Measurement and Control of Liquid-borne Particles in the Semiconductor Manufacturing Process

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1. Introduction

For a state-of-the-art semiconductor device, a hyperfine structure of 20 nm in half-pitch has been used for mass production in recent years. Controlling particle contamination in a manufacturing process or in various liquid materials used in a manufacturing process is an important target to be controlled for keeping yield or quality, with the practical use of many new materials such as a high-dielectric gate-insulating film and a metal gate, along with the complication of a process represented by a lithography based on multi-patterning as a background. The measurement technology of the attached contamination particles on a wafer enables a particle of 30 nm or less in size to be detected under specific conditions. However, a particle counter using a light scattering method that measures particles in a liquid phase in situ is also still useful for different points of view, as a particle measurement method, because of the lower limit of the actual number concentration in which quantitative evaluation can be performed or because of the characteristics or restrictions in operation (for example, measurement information being after the fact). This paper describes the technology development situation of a liquid-borne particle counter (LPC) and a theme on the detection of ultra-fine particles, with the latest management trends of liquid-borne particles as a background.

2. Latest measurement trends of liquid-borne particles

In the semiconductor technology roadmap of the ITRS,[1] created to share the objective of semiconductor technology development on an international scale, the size of contamination particles to be controlled or the numerical target of number concentration is set, and the measurement and control points of particle contamination are also defined. With the wet cleaning process as an example, each measurement point defined by the ITRS is shown in Figure 1. In general, pure water or chemicals are supplied from a supplying equipment feeder to a cleaning device through a piping system. In many cases, they are cleaned in front of the inlet of the cleaning equipment or in the circulation system inside the cleaning equipment by filtration. In sequence, with the storage tank

(POS: Point of Supply) of the liquid materials as an uppermost stream position, the measurement and control positions are defined downstream as the outlet of a supplying equipment (POD: Point of Delivery), a branch connection point (POC: Point of Connection), the entry of a cleaning equipment (POE: Point of Entry), the connected point with a process chamber (POU: Point of Use), and the process contacting a wafer (POP: Point of Process).

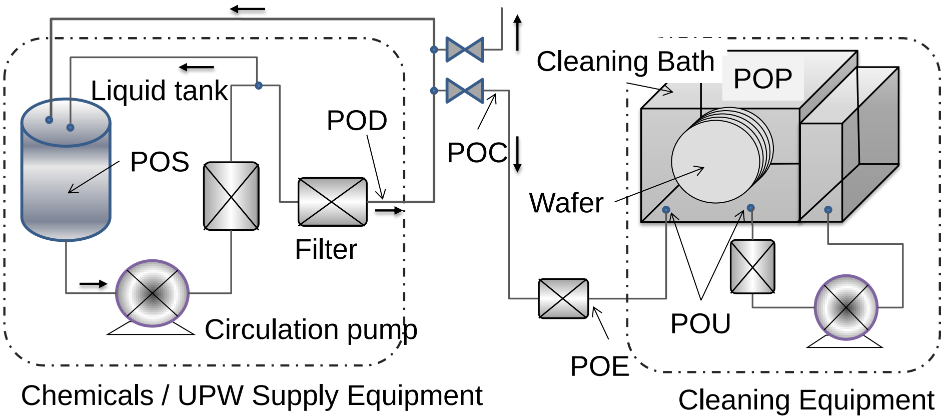


Fig. 1 Particle measurement points in the wet process.

In the ITRS, maintaining a yield of 99.9% requires the number of wafer-attached particles to be less than 12.3/wafer (300 mm in diameter) per process. It is presumed that the number concentration of liquid-borne particles contacting a wafer that satisfies the required value must be less than 1,000/L at the POP of a standard cleaning process.[2] On the other hand, the number concentration measurement in controlled particle size (Critical Particle Size, indicated in the ITRS) that ITRS requires is not actualized irrespective of the method. Therefore, the number concentration becomes approximately 125/L for 40 nm in particle size (approximately 64/L for 50 nm in particle size) when a third-power law model[1] is assumed for the particle size distribution of the number concentration. Each number concentration of particles becomes 10 times as high as the normal one when a yield of 99% is used as a standard. In any case, the number concentration of approximately 100 to 1,000/L must be measured and controlled near 50 nm in particle size.

