Both phenomena cause overestimate of sizing and underestimate of concentration.
• Bubble suppression: Significant pressure drop may happen when liquid passes through a small cross-sectional area. If the pressure before or within the sensing volume is reduced to a point below the saturation vapor pressure of the liquid, bubbles will be generated. Most instruments cannot distinguish particles and bubbles, and bubbles are also counted as particles. Therefore, it is important to make sure that no bubbles are generated during measurements.

• Refractive index contrast: Most liquidborne laser particle counters are calibrated with polystyrene latex (PSL) spheres of refractive index 1.59 suspended in water with refractive index 1.33 or in oil of refractive index 1.47 [2]. Therefore, the sizes reported by instruments are “PSL/Water (or Oil) optical equivalent” sizes, not their true mobility sizes.

The objective of this experiment is to study the performance and characteristics of a liquid laser particle counter. The important issues listed above are to be studied carefully. Then this LPC will be used to measure the CMP slurry with different dilution ratios.

**Background**

The state-of-the-art liquid LPCs are based on light scattering. They measure the amount of light scattered by particles when particles passing through the viewing volume. Figure 1 shows such an instrument [1].
This LPC can count and size particles as small as 0.2µm in liquids at a sampling rate of 20ml per minute. One of the major drawbacks of conventional light-scattering instruments is that they count bubbles as particles. This is especially serious when measuring liquid with high vapor pressure. To solve this problem, the pressurized sampling system as shown in Figure 2 is usually used. In this system, compressed clean air or nitrogen is fed into the pressure vessel to keep the pressure higher than the chemical vapor pressure, thus prevent creating bubbles. Table 2 shows the effect of sample pressure on particle counts in 30% hydrogen peroxide [1]. Note that applying high pressure can significantly reduce bubble counts.
Table 2 The effect of sample pressure on particle counts in 30% H$_2$O$_2$ [1]

<table>
<thead>
<tr>
<th>Sample pressure, psig</th>
<th>Particle counts per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;0.5µm</td>
</tr>
<tr>
<td>Vacuum</td>
<td>3,470,000</td>
</tr>
<tr>
<td>10</td>
<td>75,200</td>
</tr>
<tr>
<td>15</td>
<td>58,600</td>
</tr>
<tr>
<td>20</td>
<td>51,500</td>
</tr>
</tbody>
</table>

To overcome the bubble counting problem, TSI developed a liquid particle counter based on light interference [3]. Instead of measuring the intensity of scattered light, this instrument measures a phase shift in light waves. Because bubbles have a lower refractive index than the surrounding liquid, they produce phase signals of a polarity opposite to those of particles. Hence it can distinguish between particles and gas bubbles. The operating principles can be illustrated using the Mach Zehnder-type interferometer shown in Figure 3.

![Figure 3 Schematic of the Mach Zehnder-type interferometer](image)

An incoming laser bin with intensity $P_0$ is divided into two equally intense beams. The phase of beam 1 is changed 90°. Then the two beams are combined and split again to form Beams A and B with intensity $P_a$ and $P_b$, respectively. Particles or bubbles passing through beam 1 and beam 2 can cause phase shift of these two beams. But particles and bubbles have opposite effects on phase change, and they produce different signal as
shown in Figure 4. Therefore, we can easily distinguish particles and bubbles with an interferometer. Interferometric phase shift can be calculated as follows:

\[
\text{Phase shift} = \frac{-NA^2}{2m_w} \text{Im}[S(0^0)],
\]

where

\[
\begin{align*}
\text{NA} &= \text{numerical aperture} \\
\text{m}_w &= \text{refractive index of liquid} \\
S(0^0) &= \text{scattering matrix function}.
\end{align*}
\]

Scattering matrix is a function of refractive index contrast, m, which is defined as

\[
m = \frac{m_p}{m_w},
\]

where \(m_p\) is the refractive index of particle.

A detailed description of this kind of instrument is referred to [3].