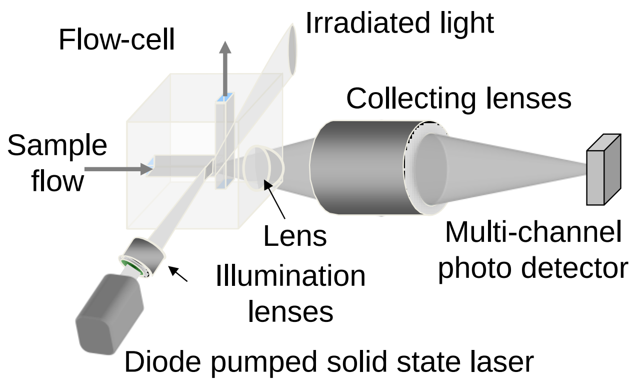
In the current ITRS, the number of particles at POC is described in a roadmap as a controlled value. In practice, the estimated number of controlling particles at POP is directly used as the number of controlling particles at POC. There will not be always a good correlation between the particle behavior at POP and the particle count behavior at POC/POE or POD. However, LPC has been recently developed and produced on a commercial scale, with particle control in the supply system required by the ITRS as an operation form.

The latest trend of LPC is described below and it is intended for measuring the particles in liquid materials in batch (applicable to POS in many cases) or for performing in-line measurement in a supply system (POD/POC/POE).

3. LPC for 40-nm particles

In LPC, in which a light scattering method is used, the relation between the minimum measurable particle size and the increase in an effective sample flow rate is contrary to each other when judged from the viewpoint of a principle. LPC, in which a particle of 100 nm or more in size is treated for measurement, enables the majority of sample to be treated for measurement. This ensured high detection efficiency.[3] For the light scattering behavior of a particle with a size of 100 nm or less, the particle size is much smaller than its wavelength. Therefore, the light scattering Rayleigh method shown in expression (1) can be applied as the approximate solution of the Mie light scattering theory.[4] Light scattering intensity (I_R) is proportional to the 6th power of the particle size and is inversely proportional to the 4th power of its wavelength.

$$I_R = I_0 \frac{\pi^4 d^6}{8R^2\lambda^4} \left(\frac{\left(\frac{m}{n}\right)^2 - 1}{\left(\frac{m}{n}\right)^2 + 2} \right)^2 (1 + cos^2\theta) = I_0 \frac{\pi^4 d^6}{8R^2\lambda^4} (1 + cos^2\theta) f_1(m,n) \qquad (1)$$



Enlarged the scattered light-collecting system

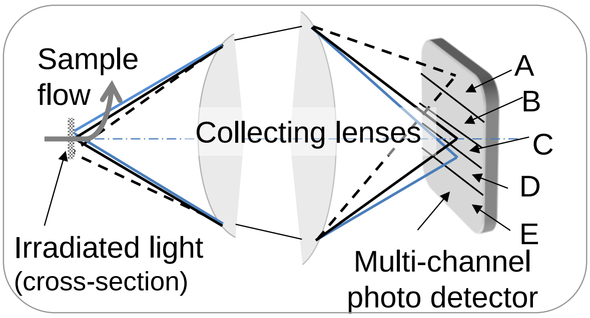


Fig. 2: Particle detection part of the 40nm compatible liquid-borne particle counter.

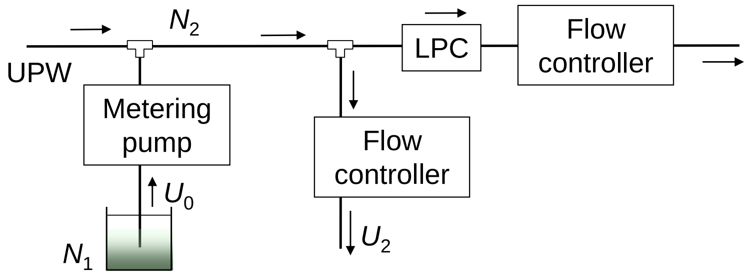
Where, I_0 is irradiated light intensity, d is particle size, R is the distance from a measurement target, λ is the wavelength of irradiated light, m is the complex refractive index of a particle, n is the complex refractive index of a medium (liquid in this paper), and θ is the azimuth angle of scattered light.

The scattered light intensity of a particle with a size of 40 nm is lower than that of a particle with a size of 100 nm by approximately 1/250. Particles cannot be detected by only an increase in the quantity of irradiated light based on a laser light source. A partial detection method for narrowing an irradiation area and increasing the density of light energy has thus been frequently used. In the partial detection method, the width of a flow path is wider than that of irradiated light. The energy intensity of irradiated light in a particle detection area is thus put in the form of Gaussian distribution. In this case, it is difficult to make the density of light energy in an irradiation area uniform. Therefore, the scattered light intensity of particles with the same size varies depending on the difference in the position of particles that pass through the irradiation area. The phenomenon such that the detection efficiency of a particle (i.e., the counting efficiency of the measuring equipment) depends on the particle size was a theme to be solved. However, the quantitative performance of the measured value has been improved by using the particle detection system (KS-18F, RION) shown in Figure 2.[5]

To detect a particle of about 40 nm in size, the second harmonic (wavelength: 532 nm, output: 500 mW) of a semiconductor-laser-excited YVO_4 laser is used as a high-output and short-wavelength light source. A light receiving system can be set in a position opposing the flow line direction of a sample flow by using an L-shaped flow cell (made of sapphire) as a flow path. The scattered light of particles focused on the surface of a photo-detector is focused at the fixed point without drawing a trajectory. The focusing position applies to the position where the particles in irradiated light passes. Therefore, the passing position of the particles is determined using a photo-detector of a multi-channel type . Moreover, selection or rejection is judged for each particle sensing signal, or the size of the signal is corrected. As a result, the size of a particle detection area or the detection sensitivity can be kept constant. In the example given in the enlarged illustration in Figure 2, the measurement area in channels B, C, and D is set as an effective particle detection area. Channels B and D are set to the detection sensitivity equal to that of channel C with the amplification factor of a photoelectric conversion signal adjusted as required. The scattered light of the particles may also enter channels B, C, and D when large particles pass through the outside of an effective particle detection area. However, counting efficiency can be kept constant by eliminating the error detection in channels B, C, and D using the signal detection information in channels A and E.

4. Evaluation of LPC counting performance

LPC specifications or LPC performance evaluations are prescribed in JIS B 9925[6] and ISO 21501-3.[7] However, the size of the particles to be measured is prescribed to be 100 nm or more. In addition, the way to evaluate counting efficiency with the reference instrument as a standard is also prescribed in this case. However, the number concentration of liquid-borne particles is not quantitatively evaluated by methods other than LPC. In reality, LPC is also thus used as a reference instrument. Consequently, it is difficult to extend the method of JIS or ISO for operations up to a particle size of 100 nm or less that can be measured only using a partial detection method. A method to evaluate the counting efficiency of LPC using a sample, in which the number concentration is given, created by quantitatively diluting a test particle’s undiluted solution in which the mass density is known, is shared.[8] PSL (Polystyrene Latex) particles, which are an actual standard sample as calibration and test particles of LPC, are on the market with a well-known mass density dispersed in pure water. The PSL particles generated by an emulsion polymerization reaction are almost uniformly spherical in form and constant in specific gravity (1.05 g/cm^3). Moreover, a PSL particle of 50 nm or more in size is very low (generally 3% or less) in the dispersion of size for a CV value (the ratio of a particle size's standard deviation to a number's average size). It can be treated as a spherical particle in which its number's average size is used as a representative particle size. Consequently, the existence rate of particles much larger than the number's average size can be quantitatively converted from mass density to number concentration under conditions that it can be almost ignored. Then, the counting performance of LPC can be evaluated with the known test particle's number concentration as a standard by diluting the undiluted solution of PSL particles quantitatively up to the measurable density range of LPC.



N_2 : Sample number concentration
U_1 : Measured sample flow rate
U_0 : Flow rate of the primary diluting fluid
U_2 : Bypass flow rate
N_1 : 3-10. Number concentration of the primary diluting fluid

Fig. 3: Block diagram of the quantitative dilution test.

The test procedure of counting performance by quantitative dilution is shown in Figure 3. Test particles with known number concentration N_1 are quantitatively injected into the pure water, at flow rate U_0, which is supplied at a fixed flow rate. The sample flow rate U_1 of LPC is controlled on the downstream side, and flow rate U_2 at which water is drained to a bypass is controlled at a fixed value. In consideration of the control accuracy of measuring equipment such as a flow meter, a dilution ratio of about 10^6 times is considered a practical limit. The undiluted solution's mass density of commercially available PSL particles is approximately 1%. For a particle diameter of 50 nm, therefore, the undiluted solution's number concentration becomes approximately 1.5 x 10^{14}/cm^3. Accordingly, the procedure for injecting the primary diluting fluid, in which the undiluted solution was diluted to about 10$^{5\text{-}6}$ times, into pure water, is required in this case. To prepare a primary diluting fluid, a undiluted solution is quantitatively (V_0) sampled using a micropipette and dispersed in the pure water of volume V_1. The number concentration N_2 of the PSL particles introduced into LPC is obtained by the expression below. The counting efficiency of LPC is obtained by comparing the counting value of LPC and N_2.