![Figure 4 Signals from interferometer when a particle or a bubble crosses both beams](http://www.chem.vt.edu/confchem/2000/a/rockwell/rockwell.htm)

Chemical Mechanical Polishing (CMP) is a process that is used for the planarization of wafers. The goal of CMP is to achieve planarization globally across the wafer to allow each successive layer to be formed over a flat surface. It is accomplished by applying a load force to the back of a wafer while it rests on a pad. Both the pad and wafer are then counter rotated while the slurry containing both abrasives and reactive chemicals is passed underneath \(^1\). One of the major problems with CMP is that the pad tends to scratch the wafer, resulting microscratches. This can lead to stringers in later

\(^1\) [http://www.chem.vt.edu/confchem/2000/a/rockwell/rockwell.htm](http://www.chem.vt.edu/confchem/2000/a/rockwell/rockwell.htm)
processing, a defect mode where a thin metal line is trapped within the dielectric, causing shorts between adjacent metal lines or between VIAs\(^2\). Therefore, CMP requires good quality of slurry. Normally, in the cleanroom, particle size distribution, specific gravity, PH value, percent solid by weight and zeta potential are measured as part of CMP process control. Among these factors, the particle size distribution is the most direct index of slurry health\(^3\). One example of slurry size distribution is shown in Figure 5. The liquidborne laser particle counter can be used to measure the size distribution of CMP slurry, and to monitor the existence of unwanted large particles.

![CMP slurry size distribution](image)

**Figure 5** Particle size distribution of SS-25 (From experiment handout)

**Experimental Methods:**

In this experiment, a TSI 7750 LIQUITRAK liquidborne particle counter based on interferometry was evaluated and studied. Figure 6 shows the experiment setup.

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\(^2\) [http://www.semiconductors.net/technical/CMP.htm](http://www.semiconductors.net/technical/CMP.htm)

\(^3\) Cited from experiment handout
Note that this system is not the pressurized system discussed in the previous section. Contrarily, this is a vacuum system. Their reasons for using this design were:

- First, the plumbing for the pressurized system is pretty complicated and the tubes are relatively long. Hence it takes a longer time to purge when switching from one kind of particle to another. This is not very efficient. On the other hand, the vacuum system is pretty simple, and it works more efficiently.

- Second, the liquid used in this experiment was water, whose vapor pressure was low enough to use this system without creating bubbles.

- Third, the LPC used in this experiment was based on interferometry. It could distinguish bubbles and particles. Therefore, we did not need to worry about bubbles.

This experiment consisted of two steps. First, three sizes of PSL spheres (0.2µm, 0.3µm, 0.4µm) were successively introduced into deionized (DI) water. The LPC sizing accuracy, refractive index contrast, and sample volume was studied. Then, the particle size distribution of a fumed SiO2 CMP slurry, Semi-Sperse® 25 (SS-25) by Cabot Microelectronics (Aurora, IL) was measured. Since the concentration of bulk particles in these slurries was more than 10^{15}#/cc, which was far above the concentration limit of the LPC. Therefore, the slurry was diluted by different dilution factors in this experiment, and the issues of counting accuracy (coincidence and saturation) were addressed.

**Results:**

1. **Sizing accuracy**

   To verify the LPC counting accuracy, three different sizes (0.2µm, 0.3µm, 0.4µm) of PSL was introduced to DI water and measured by the LPC. The raw data is listed in
Appendix B. The measured size distributions are plotted in Figure 7.a to 7.c. The statistics is listed in Table 3.

Figure 7.a 0.2µm PSL

Figure 7.b 0.3µm PSL

Figure 7.c 0.4µm PSL

Table 3 Statistics of PSL size distribution measurements

<table>
<thead>
<tr>
<th>PSL size</th>
<th>Average diameter</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2µm</td>
<td>0.22</td>
<td>0.05</td>
</tr>
<tr>
<td>0.3µm</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>0.4µm</td>
<td>0.40</td>
<td>0.06</td>
</tr>
</tbody>
</table>
From the above results, we can conclude that this LPC has a very accurate sizing capability. Note that in Figure 7.c, there is an increase in counts in the last size bin. This is because all particles bigger than 0.48µm are assigned to this size bin.

One of the major drawbacks of this interferometer is its inspected sampling volume. Only about 1/200 of the total flow rate is examined. That is why we see huge concentration values while only small number of particles were detected as shown in Appendix B. This causes large counting uncertainties in the concentration results.

2. Effect of refractive index contrast

The liquidborne LPC used in this experiment was calibrated with PSL in DI water by the manufacturer. Therefore, the reported sizes are always PSL/DI water “optical equivalent” sizes, i.e. the sizes of PSL spheres that would produce the same amount of phase change. If the measured particle has a refractive index different from that of PSL, or the liquid has a refractive index different from DI water, the refractive index contrast must be corrected to obtain the true particle size. As indicated in Equation 1 and Equation 2, Interferometric phase shift is a function of refractive index contrast: the higher refractive index contrast, the larger phase shift. Figure 8 illustrates the relationship between LPC response, particle size, particle and liquid refractive indices.
For example, if I use a particle counter, which was calibrated by PSL in DI (Refractive index contrast = 1.19), to measure PSL particles in $\text{H}_2\text{SO}_4$ (Refractive index contrast = 1.09), the true size of the indicated “optical equivalent” diameter $D_{p1}$ will actually be $D_{p2}$. Therefore, the LPC underestimate the true size in this case. Another example to illustrate this refractive index contrast effect is to use this LPC to measure SiO$_2$ particles with actually diameter of $D_{p2}$. The indicated diameter will be $D_{p1}$, which is smaller than $D_{p2}$.