$$N_2 = N_1 \frac{U_1}{(U_0+U_1)} \qquad (2)$$

$$\text{where}, N_1 = N_0 \frac{V_0}{(V_0+V_1)} \quad (3)$$

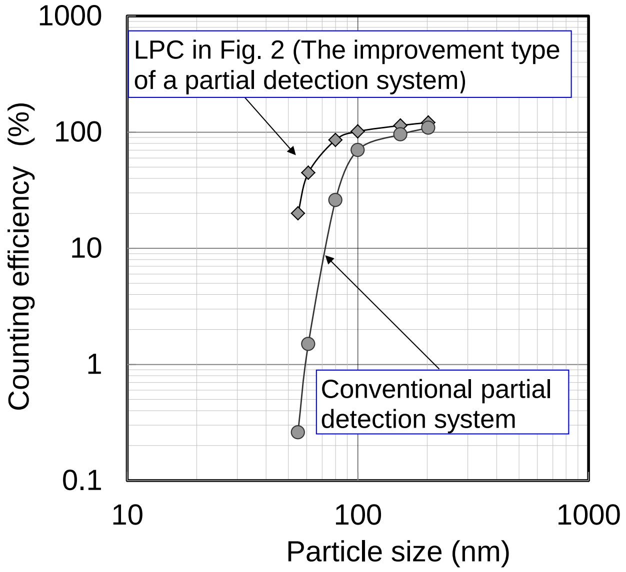


Fig. 4 Evaluation of particle counter performance by a quantitative dilution method.

Shown in Figure 4 is the result obtained when the counting performance of LPC near 50 nm at a minimum measurable particle size is evaluated with the number concentration obtained using a quantitative dilution technique as a standard. The horizontal axis indicates the size of the PSL particles used for a test. The vertical axis indicates the ratio of the particle count, to be counted, obtained from the specifications of each LPC’s effective sample flow rate (= introduced sample flow rate x counting efficiency) to the counted value of each particle size measured using a minimum particle size’s threshold value. This shows that the degree of improvement in the particle size dependency of LPC’s counting efficiency shown in Figure 2 can be quantitatively evaluated at 100 nm or less in particle size.

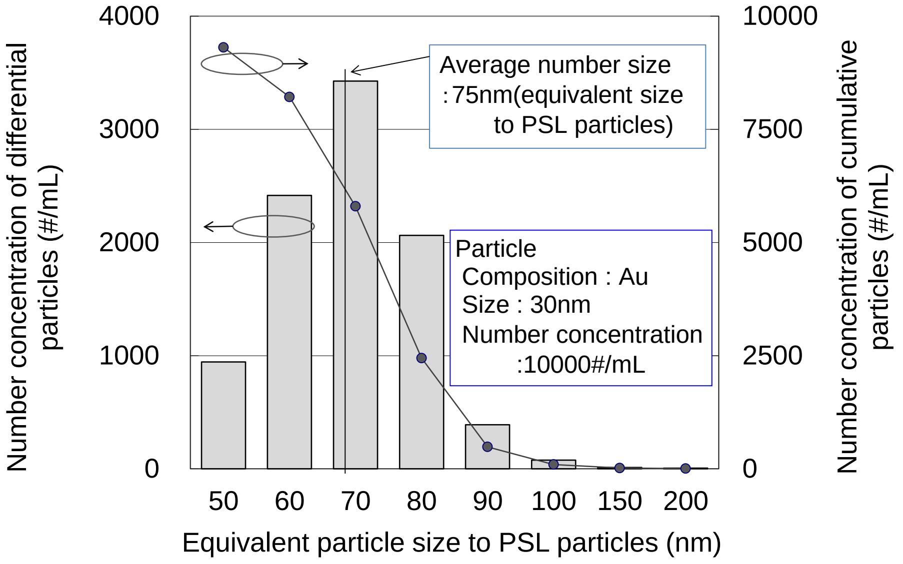


Fig. 5: Particle size distribution of 30 nm Au particles measured by LPC.