There are two ways to account for this refractive index contrast effect. One is to calibrate the LPC with particle and liquid to be measured and set size bin boundaries according to the calibration. The other is to calculate theoretical responses of calibrated and measured particle/liquid system, and correct the result for the differences between these two responses as shown in Figure 8.

3. **Counting accuracy: coincidence and saturation**

As mentioned earlier, the particle concentration of CMP slurry was so high that it exceeded the maximum limit of the LPC. In this experiment, it was diluted 10,000,
100,000, and 1,000,000 times successively to study the effect of coincidence and saturation and to measure the actual size distribution of the slurry.

When the slurry was diluted 10,000 times, almost no particles were reported. However, when we looked at the LPC signal output, we found a lot of pulses appeared simultaneously. This suggested that the LPC was totally saturated. Figure 9 compares the size distributions measured at 100,000 and 1,000,000 dilution ratios, respectively.

![CMP slurry size distributions at different dilution ratios](image)

Figure 9 CMP slurry size distributions at different dilution ratios

Note that the dilution ratio in case b is 10 times higher than that in case a, however, the concentration in case b is much higher than case a for almost all sizes. This suggests that in case a, the LPC was still saturated, and the concentration was not correct. Figure 10 shows the measured particle counts as a function of dilution ratio. The counts were normalized to those of dilution ratio 100,000. Since we only measured at three dilution ratios, we cannot determine the concentrations at intermediate dilution ratios. But it illustrates the trend that when saturation and coincidence happens, detected concentration increase as dilution ratio increase. Then the concentration will keep constant.
Concentration vs. dilution ratio

Figure 10 Effect of dilution ratio on detected particle concentration

Theoretically, when concentration is so high that saturation happens, coincidence will also happen. This will result in underestimation of concentration and overestimate of particle sizes. As shown in Figure 5, the peak concentration of the slurry appears around 0.1µm, which is below the detection limit of the LPC we used. If coincidence happens for those small particles, then they will be reported as bigger particles and detected by the LPC. Thus both size and concentration will be overestimated. However, because we didn’t know the actually concentration of the CMP slurry, we had no way to justify the effect of coincidence. Again, we see huge concentration in the last size channel of the LPC in Figure 9.b, caused by counting every particle bigger than 0.48µm to be counted in that channel.

Conclusions:

In this experiment, we used a liquidborne laser particle counter based on interferometry to measure liquid particle concentration. The sizing accuracy of this counter was evaluated by measuring PSL spheres of know sizes in DI water. The results showed that this LPC could measure particle sizes very accurate. The maximum sizing error, which was about 10%, happened near the low detection limit. Since the LPC response is dependent on particle/liquid refractive index contrast, the effect of refractive index contrast should be accounted for when obtaining true size distributions. Electronic
circuit saturation and coincidence are two major sources of counting errors. Both of them happen when the measured particle concentration is too high. In this experiment, the counting accuracy problem was addressed by measuring the CMP slurry concentrations. A dilution ratio as high as 1,000,000 was required to obtain reasonable concentration value. Usually, liquidborne LPCs suffer from counting bubbles, and pressurized system is required to suppress bubbles. However, the LPC used in this experiment can distinguish bubbles and particles. Therefore, simple vacuum sampling system was used.

References:

Appendix A: Instruments list
- TSI 7750 LIQUITRAK Liquidborne Particle Detector
- IBM personal computer
- Pressurized sampling system
- Sampling bottle with vacuum source
- Oxford adjustable macropipettors
- Magnetic stirrer

Appendix B: Raw data

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Counts(interval)</th>
<th>Counts (total)</th>
<th>Concentration (Interval)</th>
<th>Concentration (total)</th>
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</thead>
<tbody>
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<td>0</td>
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<td>0.48</td>
<td>12</td>
</tr>
</tbody>
</table>

**0.3µm PSL**

**0.4µm PSL**

**CMP slurry:**

**Dilution Ratio:** 1:100,000 1:1,000,000

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Counts (interval)</th>
<th>Particle size</th>
<th>Counts (interval)</th>
</tr>
</thead>
<tbody>
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