5. For the measurement of liquid-borne particles with a size of 40 nm or less

(1) Performance evaluation of LPC using colloidal Au particles

The method shown in Figure 3 is not restricted in application by the composition of particles if mass density, particle size distribution, or dispersibility to a medium is well known. Colloidal Au particles can be created in more uniform particle size and shape. In a specific particle size, the National Institute of Standards and Technology (NIST) authenticates[9] the reference substance on a particle size. It is also confirmed that colloidal Au particles can be dispersed without being agglomerated into pure water.[10]

The particle size distribution characteristics of colloidal Au particles dispersed in pure water and the quantitative performance of number concentration were evaluated by LPC. A colloidal Au particle of 30 nm in size (undiluted solution's mass density: 0.01%) is adjusted to approximately 10,000/mL in number concentration by a dilution technique in Figure 3 and supplied to LPC shown in Figure 2. The measurement result is shown in Figure 5. The left vertical axis indicates the particle number concentration between the particle sizes of a horizontal axis. The right vertical axis indicates the number concentration of particles exceeding the particle size of a horizontal axis. The number concentration of particles, with a size equivalent to that of PSL particles, exceeding a threshold value of 50 nm is approximately 9,400/mL. In general, the number concentration based on a dilution technique is evaluated to match with the measured value of LPC. The particle sensing signal of LPC is distributed in the form of mono-dispersion (CV value [= standard deviation/center diameter]: approximately 5.4%). It is confirmed that the particle size is accordingly uniform. The average number size is equivalent to the size of PSL particles. It is approximately 75 nm.

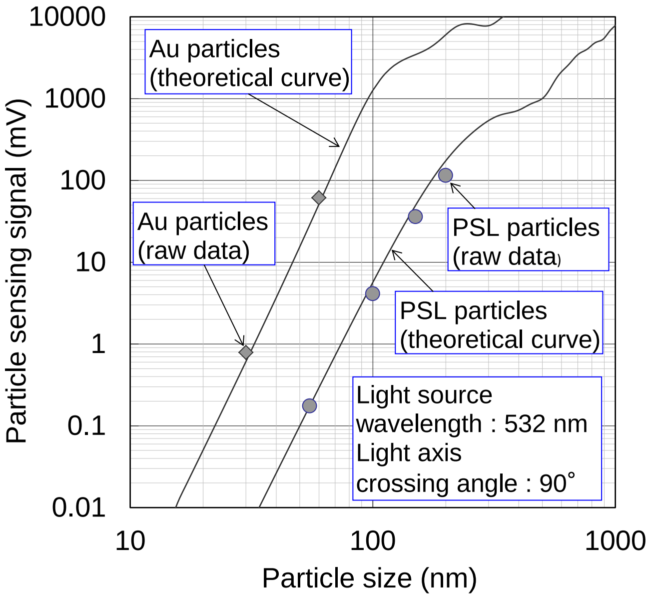


Fig. 6: Light scattering characteristics of PSL particles and Au colloidal particles.

Figure 6 shows the detection characteristics of the PSL and colloidal Au particles dispersed in pure water.[11] The complex refractive index of the colloidal Au particles is supposed to be 0.467-*i*2.41 ("*i*" is a complex number).[12] The theoretically calculated value conforms to the Mie's theoretical formulas.[4] The measured value is obtained by the method shown in Figure 5. The calculated value is made to coincide with the measured value in a PSL particle of 55 nm in diameter with the size of a detection signal corresponding to the average number diameter of the particle's diameter distribution as a representative value. There is good correlation between the measured value of each particle and the calculated value. The size of the colloidal Au particles based on the intensity of the scattered light with PSL particles as a standard is judged to match with the evaluation of the geometric size.[8]

Consequently, this shows the possibility that a colloidal Au particle of approximately 20 nm in size can be detected by the existing LPC technology, which detects a PSL particle of approximately 40 nm in size. The method[9] for evaluating the filtration performance of the latest liquid filter by measuring upstream/downstream particle mass density using a mass spectrometer analyzer such as ICP-MS has been investigated. However, there is the theme, to be solved, that the information on the size of the test particles is lost. It is thus necessary to know the size distribution of test particles in a different way. A filtration performance test in which particle size information is kept is considered to be able to be performed for a particle of approximately 20 nm in size by using particles such as the colloidal AU particles that LPC easily detects.

(2) Influence of a liquid's scattered light on the detection performance of LPC

In the Mie light scattering theory, which is used as the principles of LPC, the object (particle) of a finite size with a different dielectric constant in a uniform medium as a boundary is polarized by an electric field of light, and the spherical wave generated by the vibration of a dipole depending on the level of the dielectric constant is solved as the light scattering phenomenon of the particles. In numerical analysis, the dielectric constant is proportional to the second power of a refractive index, thus the refractive index ratio of particles and the media (liquid) is generally treated as a variable. In pure liquid, in which particles do not exist, no light scattering phenomenon occurs if the dielectric constant is completely uniform. However, the behavior of the background light (stray light) caused by a light scattering phenomenon depending on the liquid itself is actualized in an extremely weak light detection system corresponding to the light scattering phenomenon of particles, of a size of less than 50 nm . The light scattering in pure liquid becomes slightly heterogeneous in density distribution by liquid, because the boundary face of a minute dielectric constant exists (scattered points being localized). The scattered light intensity (I_E) of a medium (liquid) is obtained by the idea of Einstein's light scattering by molecular density fluctuation given in expression (4).[13] The quantitative evaluation of I_E depends on the volume of liquid to be irradiated. Therefore, I_E is evaluated as a relative value in this case.

$$I_E = I_0 \frac{\pi^2}{9R^2\lambda^4} \frac{(n^2-1)^2(n^2+2)^2}{n^4} KT\beta = I_0 \frac{\pi^2}{9R^2\lambda^4} KT\beta f_2(n) \qquad (4)$$

Where, K indicates a Boltzman's constant, T indicates absolute temperature, and β indicates isothermal compressibility. The relation shown in Figure 7 is given from the ratio of a complex refractive index's functions f_1 and f_2 in expressions (1) and (4). The horizontal axis indicates the real part's refractive index (0 for an imaginary part) of the particles. The vertical axis indicates the ratio of f_1 and f_2 based on the refractive index of the medium. The ratio of f_1 and f_2 indicates the relative relation between the scattered light intensity of the liquid and the scattered light intensity of the particles.

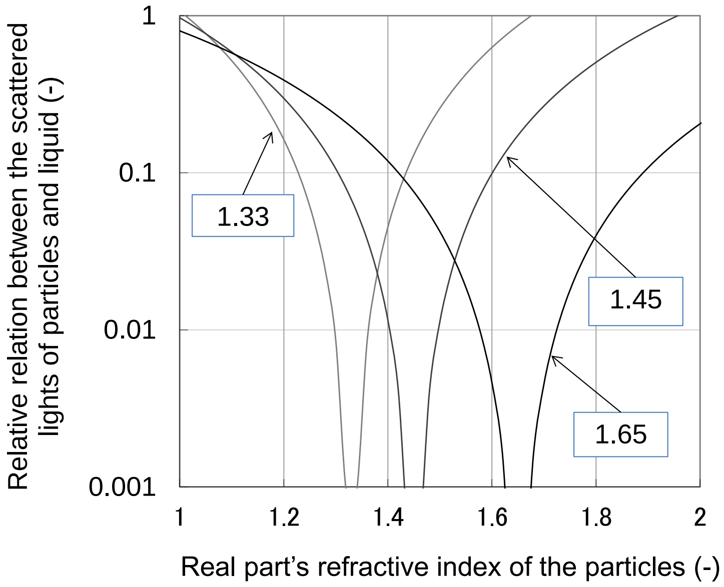


Fig. 7: Relation of scattered-light intensity depending on the refractive index of the particles and the medium. Parameter: Refractive index of the medium

In case of the same refractive index of the particles and the liquid,the vertical axis is converged to 0 because the scattering phenomenon of the particles does not occur in a value. The phenomenon in which the ratio of f_1 and f_2 increases depending on the refractive index ratio of the particles and the liquid is the same as the inclination that Rayleigh scattering indicates. However, if light scattering by fluctuation of the liquid molecular density is taken into consideration, the inclination becomes loose when the refractive index of the liquid increases. For example, this suggests the possibility that the scattered light of particles is more easily separated from the scattered light of liquid when particles (bubbles) with refractive index 1 exist in liquid with a refractive index 1.33 than when they exist in liquid with a refractive index 1.65.

The relation of the scattered light intensity given from the scattered light intensity of liquid and expression (4) is obtained. Liquid with different isothermal compressibility (β) is introduced into the particle detection area of LPC shown in Figure 2 so as to measure the intensity of the liquid's scattered light incoming to a photo detector. Figure 8 shows the relative relation between the scattered light intensity and the scattered light intensity of each liquid when the measured value of the scattered light intensity in pure water and the calculated value of the light scattering of liquid by expression (4) are based. The value in a reference is used as the isothermal compressibility of each liquid.[14]

There is a good relation between the scattered light intensity in liquid received by LPC and the scattered light intensity in liquid based on the conception of oscillating light scattering. The scattered light intensity based on a particle of approximately 40 nm in size is about several 1/10 of the scattered light intensity in pure water that LPC receives.

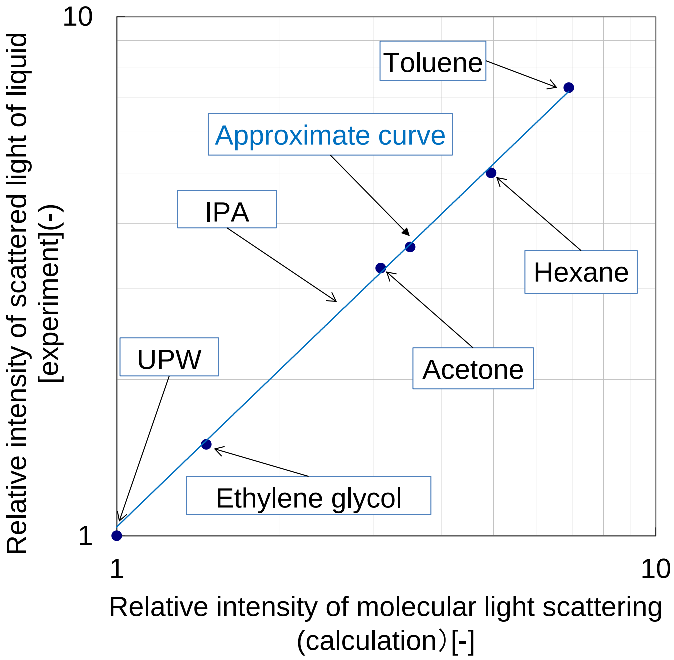


Fig. 8: Light scattering in liquid received by the particle detection system of LPC.

The sensing signal of particle, which is pulse-shaped, and the scattered light in liquid, which is DC light, can be separated by using the frequency band filter of a signal. Therefore, the signal of particles with a size of 50 nm or less can be detected. For the photo detector, such as a photodiode, however, the level of the random noise superimposed on an output signal generally varies depending on the quantity of incidental light. Consequently, reducing the received quantity of the scattered light by a medium is important to improve the detection performance of smaller particles in each liquid. The LPC shown in Figure 2 can reduce the influence of scattered light in liquid by a multi-channel photo detector. It is confirmed that LPC can also detect a particle of 50 nm or less in size in liquid, with strong scattered light, such as in toluene, as shown in Figure 6. However, it is necessary to reduce the influence of the scattered light by liquid, more efficiently when measuring even smaller particle sizes.

6. Conclusion

In the particle detection area of LPC for which a light scattering phenomenon is utilized, light is also necessarily irradiated to medium carrying particles. In LPC that is used for a particle of approximately 50 nm size, an organic solvent, acid or alkali liquid that could be regarded to be optically transparency until now proved to indicate the light scattering behavior of a significant value for the detection of particles. With the use of a nanofabrication of semiconductor or a new structure called “More than Moore,” the necessity for the particle contamination control of materials (for example, the polymer solution of a photo-resist or antireflection coat or a metallic complex or a monomer-mixed liquid that has been introduced as new materials) that have a remarkable correlation with light is on the increase. The practical application of a light scattering phenomenon has been still expected as one of the most promising methods when quantitatively measuring smaller particles in liquid. However, it is required to understand the light scattering phenomenon of various liquid materials in full detail.

Moreover, it will be also necessary to review the effective operation of particle measurement for controlling contamination. At present, LPC usage methods often involve managing a liquid supply system such as POD or POC/POE. The necessity for on-site particle measurement at POU or POP has been proposed from before. However, cooperation with an equipment manufacturer or device manufacturer as well as the theme of new measurement technology development is indispensable for development. The consecutive understanding of particle behavior, such as the adhesion of particles on a wafer and the separation of particles from a wafer, is necessary for efficient pollution particle control. First of all, it is desirable to share such a discussion.

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